



Surface extended catalyst support structures for hydrogen energy applications

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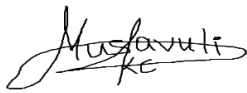
Solemn declaration

I, Kyatsinge Cédric Musavuli, declare herewith that the thesis entitled:

“Surface extended catalyst support structures for hydrogen energy applications”,

submitted in fulfilment of the requirements for the degree *Doctor of Philosophy in Engineering with Chemical Engineering*, is my own work, except where acknowledged in the text, and has not been submitted to any other tertiary institution, in whole or in part.

Signed at the North-West University (Potchefstroom Campus)



Kyatsinge Cédric Musavuli

17th February 2025

Date

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Abstract

In the current study, metal foams are evaluated as process-intensifying, surface extended catalyst support structures for three hydrogen (H_2)-based applications, namely the dehydrogenation of perhydro-dibenzyltoluene ($H_{18}DBT$), the passive autocatalytic recombination (PAR) of H_2 and the direct- CO_2 -to-methanol (MeOH) synthesis. For these applications, suitable in-house developed or commercial catalysts were washcoated on the surface of metal foams. They were investigated during catalytic activity tests using methods selected from the available literature. Their performances were then compared experimentally or using computational fluid dynamics (CFD) simulation to those of typical catalyst systems used in reactors conventionally used for the same processes.

The dehydrogenation of $H_{18}DBT$ was conducted in an unstirred tank reactor and a fixed-bed reactor (FBR). An in-house developed Pt/ Al_2O_3 catalyst was coated on aluminium (Al) foams and tested in the tank reactor. The performance of the foam-supported catalyst was later compared to that of the same amount of Pt/ Al_2O_3 pellets. Experiments were conducted at $300^\circ C$, and Pt/ $H_{18}DBT$ mol. ratio of 0.05–0.4 mol.%. H_2 productivities were 12–59% higher in the foam-based than the pellet-based tank reactor. The higher performance of the foam-based reactor was attributed to the geometric properties of the coated foam. The Pt/ Al_2O_3 -coated foams also demonstrated a high catalytic stability for more than 16 h on stream in a FBR. The relatively low degree of dehydrogenation obtained in a single pass in the FBR was improved by recycling the partially dehydrogenated product three times in the reactor at the same temperature and flow conditions. However, the H_2 productivity significantly decreased with the number of dehydrogenation cycles.

The PAR tests were performed in a recombiner consisting of Pt/ Al_2O_3 -coated Al foams in the catalytic section. The feed gas, made of 2–6% H_2 in air, was introduced to the recombiner at inlet velocities of 2–10 m/s. H_2 conversions between 57 and 89% were achieved in the recombiner, while the highest temperature recorded during the operations was $172^\circ C$ lower than the self-ignition limit of a H_2 air mixture. A comparison between the foam-based, plate-based and pellet-based recombiners using the same amount of catalyst revealed that the H_2 conversions achieved on the coated foams were similar to those obtained on the coated plates. The pellet-based recombiner exhibited the lowest performance of the three systems. Non-uniform temperature profiles were observed on the coated foams/plates due to the

unpredictable, uneven gas flow distribution in the recombiner. Three-dimensional (3D) heterogeneous CFD simulations of the foam-based recombiner were successfully validated using experimental data, including H₂ conversions and maximum temperatures. The model can successfully be used as a numerical tool for the prediction of the recombiner performance at various conditions.

The direct-CO₂-to-MeOH synthesis was performed in a two-module, bench-scale FBR containing a commercial Cu/ZnO/Al₂O₃ coated on copper foams. Activity tests were conducted at weight hourly space velocities of 1.125–2.925 NL/g_{cat}/h, pressures of 30 and 50 bar and temperatures of 190–250°C. CO₂ conversions, MeOH selectivities and MeOH productivities up to 27.46%, 82.97% and 30 g_{MeOH}/h, respectively, were achieved in the reactor. This demonstrated the suitability of the coated foam for the direct CO₂ hydrogenation to MeOH. Temperatures measured at different points in the reactor revealed that the nearly isothermal conditions were achieved in the reactor.

The experimental results of the direct-CO₂-to-MeOH synthesis were used to validate a 3D pseudo-homogeneous CFD model of the foam-based modular reactor. The model included simplified and optimised kinetic expressions which were successfully used to predict the CO₂ conversions, MeOH selectivity, MeOH weight-time yield (WTY) and CO outlet concentration. The 3D model was also used as prediction tool to simulate a modular packed bed reactor (PBR). Based only on the difference in geometric properties between the two reactors, the model predicted lower CO₂ conversions, MeOH selectivities and MeOH WTY in the PBR compared to the foam-based reactor.

The performance of the coated foams varied according to the application used. This study demonstrated that the selection of a foam-based catalytic system can be motivated by its ability to enhance processes which are more strongly affected by mass transfer than kinetic limitations.

Keywords: Liquid organic hydrogen carriers, passive autocatalytic hydrogen recombination, direct CO₂-to-methanol synthesis, foam-supported catalysts, metal foams, process intensification, CFD modelling.

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List of symbols

ABBREVIATIONS

2D	Two-dimensional
3D	Three-dimensional
CFD	Computational fluid dynamics
CNT	Carbon nanotubes
CPSI	Cells per square inch
CT	Computed tomography
DME	Dimethyl ether
DoD	Degree of dehydrogenation, %
EDS	Energy dispersive X-ray spectroscopy
FBR	Fixed-bed reactor
GHSV	Gas hourly space velocity, 1/h
H ₀ DBT	Dibenzyltoluene
H ₁₈ DBT	Perhydro-dibenzyltoluene
I.D.	Internal diameter
LOHC	Liquid organic hydrogen carrier
MeOH	Methanol
MP	3-methyl-1-pentyn-3-ol
MS	Methanol synthesis (from CO ₂ hydrogenation)
NL	Normal litre
NO _x	Nitrogen oxides
NP	Nanoparticle
O.D.	Outside diameter
PAR	Passive autocatalytic recombination
PBR	Packed bed reactor
PID	Piping and instrumentation diagram
PPI	Pore per inch
PtG	Power-to-gas
PtX	Power-to-X
RWGS	Reverse water gas shift
SCE	Saturated calomel electrode
SEM	Scanning electron microscopy
STL	Stereolithography

TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
Vol. %	Volume percent, %
WGS	Water gas shift
WHSV	Weight hourly space velocity, NL/g _{cat} /h
WTY	Weight time yield, g/g _{cat} /h
XRD	X-ray diffraction

NOMENCLATURE

ΔH	Heat of reaction, J/mol
ΔH_{f-298K}	Standard enthalpy of formation, J/mol
A	Pre-exponential factor, mol/cm ³ /K/s
a_i	Stoichiometric coefficient of species i
C_p	Heat capacity, J/kg/K
D	Diffusion coefficient, m ² /s
E	Total energy per unit mass, J/kg
E_a	Activation energy, J/kmol
F	Viscous losses, N
f_i	Fugacity of species i, MPa
g_{cat}	gram of catalyst, g
H_r	Overall reaction heat, J
I	Identity tensor
J	Diffusive mass flux, kg/m ² /s
k_{eff}	Effective thermal conductivity, W/m/K
K_i	Adsorption constant of component i, 1/MPa
k_i	Kinetic rate constant for reaction i, mol/kg _{cat} /s/MPa ^{1.5}
$K_{P,i}$	Equilibrium constant of reaction i
M_i	Molar mass of species i, kg/m ³
n_i	Moles of species i
p	Pressure of the fluid, Pa
$\vec{q}$	Heat flux, W/m ²
R_i	Rate of formation/consumption of species i, kg/m ³ /s
r_i	Rate of reaction of species i, mol/kg _{cat} /s
R_u	Universal gas constant, J/kmol/K

Sc_t	Turbulent Schmidt number
S_E	Energy source per unit volume, W/m ³
S_i	Selectivity to species i, %
S_{Y_i}	Mass fraction of the source term
T	Temperature, K
T_s	Stress tensor, Pa
U	Internal energy, J
X_i	Conversion of species i, %
Y_i	Mass fraction of species i

GREEK SYMBOLS

ϵ	Porosity of the catalyst bed, %
ϵ_m	Surface emissivity
κ	Permeability, m ²
μ	Viscosity of the gas mixture (Pa.s)
v	Fluid interstitial velocity, m/s
ρ	Fluid density, kg/m ³
ρ_s	Catalyst density, kg/m ³
ω_i	Mass fraction of species i

Chapter 1. Introduction

Chapter overview

The current chapter presents a brief overview of the project and its importance in the context of renewable energy, particularly applied to hydrogen (H₂) applications, including H₂ storage, safety and utilisation. In this chapter, foam-based reactors are introduced as technologies addressing the heat and mass transfer limitations in three specific H₂-based processes. The aim and specific objectives are briefly stated, each addressing a particular research question linked to the H₂ applications studied throughout this thesis. Lastly, the chapter also outlines the layout proposed in the thesis.

1.1 Background

In the year 2015, the United Nations proposed 17 sustainable development goals as part of a plan of action for countries to implement in the just transition towards a more inclusive, sustainable and resilient path benefiting the people and the planet. Among those, Goal 7 was a challenge for various nations and stakeholders worldwide to ensure access to affordable, sustainable and modern energy for all (United Nations, 2015). Since the energy demand is ever growing due to the rapid industrialisation and the adoption of modern society lifestyle, renewable energies are expected to play a significant role in the energy mix of the future decades. Fortunately, there has also been a growing consensus among decision makers that renewable energies are the choice of predilection to bring about a world characterised by prosperous economies, sustainable societies and equitable development (REN21, 2023).

The shift from fossil fuel toward renewable energy sources is slowly taking place around the world. As of the year 2022, a total of 174 countries had adopted clearly defined policies targeting an increase in the share of renewable energy sources in their national energy generation strategies. Worldwide, the contribution of renewable energy sources towards the final energy supply has increased significantly over the past decade. In the field of heat and electricity generation, this increased has amounted to 2.6% and 8.7%, respectively (REN21, 2023).

The transition to a more sustainable economy is driven by the deployment of specific technologies. In the power sector, solar and wind power accounted for 92% of new additions

in 2022 (REN21, 2023). The wider spread of these particular technologies has been hindered by their relatively high costs (compared to conventional fossil fuels) (Hassan et al., 2024) and their seasonal variability (Paraschiv and Paraschiv, 2023). Presently, in many regions in the world including Africa, the costs of solar and wind power generation have significantly decreased thanks to technological optimisation (Hassan et al., 2024; Osman et al., 2023). The issue of fluctuating renewable energy output is currently addressed through the development of energy storage systems aiming at balancing the energy supply and the energy demand (Al Shaqsi et al., 2020; Tan et al., 2021).

Energy storage systems can be classified into various types including electrical, electrochemical, mechanical, thermal and chemical systems (Tan et al., 2021). Each presents advantages and disadvantages when considering efficiency, discharge time, storage capacity, cost, geographic location and scale (Møller et al., 2017). Arguably, chemical storage systems present several advantages over the other systems—they offer longer storage times and a wider scale of applications ranging from several megawatt- to a terawatt-hours of stored energy (Møller et al., 2017; Revankar, 2019). In a chemical storage system, energy is stored in the form of chemical bonds between atoms in a molecule and energy is released through specific chemical reactions (Revankar, 2019). The storage molecule is then referred to as an energy carrier (Revankar, 2019).

One of the most promising energy carriers is green H₂ which is a non-toxic and clean molecule (zero carbon) generated via water electrolysis fuelled using renewable energy sources (Le et al., 2023; Revankar, 2019). Table 1-1 summarises some of the properties of H₂ (Rivard et al., 2019). The high gravimetric energy density of H₂ makes it an attractive fuel for heating applications (Kozhukhova et al., 2021) or in electricity production via the fuel cell technology (Hassan et al., 2024).

Table 1-1. Physical properties of H₂

Property	Value
Energy density (MJ/kg)	120
Density at 0°C, 1 bar (kg/m ³)	0.09
Liquid density at –253°C, 1 bar (kg/m ³)	70.8
Flammability limits in air (vol.%)	4–75
Diffusion coefficient in air (cm ² /s)	0.61

There are, however, major practical challenges related to the use of H₂ as energy carrier. First, the storage of H₂ is challenging due to its low volumetric density (Modisha et al., 2019; Møller et al., 2017). The most conventional H₂ storage methods involve its compression or its liquefaction at harsh temperature and pressure conditions (Garidzirai et al., 2023; Modisha et al., 2019; Tarhan and Çil, 2021). These physical-based H₂ storage technologies present disadvantages including safety issues, boil-off losses and high operational costs (Modisha et al., 2019). To overcome these challenges, the use of alternative material-based technologies such as liquid organic H₂ carriers (LOHCs) have been extensively explored for their practical advantages. LOHCs can be catalytically hydrogenated, transported without H₂ losses over long distances using existing infrastructures, and finally catalytically dehydrogenated at the point of use (Garidzirai et al., 2023; Modisha et al., 2019).

Second, H₂ is highly flammable. Its fast diffusion speed in air (~20 m/s) makes even small leaks unsafe due to the high potential to rapidly form an explosive H₂–air mixture (Møller et al., 2017). To mitigate the risks of detonation during leaks, methods such as ventilation or the passive autocatalytic recombination (PAR) of H₂ have been used (Malakhov, 2020). Ventilation involves the natural or forced convection of an unsafe gas mixture to prevent H₂ accumulation in confined areas. Unlike ventilation, PAR mitigates the risk of H₂ accumulation more directly by catalytic oxidation to H₂O. This technique is intrinsically safe as it converts H₂ at ambient temperature and without the formation of NO_x gases typically occurring during the direct H₂ combustion at high temperatures (Du Preez et al., 2022).

Alternatively, green H₂ can also be further converted to denser compounds. This is one way to decarbonise the hard-to-abate sectors of the chemical industry. In this concept, known as Power-to-X, excess renewable energy can also be used to provide the necessary heat for the hydrogenation of nitrogen (N₂) or carbon dioxide (CO₂) to produce ammonia (NH₃), methane (CH₄) or methanol (MeOH) (Chiuta et al., 2016; Engelbrecht et al., 2016). In view of the safety issues related to NH₃ or the challenge in storing and transporting gases such as CH₄, MeOH can be considered a material of choice in the conversion of H₂ to energy-dense compounds (Olah, 2005).

All in all, H₂ is a versatile molecule that will play an important role in the transition from a fossil-fuel based economic model towards a model based on renewable energies. Nevertheless, many technical challenges still need to be addressed in each of the H₂ applications in a sustainable economy.

1.2 Problem statement

Similar to other catalytic processes, H₂ energy applications are also subjected to heat and mass transport limitations. These limitations can affect process efficiency by decreasing throughput, and conversion or selectivities towards desired product/s. Therefore, it is crucial to design suitable process-intensifying catalytic reactor beds that can improve the process performance by facilitating heat distribution and mass transport.

1.3 Motivation

The focus of this study is on specific H₂ energy applications relevant to the sector of H₂ production/release from LOHCs, the H₂ safety and the H₂ utilisation in the Power-to-X context.

a. Perhydro-dibenzyltoluene dehydrogenation

Dibenzyltoluene/perhydro-dibenzyltoluene (H₀DBT/H₁₈DBT) has been considered as one of the most promising LOHC systems for the safe storage, transportation and distribution of H₂ due to its nonflammability, low toxicity, high storage capability (56 g_{H₂}/L), low cost and compatibility with existing fuel infrastructures (Dürr et al., 2021; Xu et al., 2024). The endothermic H₂ storage on H₀DBT occurs at temperatures of 150–200°C and pressures of 30–100 bar. Its release from H₁₈DBT is exothermic and can be achieved at temperatures of 250–320°C at atmospheric or sub-atmospheric pressures (Park et al., 2021). This LOHC system is characterised by a high boiling point (~355 to 407°C) and low melting point (–39 to –34°C). This allows the LOHC to remain liquid during the release of a high-purity H₂ gas during the dehydrogenation reaction (Ali et al., 2022; Park et al., 2021). The LOHC pair generally has a good thermal stability which ensures its recyclability after multiple hydrogenations/dehydrogenations (Shi et al., 2020).

b. H₂ removal by PAR

The PAR of H₂ is a well-established technique that has been extensively used particularly in nuclear power plants to mitigate the risk of explosion during accidental H₂ release (Avdeenkov, 2018; Bezgodov, 2022). This concept is now extended to a broader H₂-based industrial sector as a safety measure to prevent H₂ concentrations from reaching ignition limits (Du Toit et al., 2018). Basically, H₂ leaks can occur at all stages of a H₂-based economy, including the production H₂ in electrolyzers, the storage and transportation in

compressed or liquid H₂ tanks and, of course, during the H₂ utilisation in fuel cells or as a feedstock in the chemical industry. As the catalytic H₂ combustion is an exothermic reaction, the development of PAR reactors is also guided by the desire to prevent hot spot formation. These hot spots are weak points at which unintended gas-phase H₂ ignition could occur (Kirillov, 2022).

c. Direct CO₂-to-MeOH synthesis

MeOH is one of the most in-demand products of the chemical industry. Its production has nearly doubled over the past decade (IRENA and Methanol Institute, 2021). Most of the MeOH available worldwide is still produced from fossil fuels and contributes to nearly 10% of CO₂ emissions of the chemical industry (Dang et al., 2019; IRENA and Methanol Institute, 2021). As a sustainable alternative, green MeOH is synthesised from captured CO₂ and green H₂ (i.e. direct CO₂-to-MeOH synthesis) (IRENA and Methanol Institute, 2021). Compared to fossil fuel-based MeOH, green MeOH can be produced from a diversity of renewable feedstocks at reduced emissions of SO_x, NO_x and particulate matter (IRENA and Methanol Institute, 2021).

MeOH production is a well-established technology with developed infrastructures. MeOH can be used as fuel in internal combustion engines (blended with gasoline) or in direct MeOH fuel cells (Olah, 2005). It is an excellent solvent and feedstock for the synthesis of various hydrocarbons including dimethyl ether, biodiesel and olefins (Pellegrini et al., 2011).

Besides being H₂-based catalytic processes, these three applications also have in common the fact that heat management and mass transfer play a significant role in their respective performances. Poor heat distribution in the catalyst bed can result in the formation of hot spots which could decrease the catalytic performance or even lead to a localised catalyst deactivation (Kozhukhova et al., 2021). Specifically, during the H₁₈DBT dehydrogenation, hot-spot formation can accelerate the degradation of the LOHC molecule and decrease its recyclability (Modisha and Bessarabov, 2020). During PAR, hot spots can increase the risk of the uncontrolled, spontaneous gas-phase combustion of H₂ (Malakhov, 2020). In the MeOH synthesis process, increased temperatures decrease the catalyst lifetime through sintering of the active metal and carbon deposition on the catalyst surface (Liang et al., 2019).

Enhancing the mass transfer between the reactants and the catalyst phases can improve the effectiveness factor of the catalytic system, the overall apparent kinetics and ultimately the catalyst performance in processes characterised by strong diffusional limitations (Ali et al., 2022; Gancarczyk et al., 2019; Gascon et al., 2015). LOHC dehydrogenation processes are characterised by high liquid–solid mass transfer resistances which often require the use of large amounts of catalytic material (Prieto et al., 2023). The PAR of H₂ is a relatively fast reaction, but limitations due to external (gas–solid) mass transfer can be important at certain hydrodynamic conditions inside a recombiner (Sandeep et al., 2019). In the direct-CO₂-to-MeOH synthesis, significant mass transfer limitations can occur in relatively large fixed-bed reactors (Silva et al., 2024).

In this investigation, metal foams were selected for use in process intensification technologies—they were utilised as catalyst support structures in reactors used for three different H₂ energy applications. Metal foams have the following advantageous characteristics (Gancarczyk et al., 2019; Ochońska-Kryca et al., 2013).

- High volumetric surface areas, which improve mass transfer through decreased reactant/product diffusion length on the catalyst coated on the metal foam surface.
- High porosities, enabling intensive radial mixing which improves convective heat transfer and facilitates gas phase diffusion.
- High thermal conductivities (due to the presence of the metallic substrate), which improves heat distribution through the catalyst bed.
- Low pressure drop in the catalyst bed, even during reactions conducted at high space velocities.
- Compact and lightweight materials, which simplifies the catalyst bed handling procedures.

These properties provide indications that coating a catalyst on the surface of a metal foam has the potential to improve the overall catalytic performance of a given process due to improved heat and mass transport characteristics. A comparison between the foam-based and other commonly used reactors will be required to confirm the benefits of the foam properties in the respective processes studied.

1.4 Aims and objectives

The aim of this study was to evaluate the performances of three foam-based catalytic reactors used for selected H₂-based processes, namely the dehydrogenation of H₁₈DBT, the PAR of H₂ and the direct-CO₂-to-MeOH synthesis.

For each of these processes, suitable catalysts were either purchased or developed in-house and then coated on the surface of metal foams of specific properties. They were characterised using well-known catalyst or foam characterisation methods. The performances of the coated foams were evaluated at appropriate experimental conditions and compared either experimentally or through computational simulations to the performances of catalytic configurations typically used for each process.

The specific objectives of this study and their related research questions are as follows.

- I. Experimentally compare the catalytic performances of in-house developed foam-based reactors with pellet-based reactors used for the dehydrogenation of H₁₈DBT with a special emphasis on the degree of dehydrogenation, H₂ productivity and catalyst durability. The dehydrogenation process will be carried out in a tank reactor and a packed bed reactor (PBR) at different operating conditions.
How do the performances of a foam-based and pellet-based reactors compare in batch and continuous LOHC dehydrogenation systems?
- II. Experimentally assess the H₂ removal efficiency and temperature distribution in a foam-based recombiner and compare its performance to those of a plate-based and pellet-based reactors used for the PAR of H₂.
How do the performances of a foam-based, plate-based and pellet-based reactors compare during the PAR of H₂?
- III. Experimentally investigate the catalytic performance of a commercial catalyst and the temperature distribution during the catalytic tests in a foam-based, bench-scale, modular reactor designed for the direct-CO₂-to-MeOH synthesis process.
What is the effect of the reaction conditions on the catalytic performance and temperature profile of the foam-based reactor?
- IV. Make use of a 3D homogeneous computational fluid dynamics (CFD) simulation—validated by experimental data—for the description of reaction

phenomena inside the reactor modules and for the comparison of the performances of foam-based and pellet-based direct-CO₂-to-MeOH synthesis reactors.

Can pseudo-homogeneous 3D CFD models using adapted kinetics be used to simulate the performances of a foam-based reactor and predict that of a pellet-based reactor?

1.5 Thesis layout

This thesis comprises seven chapters. At the time of the final submission of the thesis (February 2025), the content of three chapters (Chapters 3, 4 and 5) have been published in accredited peer-reviewed journals.

Chapter 1 is an introductory chapter. It briefly describes how this investigation fits in with the general context of the H₂ economy. Furthermore, it presents the overall aim and the objectives of the investigation.

Chapter 2 presents a literature review of the methods used in the development of foam-based reactors used in various H₂-based processes. It provides detailed information on the manufacture of metal foams and catalyst coating methods. Moreover, typical foam-based reactor designs used in biphasic and triphasic H₂ applications are explored and compared with conventional catalytic systems where possible. Lastly, different methods of foam-based reactor simulations are briefly reported on.

Chapter 3 reports the experimental results obtained during the study of performance evaluation of foam-based reactors in the dehydrogenation of H₁₈DBT. A comparison between foam-based and pellet-based reactors' catalytic activity results was carried out in an effort to understand the possible roles of the foam properties on the differences in their performances. The results obtained in this chapter have recently been accepted for publication as a research article [Musavuli, K.C. *et al.* 2025. Metal Foam as Surface-Extended Catalyst Support Structure for Process Intensification in the Dehydrogenation of Perhydro-Dibenzyltoluene on a Pt/Al₂O₃ Catalyst. *Catalysts*, 15(1): 44].

Chapter 4 reports both experimental and CFD modelling results obtained during the investigation of a foam-based reactor used for the PAR of H₂. The performance of a foam-based recombiner was assessed and compared to two other configurations, namely: plate-based and pellet-based recombiners. The results obtained for these experiments have recently been accepted for publication as a research article [Musavuli, K.C. *et al.* 2024. Passive autocatalytic

recombination of hydrogen on a Pt/Al₂O₃-coated metal foam: Experimental evaluation and CFD modelling. *International Journal of Hydrogen energy*, 94,1374–1388].

Chapter 5 reports the results of an experimental investigation of a foam-based reactor used for the direct-CO₂-to-MeOH synthesis at different operating conditions. The performance of the reactor was evaluated and the temperature profiles are shown for a selected reactor operating condition. The results reported herein have been published as a research article [Musavuli, K.C. *et al.* 2023. Experimental evaluation of a coated foam catalytic reactor for the direct CO₂-to-methanol synthesis process. *ChemEngineering*, 7(2):16].

Chapter 6 reports the simulation results of the performance of the bench-scale reactor investigated in Chapter 5. Experimental results reported in Chapter 5 were used to validate the kinetic model used in the CFD simulations. The model was further used to compare the performance of the foam-based reactor to that of a PBR.

Chapter 7 presents the conclusions of this study and offers recommendations for future studies on the application of catalytically activated foams for H₂ applications.

Throughout the thesis, the referencing style follows the guidelines recommended by the North-West University, except in the chapters that have been published in peer-reviewed articles (i.e. Chapters 3, 4 and 5). In these chapters, the referencing style was kept as stipulated by the respective journals in which they were published. However, for enhanced clarity, the numbering of the sections, equations, figures and tables was adapted to match the style used in the thesis.

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Chapter 2. Literature review on the stages of development and the configurations of metal foam-based structured reactors for catalytic hydrogen applications

Chapter overview

This chapter summarises recently reported steps in the design of structured reactors using metal foams as catalyst support structures for process intensification in various hydrogen (H_2) applications. First, metal foam manufacturing methods provide an insight into the origin of their unique geometric features. Second, the methods of catalytic activation of the metal foam substrates are described for various H_2 applications. Third, the configuration of different foam-based reactors used for H_2 applications are explored and compared to conventional reactors. Finally, the foam reactor simulation methods are briefly discussed to understand the options available for the modelling and optimisation of foam-based reactors.

2.1 Introduction

The increased interest in CO_2 emission reduction and climate change mitigation has resulted in several research works directed towards the development of more sustainable chemical processes that incorporate a greater input of renewable sources while targeting improved process efficiencies through reduced material and energy consumption as well as minimum waste generation (Tafete and Habtu, 2023). Several of these processes involve multiphase systems that have heat and mass transport limitations. To overcome these limitations, new types of process-intensifying technologies have been developed, which enabled the design of more efficient reactors grouped under the term ‘structured reactors’ (Gascon et al., 2015).

Structured reactors have received increasing attention from the scientific community after the St. Petersburg (Russia) seminar on monolithic catalysts in 1995, followed by the ‘International Conference on Structured Catalysts and Reactors’ (ICOSCAR) conferences which provided an overview of the development of structured materials for catalytic processes (Kapteijn and Moulijn, 2022).

Cybulski and Moulijn (2010) described structured reactors, generally, as devices whose catalytic section is characterised by well-defined, detailed geometric structures, which greatly simplify the fluid hydrodynamics by enabling a nearly uniform and laminar flow while

improving the contact between the active catalyst and reactants at decreased pressure drops. Additionally, structured reactors exhibit good mechanical stability (Laguna, 2016). Fig. 2-1 shows some of the most common catalyst support configurations used in structured reactors, including the monoliths, microchannels, corrugated plates, wire meshes and foam reactors (Kapteijn and Moulijn, 2022; Porsin et al., 2016).

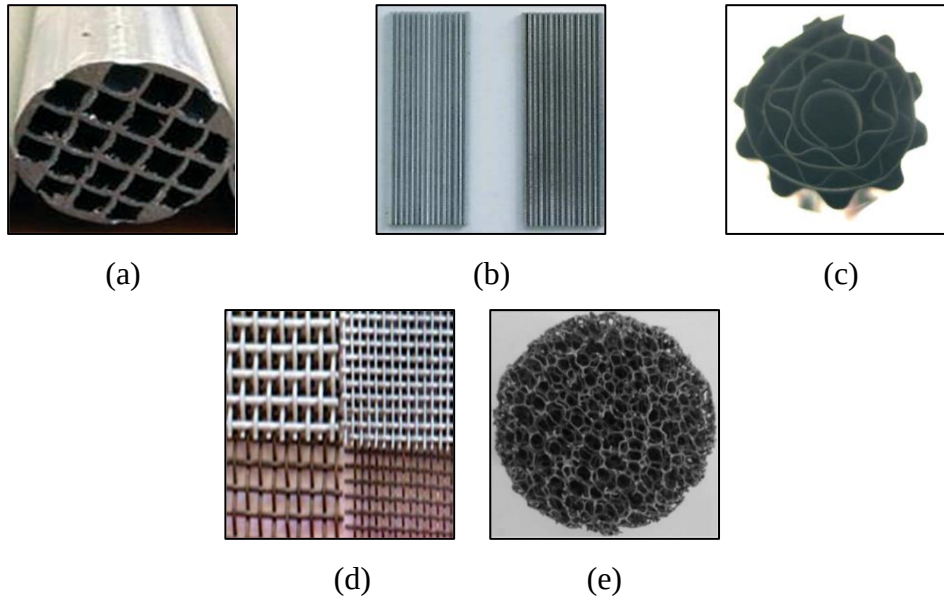


Figure 2-1. Illustrations of surface-extended catalyst support structures: (a) monolith (Montebelli et al., 2014a), (b) microchannel plate (Meille, 2006), (c) corrugated plate (Montebelli et al., 2014a), (d) wire mesh (Porsin et al., 2016) and (e) foam (Lali, 2016)

Monolith reactors, also referred to as ‘honeycombs’, consist of parallel, segregated channels whose walls are coated with a thin layer of catalyst (Fig. 2-1a). They can be manufactured using extrusion methods or by the alternate arrangement of corrugated and flat foils (Montebelli et al., 2014a). Monolith reactors have porosities of 70–90% and they are often characterised by the number of cells per square inch (Govender and Friedrich, 2017). The small size of their cells combined with the thin catalyst washcoat layer result in very laminar flows and improved mass transfer between the reacting and catalytic phases (Montebelli et al., 2014a; Palma et al., 2019). Monoliths have been used in several processes such as selective CO oxidation (Zhang et al., 2012.), Fischer–Tropsch synthesis (Zhu et al., 2021) and steam reforming of natural gas (Roh et al., 2010). Unfortunately, the geometric features of the honeycomb reactors do not allow for radial mixing and cause the process to work under adiabatic conditions which renders temperature control more difficult than in conventional packed bed reactors (PBRs) for instance (Kapteijn and Moulijn, 2022; Montebelli et al., 2014a).

Microchannel reactors are miniaturised compact devices consisting of a network of capillary channels ($< 1\text{ mm}$) coated with thin layers of catalyst (Suryawanshi et al., 2018) (Fig.2-1b). These reactors are manufactured by precise chemical or laser etching of metallic plates, with subsequent coating of the active catalysts on the walls of resulting channels. They have high surface-to-volume ratios of $\sim 10000\text{--}50000\text{ m}^2/\text{m}^3$ (Castaldi, 2009). Compared to conventional reactors, microchannel reactors offer the advantages of high heat and mass exchange, intrinsic safety and precise reaction parameter control (Dong et al., 2021). Due to their reduced dimensions, they naturally have low throughput; however, this problem is easily overcome thanks to their modular nature which allows processes to be scaled-out by the numbering up of identical reactors or by increasing the length of the channels (Engelbrecht et al., 2020). The applications of microchannel reactor technology in catalytic reactions include CO_2 methanation (Engelbrecht et al., 2016), formic acid dehydrogenation (Ndlovu, 2018), ammonia decomposition (Chiuta et al., 2016) and perhydro-dibenzyltoluene dehydrogenation (Ali et al., 2022a). Despite their apparent advantages, microchannel reactors are generally costly to produce, their channels can be easily clogged by reaction species (e.g. precipitation reaction or highly viscous liquids) and high pressure drops could result from operating them at high throughputs (Dong et al., 2021).

Corrugated plates (Fig. 2-1c) are structures commonly used in the chemical industry, for instance as packings for absorption or reactive distillation processes. They can be arranged in parallel sheets with the corrugations oriented inclined to their axes. They are characterised by high thermal conductivities, geometric surface areas and high porosity, which result in low pressure drops and efficient radial mixing (Cybulski and Moulijn, 2010; Pangarkar et al., 2008). Corrugated plates have been used for non-catalytic applications such as flame quenching materials during H_2 explosions (Nie et al., 2024). They have also been used as catalyst support structures for H_2 applications such as the dehydrogenation of perhydro-dibenzyltoluene (Nathrath et al., 2024).

Wire meshes consist of interwoven metal wires which can be coated with a thin layer of a catalyst (Fig. 2-1d). Their high mechanical strength and thermal conductivity make them suitable for fast, highly exothermic reactions (Matatov-Meytal and Sheintuch, 2002). Metal meshes have been used for the catalytic combustion of H_2 (Du Preez et al., 2020a) or syngas (Li et al., 2009). Mass transfer coefficients in metal meshes are much higher than in monoliths. Radial mass transfer and high thermal conductivity result in uniform flow and temperature

distribution in the reactor (Porsin et al., 2016). Wire meshes are also characterised by a low specific surface area. Conventional catalyst deposition methods result in non-uniformity and poor adhesion. Preferably, only thin catalyst layer ($< 50\ \mu\text{m}$) should be coated on wired mesh (Matatov-Meytal and Sheintuch, 2002).

Lastly, foam-based reactors have reticulated, sponge-like structures that comprise a highly porous material coated with an active catalyst (Fig. 2-1d). They are characterised by their open cells, interconnected struts and high porosity ranging between 80 and 98% (Banhart, 2001; Giani et al., 2005). The geometric configuration of the foam-based catalyst bed enables low resistance to fluid flow, high tortuosity and high turbulence causing rapid reactant mixing within the catalyst bed (Banhart, 2001; Lucci et al., 2015; Vicente et al., 2006). Foam structures are generally made of ceramic (alumina, silicon carbide) or metallic substrates (Al, steel, Cu, Ni, NiFeCrAl, FeCrAl) characterised by their low density, high mechanical strength and high surface-to-volume ratios (Kolaczowski et al., 2016; Voltolina et al., 2017). Foam-based reactor beds typically have low gravimetric surface areas, but this limitation is compensated for by their high volumetric surface areas, which result in higher effectiveness factors than those obtained on conventional pellet-based catalyst beds (Kolaczowski et al., 2016). The specific surface area of the foam is usually improved by coating a high-surface-area catalyst on the surface of the struts (Kolaczowski et al., 2016). Coating an active catalyst on ceramic foams is usually easier than on metal foams because of the higher surface roughness of the former (Montebelli et al., 2014a). Besides, ceramic foams are brittle, exhibit poor resistance to mechanical stress and can easily be clogged (Lali, 2016). Metal foams are particularly advantageous in processes involving highly exothermic or endothermic reactions as they prevent the formation of hot spots because of their relatively high thermal conductivities (Bianco et al., 2021; Vicente et al., 2006). Foam-supported catalysts have been used as catalyst support structures in various processes including methanol (MeOH) synthesis (Montebelli et al., 2014b), methane (CH_4) steam reforming (Wang et al., 2021; Zhou et al., 2017), Fischer–Tropsch synthesis (Aguirre et al., 2021; Egaña et al., 2018), partial oxidation of CH_4 (Maestri et al., 2005), catalytic H_2 combustion (Fernández et al., 2016a), H_2 and O_2 evolution reaction (Park et al., 2022; Pérez-Alonso et al., 2015).

Several reviews discussing foam-based catalytic structures have been published to date. Makhania and Upadhyayula (2022a) provide a brief overview of catalytic foam preparation methods and the processes in which foams were used as catalyst beds, as well as the modelling

attempts of foam-based catalytic processes. Interestingly, the review mentions some of the disadvantages observed in foam-supported catalysis; these include lower catalyst inventory than in conventional PBRs of the same volume, the tendency towards pore clogging, low adhesion of the catalyst washcoat, occasional diffusion resistance and active component leaching from the washcoat. Meille (2006) and Montebelli et al. (2014a) extensively reviewed the surface pretreatment techniques to improve catalyst adhesion, washcoating and catalyst activation methods to coat the active material onto the support structures, including foams. Their extensive reviews offer insight into the most appropriate methods to use considering the nature of the substrate and the desired properties of the catalyst layer deposited on it. In a review more specific to photocatalytic processes, Warren (2023) describe the foam manufacturing methods, proposed a classification of foams based on their pore size and identified the potential benefits of using foam-based catalytic water treatment reactors compared to slurries and other immobilised catalysts. A review by Yang et al. (2021) presents the main governing equations of fluid flow in open-cell metal foams, with special emphasis on the development of pressure drop correlation for various models reported in the literature.

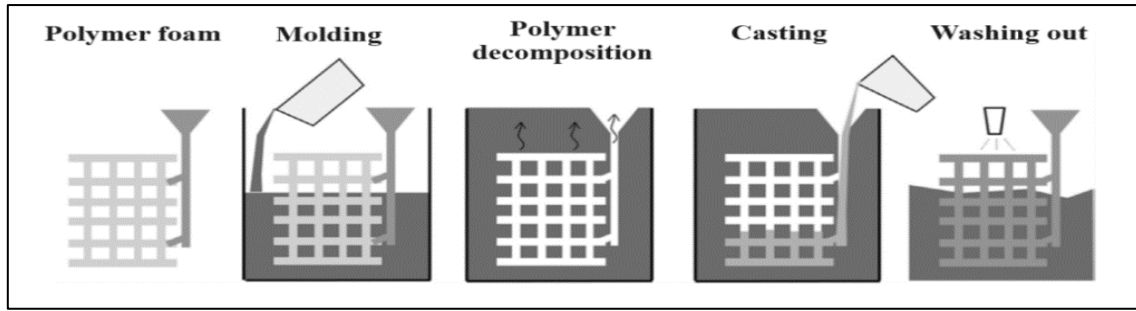
In this chapter, the main processes involved in the development of catalytically activated open-cell metal foam reactors used for H₂ applications will be addressed. Firstly, metal foam manufacturing methods will be briefly explored to understand the origin of foam's unique physical and geometrical properties. Secondly, an overview of the catalyst deposition methods will summarise the steps taken to develop the active catalyst layer on the surface of the foam. Thirdly, experimental foam-based reactor configurations for H₂-based processes will be briefly described. Performance comparison with conventional reactors will be reported to assess the advantages of foam-based structures in H₂-based catalytic processes. Lastly, different numerical modelling and simulation techniques of foam-based H₂ processes will be provided to understand the potential of computational methods in the process description and, eventually, the optimisation of foam-based reactor technology.

2.2 Open-cell metal foam features and methods of fabrication

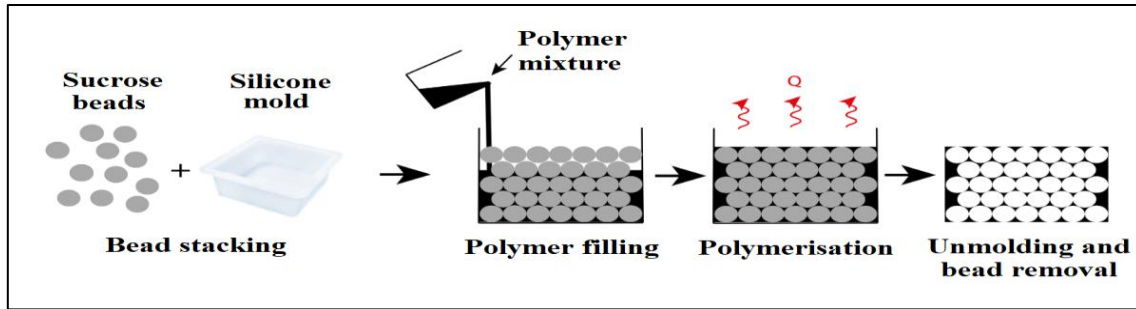
As foam support structures constitute the heart of foam-based catalytic reactors, it is pertinent to understand what the important features of these materials are and how they are manufactured. Foam structures can be broadly classified into two categories: open-cell and closed-cell foams. Open-cell foams are highly-porous, reticulated materials made up of a network of generally irregular, interconnected pores, delimited by thin metal wires called

struts, interlinked through lumps called junctions (Bianco et al., 2021; Inayat et al., 2011b; Voltolina et al., 2017). They are opposed to closed-cell foams whose pores are separated by thin walls and which, for obvious reasons, are generally not suitable for catalytic applications. Open-cell foams are considered excellent support structures for catalytic processes because of their low density, high porosity, high volumetric surface area and superior thermal properties (Duan et al., 2006; Inayat et al., 2011b, 2011a; Lucci et al., 2015). Their low density makes them ideal candidates for the design of light reactors (Dukhan, 2006). The foam's reticulated structure and high porosity enhance the tortuosity of the fluid flow and improves reactant mixing. In heterogeneous catalytic processes, high effectiveness factors can be achieved because of their high porosity and high volumetric surface area. Rapid heat dissipation can be achieved by different transport mechanisms, namely convection and radiation through the pores, as well as conduction through the struts in the case of metal foams. These advantageous properties of the open-cell foams are a function of the foam's cell size, strut diameter and pore density often expressed as 'pores per inch' (PPI), which are tuned up during the manufacturing process of the material (Montebelli et al., 2014a, Ashby et al., 2000).

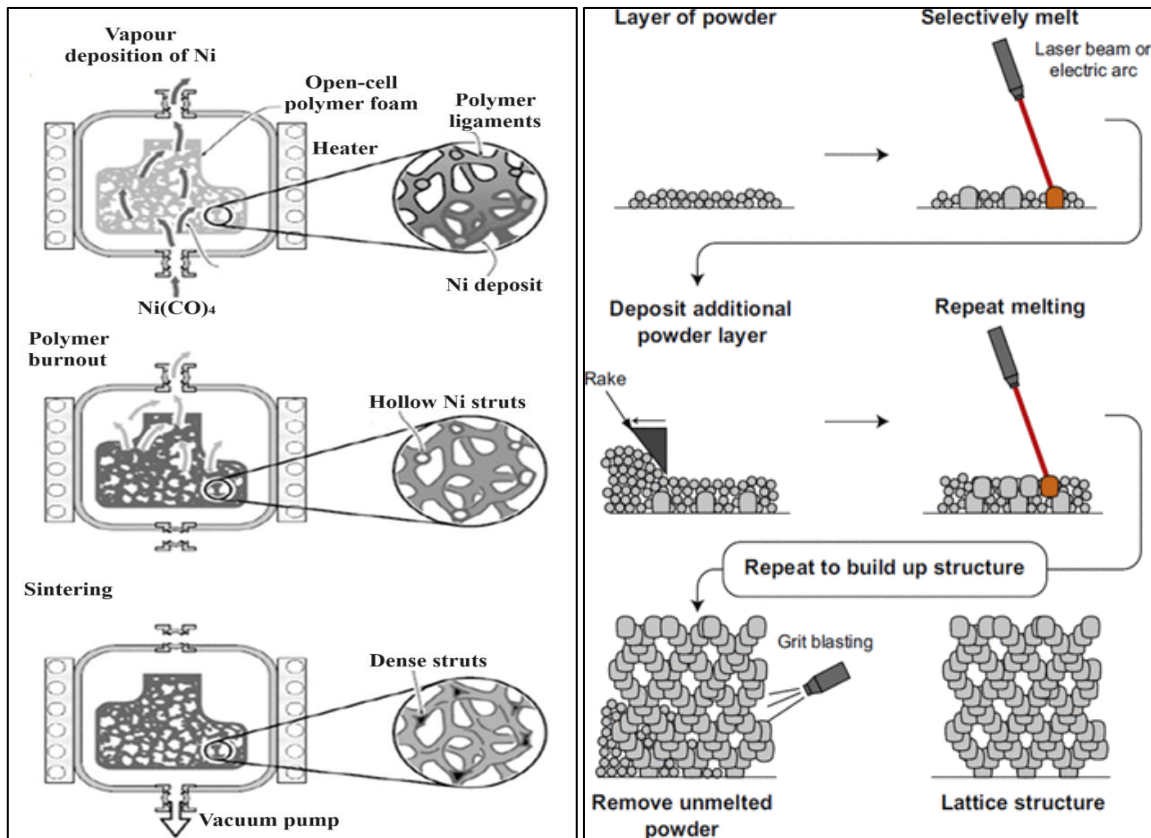
Various methods of open-cell metal foam production have been developed. They can be produced by investment-casting, metal deposition, leaching or space holder technique and 3D printing. These methods are illustrated in Fig. 2-2. In the investment-casting method, a mould is created using an open-cell polymer precursor (Fig. 2-2a). The mould is then coated with ceramic and later embedded in casting sand. The mixture is then subjected to high temperatures that cause the decomposition of the polymer precursor and the hardening of the casting sand. Molten metal or alloy is then poured into the resulting hollow structure, cooled down and extracted from the mould to form open-cell foams of pore sizes 1–5 mm and relative densities of ~ 0.05 (Ashby et al., 2000). Kapłan et al. (2022) used the investment casting method to manufacture open-cell Mg alloy foams (10 and 20 PPI) shaped by a polyurethane precursor which was burned at 730°C before the Mg alloy was cast in at 660–680°C. Firoozbakht et al. (2023) manufactured 10 PPI open-cell Al alloy foams using polyurethane precursor embedded in a commercial investment powder. The mixture was thermally treated to remove the precursor and stabilise the block mould. In efforts to gather understanding of the effect of casting condition on the foam properties, Al alloy was subsequently cast at temperatures of 700 and 740°C, while the mould temperature was varied between 575 and 750°C.



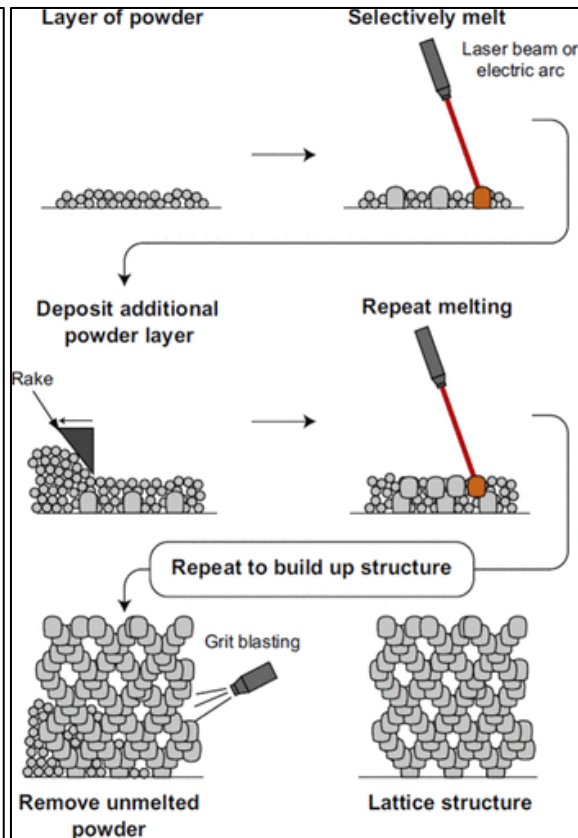
(a)



(b)



(c)



(d)

Figure 2-2. Illustrations of open-cell foam manufacturing methods by (a) investment casting (Kaplon et al., 2022) (b) space holder technique (Kubelka et al., 2022), (c) metal (Ni) deposition (Ashby et al., 2000) and (d) 3D printing (Hassan and Alnaser, 2024)

Metal foams can also be manufactured by the space-holder technique which involves co-compacting two materials, a metallic powder and a soluble material (Kaplon et al., 2022) (Fig. 2-2b). The space-holder consisting of soluble material such as NaCl, NaAlO₂ is removed by a suitable solvent after the mixture has been consolidated and subjected to heat in order to sinter the metal powder. A variation of this method consists in pouring molten metal to fill the void around the space holder, subsequently cooling the mixture and removing the space holder after solidification of the metal (Firoozbakht et al., 2023). In general, the space holder method results in very uniform foam materials with relative densities of 0.3–0.5 and cell size between 10 µm and 10 mm (Ashby et al., 2000). Gök (2021) produced a highly porous Ni foam using KBr as space holder. The method involved mixing Ni powder with KBr at a volumetric ratio of 3:7. The mixture was subjected to a pressure of 200 bar then to temperature of 1050°C to sinter the Ni powder. After cooling, KBr was removed by dissolution in water. The space holder and the investment casting techniques can also be combined into a two-step foam manufacturing method. For instance, Kubelka et al. (2022) used this method to manufacture regular body-centred open-cell Al foams. In the first step, sucrose beads (diameter: 6 mm) were used as space holders while epoxy resin was the polymer precursor for the Al foam. After the sucrose was dissolved in water, the remaining matrix was embedded in ceramic and burned out at 720°C before Al was cast into the resulting mould at 750°C.

The metal deposition method is used for obtaining open-cell foams with hollow struts (Fig. 2-2c). This technique uses chemical vapour deposition, electrodeposition or evaporation to coat a polymer foam template with a metal layer (e.g. Ni or Ti). The polymer is then burned away leaving a foam of the desired shape and size. Pore sizes 100–300 µm and relative densities of 0.02–0.05 can thus be generated (Ashby et al., 2000). INCOFOAM[®] Ni foams (5–130 PPI) were produced by chemical vapour deposition Ni(CO)₄ on polyurethane foam. Densities of 0.2–2.6 g/cm³ and porosities up to 98% are obtained using this process (Paserin et al., 2003). Besharati and Paydar (2023) produced a 10 PPI Cu foam by electrodeposition of Cu (from Cu plate anodes) on polyurethane precursor. The process was carried out by immersing the polyurethane foam (cathode) in the electroless Cu plating bath at 55°C and at a pH of 12.5–13.0.

With the progress of computer technologies, computer-aided design software can be used to accurately design a foam geometry which can then be 3D printed by alternatively depositing a layer of metal powder and melting it using laser or electron beam melting until the desired 3D

object is finalised (Hassan and Alnaser, 2024) (Fig. 2-2d). Zhou et al. (2022) applied the selective laser melting technique to produce metal foams from an Al alloy for a thermal energy storage process using a paraffin as phase change material. Their foam fabrication method produced structurally controlled metal foams and could be used in the creation of free-form, optimised foam structures with complex geometries. Costanza et al. (2021) combined 3D printing and investment casting to produce regularly shaped foam composed of truncated octahedron cells. The originality of their method lays in using the fused deposition modelling technique to print polylactic acid which was to be used, instead of wax, in the generation of the mould into which Al was to be casted. The elementary cell thus obtained had a thickness of 1.5 mm and a cell length cell of 2.8 mm.

2.3 Catalyst deposition process on open-cell metal foams

In chemical reactors, open-cell metal foams are generally catalytically inert materials. They act as catalyst support substrates, which are expected to improve the following: (1) mixing, because of the tortuous nature of the fluid flow imposed by their geometric structure; (2) the mass transfer and effectiveness factor of the process, because of their high surface-to-volume ratio and (3) the heat transfer process, because of their high thermal conductivity and high porosity. The catalytic deposition process on the foam substrate involves the following general steps: substrate cleaning, surface pretreatment, support activation (i.e. growth of the catalyst phase on the metal foam) and thermal post-treatment. Techniques related to these steps were extensively reviewed by Meille (2006) and Montebelli et al. (2014a) and will only be briefly summarised in this section with an emphasis on their application in H₂-related processes.

As closed-cell foams are generally not suitable for catalytic applications, in the following sections the term ‘foam’ will be used to exclusively refer to open-cell foams.

2.3.1 Surface cleaning

The cleaning of the surface of metal foams has often been reported as a step aiming at the removal of dust and organic matter from the metal surface. Organic solvents such as acetone and ethanol, or diluted acids such as HCl are often used in this process (Shen et al., 2021; Yu et al., 2007; Zhou et al., 2017). Deionised water can also later be used as rinsing agent (Montebelli et al., 2014b; Shen et al., 2021; Shultz et al., 2022). Increased temperatures (e.g.

80–100°C) or an ultrasonic bath can be used in some cases to improve the efficiency of the impurity removal process (Shultz et al., 2022; Zhou et al., 2017).

The surface cleaning process can be simple, and executed in one step, as reported by Zhou et al. (2017) in their study on H₂ production via MeOH steam reforming using coated Cu foams, where the organic impurities were removed by cleaning the foam in ethanol in an ultrasonic bath. An example of a more complex cleaning is reported by Tang et al. (2024). Prior to their experiments on CO₂ hydrogenation to CH₄, they cleaned their Ni foams by first sonicating them in acetone for 20 min to remove organic impurities, followed by immersing them in 0.1 M HCl for an additional 20 min at ambient temperature in order to remove the Ni oxide from the metal surface. The resulting foams were finally rinsed in deionised water. The surface cleaning process is not expected to alter the chemical composition of the foam substrate. The solvent is often carefully chosen to selectively dissolve and remove the superficial impurities while leaving the substrate intact. For instance, long exposures to a strong acid such as HCl could lead to the complete dissolution of Al foams. For this reason, some authors choose to clean with non-aggressive agents such as deionised water, ethanol or acetone (Löfberg et al., 2011; Montebelli et al., 2014b).

2.3.2 Substrate surface pretreatment

Coating metallic substrates is challenging due to the low adhesion strength of the catalyst washcoated onto the smooth substrate surface. This causes the catalyst to detach from the foam while being handled or during the chemical reaction process. Surface pretreatment methods are therefore used to increase the foam surface roughness. This not only improves its surface area but also the adhesion strength of the catalyst washcoat layer. The main surface pretreatment methods developed for catalytic applications include the oxidation (anodic or thermal), the chemical treatment and the primer deposition (Meille, 2006; Montebelli et al., 2014a).

Oxidative pretreatment methods involve the generation a porous oxide layer by subjecting the substrate to electrochemical (anodic oxidation) or thermal treatment (thermal oxidation). During anodic oxidation, a direct voltage is applied to an electrolyte in which the substrate is immersed. This process increases the surface roughness not only through the formation of an oxide layer but also through the partial dissolution of the substrate into the electrolyte solution. Temperature, current density and voltage are crucial parameters affecting the properties of the oxide layer. To obtain a rough Al surface for better adhesion of a Fischer–Tropsch catalyst,

Almeida et al. (2007) pretreated their Al foams in oxalic acid at a temperature of 50°C and a current density of 2 A/m² for 40 min. The surface treatment resulted in a homogeneous and well-adhered catalyst coating. On the other hand, thermal pretreatment involves calcining the substrate at high temperatures to promote the formation of an oxide layer on the foam surface. This method was applied by Egaña et al. (2018); they thermally treated Al foams and FeCrAl foams in air at 500°C for 2 h and 900°C for 22 h, respectively. Adherence tests conducted using ultrasonication for 30 min at room temperature, resulted in no more than 5% loss for their Fischer–Tropsch catalyst.

During the chemical treatment, metal foam samples are immersed in a strong acidic or basic solution which, by etching or oxidizing the substrate, causes an increase in the surface roughness. For instance, after a cleaning step, Ho et al. (2021) etched the surface of their NiCrAl foam discs in a 5M HCl for 15 min before coating it with a Ru-based catalyst for CO₂ methanation. Chemical treatment can also be combined with thermal oxidation in the metal foam pretreatment step. Such a two-step pretreatment method was used by Catillon et al. (2004) to increase the roughness of their Cu foam used in H₂ production by MeOH steam reforming. For syngas methanation experiments, Li et al. (2016) subjected their Cu, Ni and CuNi alloy foams to etching solutions containing a mixture of acetic acid, sodium dodecyl sulphate and Al(NO₃)₃ or Ni(NO₃)₂ before calcining the Cu and CuNi foams at 300°C and the Ni foam at 500°C for 2 h. Chemical etching resulted in a well-adhered NiO-Al₂O₃ composite on the foam struts.

In some cases, the affinity between the catalyst and the metal foam is low and needs to be improved by the coating of a material, called a primer. Materials such as boehmite, silica or alumina often play the role of primers, used prior to coating the active catalyst (Montebelli et al., 2014a). Chen et al. (2008) coated alumina as primer layer on a CuZn foam before coating the CuZnAlZr catalyst for the H₂ production by steam reforming of MeOH. For H₂-related processes, primer deposition is scarcely reported, anodic or thermal oxidation and chemical treatment are the most commonly used surface pretreatment methods.

2.3.3 Catalyst deposition

Catalysts generally consist of (1) an active metal, which interacts with reactant species and (2) a morphological support, usually a material of high gravimetric surface area, which keeps the active metal well dispersed. These two components can be coated in two separate steps or both

at once. Metal foams are generally inert materials that only play the role of support structures in catalytic processes. Therefore, to be used for catalytic processes, they need to be activated by dispersing a catalyst onto their surface (Fig. 2-3). Methods of morphological support deposition include plasma spraying, electrophoretic deposition, chemical vapour deposition and wet coating. The active metal addition, also referred to as ‘support activation’, can be done by impregnation, electrochemical deposition, electroless plating, deposition precipitation, ion exchange or physical vapour deposition methods such as cathodic sputtering, electron-beam evaporation, pulse laser deposition or flame assisted vapour deposition. Details of these techniques are presented in reviews available in recent literature (Makhania and Upadhyayula, 2022b; Meille, 2006; Montebelli et al., 2014a; Pauletto et al., 2020).

In this sub-section, the focus is on catalyst deposition methods on metal foams commonly used in H_2 applications. They will be classified in two categories, namely: the deposition of supported-metal catalysts and the direct deposition of the active metal on the metal foam.

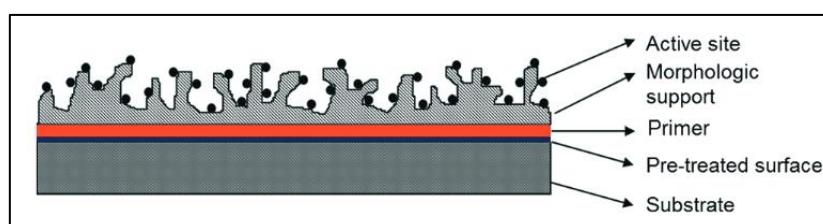


Figure 2-3. Schematics of a foam-supported catalyst (Montebelli et al., 2014a)

2.3.3.1 Deposition of supported-metal catalysts of metal foam surface

The deposition of a catalyst consisting of an active metal and a morphological support is generally performed in liquid phase, which can be a suspension of solid particles in powder form (slurry) or a colloidal dispersion of suitable precursor (sol–gel) (Montebelli et al., 2014a). The coating process steps include: (1) preparing a suitable suspension or sol–gel with determined physicochemical properties (concentration, solid content, viscosity, pH, temperature, etc.), (2) bringing the foam into contact with the liquid phase by either dipping the foam into the liquid mixture (dip-coating) or by spraying the liquid on the foam (spray-coating), (3) removing the excess liquid by blowing inert gas at constant pressure or by spinning the foam at constant velocity, (4) drying the coated foam and (5) repeating the procedure (steps 2 to 4) until the desired loading is achieved (Pauletto et al., 2020). At the end of the wet coating process, the foam-supported catalyst can be subjected to catalyst stabilisation and activation steps which include calcination at elevated temperatures (Aguirre et al., 2021).

a. Suspension or slurry method

Typical suspensions are prepared by mixing a powder, a binder, an acidic dispersant and a solvent. The powder is obtained by crushing a catalyst or a morphological support to a suitable particle size. Smaller particles (e.g. 3 μm) generally result in more adherent catalyst layers than larger particles (e.g. 50 μm) (Mehla et al., 2019). Ball mills are often set to specific parameters to achieve such particle sizes. To prepare their catalyst washcoat, Wang et al. (2021) crushed a commercial $\text{CuO}/\text{Zn}/\text{Al}_2\text{O}_3$ catalyst for 3 h at 1200 rpm to obtain the powder to coat a copper foam used in the MeOH steam reforming process. Similarly, for CH_4 steam reforming tests on FeCr alloy foams, Cristiani et al. (2012) used ZrO_2 balls to crush $\text{Ni}/\text{MgAl}_2\text{O}_4$ powders (mass ratio ball:catalyst = 10:1) dispersed in an aqueous solution of HNO_3 for 24 h. In their experiments on MeOH synthesis from syngas, Montebelli et al. (2014b) obtained stable dispersions by ball-milling a mixture of 20 wt.% commercial Cu-based catalyst, 79.4 wt.% deionised water and methylhydroxyethylcellulose in a 250 mL jar at 40 rpm overnight.

Chemical binders such as boehmite, polyvinyl alcohol or isopropyl alcohol are added to maintain the mixture at the desired viscosity and to ensure a better adherence of the catalyst onto the struts of the metal foams. The binder concentration in the slurry not only plays a critical role in the rheological properties of the mixture but also in the coating process and, consequently, the geometric characteristics of the coated foam. Yun et al. (2015) demonstrated the effect of 1–5 wt.% binder (polyvinyl alcohol) content on the final properties of the catalyst slurry and the coated foam. They observed that increasing the binder content from 3 to 5 wt.% resulted in a nearly fivefold increase in the slurry viscosity to 10000 cP. Higher viscosities decreased the number of coating steps necessary to achieve a desired catalyst loading on the foam. High viscosities can also lead to a tendency to pore blocking. Therefore, binder content should be kept to ~1–2 wt.% in the catalyst slurry. Wang et al. (2021) mixed $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst powder in a 1 wt.% polyvinyl alcohol solution to obtain a suitable viscosity of the slurry used to coat Cu foams for MeOH steam reforming experiments. In the development of a foam-supported Co catalyst for Fischer–Tropsch synthesis, Aguirre et al. (2021) used boehmite and polyethylene glycol as binders to increase the viscosity of the suspension used in the coating process of Al_2O_3 and TiO_2 on Al foams, respectively.

Dispersants are generally acids used to regulate the pH which, in turn, affects the rheological properties and the stability of the suspension. High viscosities can result from the addition of acids which can catalyse cross-linking reactions in the slurry (Montebelli et al., 2014a). Typical

acids used in the suspension preparation include HNO_3 , HCl or citric acid. For their hydrogenation experiments, Lali et al. (2015) used HNO_3 to maintain the pH of an Al_2O_3 suspension below 3.5. They argued that higher pH values inhibit the dissolution of Al_2O_3 . In some cases, the use of acidic dispersants could result in changes in the chemical properties of the catalyst due to the dissolution of the active metal. Montebelli et al. (2014b) resorted to use methylhydroxyethylcellulose as dispersant since they noticed that using HNO_3 resulted in Cu and metal losses in the mother liquor.

Different solvents can be used in the catalyst coating process. Deionised water is by far the least costly, most accessible and most commonly used solvent in H_2 applications (Chen et al., 2008a; Egaña et al., 2018; Lali et al., 2015; Shen et al., 2021). Other solvents include diethyl ether, ethyl acetate, diethyl ether and some alcohols such as ethanol (Montebelli et al., 2014a).

b. Sol–gel method

The sol–gel method has been widely used during the catalyst coating processes on metal foams used in H_2 applications. It entails the preparation of a solution or colloidal dispersion of the chemical precursors of the materials to be coated on the metal foam. A typical sol comprises a solution containing a precursor, an acid for particles dispersion and the solvent (usually deionised water) (Park et al., 2014). A chemical binder such as polyvinyl alcohol can also be used to increase the viscosity of the solution (Jin and Kwon, 2009). In some instances, the morphological support is added to the colloidal dispersion containing its precursor. In this case, the sol also plays the role of a binder (Meille, 2006). Prior to the coating process, the dispersion can be aged for some time (from a few minutes up to several days) to allow gelation of the solution (Meille, 2006). Subsequently, a thermal treatment involving drying and calcination steps is required to generate the desired properties of catalyst morphological support on the surface of the foam.

The sol–gel coating method has been used by several researchers working on H_2 -related processes. For instance, in preparations for the MeOH steam reforming experiments on Cu foams, Catillon et al. (2004) prepared a sol by mixing an acidified colloidal dispersion of α -alumina in water to γ -alumina powders. The foam samples were dried at 100°C for 1 h. To prevent the migration of alumina particles, the samples were subsequently calcined in air—the temperature was increased from 25 to 300°C at a rate of $1^\circ\text{C}/\text{min}$. Jin and Kwon (2009) used sol–gel method to coat alumina on the surface of Ni foams to be used for catalytic H_2

combustion. $\text{Al}(\text{OH})_3$ was produced by the hydrolysis of isopropoxide ($\text{Al}(\text{OC}_3\text{H}_5)_3$) in water. Polyvinyl alcohol was later added to the mixture to increase the viscosity. The mixture was acidified by adding HNO_3 and aged for 30 min. After coating the foams with the precursor, samples were dried at 100°C for 30 min and later calcined in a furnace at 500°C for 12 h. The aim of the alumina layer was to increase the gravimetric surface area of the foam structure before the deposition of the active metal.

c. Active metal deposition

When the morphological support is coated first on the foam surface, a necessary subsequent step then requires the deposition of the active metal on the surface of the support covering the surface of the foam. For H_2 -related catalytic applications on metal foams, this step can be performed using various techniques, including impregnation and coprecipitation methods.

Impregnation is one of the most reported methods of deposition of the active metal of the catalyst on the surface of the foam used for catalytic H_2 processes. In this method, a solution containing a suitable precursor is brought into contact with the foam coated with a high-surface morphological support (Montebelli et al., 2014a). The contact between the foam and solution can be done by wet impregnation or incipient wetness impregnation (Giani et al., 2006; Lacroix et al., 2011). Wet impregnation involves dipping the foam in a solution containing a predetermined amount of precursor of the active metal. On the other hand, incipient wetness impregnation is performed by feeding a determined amount of precursor solution in a dropwise manner onto the foam coated with porous catalyst support. The impregnation is then followed by a drying step, the aim of which is to remove the liquid solvent from the coated pores of the foam. Lastly, the impregnated foam undergoes calcination and reduction steps to generate the active metal phase on the foam. The temperature, the pressure and the duration of the drying, calcination or reduction steps are the main control parameters in the impregnation method (Cimino et al., 2020; Garidzirai et al., 2021; Jo et al., 2010; Lacroix et al., 2011; Lali et al., 2015). Well-dispersed Pd nanoparticles for a hydrogenation reaction were obtained by Lali et al. (2015); they used the wet impregnation method in the deposition of Pd on pre-anodised Al foam samples coated with alumina. Pd acetate was used as precursor. The samples were dried at 100°C for 1 h, then calcined and reduced for 4 h at 300 and 250°C respectively. Jo et al. (2010) used the incipient wetness method to deposit Pt on the surface of Al foam coated with an alumina washcoat layer. The precursor solution consisted of hexachloroplatinic acid (H_2PtCl_6) in acetone. The evaporation of acetone left H_2PtCl_6 particles uniformly spread on the

surface of the alumina-coated foam. Multiple impregnation–drying steps can also be performed on the same foam sample to achieve the desired amount of the active metal in the pores of the support. Jin and Kwon (2009) used this method to deposit Pt on alumina-coated Ni foam. Each step involved the absorption of 100 μL H_2PtCl_6 and 30 min of drying at ambient temperature.

Deposition by coprecipitation of the catalyst active metal is usually carried out by gradually modifying the pH of the solution containing suitable precursors. For instance, Catillon et al. (2004) activated their alumina-coated Cu foam by immersing it in a solution of Cu and Zn nitrates mixed with urea at a temperature of 90°C. As the urea decomposed at 90°C, the pH of the solution increased from 3.8 to 5.8 within 2 h. In their production of H_2 from NH_3 decomposition, Koo et al. (2024) activated their Mg- AlO_x -coated FeCrAl foam through the deposition of Ru by precipitation, using $\text{Ru}(\text{NO})(\text{NO}_3)_x(\text{OH})_y$ as precursor and NH_3 solution as precipitant.

2.3.3.2 Direct coating of active metal on the metal foam surface

In numerous cases the active metals of the catalyst are coated directly on the foam surface without prior coating of a morphological support. In these cases, high catalyst activity can still be achieved by the active metal without interaction with a high-surface morphological support. For H_2 -related catalytic applications on metal foams, the following techniques can be used: electrochemical deposition, electrophoretic deposition, electroless plating and sputter coating.

The electrolytic deposition or electrodeposition method uses an electric current to reduce metal ions in a solution to metals deposited on the surface of a conductive substrate (Saidin et al., 2011). Metal foams used for electrochemical processes have been coated using this method. The size and nature of the deposited metal layer depends on factors that include the deposition time, the current density, the temperature, the chemical properties of the solution, the physicochemical properties of the substrate (e.g. metal foam) as well as the presence of impurities in the solution. Lotfi et al. (2020) developed a highly stable and active foam by multiple-step electrodeposition of Ni, Cu, graphene oxide and Pt on Ni foams. Each deposition step was performed at different conditions. The deposition of Ni and Cu was performed at ambient temperature, a current density of 2 A/cm^2 and pH of 1, over a period of 40 min, while the graphene oxide was deposited at 50 and 20 mA/cm^2 and pH of 9–10, over a deposition time of 120 s. Pt nanoparticles were deposited under a potential of -0.4 V vs SCE. In their study on CO_2 methanation, Ho et al. (2021) coated their NiCrAl foam samples by electrodeposition of

CeO₂, Ni_xCe_y or Ru_xCe_y using nitrate precursors at –1.2 to 1.3 V vs SCE for 600 s. The coating process was completed by a calcination step at 600°C for 6 h. Well-dispersed Ru and Ni species were obtained using this catalyst coating method.

The electrophoretic deposition method uses an electric current to attract the charged solid particles present in a colloidal suspension to electrodes of opposite charge. Important parameters that affect the properties of the coating include the current voltage, the chemical properties of the suspension and the deposition time (Montebelli et al., 2014a). Mohammadi et al. (2016) used the electrophoretic deposition method to coat carbon nanotubes (CNT) on Ni foam of nanoscale porosities in a H₂ storage process. In their study, an annealed Ni foam sample (anode) was dipped in a suspension of acetone and CNT which was subjected to a deposition voltage of 300 V for 2 min. They investigated several parameters such as the intensity of the current, the number of charge and discharge cycles and the effect of annealing. They found that annealing the CNT electrodes and increasing the number of charge and discharge cycles had a beneficial effect on the H₂ discharge capacity of their system.

The electroless plating method makes use of the difference in electronegativity between the substrate and the metal to be coated on it. This technique involves a metal deposition on the surface of a less electropositive metal foam by a redox reaction. Key parameters affecting the process include the composition of the electroless bath (i.e. source of metal ions, complexing agent, reducing agent and stabiliser), the pH and the temperature of the electroless bath (Pérez-Alonso et al., 2015; Tian and Guo, 2010). This method has also been often used to coat foam samples used in H₂ evolution reactions (Montebelli et al., 2014a). For instance, Yang et al. (2018) used electroless plating to deposit a 1 µm layer of a ternary Ni-Co-P alloy on the surface of Ni foam. The precursor solution consisted of NiSO₄·6H₂O, CoSO₄·7H₂O and NaH₂PO₂·H₂O. The coated foam exhibited promising H₂ evolution reaction performance in basic medium at overpotentials of 107 and 125 mV for current densities of 10 and 20 mA/cm² respectively. Pérez-Alonso et al. (2015) used electroless plating to deposit Ni-Co on Ni foams. Their plating bath consisted of Na citrate as complexing agent, dimethylamine borane as reducing agent, and NiSO₄·6H₂O and CoSO₄·6H₂O as metal sources. Their study highlighted the effect of different Ni/Co ratios on the O₂ and H₂ evolution reactions' performances and on the plating layer thickness.

Sputter coating is a physical deposition method in which a capacitive plasma, generated under vacuum, causes sputtering of single metal atoms of the coating material (anode side) onto the

substrate surface (anode) (Meille, 2006). Tian et al. (2021) developed a ppb-level H₂ sensor using a Ni foam coated with Pd by magnetron sputtering. The detection limit of the sensor was 7 ppb and the device was reported to have high cycling stability and selectivity. The sensor was therefore found to be a promising candidate for safety applications in various industries.

2.3.3.3 Packed foams

The foam coating process requires several parameters to be considered in order to achieve optimum textural, chemical and mechanical properties of the catalytic washcoat. Besides, the coating process often results in very low catalyst inventory inside the PBR. For these reasons, packed foams were proposed to combine the advantages of structured reactors (i.e. foams) with those of conventional PBRs. Such a catalytic system can benefit from both a high catalyst loading and the high thermal conductivity of metal foams. Packed foams are able to achieve high catalytic performance while maintaining nearly-isothermal reaction conditions in catalyst beds (Ambrosetti et al., 2020, 2022; Fratalocchi et al., 2018).

2.4 Designs and configurations of foam-based reactors

Processes involving catalytic H₂-based reactions vary in their nature from highly exothermic or endothermic, two- or three-phase processes which may run in kinetic- or diffusion-controlled regimes at different pressure and fluid flow conditions. These processes have been conducted in several types of reactors, including packed bed continuous reactors, microreactors, stirred tank reactors and slurry reactors. These reactor designs have several disadvantages, including a high pressure drop, formation of hot spots (e.g. PBRs), cost of manufacturing (e.g. microreactors), and difficult separation between catalyst and products (e.g. stirred tank and slurry reactors) (Lali, 2016). Foam-based structured reactors can be used to overcome some of the shortcomings associated to these reactor types (Kapteijn and Moulijn, 2022). Foams used as catalyst support structures are light, highly porous and have high thermal conductivity, enabling high mixing, low pressure drops and the prevention of hot spots formation (Aguirre et al., 2020; Yu et al., 2007). The reactor types in which metal foam structures have been used as catalyst beds or simply heat exchange materials for H₂-related processes are summarised below.

2.4.1 Tubular fixed-bed reactor

Fixed-bed reactors (FBRs) are the most commonly used reactor type for H₂-based reaction processes conducted on catalytically activated metal foams. Their construction is relatively simple—catalytically activated foam samples are inserted in a tube often heated from its walls. The size and shape of the foam samples is chosen to maximise contact with the reactor wall (Fratalocchi et al., 2018; Ho et al., 2020a). In cases of poor foam–wall contact, the foam samples can be wrapped in materials such as quartz wool, Al foil or polytetrafluoroethylene strips to avoid bypassing of the reactants or channelling effects (Egaña et al., 2018; Lali, 2016; Montebelli et al., 2014b). The FBR inlet and outlet sections can be sealed with inert materials to ensure even flow distribution through the catalyst bed or to prevent eventual catalyst loss (Giani et al., 2005; Kapteijn and Moulijn, 2022; Montebelli et al., 2014b).

Foam-based FBRs have been considered suitable for several processes as reported in recent scientific literature. Koo et al. (2024) produced H₂ from NH₃ in a laboratory-scale FBR consisting of a jacketed Inconel tube (length 25.4 mm, I.D. 22.1 mm) containing a FeCrAl foam (20 or 40 PPI, height 6.35 mm, diameter 22 mm) coated with Ru/Mg-Al oxide. Their tests were conducted at atmospheric pressure, reaction temperatures of 550–700°C and gas hourly space velocities (GHSV) of 3000–10000/h. The foam-based catalyst beds exhibited high performances at temperatures higher than 650°C and GHSV as high as 6000/h while demonstrating excellent heat transfer capabilities. Furthermore, the foam-supported catalyst was tested in a NH₃ decomposition reactor (H₂ production capacity 20 Nm³/h) using 480 doughnut-shaped coated foams (20 PPI, O.D. 43.2 mm, I.D. 15.9 mm, height 6.35 mm). A minimum NH₃ conversion of 99% was maintained for 100 h on stream at an operating pressure of 8 bar and GHSV of 3000/h. During this long-term test, the average temperature of the outlet foam was kept at 800°C. The foam-based catalyst proved to be a promising catalytic system for large scale H₂ production from NH₃ decomposition.

Sang et al. (2012) conducted dry reforming of CH₄ experiments on stainless steel foam discs (~60 PPI foam, diameter 20 mm, thickness 6.35 mm) coated with Ru, Ru/Al₂O₃ and Ni/Al₂O₃ in a FBR consisting of a quartz tube (I.D. 20 mm). Their tests demonstrated the importance of coating a high-surface area morphological support on the foam. CH₄ conversions of ~75 and < 10% were obtained on the Ru/Al₂O₃-coated and Ru-coated foams, respectively, at a temperature of 800°C and weight hourly space velocity (WHSV) of 60 L/g_{cat}/h. The conversion of CH₄ on the Ni/Al₂O₃-coated foam was ~20% at the same operating conditions due to carbon

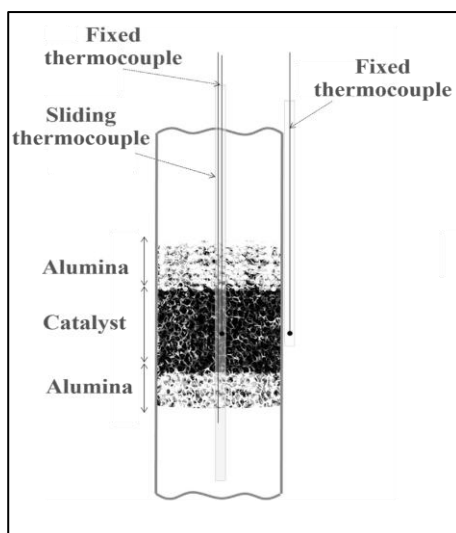
deposition on the surface of the catalyst. The Ru/Al₂O₃-coated foam proved to be stable as a constant catalytic activity was maintained over a period of 100 h operation.

To improve the FBR performance in specific processes, two major variations in the design are proposed in the literature on H₂ applications: the packed-foam reactor and the membrane reactor.

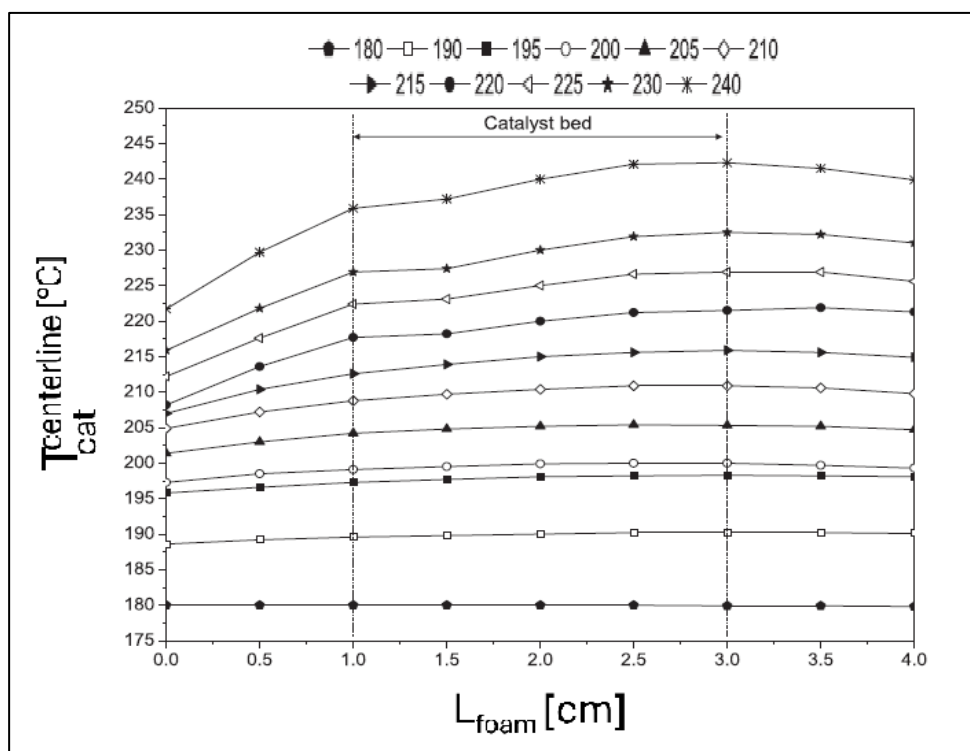
2.4.1.1 Packed-foam reactor

For sluggish chemical reactions, the catalyst inventory in the FBR becomes an important factor. As mentioned earlier (Section 2.3.3.3), for similar bed volumes, higher amounts of catalyst can be loaded in a conventional pellet-based bed than on the surface of metal foams (Ambrosetti et al., 2022). To take advantage of both the high catalyst inventory offered by conventional PBRs and the enhanced heat transfer capabilities of metal foams, some researchers have considered the use of packed foam configurations for different processes.

Fratilocchi et al. (2018) conducted Fischer–Tropsch experiments in a packed-foam reactor consisting of a stainless steel tube (I.D. 27.8 mm, length 850 mm) containing 7.2 g of Co/Pt/Al₂O₃ pellets (diameter 0.3 mm) loaded into the matrix of a 40 PPI Al foam (height 40 mm, diameter 27.8 mm) (Fig. 2-4a). Catalytic activity tests were conducted continuously at temperatures of 170–240°C, at a pressure of 25 bar, H₂/CO mole ratio of 2 and a WHSV of 6410 mL/g_{cat}/h. CO conversions of 3.7% were recorded at temperatures as low as 170°C; conversions increased with temperature, reaching 67.5% at 240°C. The selectivities to CO₂ and C₁–C₄ hydrocarbons increased from 0.5 to 2.8% and 11.5 to 16.0%, respectively as temperature increased from 195 to 225°C. In the same temperature range, selectivities to higher hydrocarbons and olefins decreased from 76.6 to 56.3% and 19.2 to 4.6%, respectively. Additionally, temperature gradients in the catalyst bed were very low even at high volumetric heat duty. The temperature differences were found to be 1°C at 195–205°C with CO conversions up to 22% and 6°C at 240°C where the CO conversion was 67.5°C (Fig. 2-4b).



(a)



(b)

Figure 2-4. (a) Schematic of the packed foam reactor. (b) Axial temperature profiles obtained in the reactor at WHSV of 6410 NmL/g_{cat}/h, and pressure of 25 bar (Fratalocchi et al., 2018)

Legend. $T_{cat}^{centerline}$: temperature at the centreline of the foam; L_{foam} : foam length.

Balzarotti et al. (2020) conducted CH₄ steam reforming experiments in a packed foam tubular reactor (I.D. 29.5 mm) (Fig. 2-5a). Three different foam matrixes filled with Rh/Al₂O₃ catalyst pellets (0.6 mm spheres) were tested: FeCrAlY foam (12 PPI) and Cu foams (10 and 40 PPI). The total amount of Rh/Al₂O₃ catalyst in the reactor bed was 5.75 g in each configuration. SiC particles were inserted in the upper part of the reactor to allow reactant mixing. Temperature

profiles and wall-centre temperature differences observed during catalytic tests at a GHSV of 10000/h clearly showed higher heat dissipation capabilities of Cu foams compared to the FeCrAlY foam (Fig. 2-5b). Efficient axial and radial heat transfer on the Cu foams was attributed to the much higher thermal conductivity of Cu (380 W/m/K) than that of FeCrAlY (16 W/m/K). Moreover, a comparison between the 10 and 40 PPI Cu matrixes in the reactor bed revealed that using a higher pore density resulted in a higher wall heat transfer coefficient which improved the temperature distribution across the reactor bed.

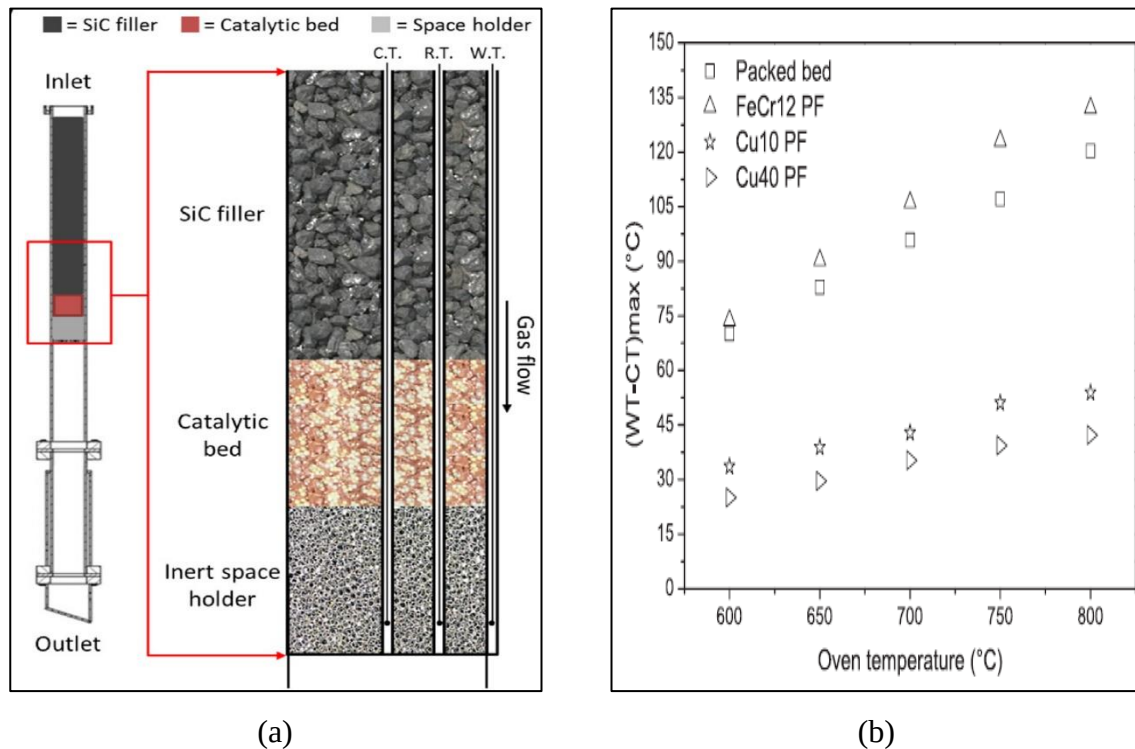


Figure 2-5. (a) Schematic of the packed foam reactor and (b) maximum wall-centre temperature differences at different oven temperatures (Balzarotti et al., 2020)

Legend. C.T.: centre temperature; W.T.: wall temperature; R.T.: radial temperature; PF: packed foam; FeCr12: 12 PPI FeCr foam; Cu10 PF: 10 PPI Cu foam; Cu40 PF: 40 PPI Cu foam.

2.4.1.2 Membrane reactor

In equilibrium-limited H_2 production processes such as the reforming of natural gas, removing H_2 from the reaction medium is beneficial in order to shift the reaction equilibrium towards the formation of products (Le Chatelier principle) (Alamdari, 2015). It is for this reason that H_2 -permeable membranes have been used in FBRs. The utilisation of highly selective membranes (e.g. Pd-based membranes) results in higher H_2 throughputs compared to those of conventional FBRs (Alamdari, 2015). Theoretically, membrane reactors can achieve maximum fuel processor and overall power plant efficiencies for reforming processes (Shigarov et al., 2017).

Their high potential for process intensification can enable the design of simplified processes, cost savings and simple parallel scale-up (Yan and Cheng, 2022).

Shigarov et al. (2017) designed two foam-based membrane reformers to produce pure H_2 from CH_4 . The reformers contained a Pd-Ag membrane and a Ni/MgO-coated Ni foams (60 PPI, diameter 85 mm, height 14 mm). The designs differed mainly in the gas flow arrangements in the reactor, namely: consecutive flow (type I) and symmetrical flow (type II) of the reaction mixture along the two sides of the membrane (Fig. 2-6). The 7% higher H_2 productivity observed experimentally on the type II configuration was attributed to the more even temperature profile causing nearly isothermal conditions around the membrane. A comparison between the foam-based membrane reactor (type II configuration) with reactors reported in the literature revealed its superior performance to that of tubular reactors and pilot fluidised bed membrane reactors.

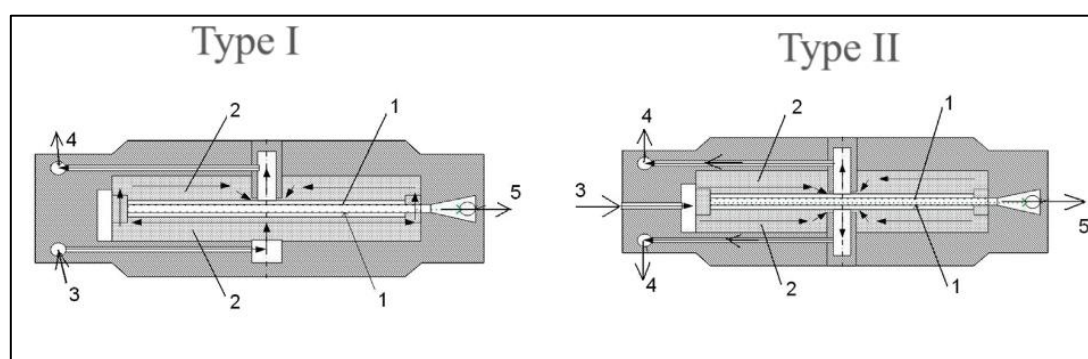


Figure 2-6. Schematic of foam-based membrane reactor designs (Shigarov et al., 2017)
 Legend. 1. Composite membrane Pd-Ag/porous steel; 2. Ni foam discs; 3. Reactant inlet; 4. Retentate gas outlet; 5. Pure H_2 outlet

2.4.2 Tank reactor

Tank reactors have been used in processes involving gas, liquid and solid phases such as hydrogenation, dehydrogenation or photocatalytic H_2 production. In these triphasic processes, kinetic rates are affected by mass transfer resistance due to gas–solid, liquid–solid or gas–liquid phase diffusion (Leon et al., 2012). Catalytically activated metal foams are considered suitable for their high volumetric surface area and reticulated porous structure, enhancing mass transfer (Leon et al., 2011). Other reported advantages of metal foams include their magnetic properties, electrical and thermal conductivities, which enables them to be used in processes involving relatively advanced heat transfer mechanisms such as induction heating (Wang et al., 2022). Several types of foam-based batch reactors reported in the literature on H_2 -based processes.

They are now grouped in two major categories, as described further below: unstirred and stirred tank reactors.

2.4.2.1 Unstirred reactors

In unstirred foam-based tank reactors, the foam is placed inside a vessel which contains the reactant, without a stirring device. Here, metal foams mainly play the role of immobilising the catalyst particles in the reactor (Fig. 2-7a). Such a system has been studied by Sousa et al. (2012) who conducted a study on the H_2 production from an alkaline $NaBH_4$ aqueous solution (2 wt.% $NaBH_4$, 2 wt.% $NaOH$). The reaction was performed on a Ru-coated Ni foam placed in an unstirred tank reactor. Experiments were carried out at temperatures of 30–60°C for 15 min (Fig. 2-7b). The total volume of the solution was 75 mL. The reactor temperature was controlled using a water bath. At 30 and 60°C, 2 L of H_2 was produced within 7.5 and 1.17 min, respectively. Kinetic studies were conducted and results revealed that the reaction rate was well described by a classical Langmuir–Hinshelwood model.

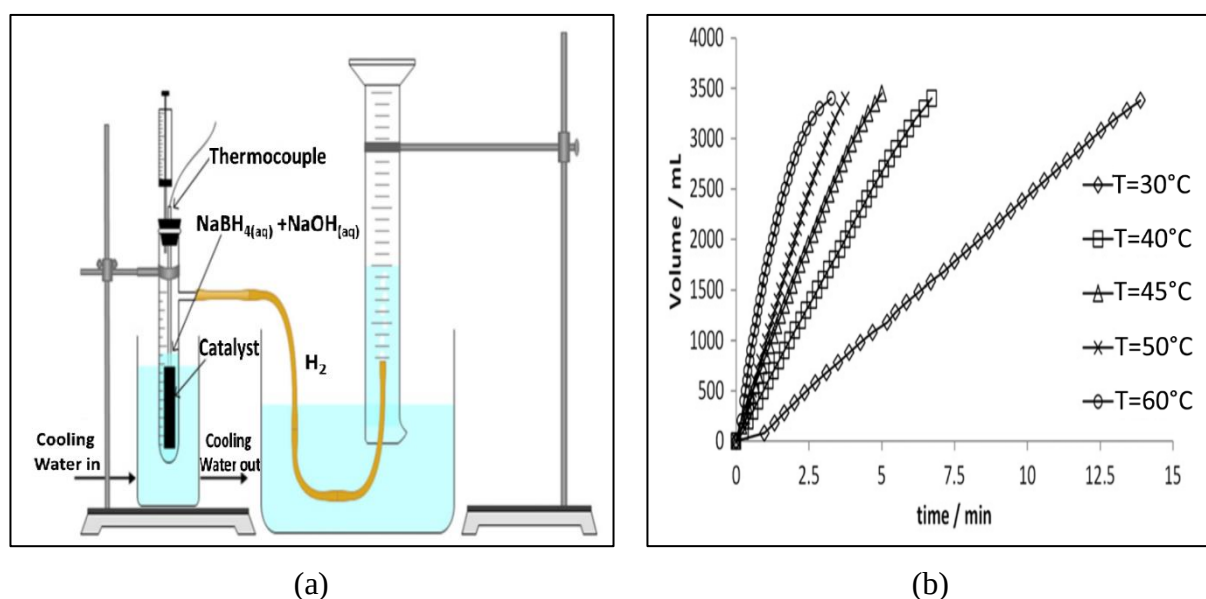


Figure 2-7. (a) Schematic of the experimental set-up used for the $NaBH_4$ dehydrogenation reaction and (b) the H_2 cumulative volume produced at different reaction temperatures (Sousa et al., 2012)

Wang et al. (2022) used Ni foam coated with TiO_2 for the photocatalytic H_2 production from water under simulated solar radiation in an unstirred tank reactor (Fig. 2-8a). The effects of the position of the foam, the reaction temperature and the heating method on the catalytic activity were investigated. Results revealed that low H_2 evolution rates were obtained when the catalytic foam was fully immersed into water (T/NF-sink) (Fig. 2-8b). The low H_2 rates were

comparable to those obtained using an immersed a powder catalyst. H_2 bubbles that formed on the solid surface could cause light scattering effects which would hinder efficient H_2 formation. The best H_2 evolution rates were obtained when the coated foam was placed at the air–water biphasic interface, with half of the coated foam immersed in water (T/NF-float). In this configuration, the heat released by the TiO_2 -coated foam under light exposure (photothermal effect) will promote steam generation, which will boost H_2 formation on the TiO_2 surface. The study also indicated that increasing the reactor temperature from 35 to 70°C led to an increase in the H_2 production rate from 31.2 to 71.8 $\mu\text{mol/h}$ on the T/NF-float. Directly heating the partially immersed foam to 70°C using induction heating significantly improved the H_2 production rate; a H_2 production rate of 104 $\mu\text{mol/h}$ was achieved. Wang et al. (2022) argued that the alternative magnetic field not only induced heat on the foam but improved the electron transfer behaviour.

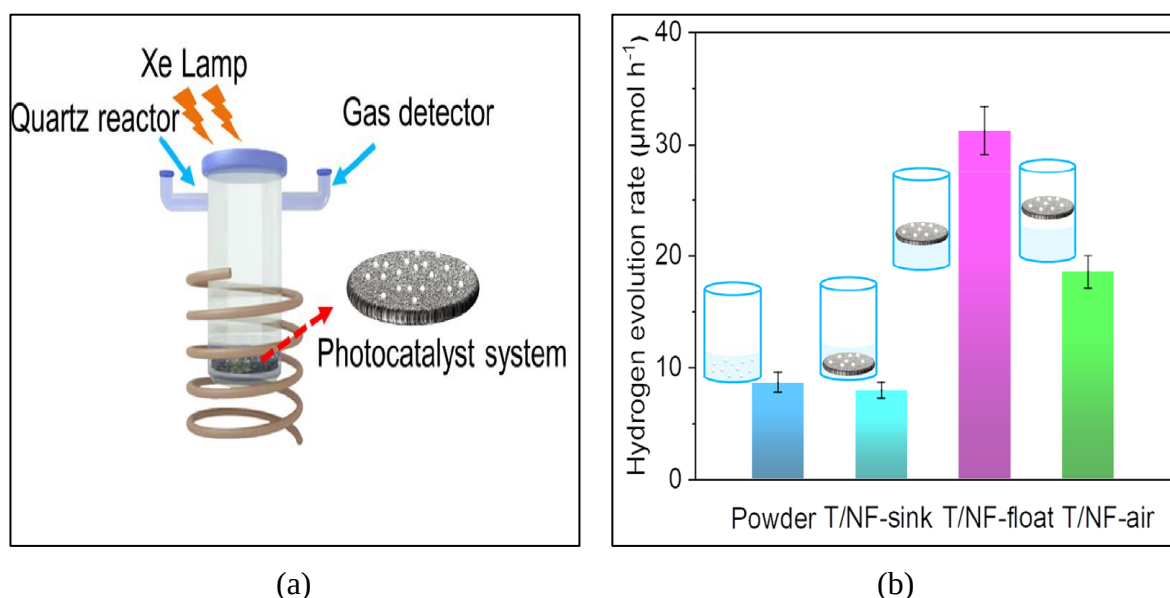


Figure 2-8. (a) Schematic of the experimental set-up used for the photocatalytic H_2 production under alternative magnetic field. (b) Effect of the catalyst configuration and position on the H_2 evolution rate (Wang et al., 2022)

Legend. T/NF-sink: foam fully immersed in water; T/NF-float: foam positioned at the air–water interface; foam positioned above the water.

2.4.2.2 Stirred reactor

Stirring benefits processes by increasing turbulence in a fluid and reactant mixing. The presence of metal foams amplifies these turbulences because fluid streams contacting the foam struts split and recombine in the pores. This phenomenon can be repeated as many times as the fluid encounters more struts throughout the course of the stream flow. Stirred foam reactors have showed high rate of mass transfer between the liquid and the gas phases due to the

formation of fine bubbles (Benamara et al., 2018; Leon et al., 2011). On the solid surface, stirring also enhances liquid–solid mass transfer because of the regular supply of fresh reactant at the solid-liquid interface (Leon et al., 2011). Stirring can be performed in two ways. In the first method, a mechanical device (e.g. impeller or magnetic stirrer) is used to stir the fluid while the foam is stationary (Benamara et al., 2018). Precautions need to be taken to prevent contact between the device and the foam so as not to damage the foam structure. In the second method, the foam itself is used as a stirring device (Leon et al., 2011, 2012; Yang et al., 2019).

Benamara et al. (2018) conducted experiments on α -methylstyrene hydrogenation in a 300 mL autoclave fitted with an impeller (height 43 mm, diameter 24 mm) (Fig. 2-9a). The reactor contained a cylinder-shaped foam block (40 PPI, O.D. 45 mm, I.D. 25 mm, height 55 mm) partially coated with Pd/Al₂O₃ catalyst for 11 mm at the foam mid-height (Fig. 2-9b). The reactions were carried out on the foam at 30°C and 20 bar, for 20 min. The effect of stirring was clearly demonstrated; the H₂ consumption rate increased significantly from ~0.004 to ~0.009 mol/g_{Pd}/s when the stirring speed was increased from 500 to 2000 rpm. The mass transfer coefficient was found to be insensitive to the stirring rate below 900 rpm. It was only above this critical value that the stirring power was high enough to generate the depression required to induce gas bubbles through the hollow shaft.

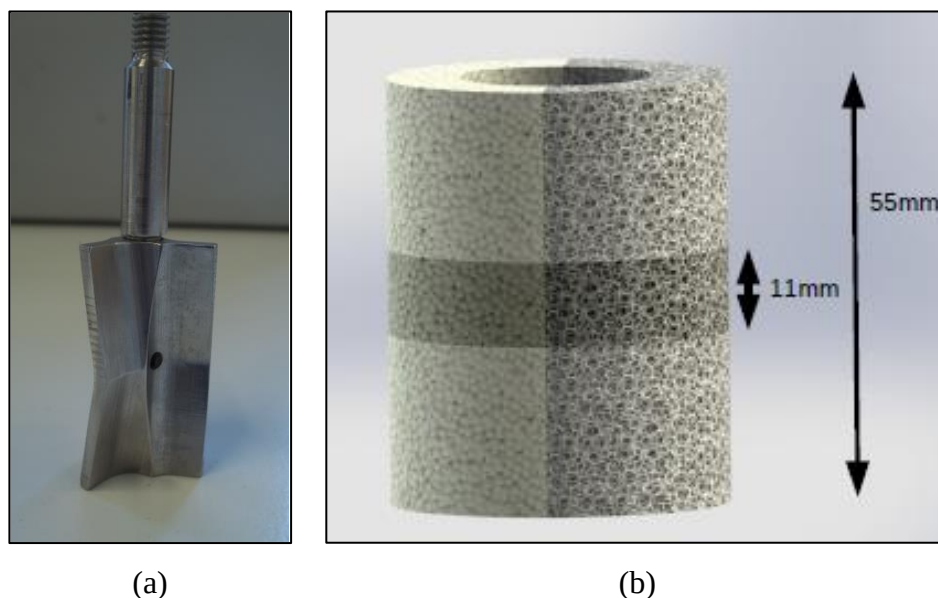


Figure 2-9. (a) Gas-inducing impeller. (b) Representation of the catalyst position (11 mm, mid-height) in the foam bed and pellet bed, used for comparison (Benamara et al., 2018)

The hydrogenation of 3-methyl-1-pentyn-3-ol (MP) was conducted by Leon et al. (2011) in a 5 L batch reactor equipped with a foam blade stirrer (blade size $50 \times 50 \times 20$ mm) and equally-spaced baffles fitted to the reactor wall (Fig. 2-10a). The hydrogenation activity was conducted at 25°C and 1.2 bar H_2 , using a concentration of 30 mol/m^3 MP in 3 L solvent.

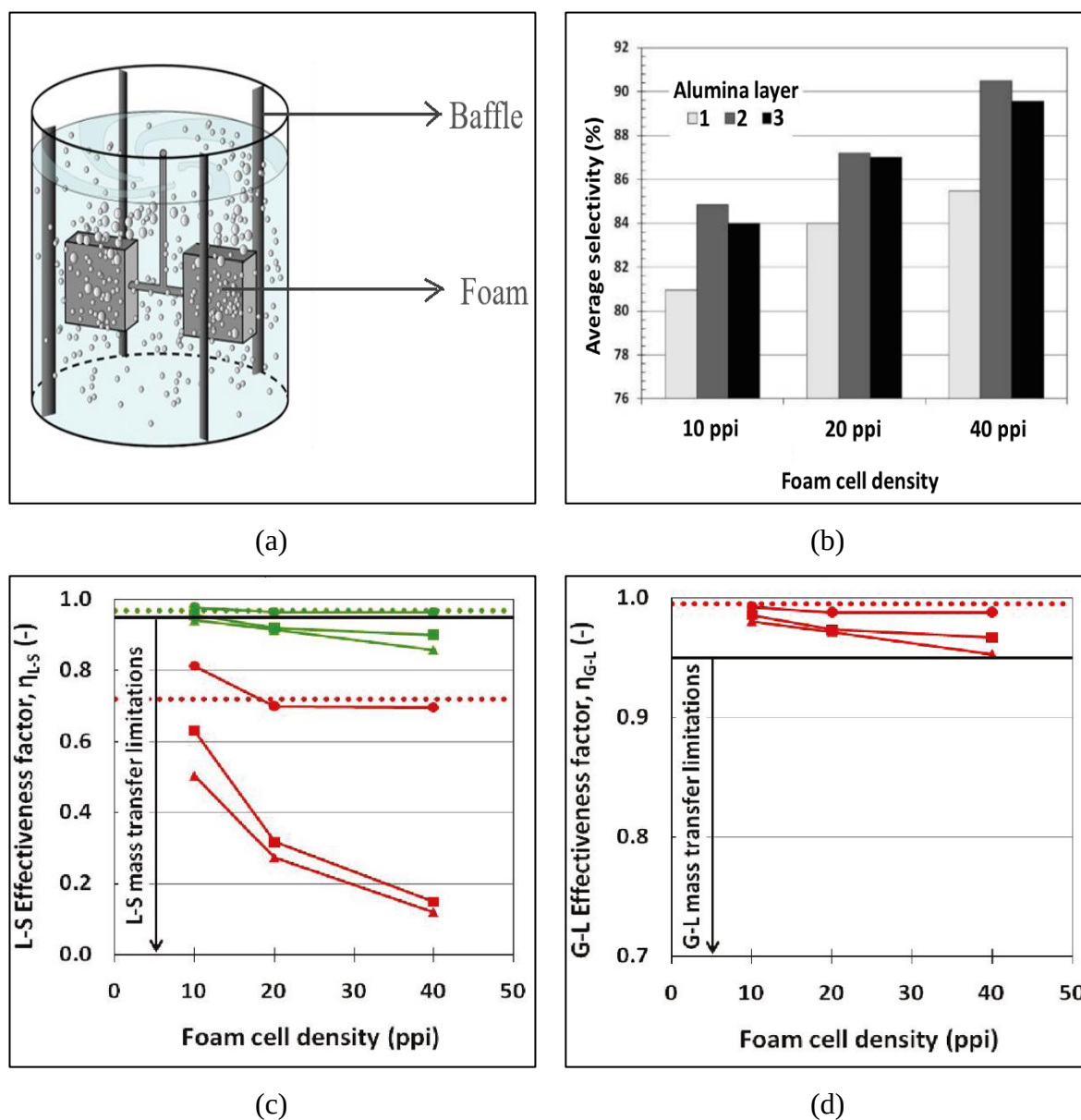


Figure 2-10. (a) Schematic of the foam-based stirred reactor used for the hydrogenation of MP. (b) Average catalytic activities on 10, 20 and 40 PPI loaded with alumina washcoat layers of 30 (●), 40 (■) and 50 μm (▲) (1–3 layers). (c) Liquid–solid (L–S) effectiveness factor and (d) gas–liquid (G–L) effectiveness factor calculated using Carberry number (Leon et al., 2011).

Legend. Solid lines: foam catalyst; dotted lines: slurry catalyst. Red, H_2 ; green, MP.

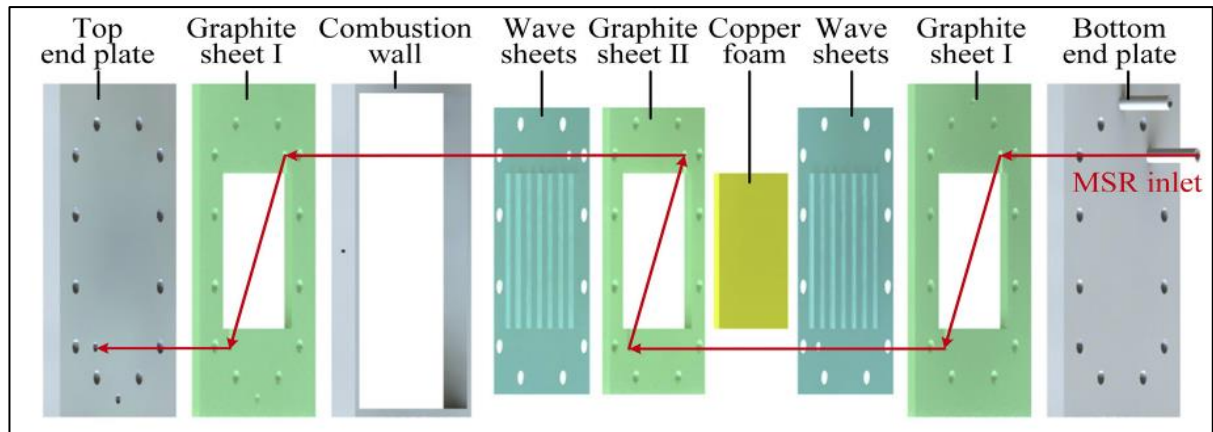
The effect of the pore density on the catalytic activity was studied using 10, 20 and 40 PPI foams. The average hydrogenation activity per foam volume increased at higher pore densities (Fig. 2-10b). The reason for this is that more catalytic active sites are accessible as the pore density increases. However, the activity per unit mass was lower on the foams of higher pore densities. This was attributed to the lower access of the liquid to the internal pores of the foam blades. It was interesting to note that an increase in the catalyst coating thickness had a beneficial effect on the average volumetric hydrogenation activity and selectivity on all the foam samples here. This beneficial effect, however, comes at the expense of the liquid–solid (L–S) effectiveness factor (Fig. 2-10c). It was argued that increasing coating thickness would result in lengthening the diffusion path taken by MP species through the micropores towards the external surface. Based on the calculated gas–liquid (G–L) effectiveness factors, gas–liquid mass transfer limitations were considered negligible (Fig. 2-10d). This study revealed that the performance of the foam is not only linked to the intrinsic activity of the catalyst but also to the geometric and textural properties of the foam.

2.4.3 Microreactor

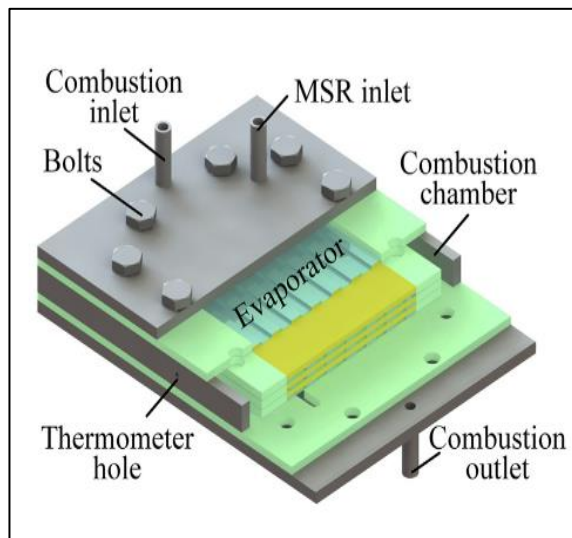
According to Seelam et al. (2013), microreactors are miniaturised reactor devices with geometric features generally in the range 10–1000 μm . Microreactors can be made of ceramics, stainless steel, silicon or polymers (Yao et al., 2015). These process-intensifying devices have several advantages for chemical industries; they offer a high-surface-to-volume ratio, improved heat transfer rates, compactness, increased safety and enhanced process control (Engelbrecht et al., 2020). Such microfluidic devices naturally have low throughput but can be easily be scaled-out by the numbering-up of several units (Seelam et al., 2013). Due to their small dimensions, the flow in a microreactor is generally laminar (low Reynolds number). Their reduced heat and mass transfer diffusion paths makes them suitable for transport-limited reactions (Kim et al., 2015; Seelam et al., 2013; Yao et al., 2015). Depending on the field of application, there are various types of microreactors, including micromixers, membrane microreactors and microchannel reactors. Metal foams have been fitted in microreactors in various configurations. Generally, they have been reported to maintain high activity and improve the heat distribution in the microreactors used in various processes, including H_2 applications (Kim et al., 2015; Liu et al., 2019; Yu et al., 2007; Zhou et al., 2017).

Wu et al. (2022) successfully developed a complex MeOH steam reforming microdevice which was composed of a foam-based catalyst bed, staked wave sheets (microchannel plates),

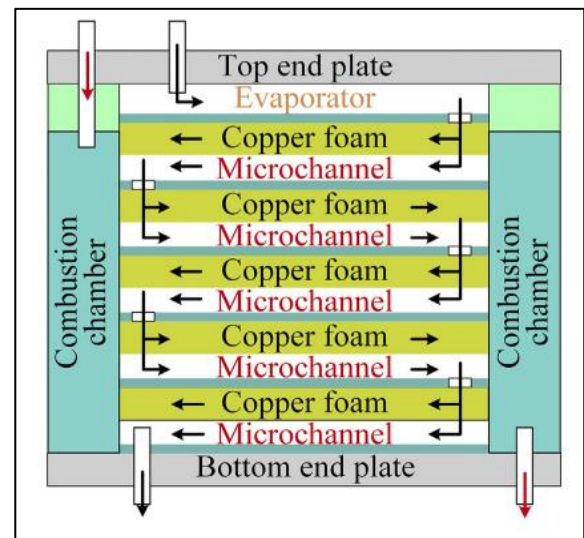
graphite sheets, a combustion wall and two end plates (Fig. 2-11a–c). The Cu foams ($65\text{ mm} \times 65\text{ mm} \times 2\text{ mm}$) had a porosity of 96%, a pore density of 110 PPI, and was coated with 19.4 g of a commercial CuO/ZnO/Al₂O₃. Each wave sheet ($120\text{ mm} \times 90\text{ mm} \times 0.2\text{ mm}$) consisted of microchannels ($65\text{ mm} \times 5\text{ mm} \times 1\text{ mm}$). The respective purposes of the wave sheets and the foam section were to uniformly distribute the reactant and to increase the catalyst loading in the microreactor. MeOH and steam were feed to the reactor inlet at a steam to carbon (S/C) ratio of 1.5. The heat required for the reforming process was supplied by the catalytic combustion of MeOH using a pelletised Pt/Al₂O₃ catalyst placed in the combustion chamber. The performance of the foam-based microreactor was characterised by a relatively rapid heating rate. It took 14 min to increase the temperature from 20 to 260°C. The temperature variation between the centre and edge of the foam was < 3°C (Fig. 2-11d). Catalytic activity tests were carried out at MeOH inlet flow rates of 0.6–1.4 mL/min and temperatures of 250–290°C. Based on MeOH conversions and reformat flow rates achieved, the optimum operating conditions were obtained at an inlet flow rate of 1.2 mL/min and temperature of 280°C. MeOH conversions of 65% and a reformat flow of 1 NL/min were achieved in the microreactor.



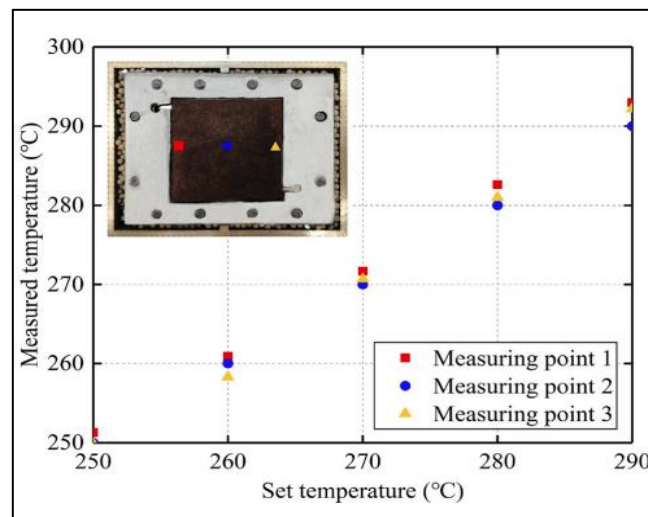
(a)



(b)



(c)



(d)

Figure 2-11. Illustration: (a) the structural design of the MeOH steam reforming (MSR) microreactor consisting of stacked wave sheets and copper foam. (b) the assembled microreactor. (c) the microreactor working principle. (d) temperature profile across the foam bed (Wu et al., 2022).

Yan et al. (2014) designed a metal foam micrometric system for the in-situ H_2 production by the steam reforming of dimethyl ether (DME) followed by a CO removal step. The system comprised a vaporiser, a mixer, a foam-based DME microreformer, a CO preferential oxidation microreactor and an electrical heater. The H_2 production reactor integrated five reforming chambers ($40\text{ mm} \times 40\text{ mm} \times 1.8\text{ mm}$), each containing two pieces of catalytically activated Ni foams ($40\text{ mm} \times 17\text{ mm} \times 1.8\text{ mm}$) (Fig. 2-12a).

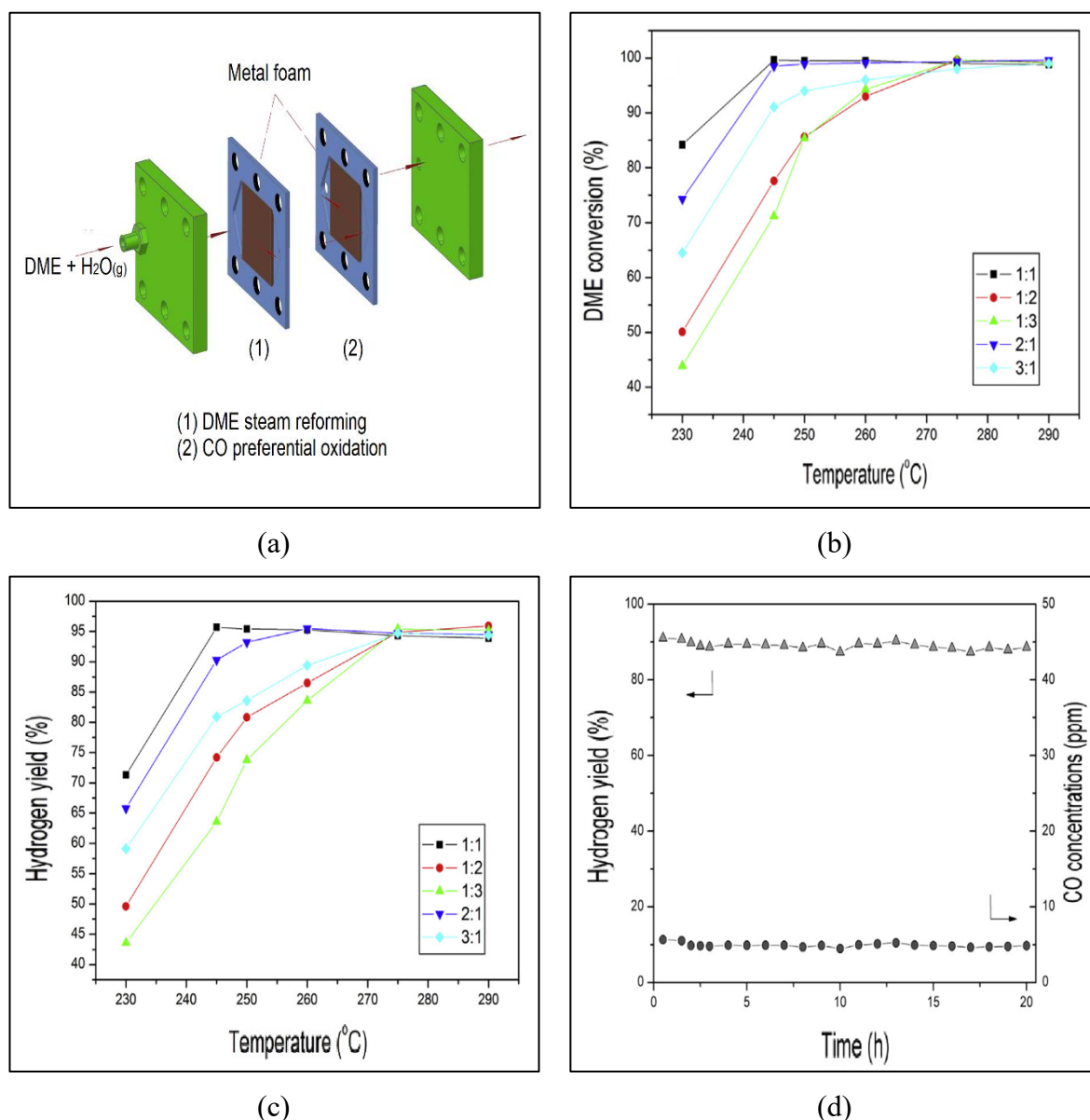


Figure 2-12. (a) Schematics of the foam-based microreactor. (b) Effect of Cu/Zn/Al/Cr to HZSM-5 mass ratio on DME conversion. (c) Effect of Cu/Zn/Al/Cr to HZSM-5 mass ratio on H_2 yield. (d) Stability test of the DME reforming–CO preferential oxidation system. Reaction conditions: steam/DME ratio = 5, WHSV = $5180\text{ mL/g}_{cat}/h$ (Yan et al., 2014)

The foams used for DME reforming were coated with Cu/Zn/Al/Cr and HZSM-5 catalysts. Pt/Al₂O₃ catalyst was coated on those prepared for CO preferential oxidation. Catalytic activity tests were conducted at different Cu/Zn/Al/Cr to HZSM-5 mass ratios; the 1:1 mass ratio was found to be optimum (Fig. 2-12b,c). CO concentrations of < 10 ppm were achieved in the CO preferential oxidation reactor at temperature of 80–90°C and at an O₂/CO mole ratio of 4. The microreactor system maintained a stable H₂ production for > 20 h of reaction (Fig. 2-12d).

2.5 Performance comparison between foam-based and other reactor types

Important factors considered in the development of reactors include the geometric configuration as well as the physical and chemical properties of the catalyst. The unique characteristics of coated metal foams have often been used as a motive for their selection over other configurations in process-intensifying devices. Their relatively high volumetric surface area has the potential to improve the catalytic activity in diffusion-limited chemical reactions (Maestri et al., 2005). Rapid dynamic responses and improved thermal and start-up/shut-down stabilities in metal foams are also anticipated because of the conjunction of heat transfer mechanisms, namely conduction, convection and radiation (Balzarotti et al., 2020; De Wild, 2000). The high porosity and reticulated structure of the foam-based catalyst beds not only improves reactant mixing—and therefore mass transfer rates—but also enables processes to be carried out with low pressure drops (Kolaczkowski et al., 2016; Yan and Cheng, 2022). However, there has also been cases where coated foams were not as beneficial to the process as were conventional catalyst structures. The causes of differences in performance observed in selected studies, where the foam-based reactors and other reactor types were compared, are now summarised, below.

2.5.1 Performance comparison in fixed-bed reactors

The large volumetric surface areas and high metal conductivities of metal foams are often advantageous in process-intensifying reactors. Comparison between the performances of foam-based reactors and other reactor types have been reported in a few studies on H₂-based processes. For instance, Montebelli et al. (2014b) compared the performances of a foam-supported (OF) with powder-based Cu/ZnO/Al₂O₃ catalysts during an investigation of MeOH synthesis from syngas. Two powder samples were used. The first was the powdered Cu/ZnO/Al₂O₃ (CC) and the second was obtained by drying, at 383 K for 24 h, the slurry used to coat the foam and calcining the resulting powder from ambient temperature to 573 K (1

K/min) for 2 h (SP). During the catalytic tests, the same amounts of Cu/ZnO/Al₂O₃ were loaded in the foam-based and powder-based FBRs. The Cu/ZnO/Al₂O₃ powders were diluted in SiC to prevent a strong temperature gradient. The catalyst bed lengths were 10 and 4 cm in the foam-based and powder-based reactors, respectively. The tests were conducted at 50 bar_a, using an inlet flow rate of 100 NmL/min and feed gas composition of 8.3% CO, 2.6% CO₂, 73.2% H₂, 5.1% CH₄ and the remainder N₂. Results revealed that the slurry preparation or calcination procedure had a detrimental effect on the performance of the Cu/ZnO/Al₂O₃ catalyst; however, the powder SP and foam-supported catalyst exhibited similar performances (Fig 2-13a,b).

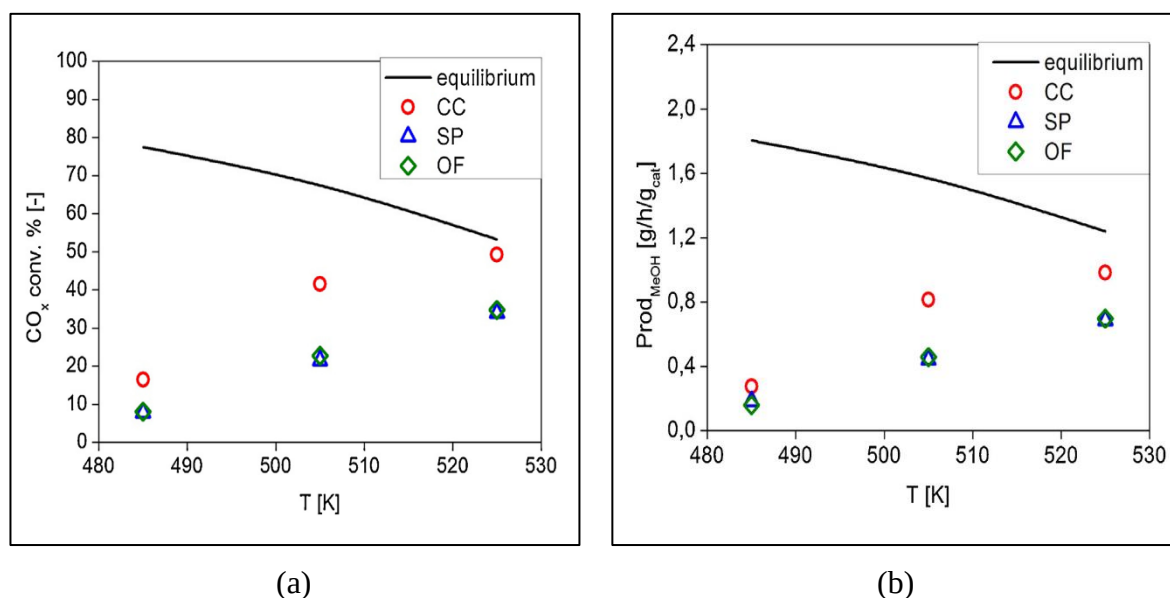


Figure 2-13. Comparison between the catalytic performances of a foam-supported and powder-based Cu/ZnO/Al₂O₃ catalysts during MeOH synthesis from syngas: (a) CO_x conversion and (b) MeOH productivity.

Legend. CC: Cu/ZnO/Al₂O₃ crushed powder; SP: Cu/ZnO/Al₂O₃ slurry powder and OF Cu/ZnO/Al₂O₃ coated on the Cu foam (Montebelli et al., 2014b)

In yet another study, an investigation of H₂ production from NH₃ decomposition was conducted by Koo et al. (2024) on Ru/Al₂O₃ in different catalyst configurations: Ru/Al₂O₃ pellets and Ru/Mg-Al oxides coated on monoliths and on FeCrAl foams. The Ru content in the pellets was 0.16 g. The monoliths used in the investigation had cell densities of 600, 800 and 100 cells per inch (CPI) and Ru content of 0.0024, 0.0015 and 0.0023 g respectively. The foam-supported Ru/Mg-Al oxides had pore densities of 20 and 40 PPI and Ru content of 0.0012 and 0.0014 g. Results of the study revealed that the highest catalytic performances at low temperatures (< 650°C) were obtained for the systems with the largest BET surface areas and highest catalyst loadings. Therefore, at reaction temperatures < 650°C and GHSV of 3000/h, it was found that the NH₃ conversions decreased in the following order: pellets > 1000 CPI monolith ~ 600 CPI

monolith > 800 CPI monolith > 40 PPI foam > 20 PPI foam (Fig 2-14a). The catalytic activity tests were subsequently conducted at 700°C and GHSV of 3000–10000/h. In this case, the foam-supported catalysts exhibited better performances than those of the monoliths but they were still lower than those of the pellets (Fig 2-14b). Naturally, the high performance of the pellets was most likely due to their much higher content of Ru (> 10 times higher). The excellent performance of the foam-based systems at these conditions of high mass transfer limitations (i.e. high GHSV) was attributed to their high porosity, and excellent heat and mass transport properties, related to their complex structure and large geometric surface area. It can be argued that, in this investigation, a comparison between the structures is not straightforward since the catalysts and amounts of Ru differed. Nevertheless, the foam-based catalysts exhibited excellent capabilities—despite their low Ru content—at conditions where heat and mass transfer are crucial for high catalytic performance. This study highlighted the fact that the performance of foam-supported catalysts may be limited by the maximum amount of catalyst that a foam can bear on its struts.

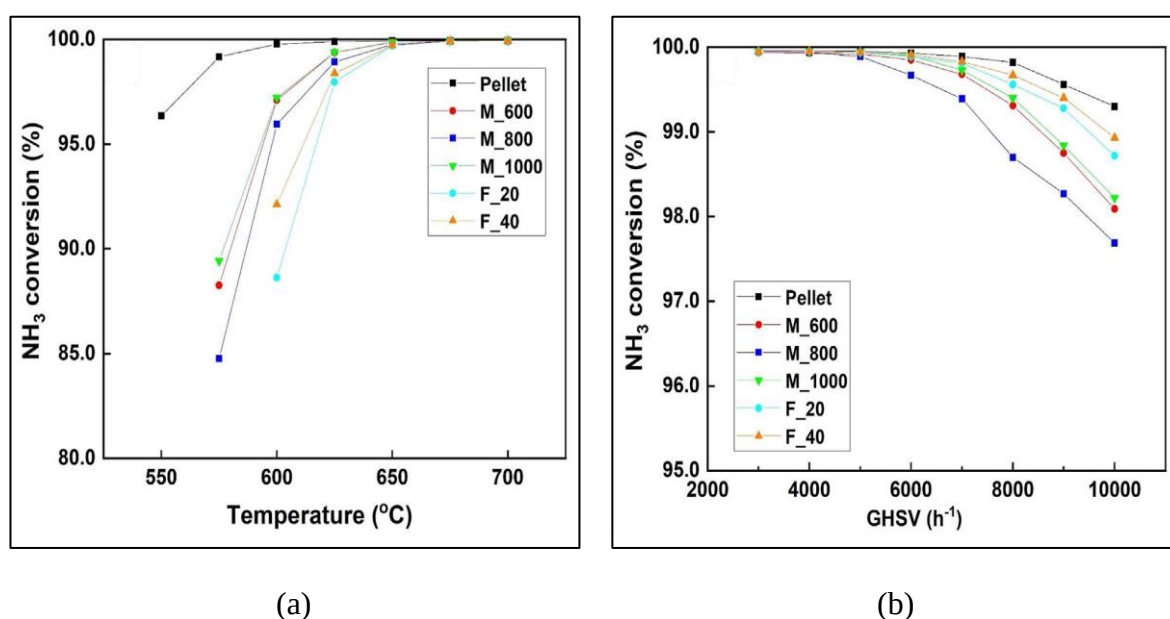


Figure 2-14. Conversions of NH_3 obtained using different catalyst configurations at (a) different reaction temperatures (GHSV of 3000/h) and (b) different GHSV (reaction temperature of 700°C) (Koo et al., 2024)

The low catalyst loading on the foam surface will limit the catalytic performance in kinetically controlled reaction processes. Packed-foam reactors were designed as reactors that can ensure the benefits of both the metal foam properties (e.g. high thermal conductivity) and those of pellet-based systems (e.g. high catalyst loading). Fratalocchi et al. (2018) compared the performance of their packed-foam reactor with that of a packed bed filled with the same amount

of Co/Pt/Al₂O₃ (7.2 g). The catalyst pellets in the PBR were diluted with inert Al₂O₃ in order to achieve the same bed length (40 mm) as in the packed foam reactor. The results of the temperature evolution recorded at the bed centre of the two reactor configurations revealed the beneficial effects of the metal foam as conductive structure dissipating the heat released through the Fischer–Tropsch process. Milder temperature conditions were obtained in the packed-foam reactor than in the conventional PBR (Fig. 2-15).

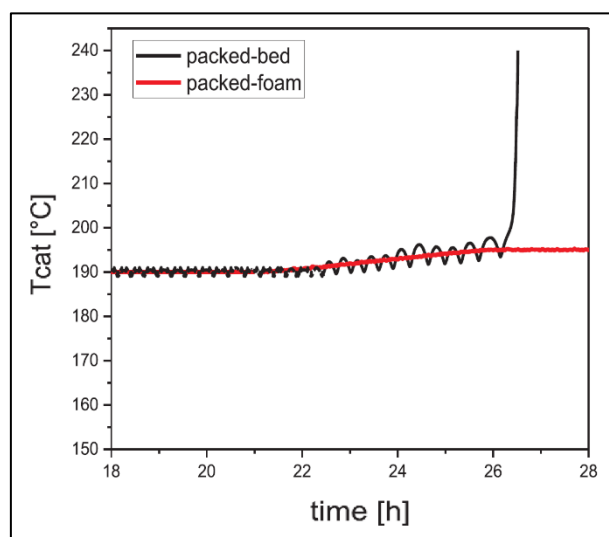


Figure 2-15. Temporal change of the temperature at the centre of the catalyst bed as the temperature was ramped from 190 to 195°C (Fratalocchi et al., 2018)

2.5.2 Performance comparison in batch processes

Mass transfer limitations are a major issue affecting the performance of tank reactors in triphasic chemical processes. The use of catalyst-coated foams has been considered as a potential solution to this problem. Their high volumetric surface area improves mass transfer between the reactant and product phases and the catalyst phase. As an example, Benamara et al. (2018) compared the Robinson–Mahoney catalytic basket with an annular foam block for hydrogenation tests in a stirred tank reactor. Higher hydrogenation rates (Fig. 2-16a) and mass transfer coefficients (Fig. 2-16b) were observed in the foam-based than in the pellet-based reactor at all stirring speeds used during their tests (300 to 2000 rpm). The better performance of the coated annular foam was mainly attributed to the geometric configuration of the foam (i.e. higher porosity).

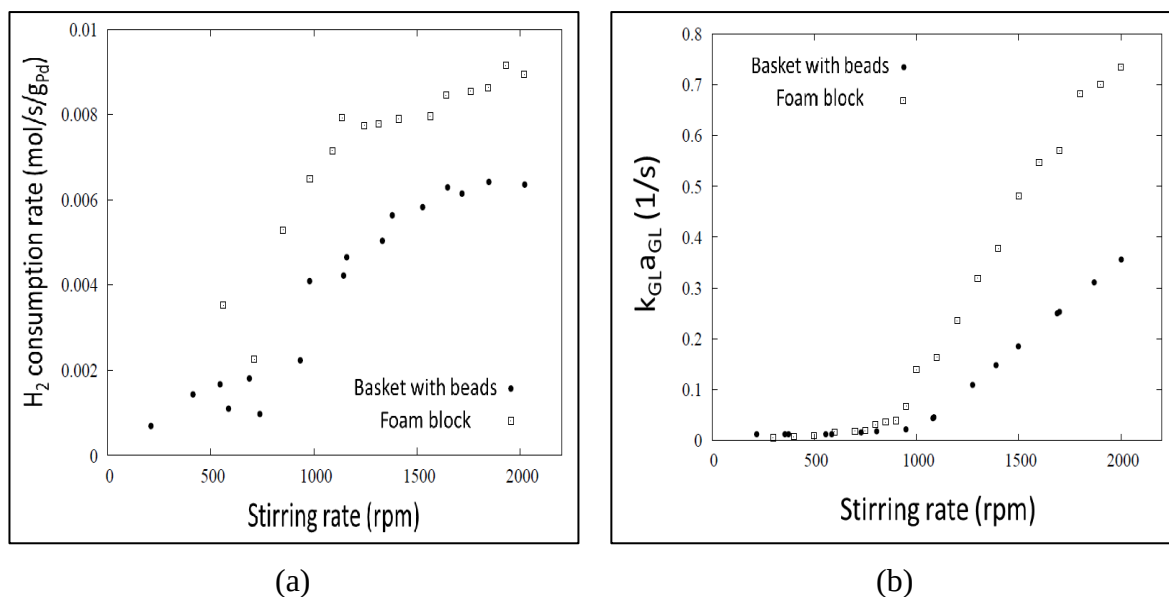


Figure 2-16. Comparison between the basket filled with catalytic pellets (beads) and the foam-supported catalyst at different stirring rates: (a) H₂ consumption rate and (b) mass transfer coefficient. The two reactors contained the same amount of Pd/Al₂O₃ catalysts (Benamara et al., 2018)

In another study, Lali et al. (2015) compared the specific activities of a catalytically activated foam stirrer with a catalytic slurry in a 600 cm³ batch reactor used for the hydrogenation of α -methylstyrol. The Pd/Al₂O₃-coated foam (30 mm × 20 mm × 12 mm) had a pore density of 30 PPI. The amount of Pd/Al₂O₃ and the hydrodynamic conditions in the slurry reactor were the same as in the foam-based reactor. Comparison tests were performed at rotation speed of 600–1500 rpm (Fig. 2-17). The specific activity of the foam-supported catalyst was lower than that of the slurry catalyst. The lower performance of the foam was attributed to higher internal mass transfer limitations due to its longer characteristic length (thickness of washcoat layer) of 17.8 μ m compared to 8.33 μ m for the slurry catalyst particles. Pd/Al₂O₃ particles were homogeneously dispersed in the slurry. This could improve the contact between the catalyst and the reactants, resulting in a better performance than that achieved with the foam-supported catalyst.

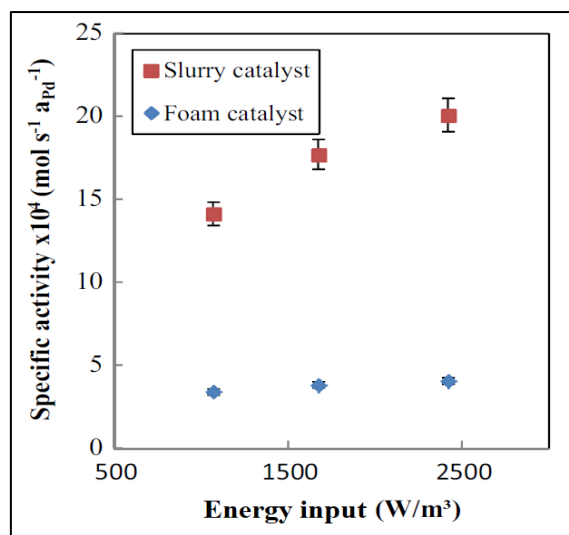


Figure 2-17. Comparison of the specific catalytic activities obtained in the hydrogenation of α -methylstyrol on a foam-based and slurry-based catalysts. The energy input of 500–2500 correspond to impeller rotation speed $\sim$ 600–1500 rpm (Lali et al., 2015)

Leon et al. (2011) observed similar results for their MP hydrogenation reaction on foam-supported and slurry catalysts. According to them, the lower performance of the foam could also be due to its lower specific surface area and lower active metal dispersion. Nevertheless, they recommend the use of foam-based systems for processes that may involve costly or time-consuming methods for separation of the catalyst from the reaction products. Unlike slurry reactors, a foam-based system greatly facilitates the reuse of the catalyst.

2.5.3 Comparison of foam-based microreactors with fixed-bed reactors

The features of foam-based microreactors combine the complex geometry of structured reactors and the reduced dimensions of microreactors. These properties are expected to lead to increased rates of heat and mass transfer in the reactor. During their DME reforming tests, Yan et al. (2014) compared the performance of a foam-based DME microreactor to that of a FBR at a steam/DME ratio of 5, WHSV of 5180 mL/g/h and a temperature of 250°C. The DME conversion and H₂ selectivity obtained in the microreactor were, respectively, 34 and 36% higher than those obtained in the FBR. This higher performance of the microreactor was attributed to higher heat and mass transfer rates in the microreactor. Furthermore, stability tests showed that the catalyst in the foam-based microreactor was more stable than the catalyst in the FBR (Fig. 2-18). The more rapid deactivation of the latter was due to carbon deposition on the catalyst surface. Better heat distribution in the foam-based microreactor prevented the formation of hot spots, which are known to increase carbon formation on the catalyst surface.

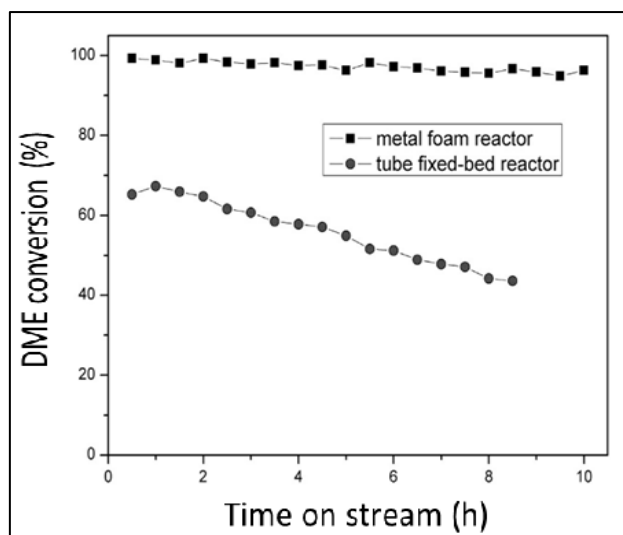


Figure 2-18. Comparison between the long-term performances of the structural microreactor and FBR used for the steam reforming of DME (Yan et al., 2014)

The superior performance of a foam-based microreactor over that of a PBR was also observed by Kim et al. (2015) in the H_2 production by partial oxidation of DME. The PBR consisted of a quartz tube (I.D. 8 mm, O.D. 10 mm) containing Rh/ Al_2O_3 pellets (diameter 1.7–2.0 mm). The catalyst bed in the microreactor consisted of a Rh/ Al_2O_3 -coated FeCrAl foam (20 mm × 40 mm). The specific surface areas of the catalyst pellets and Rh/ Al_2O_3 washcoat were 164.2 m^2/g and 97.4 m^2/g , respectively. Experiments in the foam-based microreactor and FBR were conducted at temperatures of 200–750°C, and DME and O_2 flow rates of 6 and 5 mL/min, respectively. The Rh loadings on the Rh/ Al_2O_3 catalyst were 0.05, 0.1 and 0.5 wt.%, corresponding to 0.18, 0.36, 1.8 mg Rh, respectively. At a Rh loading of 0.5 wt.%, the highest DME conversions and H_2 yield were obtained at lower temperatures (i.e. 400–600°C) in the foam-based microreactor than in the PBR. The better catalytic performance of foam-based microreactor was attributed to the higher thermal conductivity of the foam, enabling better heat dissipation. At temperatures > 600°C, the performances of the two reactors were similar (Fig. 2-19a). The effect of Rh loading was investigated during a 600 min activity test conducted at a temperature of 700°C. The superior performance of the foam-based microreactor compared to that of the PBR was very evident at low Rh loadings (e.g. 0.05 wt.% Rh/ Al_2O_3) (Fig. 2-19b). The foam-based microreactor could sustain high conversions (> 90%) for > 1200 h on stream, i.e. 10 times longer than the FBR (Fig. 2-19c,d). Less severe carbon coking in the foam-based microreactor was attributed to high turbulence of the gas inside the highly porous catalyst bed.

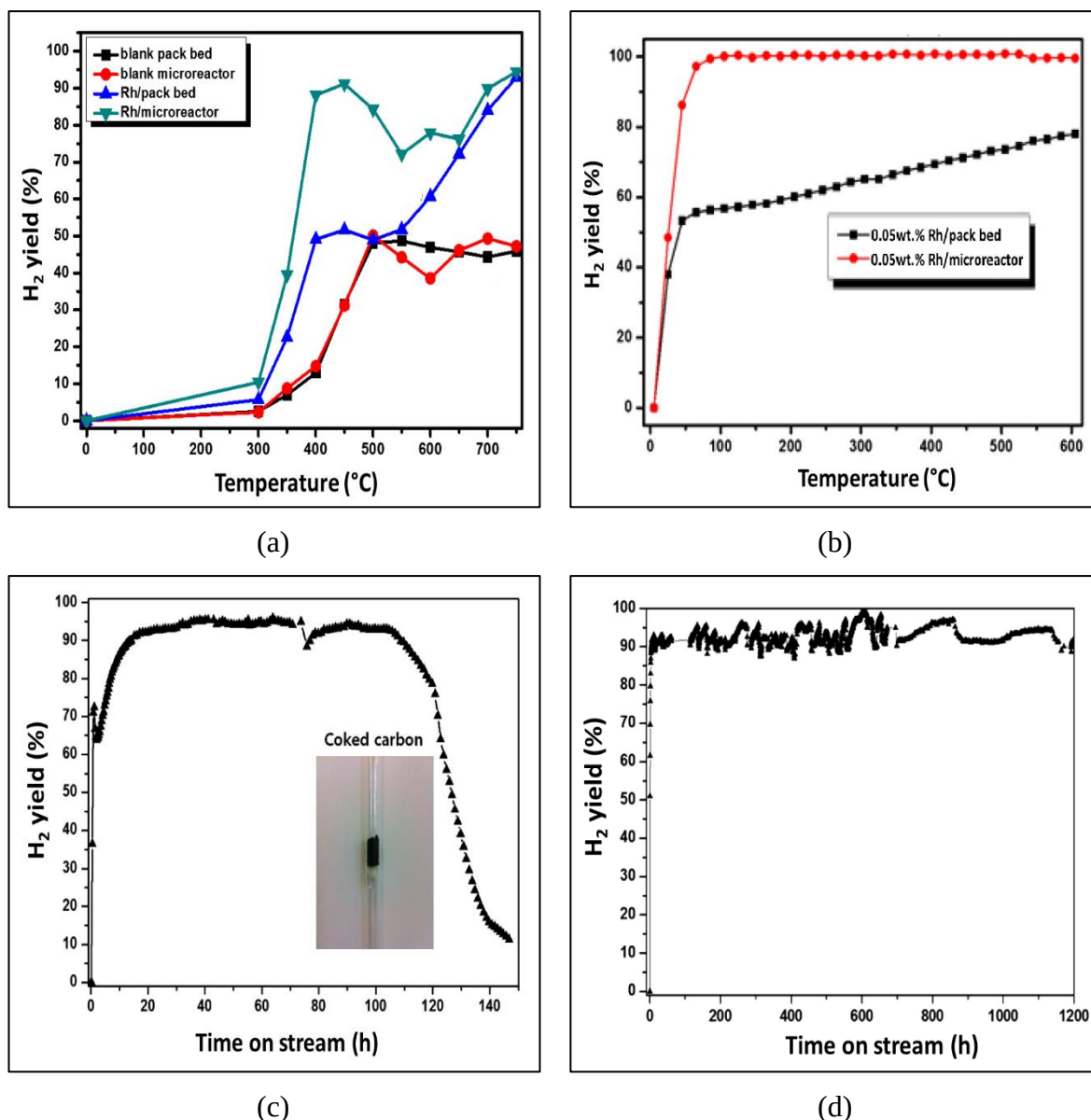


Figure 2-19. (a) Effect of reactor configuration on H₂ yields obtained in catalytically activated and blank reactors. (b) Effect of reactor configuration on the H₂ yield at a Rh loading of 0.05 wt.% and a temperature of 700°C. (c) H₂ yield obtained during the durability test in the PBR. (d) H₂ yield obtained in the foam-base microreactor during the durability test at 700°C (Kim et al. 2015)

2.6 Selected foam-based chemical systems reported in the literature

Sections 2.2–2.4 of this chapter demonstrated the versatility of metal foams in their applications as catalyst support structures in H₂-based processes. From the literature, the motivation behind the choice of a specific foam material in a particular process is generally unclear. Although physical properties such as thermal or electrical conductivities may guide the choice of the substrate, it is not unusual to encounter instances where the surface of the metal foam is oxidised to grow an oxide layer, used as a morphological support for an active metal to be

deposited on. It can also be deduced from the literature that the physical and chemical stability of the active metal and the foam substrate as well as the foam resistance to corrosion are relevant factors in the choice of the substrate.

The pore densities of metal foams selected for H₂ applications can range from low PPI values of 12 PPI to values > 100 PPI. These values can be guided by the amount of surface area available on the foam (larger surfaces of high PPI foams decrease diffusion limitations), the anticipated pressure drop limits (small pores increase pressure drop) and the catalyst coating methods (larger pores decrease the probability of pore blockage).

Various catalytic activation methods have been proposed in H₂ applications. Generally, physical stability (minimal catalyst loss from the foam surface) and chemical stability (low sintering tendency) are considered in the choice of the coating method.

Foam-based reactor technologies vary from simple designs such as FBR and tank reactor to more complex designs such as membrane reactors and microreactors. Generally, biphasic processes in which high space velocities can be achieved are run continuously in conventional FBR or microreactors for enhanced mass transfer. Triphasic processes, involving liquids, have been often reported to take place in tank reactors.

Table 2-1 reports the types of coated foams and reactors used in selected recent H₂ applications.

Table 2-1. Different catalyst deposition methods and reactor types used in H₂ applications

Reference	Application	Foam used	Catalyst	Catalyst coating method	Reactor
Tarifa et al. (2022)	Biogas steam reforming	NiCrAl (cell size: 450 µm)	RuMgAl and RhMgAl	Electrodeposition	FBR
Peng et al. (2014)	CO preferential oxidation in H ₂ -rich gas	Ni (110 PPI)	CuO/CeO ₂	Sol gel	FBR
Tang et al. (2024)	CO ₂ methanation	Ni (110 PPI)	CeAlO _x /Ni	Coprecipitation	FBR
Ho et al. (2020b)	CO ₂ methanation	NiCrAl (cell size: 450 µm)	Ni/X/Al (X represents Ce, La or Y)	Electrodeposition	FBR
Ho et al. (2021)	CO ₂ methanation	NiCrAl (cell size: 450 µm)	Ru/CeO ₂ , Ni/CeO ₂	Electrodeposition	FBR
Mohammadi et al. (2016)	Electrochemical H ₂ storage	Ni (pore density not provided)	Ni-carbon nanotube (CNT)	Electrophoretic deposition (CNT) Electroplating (Ni)	Tank reactor
Egaña et al. (2018)	Fischer-Tropsch synthesis	Al or FeCrAl (10–40 PPI)	Co-Re/Al ₂ O ₃	Sol gel	FBR

Table 2-1 (continued). Different catalyst deposition methods and reactor types used in H_2 applications

Reference	Application	Foam used	Catalyst	Catalyst coating method	Reactor
Aguirre et al. (2021)	Fischer-Tropsch synthesis	Al (20 PPI)	Co/ Al_2O_3 and Co/ TiO_2	Slurry	FBR
Ping et al. (2016)	H_2 and C nanotubes production by catalytic CH_4 decomposition	Ni (110 PPI)	NiO/ Al_2O_3	Sol gel	FBR
Ma et al. (2018)	H_2 evolution reaction	Ni (pore density not provided)	Ni_2N	Magnetron sputtering	Tank (electrolysis cell)
Yang et al. (2018)	H_2 evolution reaction	Ni (110 PPI)	Ni/Co/P	Electroless plating	Tank (electrolysis cell)
Lotfi et al. (2019)	H_2 evolution reaction	Ni (35–45 PPI)	Graphene oxide/Ni/Cu and Ni/Cu	Electrodeposition	Tank (electrolysis cell)
Lotfi et al. (2020)	H_2 evolution reaction	Ni (pore density not provided)	Pt/graphene oxide/Ni/Cu	Electrodeposition	Tank (electrolysis cell)
Ho et al. (2020a)	H_2 production by partial oxidation of CH_4	FeCrAl (60 PPI)	Rh/Mg/Al	Electrodeposition	FBR
Ambrosetti et al. (2022)	CH_4 steam reforming	Cu (40 PPI)	Rh/ Al_2O_3	None (Packed foam)	FBR

Table 2-1 (continued). Different catalyst deposition methods and reactor types used in H_2 applications

Reference	Application	Foam used	Catalyst	Catalyst coating method	Reactor
Shigarov et al. (2017)	CH ₄ steam reforming	Ni (60 PPI)	Ni/MgO	Wet impregnation	Membrane reactor
Cristiani et al. (2012)	CH ₄ steam reforming	FeCr alloy (12, 30 PPI)	Ni/MgAl ₂ O ₃	Coprecipitation (MgAl ₂ O ₄) Incipient wetness impregnation (Ni)	FBR
Zheng et al. (2019)	MeOH steam reforming	Cu (110 PPI)	Cu/Zn/Al/Zr	Sol gel	Microreactor
Wang et al. (2021)	MeOH steam reforming	Cu (110 PPI)	Cu/Zn/Al ₂ O ₃	Slurry	Microreactor
Zhou et al. (2017)	MeOH steam reforming	Cu, Ni (50, 80, 100 PPI)	Cu/Zn/Al/Zr	Sol gel	Microreactor
Liu et al. (2019)	MeOH steam reforming	Cu (pore density not provided)	Cu/Zn/Al/Zr	Sol gel	Microreactor
Montebelli et al. (2014b)	MeOH synthesis	Cu (45 PPI)	Cu/ZnO/Al ₂ O ₃	Slurry	FBR
Park and Kim (2016)	NaBH ₄ dehydrogenation	Ni (pore density not provided)	Co/B, Co/P/B and Co/Ni/P/B	Electroless plating	Tank reactor
Badakhsh et al. (2021)	NH ₃ decomposition	NiCrAl (pore density not provided)	Ru and Ru/Al ₂ O ₃	Wet impregnation or slurry coating	FBR

Table 2-1 (continued). Different catalyst deposition methods and reactor types used in H₂ applications

Reference	Application	Foam used	Catalyst	Catalyst coating method	Reactor
Jo et al. (2010)	Passive autocatalytic H ₂ combustion	Al (40 PPI)	Pt/Al ₂ O ₃	Sol gel (Al ₂ O ₃) Incipient wetness impregnation (Pt)	FBR
Wang et al. (2022)	Photocatalytic H ₂ production	Ni (pore density not provided)	TiO ₂	Slurry	Unstirred tank reactor
Park et al. (2014)	Steam-CO ₂ reforming of CH ₄	Ni (pore density not provided)	Ni/Al ₂ O ₃	Sol gel (Al ₂ O ₃) Wet impregnation (Ni)	FBR
Li et al. (2016)	Syngas methanation	Ni, Cu or Ni/Cu alloy (100 PPI)	Ni/Al ₂ O ₃	Incipient wetness impregnation	FBR
Lali et al. (2015)	α -Methylstyrene hydrogenation	Al (10–45 PPI)	Pd/Al ₂ O ₃	Slurry coating (Al ₂ O ₃) Wet impregnation (Pd)	Stirred tank (rotating foam)
Ma et al. (2021)	α -Methylstyrene hydrogenation	Ni (130 PPI)	Pd/Al ₂ O ₃	Sol gel or electrodeposition (Al ₂ O ₃) Wet impregnation (Pd)	Microreactor
Lali (2016)	α -Methylstyrene hydrogenation	Al (30, 45 PPI)	Pd/Al ₂ O ₃	Slurry (Al ₂ O ₃) Wet impregnation (Pd)	FBR

2.7 Numerical modelling and simulations of foam-based reactors

To optimise the design of reactors, a cost-effective method includes describing processes using mathematical equations and using computational tools to predict, with relatively high accuracy, the physical and chemical properties of a system. Numerical modelling and simulations have been extensively used to understand the flow behaviour, pressure drop, heat and mass transport phenomena on the surface and inside the pores of coated metal foams. Typical models of foam-based catalytic processes are described by conservation of mass/species, energy and momentum, kinetic rate equations combined with equations of transport in porous medium (Palma et al., 2018; Sinn et al., 2020b; Solovev et al., 2022; Zhou et al., 2022).

Specific modelling parameters such as the heat and mass transfer coefficients, effective thermal conductivities, binary diffusion coefficients and pressure drop can be determined using correlations determined experimentally or obtained from literature (Ferroni et al., 2021; Gancarczyk et al., 2019; Inayat et al., 2011; Yang et al., 2021).

The numerical modelling of processes taking place in foam structures can be grouped into two major categories, namely: the pseudo-homogeneous and heterogeneous models (Kiewidt, 2017; Makhania and Upadhyayula, 2022a, 2022b).

2.7.1 Pseudo-homogeneous models

In pseudo-homogeneous modelling, no distinction is made between the solid phase (i.e. coated foam) and fluid phase (i.e. reactants). Both the fluid and solid are assumed to be a single homogeneous phase characterised by effective properties. This simplified approach considers neither the complex geometry of foams nor the localised physical and chemical properties of each component of the system. It is therefore a much less computationally intensive simulation method than an heterogeneous approach. For H₂-based chemical processes in foam-based reactors, pseudo-homogeneous modelling has often been used in macroscale modelling and computational fluid dynamics (CFD) simulations to describe the effects of operating parameters, catalyst properties or structural configuration on the overall reactor performance.

Luneau et al. (2017) developed a one-dimensional (1D) model describing the autothermal reforming (ATR) of biogas on Si-infiltrated silicon carbide foams coated with Ni-Rh/MgAl₂O₄ catalyst. ATR experiments were conducted in a FBR (I.D. 25.4 mm) at a pressure of 1.8 bar. The reaction mixture contained 42% H₂O, 14% CO₂, 7% O₂ and the remainder Ar. The model

assumptions included an ideal gas behaviour, plug flow conditions, the absence of radial concentration and temperature gradients, a homogeneous reaction as well as a negligible pressure drop over the foam. The governing equations included mass and energy balance equations. The external heat transfer and mass transfer coefficients were determined using Nusselt and Sherwood numbers from established correlations. Some of the kinetic parameters from previous literature were adjusted to match experimental results more accurately. Simulations were performed using 161 discretisation points, using a Fortran code. The results indicated that calculated axial temperature were in good agreement with the experimental data (Fig. 2-20a). However, there was a mismatch between the experimental and calculated H_2/CO ratios due to the difference between the calculated and experimental temperatures at the end of the catalyst bed (Fig. 2-20b). The CH_4 conversions were also underestimated because the kinetic expressions did not account for the increase in activity due to the presence of Rh in the catalyst composition.

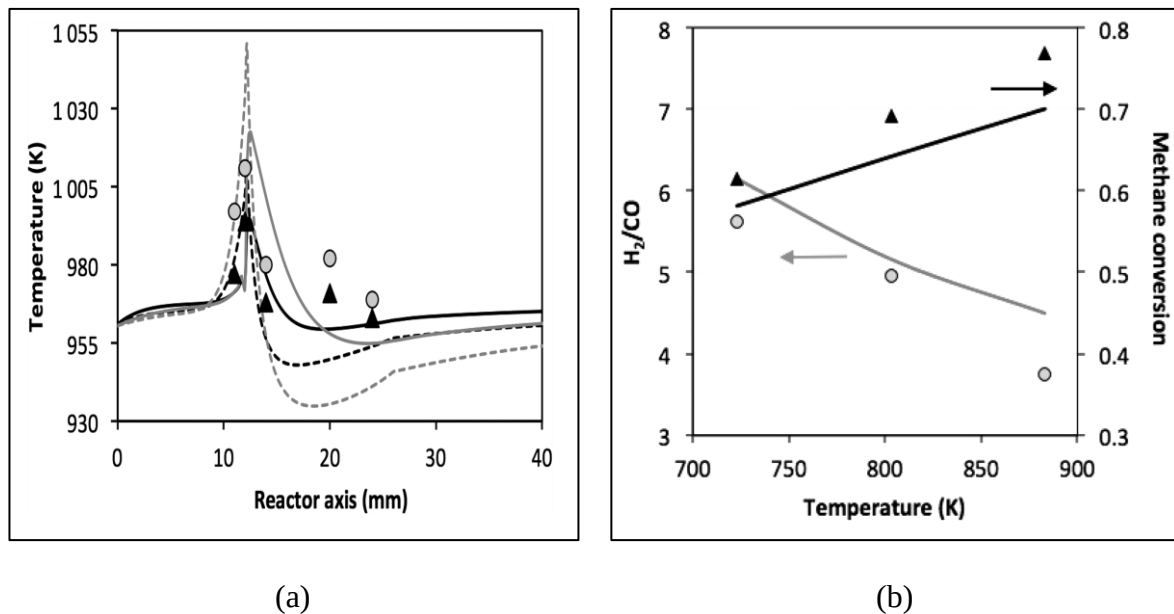
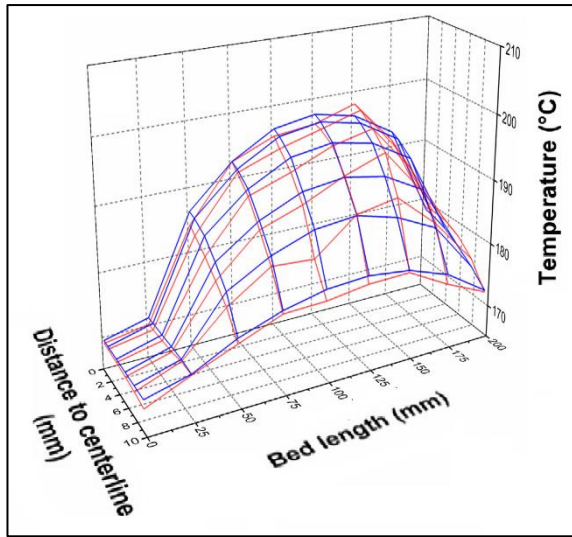
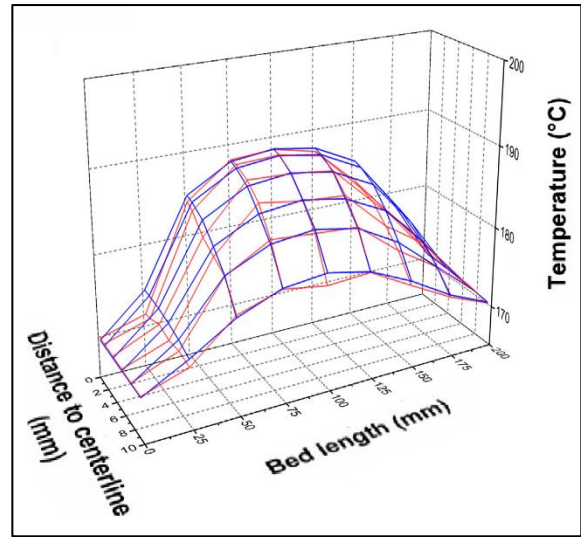


Figure 2-20. Comparison between experimental (symbols) and calculated (lines) results: (a) Axial temperatures measured at five points in the foam-based reactor. Black and grey lines represent calculated profiles at GHSV of 10000 and 20000/h, respectively. Full and dashed lines represent calculated gas and solid phase temperatures, respectively. (b) H_2/CO ratios and CH_4 conversions at different temperatures (Luneau et al., 2017).

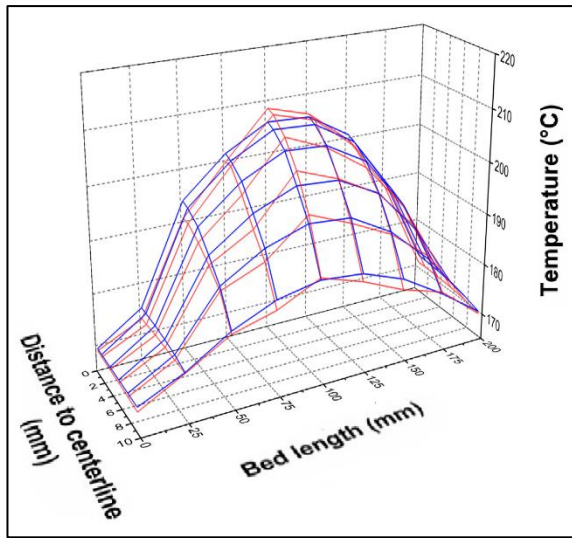
In a study by Gräf et al. (2016), a two-dimensional (2D) pseudo-homogeneous model was developed to simulate heat transport in a foam-based FBR used for the exothermic hydrogenation of benzene. The catalyst bed consisted of α -alumina or mullite foams coated with Ni/ γ -Al₂O₃. The simulations were conducted using MATLAB software. The computational geometry consisted of five zones representing the parts of the foam bed that were coated or not with the catalyst. During the simulations, steady-state conditions were assumed. Velocity profiles, temperature and concentrations were assumed to be symmetrical to the reactor centreline. Fluid properties such as specific heat capacity, viscosity and thermal conductivity were calculated using mixing rules. The heat balance equation included terms describing the enthalpy change to the fluid, axial and radial heat flow and heat production through chemical reaction. The mass balance expression accounted for the convective mass transfer, radial dispersion and kinetics. The kinetic rate expression included the chemisorption equilibria of H₂, benzene and cyclohexane. Arrhenius equations were used to implement the temperature dependence of the rate coefficients. Kinetic parameters were optimised using a least squares method in MATLAB. The simulation results indicated that calculated temperatures agreed with the temperatures measured at 108 locations in the reactor. The study showed the effects of thermal conductivity and foam pore density on the temperature distribution in the reactor. The 10 PPI α -alumina foam exhibited higher benzene conversions (i.e. 6.73 vs 5.72 mmol/min at a benzene flow rate of 300 mL/min) and a smoother temperature profile than the temperature profile obtained on the 10 PPI mullite foam (Fig 2-21a,b). This was attributed to the higher thermal conductivity of the α -alumina foam. As the pore density of was increased α -alumina foam, more benzene conversion was achieved (9.72 mmol/min), resulting in higher heat released in the foam bed (Fig 2-21c). The model predictive capability was used to show that using metal foams instead of alumina or mullite foams resulted in better heat distribution because of the high thermal conductivity of metallic substrates (Fig 2-21d).



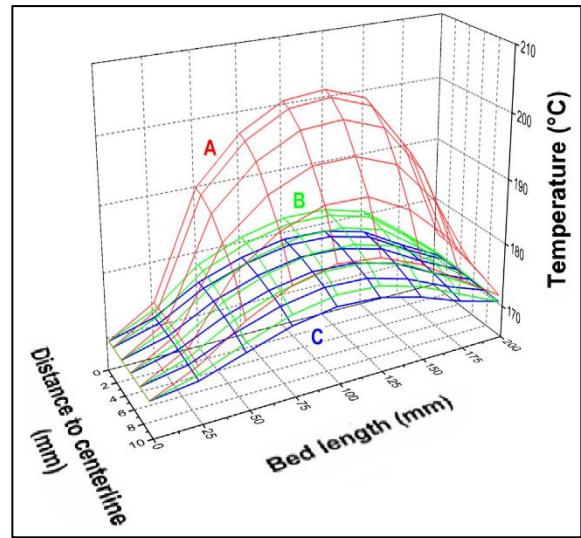
(a)



(b)



(c)



(d)

Figure 2-21. Comparison between experimental (red) and simulated (blue) temperature profiles on (a) a Ni/γ-Al₂O₃-coated 10 PPI mullite foam, (b) a Ni/γ-Al₂O₃-coated 10 PPI α-Al₂O₃ foam and (c) a Ni/γ-Al₂O₃-coated 20 PPI α-Al₂O₃ foam. (d) Comparison between simulated temperature profiles obtained on foams of different thermal conductivities: α-alumina (red), SiC-Al alloy (green) and Al (blue) (Gräf et al., 2016).

Using a pseudo-homogeneous three-dimensional (3D) modelling approach, Palma et al. (2018) simulated the water gas shift (WGS) reaction and compared the performance of a foam-based and a powder-based FBRs. The CFD modelling tool, COMSOL Multiphysics, was used to build a simplified geometry of the reactor, which was discretised into 128235 finite elements. Predefined material properties were assigned to the foam-based and powder-based catalytic domains. They included the density, heat capacity, porosity and permeability. Effective thermal conductivities of the porous domain were calculated using the volume average of the respective thermal conductivities of the fluid and foam or powder. The flow was assumed to be

incompressible and isothermal. Steady-state, incompressible Navier–Stokes equations were applied to determine the velocity profiles in the free-fluid zones. The Brinkman equation was used to model the catalytic zone of the reactor. The WGS reaction kinetics parameters (pre-exponential factor, the activation energy and heat of reaction) were calculated by the discretised Euler method. The simulations showed that the high porosity of the foam-based catalyst bed improved diffusional mass transfer in the catalyst bed. A CO conversion of 99% was achieved within 1.7 cm and 2.5 cm of the foam-based and powder-based catalyst beds, respectively (Fig. 2-22a,b).

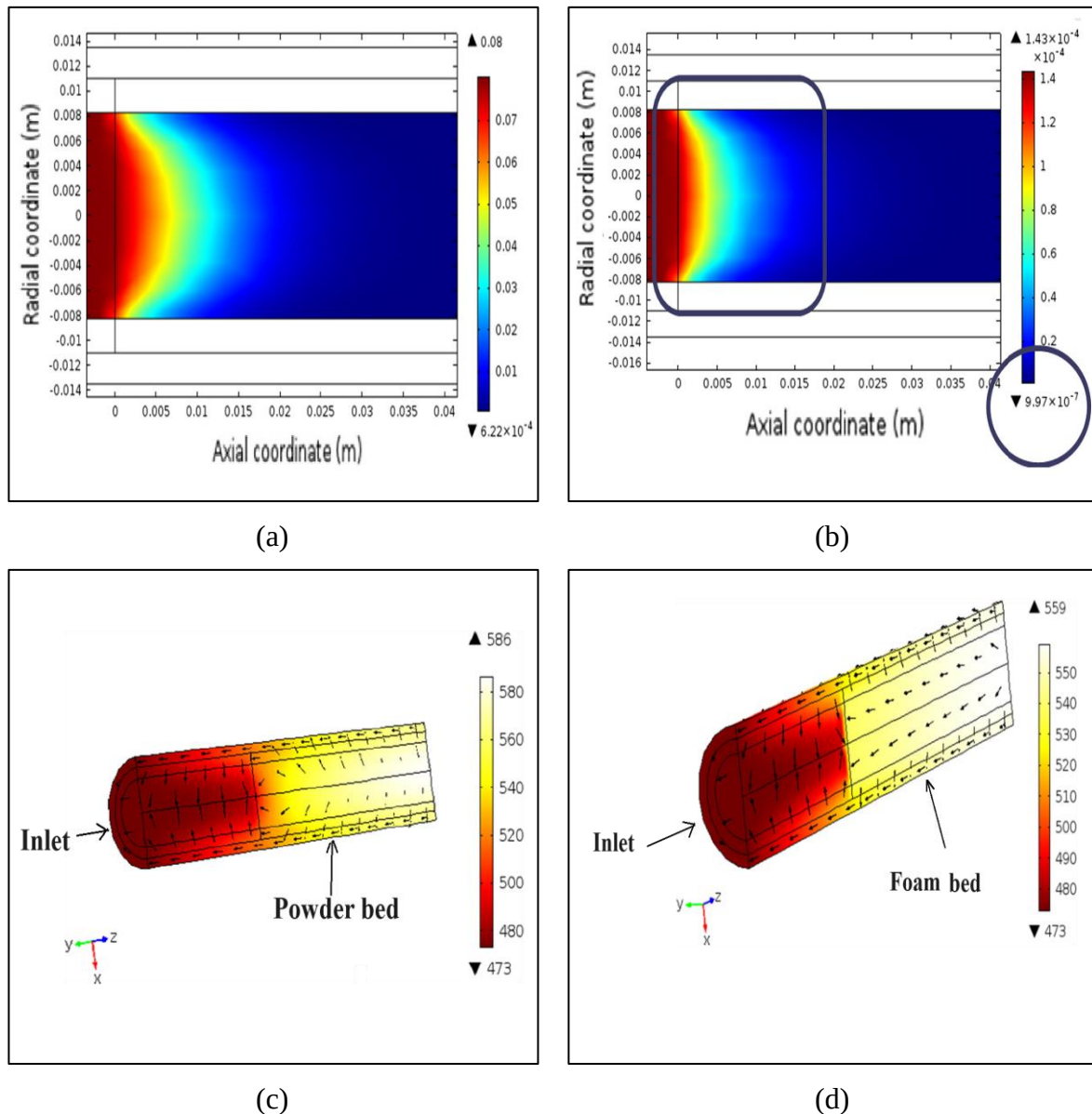
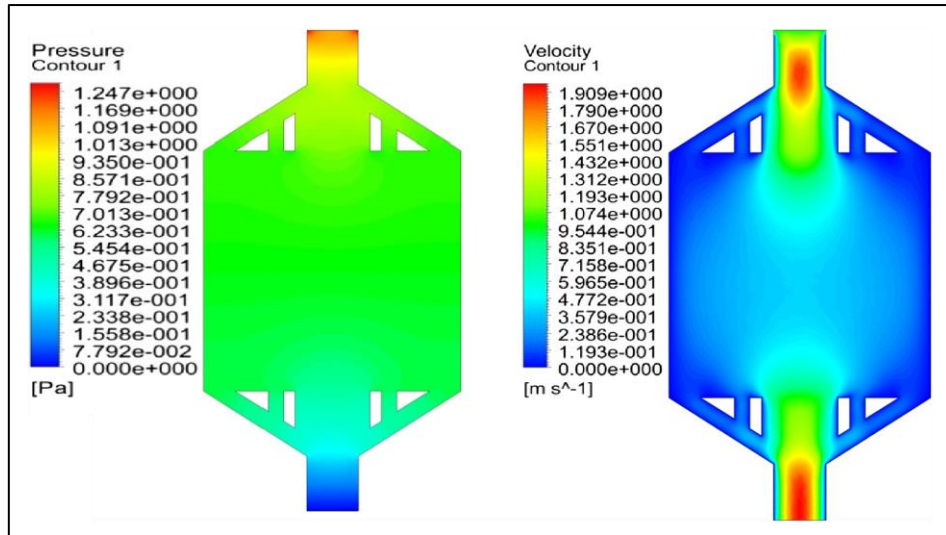


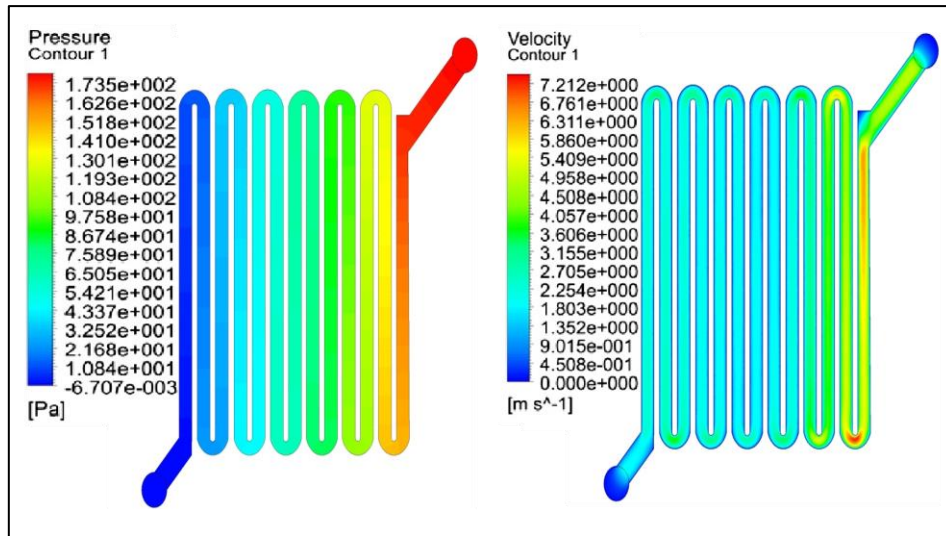
Figure 2-22. Comparison of CO mole fraction profile in the (a) powder-based reactor bed and (b) foam-based reactor bed. Temperature distribution profiles in (c) the powder-based bed and (d) the foam-based bed. (Palma et al. (2018))

Temperature profiles were more uniform in the foam-based reactor bed thanks to the high thermal conductivity of the metal foam. Moreover, the axial heat flux was higher in the foam-based catalyst bed due to the metal foam's high thermal conductivity (Fig. 2-22c,d). In this study, the CFD simulation proved to be a useful optimisation and predictive tool to establish the best parameters for the design of a single-stage WGS reactor.

Wilberforce et al. (2019) conducted and CFD simulations of polymer electrolyte membrane fuel cells fitted with metal foams used to obtain a more uniform pressure distribution on the gas diffusion layer. Their investigation focused on comparing the effects of different plate manifold designs on the pressure drop, flow regime and velocity profiles. The pseudo-homogeneous computational domains were designed using ANSYS software, consisting of a total of 250000–310000 discrete elements. Based on the calculated Reynolds number, the flow was considered laminar at all conditions throughout the simulated domains. The temperature was set to 288 K and inlet gas velocities were in the range 1–12 m/s. Their results revealed that the best design featured the inlet and outlet positioned symmetrically and aligned to the mid-section of the domain (Fig. 2-23a). This system was characterised by low pressure drops between the inlet and outlet, best described using Darcy's model. However, the velocity profile still revealed a high tendency for dead zone formation where water could potentially accumulate. It was also noted that full usage of the membrane electron assembly surface would not be achieved using this design. The performance of this foam-based design was compared to that of the serpentine design, known for its more efficient usage of the membrane electron assembly surface (Fig. 2-23b). Simulation results showed that pressure drops of 10000 and 20 Pa were obtained on the serpentine and foam-based designs respectively, at gas flow velocity of 12 m/s. This proved the suitability of using foam materials for process intensification in fuel cells.



(a)



(b)

Figure 2-23. Simulated pressure and velocity profiles in (a) the foam-based design and (b) serpentine design of the bipolar plate of the fuel cell (Wilberforce et al., 2019)

2.7.2 Heterogeneous models

In heterogeneous models, the transport properties of the fluid phase are computed separately from those of the solid phase. Heterogeneous simulations require phase-specific governing equations and therefore are more computationally intensive than homogeneous simulations (Kiewidt, 2017). Two different approaches can be used in heterogeneous modelling, namely the fully heterogeneous and the pseudo-heterogeneous approaches. Fully heterogeneous models consider the actual geometry and localised properties of the solid domain whereas pseudo-heterogeneous models do not (Kiewidt, 2017; Makhania and Upadhyayula, 2022b; Wehinger et al., 2016).

The complex foam structure can be simulated using real models or idealised geometries. Real geometries can be obtained from X-ray computed tomography or magnetic resonance imaging. These methods require complex preparation methods and they are time- and cost-intensive (Wehinger et al., 2016). For these reasons, regular polyhedral models (e.g. periodic open cell structures) have been extensively used in simulations of foam-based processes. These models include regular geometries such as the cubic, the body-centred cubic, the pentagonal dodecahedron, the tetrakaidecahedron (Kelvin cell) and the Weaire-Phelan cells (Ferroni et al., 2021; Krishnan et al., 2006) (Fig. 2-24). Due to the deterministic nature of these idealised models, random variations occurring in real foam geometries are not fully taken into account. To correct this issue, elaborate techniques such as algorithms based on the Voronoi tessellations have been used to generate more stochastic foam geometries (Lucci et al., 2017; Wehinger et al., 2016).

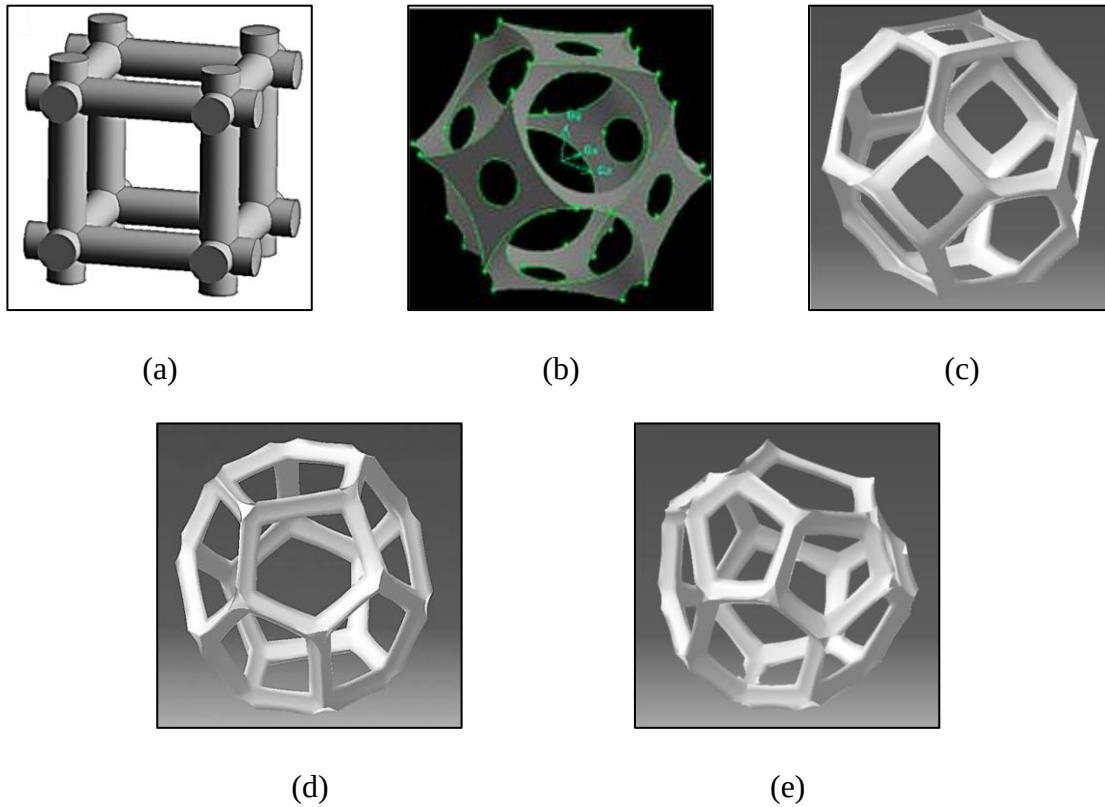
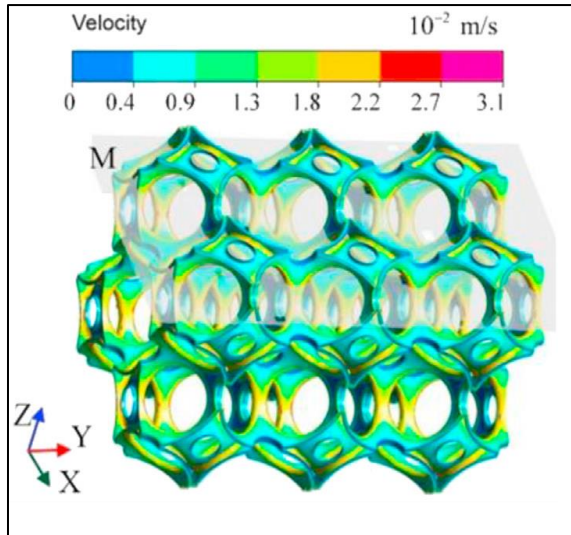


Figure 2-24. Examples of regular geometries used in periodic open cell structures: (a) cubic (Iwaniszyn, 2022), (b) body-centred cubic (Krishnan et al., 2006), (c) tetrakaidecahedron (Iwaniszyn, 2022), (d) dodecahedron (Iwaniszyn, 2022) and (e) Weaire-Phelan cells (Iwaniszyn, 2022).

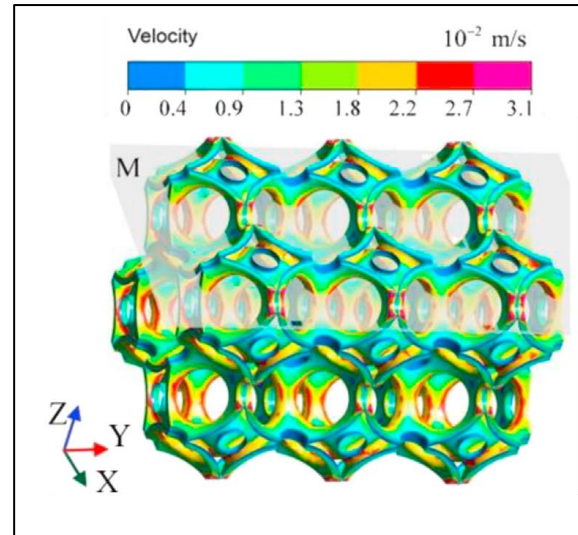
Heterogeneous simulations have been conducted in efforts to understand the effect of the foam geometry on the flow characteristics such as velocity profiles (Fan et al., 2016; Liu et al., 2019; Solovev et al., 2022; Wang et al., 2021; Zafari et al., 2015) and pressure drop (Ambrosio et al.,

2016; Fourie and Du Plessis, 2002; Wehinger et al., 2016; Zafari et al., 2015) or to provide a systematic analysis of heat transport (Ambrosio et al., 2016; Fan et al., 2016; Krishnan et al., 2006; Razza et al., 2016; Solovev et al., 2022) and mass transport (Aguirre et al., 2020; Ferroni et al., 2021; Solovev et al., 2022) phenomena in porous structures. A typical foam-based reactors consists of foams composed of hundreds or thousands of unit cells. It is usually impractical to simulate the entire reactor geometry of such systems. Therefore, to reduce computational costs, heterogeneous simulations are often conducted on a unit cell or a representative elementary volume.

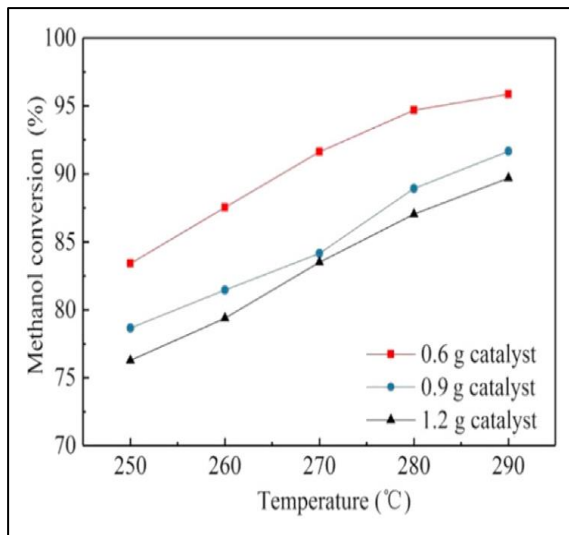
Wang et al. (2021) modelled a CuO/ZnO/Al₂O₃-coated copper foam unit (110 PPI, porosity 96%) using a body-centred cubic structure. The heterogeneous CFD model aimed at simulating flow profiles obtained at different catalyst loadings during the autothermal MeOH steam reforming process in a foam-based microreactor. The computational domain consisted of 12 cells of the coated foam. During the simulations, a steady-state, laminar, incompressible flow was assumed. The solid phase was assumed to be a homogeneous, isotropic porous zone, while the gas phase was assumed to obey ideal gas laws. A constant gas velocity and temperature were set at the inlet. A symmetry condition was imposed at the walls of the computational domain. The continuity and momentum equations were used to mathematically describe the process. The flow through the foam was described using Darcy's law. The catalyst loadings on the foam were 0.6, 0.9 and 1.2 g. The simulations results revealed that increasing the catalyst loading lead to greater gas velocity—shorter residence time—due to the more restricted flow area (Fig. 2-25a,b). The shorter residence time of the gas explained the decrease in MeOH conversion and H₂ production at high catalyst loadings (Fig 2-25c). The friction factor—and pressure drop—calculated from the simulations increased with the inlet gas velocity and the catalyst loading. Even though the catalyst loading of 0.6 g resulted in higher H₂ production and lower pressure drops, it also resulted in the lowest overall system efficiency. The efficiency of this autothermal system was found to increase with the inlet gas velocity since the heat generated from MeOH combustion would also maintain the reforming process. In this study, the optimum catalyst loading was found to be 0.9 g.



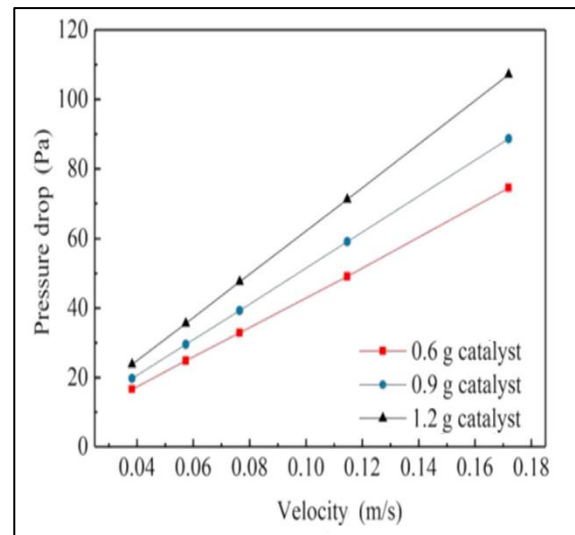
(a)



(b)



(c)



(d)

Figure 2-25. Results of simulations of MeOH steam reforming on a CuO/ZnO/Al₂O₃-coated foam: (a) velocity contour on the foam coated with 0.6 g of catalyst, (b) velocity contour on the foam coated with 1.2 g of catalyst, (c) MeOH experimental conversion at different temperatures and (d) simulated pressure drops at different catalyst loadings (Wang et al., 2021)

Sinn et al. (2020a) investigated heat transport in a foam-based catalytic reactor bed (10 PPI, diameter 12 mm, length 24 mm) by studying the effect of solid thermal conductivity, superficial velocity and surface emissivities. The actual foam geometry was generated by micro-computed tomography. The CFD simulations were run in OpenFOAM and verified using StarCCM+. Heat released or absorbed during H₂-based processes such as Fischer–Tropsch synthesis, CO₂ methanation, steam or dry reforming of CH₄ were mimicked by implementing a uniformly distributed 50 W heat source on the foam substrate. The flow through the foam was considered laminar, and governing equations included the conservation of mass, energy and momentum.

Radiative heat flow was expressed by the Stefan–Boltzman law. To understand the effect of thermal radiation on the calculated heat flow and solid temperature on conjugate heat transfer, the simulation was conducted with and without radiation model parameters (Fig. 2-26). During the study, the thermal conductivity was varied from 1 to 200 W/m/K, the velocity from 0.1 to 0.5 m/s and the surface emissivity from 0.1 to 1. The results showed that the influence of radiation on heat flow decreased but were not negligible for materials with high thermal conductivities (e.g. metal foams). This is due to the lower heat transport limitations occurring in high thermal conductivity materials. Increasing superficial velocities resulted in a decrease in the difference in heat flow between models which include radiation and models which do not consider radiation. At high gas flow, convective heat transfer increases and thermal radiation becomes less important. The role of surface emissivity in the radiation model was found to be more important at emissivity levels < 0.5 and elevated temperatures. A comparison with pseudo-homogeneous models showed that the effect of radiation modelling decreased with increasing thermal conductivity of solids and decreasing reactor temperatures. It was concluded that radiation model was influenced by the parameters in the following order: overall temperature $>$ substrate thermal conductivity $>$ superficial velocity $>$ surface emissivity.

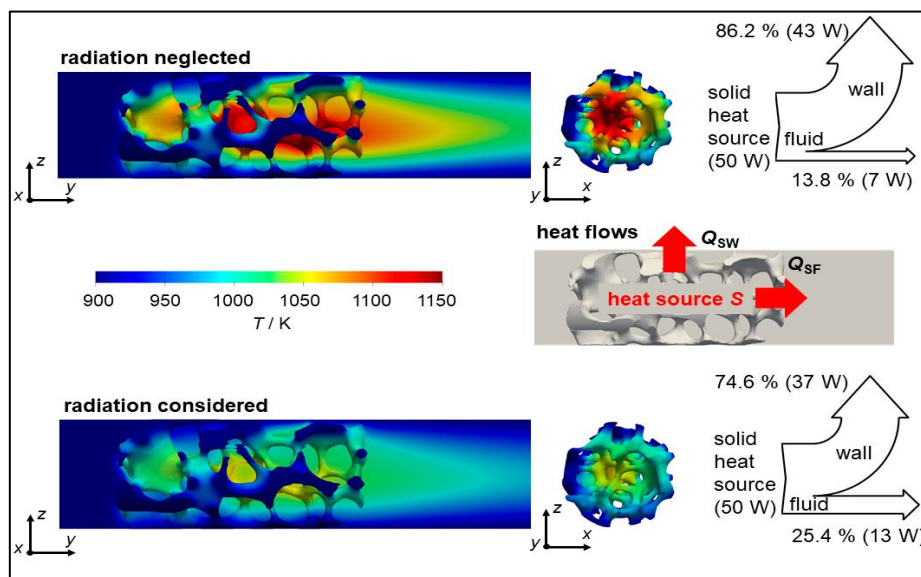


Figure 2-26. Nephogram showing the temperature fields and heat flows in models including heat transfer by radiation or not. Process conditions: wall temperature of 900°C; solid thermal conductivity of 5 W/m/K; fluid velocity of 0.5 m/s and a porosity of 0.9 (Sinn et al., 2020a). Legend. S: applied heat source, Q_{SW}: conductive heat flow to the wall; Q_{SF}: convective heat flow to the fluid.

Mühlbauer et al. (2020) simulated low-temperature WGS reaction in a foam-based reactor. The geometry was modelled using constructive solid geometry based on an inverse packing technique (Fig. 2-27a). The isotropic stochastic rotation dynamics method was used to simulate the fluid flow in the reactor (Fig. 2-27b).

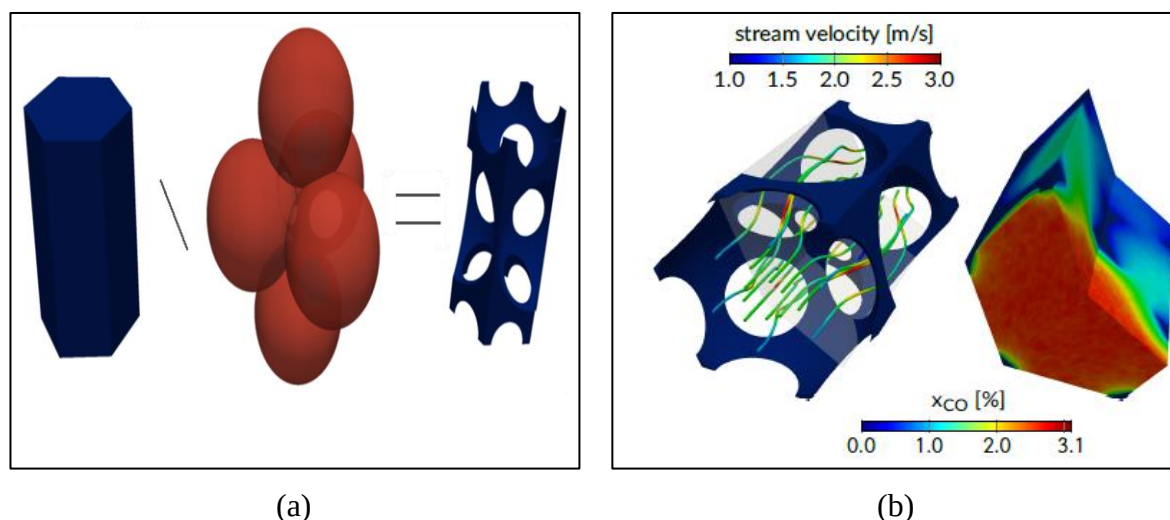


Figure 2-27. Illustration of (a) a simulated foam structure generated inverse packing method and (b) simulation result showing the velocity flow field and the CO mole fraction (x_{CO}) profile in the porous domain (Mühlbauer et al., 2020).

At the domain inlet and outlet, a periodic boundary condition was imposed for the temperature, density, velocity and pressure. Concentrations of reactants and products were assumed temporally constant at the reactor inlet. The foam structure was assumed to be uniformly coated with Cu/ZnO/Al₂O₃ catalyst. The model results showed that the effect of the Reynolds number on the pressure drop agreed better with experimental findings at low values of the Reynold number ($Re < 30$). At higher values, deviations observed between the simulated and experimental pressure drop correlations were attributed to the incompressibility effects. The correlation between the Sherwood and Reynolds numbers revealed two different mass transfer regimes. At low Reynold numbers ($Re < 10$), reactant species conversions depended more on diffusional properties than on superficial velocity; however, it was not the case at higher $Re > 10$. The deviation was attributed to the less tortuous flow path obtained in the more regular geometry of the model compared to flow in real foam structures. The study also revealed the effect of the porosity on the performance of the reactor. With an increase in porosity, both the pressure drop and the overall conversion rate decreased in diffusion-limited intermediate regimes corresponding to Thiele moduli of 16.8 and 1.34, respectively. To further assess the suitability of foam substrates, three performance indices were proposed, namely: the ratios of

conversion to dimensionless pressure drop, conversion to specific surface area and area to dimensionless pressure drop. The first two indices increased while the latter decreased with porosity. Therefore, in this study, high porosities were found to improve surface utilisation in both mass transfer limited and intermediate regimes. In reaction limited regimes, however, lower porosities are more beneficial.

2.7.3 Selected foam modelling processes reported in the literature

Numerical simulations have been conducted for several H₂ applications. Both homogeneous and heterogeneous simulations have been performed on commercial or open-source software. The objectives of some of the most recent simulation works on H₂ applications conducted on metal foams are summarised in Table 2-2.

Table 2-2. Selected recent CFD simulations of foam-based H_2 applications reported in the literature

Reference	Application	Model/simulation type	Software/code	Aim of the study
Solovev et al. (2022)	Acetylene hydrogenation	3D heterogeneous	ANSYS Fluent	Determination of the optimum geometric parameters to maximise the performance (i.e. conversion and selectivity) of the reactor.
Weng et al. (2024)	CH ₄ dry reforming over foam-supported Rh catalysts	3D heterogeneous	ANSYS Fluent	Study of the effect of the metal foam pellet structure on the reactor performance. Comparison between the performance of foam pellets and conventional ceramic pellets.
Barokh and Siavashi (2024)	CH ₄ steam reforming	3D heterogeneous	OpenFOAM	Investigation of the effect of velocity, temperature, steam-to-carbon ratio and foam porosity on the reactor performance.
Shigarov et al. (2017)	CH ₄ steam reforming on Ni/MgO catalyst supported on Ni foam	1D and 2D pseudo-homogeneous models	C++	Comparison between 1D and 2D models used for the description of the catalytic process conducted in two membrane reactor configurations. Simulation of flow conditions, temperature and pressure profiles in the reactor.
Ferri et al. (2024)	CH ₄ steam reforming on Rh/Al ₂ O ₃ in a packed foam reactor	2D heterogeneous model	MATLAB	Simulation of overall CH ₄ conversions as well as temperature distribution, reacting and product species distribution along the reactor length, at different operating conditions (GHSV, temperature).

Table 2-2 (continued). Selected recent CFD simulations of foam-based H_2 applications reported in the literature

Reference	Application	Model/simulation type	Software/code	Aim of the study
Sinn et al. (2020b)	CO_2 methanation	3D heterogeneous model	STAR-CCM+	Investigation of the effect of fluid properties, gas velocity, composition and pressure on the heat removal in the reactor.
Guo et al. (2024)	H_2 evolution reaction on Ni foam used as electrodes (Water electrolysis)	2D pseudo-homogeneous model	OpenFOAM	Assessment of the effect of the thickness of the foam electrodes on multiphase flow and ion transport.
Liu et al. (2019)	MeOH steam reforming on foam-supported Cu/Zn/Al/Zr	3D heterogeneous	ANSYS Fluent	Analysis of the effect of the size and distribution hole array on the performance of the foam-based microreactor.
Ding et al. (2010)	Partial oxidation of CH_4 on foam-supported Rh	2D axisymmetric heterogeneous model	FLUENT	Assessment of the effect of different geometric configurations and parameters, including foam material, catalyst surface area and channel size on catalytic performance.
Wehinger et al. (2016)	Partial oxidation of CH_4 on foam-supported Rh	3D heterogeneous model	STAR-CCM+	Catalytic foam modeller based on random point distribution and Voronoi tessellations was used to simulate a realistic foam structure. Simulation of species mole fraction profiles and temperature profiles in the foam-based FBR.
Upadhyay et al. (2022)	Water electrolysis in a proton exchange membrane (PEM) electrolyser	2D pseudo-homogeneous model	ANSYS Fluent	Assessment of the effect of stack temperature, cathode pressure, water feed rate, membrane thickness and porosity of the transport layer on the performance of the PEM using a foam for uniform flow distribution.

2.8 Summary of the advantages and disadvantages of techniques used in the development of foam-based catalytic systems

Metal foams have been extensively used as catalyst support structures for various H₂-based applications. To leverage the advantages of the foams in catalytic reactions, conventional chemical reactors have been modified to incorporate a foam-based catalytic section. In this chapter, the development of such foam-based reactors using metal foams as surface-extended catalyst support structures for H₂ applications was subdivided in three important stages: foam manufacturing, catalyst activation of the foam and foam-based reactor design.

Firstly, metal foam manufacturing methods, including investment casting, space holder, metal deposition and 3D printing techniques have been briefly discussed to understand the origin of their unique physical and geometric properties. Foam manufacturing by investment casting, space holder or metal deposition techniques results in the stochastic distribution of cells of different shapes. The investment casting method is well-suited for metal foams characterised by low-melting points whereas the space holder techniques can be used for metals of high melting temperatures (Hassan and Alnaser, 2024). The metal deposition technique has the further advantage of generating hollow struts, which results in lighter foams (material saving) (Ashby et al., 2000).

Despite their relative simplicity, these foam manufacturing methods present some disadvantages. For instance, when using the investment casting method, it can be difficult to completely fill the mould with liquid metal and subsequently remove the mould without rupturing the foam struts (Hassan and Alnaser, 2024; Kapłan et al., 2022). The space-holder method is limited to porosities ranging from 50–85%. Outside this range, removing the space holder material or maintaining the continuous structure of the foam can be challenging (Hassan and Alnaser, 2024).

The above foam manufacturing methods are not easily reproducible and they result in a limited variety of cell geometries. Modern techniques such as 3D printing have the potential to introduce a wider choice of simple or complex reproducible geometries that may be adapted to specific applications, including chemical processes (Constanza et al., 2021).

In general, for catalytic applications, the manufacturing methods of metal foams are seldom discussed in the scientific literature on foam-based catalytic structures. For these applications,

the foam characteristics should enable more a turbulent, tortuous reactant flow, improved reactant mixing, good heat distribution, low pressure drop and a good catalyst adhesion on the substrate surface.

Secondly, the catalyst deposition process on metal foams has been described in steps that include surface cleaning, pretreatment and catalyst coating (substrate activation). Surface cleaning is an important step in the removal of impurities that include dust and organic matter from the foam surface (Shen et al., 2021). These impurities can impair the catalytic coating process by generating flawed weak points that could affect the overall performance of the foam-based system. Cleaning agents are selected by considering the nature of the impurities expected on the foam surface. Deionised water, organic compounds (e.g. acetone, ethanol), acidic or basic solutions have been often used as cleaning agents (Lotfi et al., 2019; Park and Kim, 2016). Furthermore, cleaning agents should be carefully chosen to avoid damaging the physical or chemical nature of the metal foam (Montebelli et al., 2014b).

Substrate pretreatment methods are aimed at increasing the roughness of the foam surface to improve the adhesion of the catalyst. Oxidative and chemical pretreatment methods modify the foam by creating an oxide layer or by simply etching the surface (Meille, 2006). The advantage of the generation of an oxide layer is that it can act as an inexpensive morphological support to enhance the surface area of the catalyst and prevent the sintering of the active metal during the activity tests. Primers can be added to increase the adhesion of the catalyst (Meille, 2006, Montebelli et al., 2014). However, this results in increased amounts of materials on the foam substrate, which decreases the porosity and can lead to pore blocking in foams of high pore densities.

Catalyst deposition methods vary according to the nature of the catalyst to be coated and the process in which the catalyst is used. In some applications, active metals can be directly deposited on the surface of the pretreated foam. Direct metal coating methods such as electrochemical deposition present several advantages, including low tendency for pore blocking, uniform catalyst distribution and controlled washcoat thickness (Ho et al., 2020a). In other applications, a morphological support is required to maintain a stable and satisfactory catalytic performance of the active metal. In such cases, methods such as sol–gel coating or the slurry coating methods can be used. The sol–gel deposition technique results in thin and uniform catalyst layers on the foam struts (Montebelli et al., 2014a). For applications involving the use of commercial or ready-made catalysts, characterised by specific textural properties

that are crucial for their high catalytic performance, it may be useful to resort to the slurry coating method. The catalyst deposition is often coupled with post-treatment steps such as thermal treatment to remove traces of solvent or organic matters, to consolidate the catalyst layer on the foam. The selection of post-treatment methods should be guided by anticipated beneficial properties such as the average size of the catalyst nanoparticles, oxidation state of the active metal (Montebelli et al., 2014a).

Thirdly, the main foam-based reactor configurations used in H₂-based catalytic processes have been briefly reported on. They include FBRs, tank reactors and microreactors. These designs may involve simply replacing the conventional catalyst bed (e.g. catalyst pellets) with a coated foam or they may incorporate structured components such as foam-based impellers in tank reactors. In several cases, the foam-based reactors were found to offer better performances of processes limited by heat or mass transfer limitations (Benamara et al., 2018; Koo et al., 2024).

The high porosity and high thermal conductivity of metal foams enhances heat distribution inside the reactor. Convection, radiation and conduction heat transfer mechanisms simultaneously contribute to create the relatively uniform temperature profiles generally observed in foam-based reactors. Catalytically activated metal foams have the advantage of reducing hot spot formation in reactors, improving the selectivity to desired products and delaying catalyst deactivation (Fratalocchi et al., 2018; Kim et al., 2015; Yan et al., 2014).

The highly porous and reticulated structure of the foam also enhances mass transfer by causing a high level of reactant mixing and turbulence in the flow of chemical species inside the catalyst bed. Mass transfer in foam-based reactors is also improved because of the foam's high volumetric surface area and reduced diffusion length compared to conventional pellets, for instance (Benamara et al. 2018; Leon et al., 2011). This implies that smaller pore diameters and thin washcoat layers are beneficial for diffusion-limited processes.

However, these geometric properties place a limit on the maximum catalyst inventory available in a given reactor volume. This makes foam-supported catalyst beds less suited than catalyst pellets for kinetically limited processes. For this reason, packed foam reactors have been used to maintain high catalyst loading in the reactor while taking advantage of the desirable heat transfer properties of metal foams (Ambrosetti et al., 2022, 2020; Fratalocchi et al., 2018). To select an appropriate reactor bed configuration, it is therefore important to consider the relative importance of the kinetic and diffusion limitations characterising the chemical process.

Lastly, numerical modelling and simulation were mentioned as modern, cost-effective tools in the design and optimisation of foam-based reactors used in H₂ applications. The main modelling approaches that have been investigated were grouped into two categories: the pseudo-homogeneous and heterogeneous models. The selection of an approach depends on the expected level of detail in the estimation of simulated parameters and consequently, the available computational power.

Pseudo-homogeneous models can be used in cases where an entire reactor unit needs to be simulated to understand the overall process. The properties of the reactor components are simplified to averaged and effective physical properties (Palma et al., 2018). This approach has the advantage of simplicity and being less computationally intensive. It could be used by engineers for the optimisation of the overall process parameters or the reactor unit.

On the other hand, heterogeneous models are more detailed. They take into account the actual or approximated (idealised) geometry of the foam and more detailed properties of the different phases present in the process (Makhania and Upadhyayula, 2022a). This approach is beneficial for the determination of the effect of the foam geometry on specific parameters such as heat or mass transfer coefficients and pressure drop and the reactor performance. Generally, both pseudo-homogeneous and heterogeneous simulations are ways to select the main geometric or material properties of foam-based catalyst beds and to confirm the benefits of foam-based reactors in the intensification of catalytic processes.

2.9 Conclusions

This chapter presented an overview of important steps in the development of foam-based reactors used for H₂ applications. The scientific literature has shown that the foam-based structured reactor can suitably be used for a variety of chemical processes. Depending on the application involved, the foam-based reactor beds contributed differently to the reactor performance. Generally, the foam contributes to improving the performance of processes subjected to heat and mass transfer limitations. Thanks to their high thermal conductivities, metal foams enhance heat distribution or dissipation in the catalyst bed. Their high volumetric surface area improves the contact between the reactants and the catalyst active phase. This results in better effectiveness factors than in conventional pellet-based reactors, for instance.

In the design of a suitable foam-based reactor, several important aspects should be considered. During the manufacturing stage—or when acquiring a ready-made foam—the foam should be selected by anticipating the beneficial physical and chemical properties as well as the stresses which the foam will undergo. High thermal conductivity and resistance to chemical or mechanical stresses depend on the substrate material. The diameter of pores and struts of the foams will determine the surface available for catalyst deposition as well as the tendency for the occurrence of defects such as pore blocking.

The method of catalytic activation of the foam substrate is also crucial to obtain the desired catalytic properties which, in synergy with the foam characteristics, will contribute to the reactor performance. During the catalyst deposition step, process-specific beneficial catalytic properties should be carefully assessed to establish the need for the use of primers, binders or morphological supports. The choice of a suitable catalyst treatment method (i.e. calcination, reduction) is also guided by the desired chemical properties of the catalyst coated on the foam.

The beneficial effect of the foams is generally evidenced in reactor designs through the enhancement of both transport and kinetics properties. Heat and mass transport characteristics are usually improved by the foam properties (thermal conductivity, surface area and porosity). These properties are of little use when catalyst coating processes limit the benefits of the catalyst intrinsic properties (e.g. by decreasing the availability of active sites through pore blocking and thick washcoat layer thicknesses). The reactor design can be aided by numerical simulations in which suitable models are implemented for the prediction of the reactor performance.

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Chapter 3. Metal foam as surface-extended catalyst support structure for process intensification in the dehydrogenation of perhydro-dibenzyltoluene on a Pt/Al₂O₃ catalyst

Chapter overview (Abstract)

Dibenzyltoluene/perhydro-dibenzyltoluene (H₀DBT/H₁₈DBT) is considered a promising liquid organic hydrogen carrier (LOHC) pair for the storage and transportation of green hydrogen (H₂). However, at the point of use, the catalytic dehydrogenation of H₁₈DBT is still limited by mass transport limitations. To address this issue, the dehydrogenation of H₁₈DBT was successfully conducted on Pt/Al₂O₃-coated foams in both an unstirred tank reactor and a fixed-bed reactor (FBR). A performance comparison between coated foams and pellets in the tank reactor revealed that H₂ productivities were 12–59% higher in the foam-based reactor than in the pellet-based reactor. Since the textural properties of the foam-supported and pellet-based catalysts were similar, the higher degree of dehydrogenation (DoD) and H₂ productivity achieved by the former were attributed to the geometric properties of the foam structure. Long-term tests performed in the FBR demonstrated the ability of the coated foams to maintain steady activity for >16 h on stream. However, the single-pass DoDs achieved were 34–38%. By recycling the partially dehydrogenated products three times into the FBR, the DoD improved to 63%. The results of this study demonstrated the capabilities of the coated foams in the process intensification of LOHC dehydrogenation reactors.

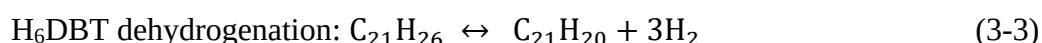
3.1 Introduction

In recent decades, green hydrogen (H₂) has been considered a very attractive energy carrier. It is a gas of high energy density (120 MJ/kg) that can be converted into energy through environmentally friendly processes [1]. H₂ also has the potential to minimise the gap between energy supply and demand caused by the fluctuating nature of widely used renewable energy sources such as wind and solar power [2–4]. Due to the low density of H₂ at normal temperature and pressure conditions and its tendency to diffuse through metals, establishing an energy distribution system partly relying on the storage of excess renewable energy in the form of green H₂ presents several practical challenges. For instance, the current methods of H₂ storage and transportation are energy-intensive, relatively unsafe; and, therefore, costly [5,6]. Compressed and liquid H₂ requires harsh conditions such as elevated pressure (e.g., 700 bar)

and a low temperature (-253°C), and specially designed pipelines are required to transport H_2 over long distances [7,8]. H_2 can also be stored by physisorption and chemisorption mechanisms in solid compounds on metal–organic frameworks and metal hydrides or by a reversible catalytic reaction in unsaturated aromatic compounds known as liquid organic hydrogen carriers (LOHCs) [1,9–11]. Compared to existing H_2 storage methods, LOHCs offer important advantages, including a high H_2 gravimetric storage capacity, compatibility with existing transport infrastructures, a mature industrial synthesis technology, and cost-efficiency [6,12,13].

One of the most promising LOHCs is dibenzyltoluene (H_0DBT), also known as Marlotherm SH[®], which is currently used as an industrial heat-transfer fluid [4,14]. H_0DBT is a non-toxic, non-flammable aromatic liquid at room temperature [15,16]. Its hydrogenated version, perhydro-dibenzyltoluene (H_{18}DBT), contains 6.2 wt.% H_2 . H_2 storage in H_0DBT is achieved through an exothermic reaction at relatively high pressures (10–50 bar) and low temperatures (150–300 $^{\circ}\text{C}$), while the dehydrogenation of the H_2 -rich molecule (H_{18}DBT) can be performed at atmospheric pressures and higher temperatures (e.g., 280–320 $^{\circ}\text{C}$) [17]. Both reactions require the presence of highly active catalysts such as Pt-, Ni-, or Ru-based catalysts for the hydrogenation reaction and Pt-based catalysts for the dehydrogenation reaction.

The dehydrogenation of H_{18}DBT is a complex endothermic reaction ($\Delta\text{H} = 65 \text{ kJ/mol}_{\text{H}_2}$); it takes place in three steps (Eqs 3-1–3-3) [18–20]. Practically, this process generally results in the production of H_2 in the gas phase and a mixture consisting of partially dehydrogenated products or intermediates (H_{12}DBT and H_6DBT) and a fully dehydrogenated product (H_0DBT) [11].



Harsh reaction conditions during catalytic dehydrogenation can cause the cracking of the H_{18}DBT molecule into undesired by-products, which not only prevent its recyclability as a H_2 storage molecule but eventually accelerate the deactivation of the catalyst [21,22].

To mitigate this issue, research has been conducted on the optimisation of the properties of catalysts. Suitable catalysts are characterised by high activity and high selectivity towards the fully dehydrogenated product [23]. Pt-based catalysts are preferred for the dehydrogenation of LOHCs because of their ability to facilitate the activation of adsorbed aromatic hydrocarbons and their higher selectivity towards the functionalisation of C-H bonds rather than C-C bonds [24]. More specifically, Pt/Al₂O₃ catalysts have been extensively studied for H₁₈DBT dehydrogenation. To further improve the dehydrogenation performance of Pt/Al₂O₃, several catalyst modification methods have been proposed. Garidzirai et al. [25] observed that the use of Mg as a dopant for Pt/Al₂O₃ resulted in better Pt dispersion and lower Al₂O₃ acidity—and, consequently, a significant increase in H₂ productivity and selectivity towards H₀DBT. Shi et al. [26] observed that Pt doped with Mo resulted in the formation of fewer by-products due to better H₂ spillover on Pt/Mo_xC-Al₂O₃. Modisha et al. [21] prepared a Pt/Al₂O₃ catalyst using a supercritical vapour deposition method that not only increased the dispersion of the Pt particles but improved the performance and reusability of the catalyst.

Other research groups have focused on process intensification methods aimed at improving heat and mass transfer in reactors [19,27–30]. Wunsch et al. [14] developed a multi-stage micro-structured reactor equipped with intermediate membrane-based H₂ separation units, with the aim of avoiding the use of high reaction temperatures necessary for increased H₂ production and mitigating the negative effect of the gas phase on the LOHC residence time. Müller et al. [30] proposed a decrease in the LOHC dehydrogenation temperature by overcoming reaction equilibrium limitations; three approaches were employed: reaction under vacuum pressure, H₂ dilution with inert gas, and reactive distillation. Solymosi et al. [28] prepared stainless steel plates coated with Pt/Al₂O₃ modified by sulphite impregnation. They proposed that such plates could be used as catalytically activated heat-transfer materials that could be incorporated into high-temperature fuel cell systems. Ali et al. [19] utilised a microchannel reactor because of its high thermal and mass transfer capabilities, precise temperature control, and quick phase separation. They demonstrated the improved performance of a microchannel reactor washcoated with Pt/Al₂O₃ compared to that of a stirred tank reactor. The results of the studies by Solymosi et al. [28] and Ali et al. [19] suggested that surface-extended catalyst support structures could improve heat and mass transfer—and, therefore, reactor performance—in highly endothermic LOHC dehydrogenation processes. These processes are subject to both kinetic and diffusion limitations.

In this study, metal foams were selected as surface-extended catalyst support structures for the dehydrogenation of H_{18} DBT. Typically, the dehydrogenation of H_{18} DBT is mostly conducted on pellet-based or powder-based catalysts. According to the literature, the reported benefits of metal foams as catalyst support structures include the following: improved heat distribution (essential for the prevention of hot spots), enhanced mass transfer due to an increased surface-to-volume ratio, high porosity and tortuosity, mechanical stability, and ease of catalyst handling in the reactor [31–37]. The benefits of foam-based reactors over conventional catalytic systems were demonstrated in several processes, including those involving liquid phases. For instance, Benamara et al. [38] compared the performance of foam-based and pellet-based reactors used for the adsorption of H_2 in α -methylstyrene. Their results showed that the gas/liquid mass transfer coefficient obtained in the foam-based reactor was twice as high as that obtained in the pellet-based reactor. In another study, Leon et al. [39] compared the performance of a rotating foam reactor and a slurry reactor for the hydrogenation of 3-methyl-1-pentyn-3-ol. They stated that the foam-based reactor presented the advantages of easier catalyst separation from the reaction medium; catalyst reusability; and improved safety, especially for highly exothermic reactions.

In the current investigation, H_{18} DBT dehydrogenation experiments were performed on 5 wt.% Pt/ Al_2O_3 catalyst coated on aluminium (Al) foam in a tank reactor and an FBR. The tank reactor was selected because of its suitability for screening and comparison tests using small reactant volumes and low catalyst amounts. The foam-based FBR was used to extend the study towards continuous H_2 production, which is more typical of large-scale operations [40]. The objectives of this study were the following: (1) to assess the effect of catalyst coating on the textural properties of the Pt/ Al_2O_3 catalysts; (2) to evaluate the effects of various parameters, including the Pt/ H_{18} DBT ratio and the temperature, on the performance of the Pt/ Al_2O_3 -coated foam and Pt/ Al_2O_3 pellets in an unstirred tank reactor; and (3) to assess the effect of long-term reaction and product recycling on the performance of the foam-supported catalyst in an FBR.

3.2 Results and discussion

This section first reports on the catalyst's textural properties determined using the characterisation methods, including scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), thermogravimetric analysis, X-ray diffraction (XRD), and CO pulse chemisorption. The catalytic performance results from the tank reactor and the FBR are summarised and discussed later.

3.2.1 Catalyst characterisation

SEM micrographs and EDS spectra of samples of Pt/Al₂O₃-coated foam and Pt/Al₂O₃ pellets are shown in Fig. 3-1. The presence of the catalyst washcoat layer on all the struts confirmed the effectiveness of the catalyst coating process. The cracks observed in Fig. 3-1a could have originated from the superposition of multiple layers of catalyst during the coating process. During slurry coating, a single cycle of dip-coating and drying often results in insufficient catalyst inventory on the surface of the foam. Generally, high catalyst loading is necessary to improve the catalytic activity in kinetically limited processes [41]. To increase the catalyst loading on the foam, multiple coating cycles are, therefore, necessary. The disadvantage of this is that weak spots can be created between adjacent layers. The most adhesive catalyst layers are those closest to the foam substrate. As the loading increases, subsequent layers will tend to detach more easily from the foam structure when subjected to increased mechanical stresses [42]. This then suggests that only a limited amount of catalyst can be coated on a foam, even one of low pore density (i.e., large pores). A foam of higher pore density (e.g., 40 PPI) has a higher volumetric surface area available for catalyst coating but also a higher pore-blocking tendency at increased catalyst loadings.

The high surface roughness of the foam could have originated from the decomposition of the binder (polyvinyl alcohol) during the calcination process. A high level of rugosity on the surface is beneficial to diffusion-limited catalytic processes because it increases the volumetric surface area of the coated foam. As mentioned earlier, the dehydrogenation of H₁₈DBT is generally accepted as being a three-step process. The first step (Eq. 3-1) is the fastest, while the second and third steps (Eqs 3-2 and 3-3) are rate-limiting [19]. The 10 PPI foam used in this study was selected for its ability to support relatively high catalyst loading while maintaining a larger volumetric surface area compared to conventional catalyst structures such as pellets.

Pt/Al₂O₃ pellets typically have gravimetric surface areas >170 m²/g [43]. Some major cracks were also evident on the surface of the Pt/Al₂O₃ pellet (Fig. 3-1b). These cracks can be attributed to mechanical stresses during the handling of the catalyst. The EDS data confirmed the presence of Pt (highlighted on the spectra in Fig. 3-1) and alumina (Al and O) along with traces of other elements, including Cl, Ca, Fe, K, S, and Rh (Fig. 3-1a,b). The Cl peak can be attributed to the presence of small amounts of precursor (H₂PtCl₆·6H₂O) that may have

remained on the catalyst after the thermal treatment [44]. The remaining elements originated from a misidentification of minor peaks by the software during the analysis [45].

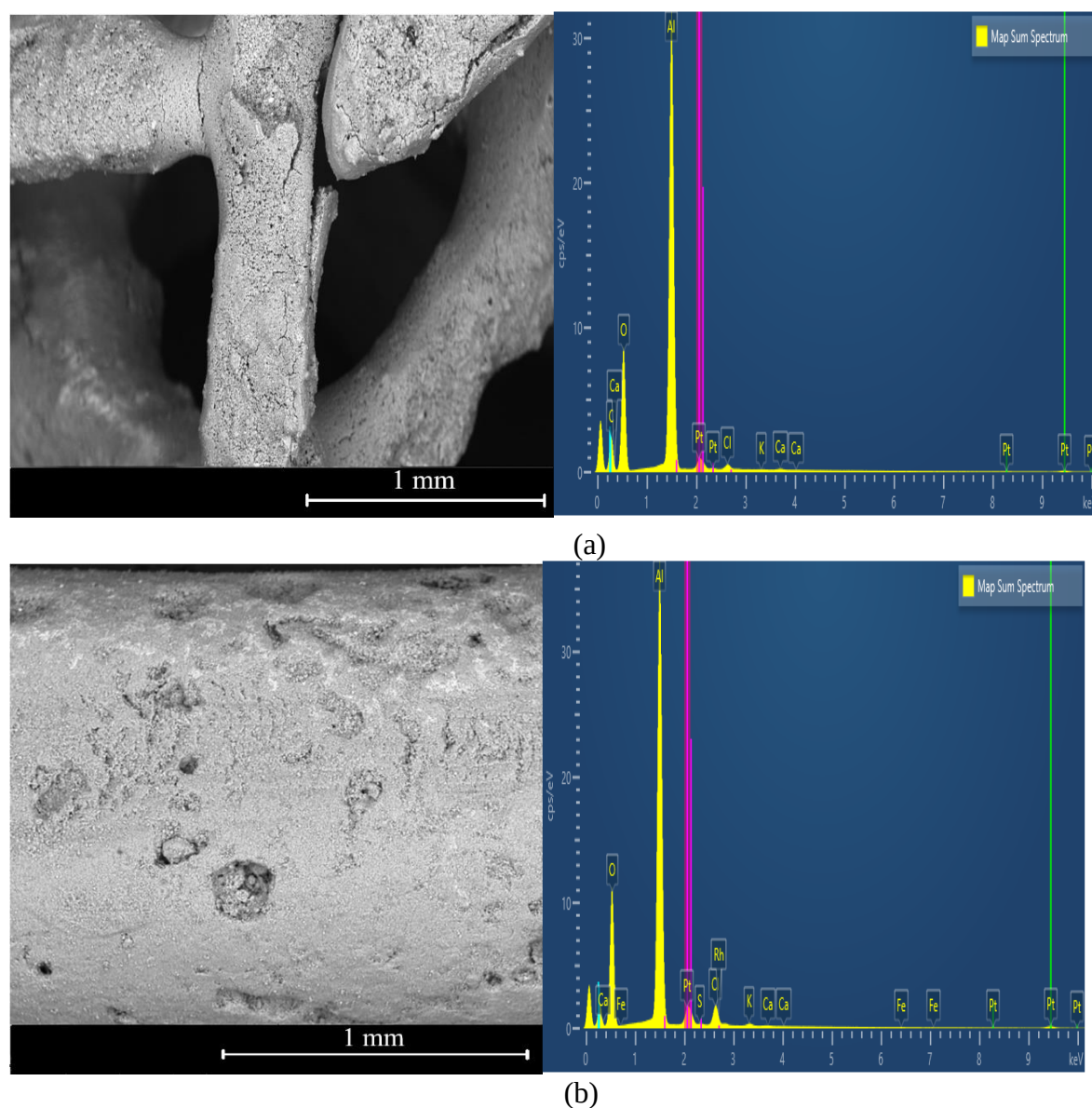


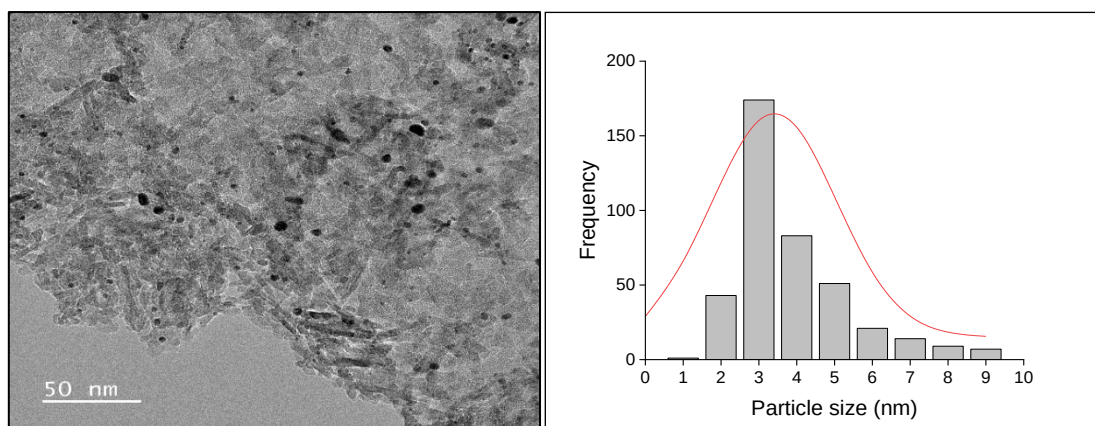
Figure 3-1. SEM micrographs and EDS spectra of (a) Pt/Al₂O₃-coated foam struts and (b) Pt/Al₂O₃ pellets.

Pt was found to be well distributed on the surface of the pellet-based and foam-supported catalysts. However, the surface compositions differed. The Pt content of the pellets and coated foam surfaces were 7.4 and 5.3 wt.%, respectively (Table A-1, Appendix A). The Pt content of the foam catalyst layer is closer to the value targeted during the catalyst preparation. This difference can be attributed to the difference in preparation methods. The pellets were prepared by wet impregnation of Pt from an aqueous H₂PtCl₆ precursor solution. This preparation method resulted in an eggshell structure in which the Pt nanoparticles were more concentrated on the surface than in the centre. The catalyst coated on the foam was first crushed and

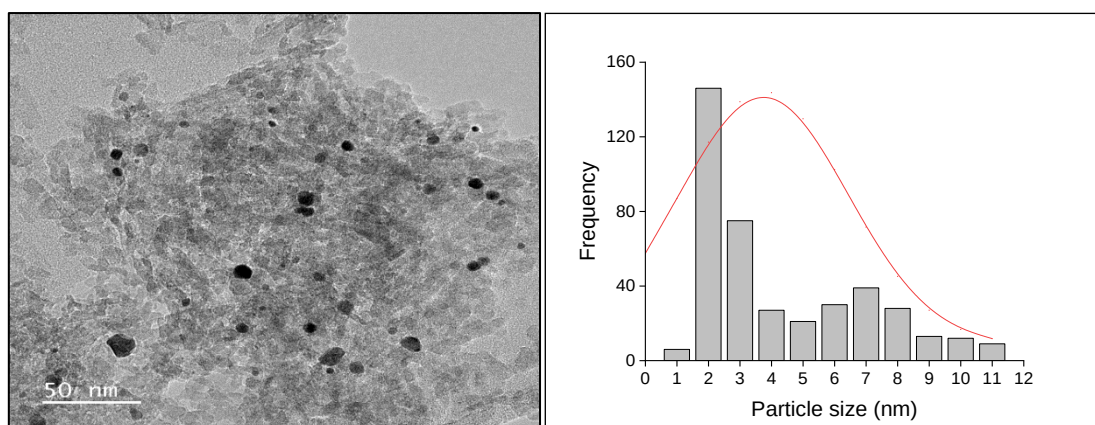
homogenised during the preparation of the slurry used to coat the Al foam. This resulted in Pt being more uniformly distributed in the washcoat layer.

Catalyst powders obtained from the pellets and extracted from the washcoat layer of the foam were also analysed using TEM, TGA, and XRD. The results obtained for the two catalyst configurations are shown in Fig. 3-2.

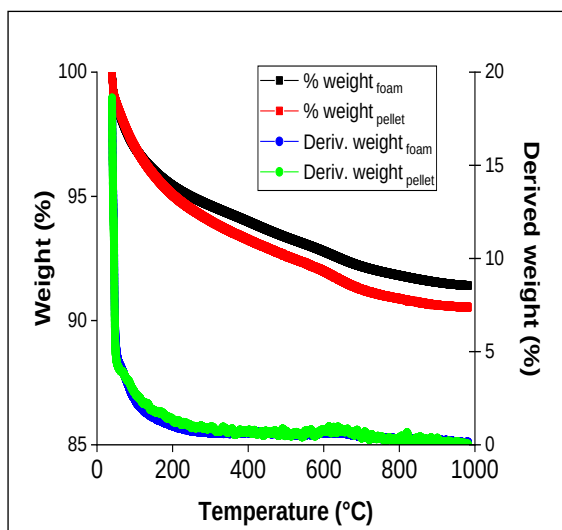
Despite the slight difference in particle size distribution, the mean Pt nanoparticle sizes calculated from TEM (Fig. 3-2a,b) were found to be similar: 3.4 and 3.8 nm for foam-supported and pellet-based catalysts, respectively. The similarity between the two TGA thermograms (Fig. 3-2c) confirmed the absence of residual organic matter that could have originated from the catalyst coating procedure on the foam. Furthermore, the two similar XRD diffractograms (Fig. 3-2d) revealed the presence of Pt and PtO_x on the foam-supported and pellet-based catalysts. The relatively broad peaks in Fig. 3-2d suggest an overlap between the Pt and Al₂O₃ peaks [46–48]. Nevertheless, signals corresponding to Pt (111), Pt (200), Pt (220), Pt (311), and Pt (222) can be recognised at diffraction angles of 37°, 46°, 67°, 81°, and 86° [46,49]. Reflections corresponding to PtO_x could be observed in both diffractograms at diffraction angles of 26°, 34.5°, 52°, 57°, and 61°, corresponding to Pt (0002), Pt (10-10), Pt (0004), and Pt (110) [50]. They were generally characterised by sharp peaks, indicating the high crystallinity of the oxide particles [50]. The presence of these oxides could be attributed to the fact that some Pt nanoparticles remained oxidised after the calcination–reduction pretreatment during the catalyst preparation [49].



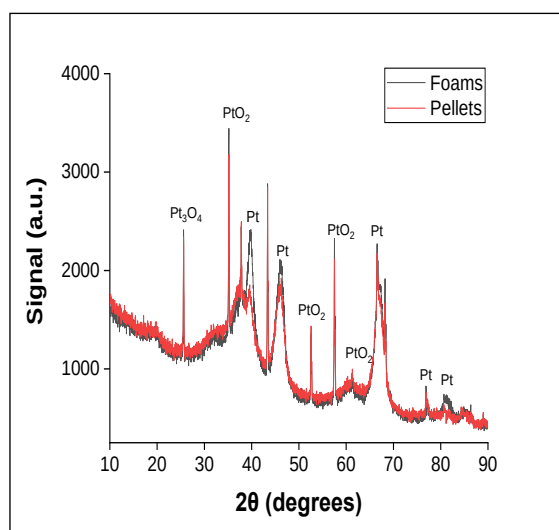
(a)



(b)



(c)



(d)

Figure 3-2. (a) TEM micrograph and particle size distribution of the catalyst extracted from the coated foam; (b) TEM micrograph and particle size distribution of the powder from crushed pellets; (c) TGA thermogram of the catalyst from the foam and pellets; and (d) XRD diffractogram of the catalyst from the foam and pellets.

The dispersions and surface areas of the Pt were estimated using CO pulse chemisorption. The results are tabulated in Table 3-1. For the same amounts of Pt/Al₂O₃ catalyst, the Pt dispersions and surface areas on the Pt/Al₂O₃ pellets and on the Pt/Al₂O₃-coated foams were generally similar. The slightly higher Pt metal dispersion and surface area on the pellets suggest that the foam coating process resulted in the dilution of some Pt nanoparticles in the morphological support (Al₂O₃). Although the Pt particle sizes calculated using this method were found to be relatively similar in the two configurations, they were higher than the sizes calculated using TEM. This was also observed by Modisha et al. [43], who explained that particle sizes obtained from TEM analysis are specific to the area/s selected during the imaging process. The CO pulse chemisorption results, however, are calculated from the total amount of CO adsorbed on the Pt active sites. These include the active sites on single atoms and small nanoparticles (not easily observed by TEM) as well as relatively large nanoparticles. The assumption of monomolecular CO adsorption on Pt atoms may have led to an overestimation of the Pt particle size calculated by the CO pulse chemisorption technique [8].

Table 3-1. Results of CO pulse chemisorption analysis.

Sample	Metal dispersion (%)	Pt Surface area (m²/g)	Pt particle size (nm)
Pellets	21	51	5
Foam	19	46	6

In general, the characteristics of the Pt/Al₂O₃ catalysts extracted from the pellets and from the washcoat layer on the foam were comparable. These results prove that the coating procedure and thermal treatment of the Pt/Al₂O₃ catalyst on the foam did not significantly alter the textural properties of the catalyst. Differences in catalytic performance between coated foams and pellets were, therefore, mainly attributable to the difference in structural configurations.

3.2.2 Catalytic performance

In all the experiments conducted in this study, the dehydrogenation products mainly consisted of a mixture of unreacted H₁₈DBT, intermediate dehydrogenation products (H₁₂DBT and H₆DBT), small amounts of H₀DBT and by-products (Fig. A-1, Appendix A). Dehydrogenation did not generate any detectable gaseous products other than H₂ (Fig. A-2, Appendix A).

3.2.2.1 Effect of Pt/H₁₈DBT molar ratio on H₁₈DBT dehydrogenation performance

A comparison of the H₂ release rates obtained during H₁₈DBT dehydrogenation on the Pt/Al₂O₃-coated foam and Pt/Al₂O₃ pellets is shown in Fig. 3. The operational advantage of the coated foam over the pellets is evident at Pt/H₁₈DBT molar ratios of 0.05–0.2 mol.%. The maximum H₂ flows were 1.7–2.7 times higher in the foam-based reactor than in the pellet-based reactor. The maximum H₂ release rates from the foam-based reactor were lower than, or similar to, those obtained from Pt/Al₂O₃ powders (Fig. A-3, Appendix A). The highest H₂ release rates were obtained during the first 20 min of the reaction.

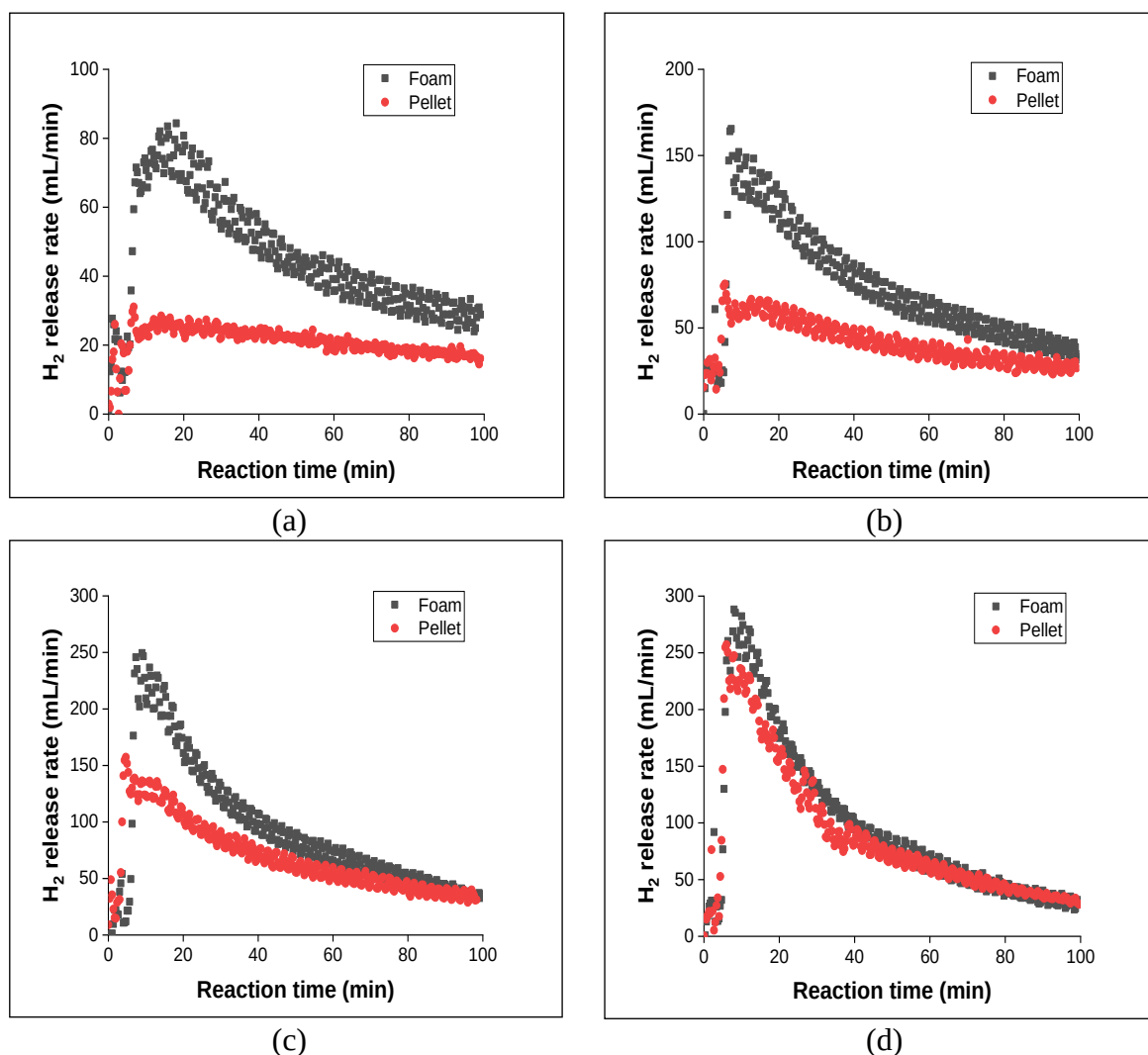


Figure 3-3. Evolution of the H₂ release rate with reaction time at various Pt/H₁₈DBT ratios: (a) 0.05, (b) 0.1, (c) 0.2, and (d) 0.4 mol.%. H₁₈DBT volume, 20 mL; reaction time, 100 min; reaction temperature, 300°C.

During that time, it is possible that most of the H_2 was released mainly through the conversion of $H_{18}DBT$ into $H_{12}DBT$, which is considered the fastest of the three $H_{18}DBT$ dehydrogenation steps (Eqs 3-1–3-3) [19]. The difference in exposed catalytic surface areas could explain performance disparities between the foam-based and pellet-based configurations. This then suggests that mass-transfer limitations play an important role in this first stage of $H_{18}DBT$ dehydrogenation. These limitations could originate from the triphasic nature of the $H_{18}DBT$ dehydrogenation process, which involves gas, liquid, and solid phases [16]. The larger volumetric surface area of the coated foam has improved solid–liquid mass transfer rates in the dehydrogenation reactor, resulting in greater H_2 volumes released during the first step of the dehydrogenation process.

The performance advantage of the foam decreased with increasing Pt/Al_2O_3 loadings. For instance, at a $Pt/H_{18}DBT$ molar ratio of 0.4 mol.%, the maximum H_2 release rate was only 1.2 times higher on the foam-based configuration than on the pellet-based configuration. An increase in catalyst loading on the foam inevitably results in a thicker washcoat layer. At increased layer thicknesses, the access of the reactant species to the surface of Pt can be hindered by its dilution in the Al_2O_3 morphological support phase. Thinner catalyst washcoat layers have the potential to minimise mass-transfer limitations on the foam surface [39]. To maintain high catalyst loading in thin washcoat layers on the foam substrate, one option is to use foams of higher pore densities. In practice, however, catalyst loading on foams of high pore density is more limited due to a tendency towards pore blocking [39].

At reaction times of 40–100 min, the H_2 release rates in the foam-based and pellet-based reactors slowly converged. The second and third dehydrogenation steps are characterised by slower kinetics [19]. Knowing the catalyst amounts of the foam and pellets to be identical, the difference in surface areas has less impact on the catalytic performance in these dehydrogenation steps than in the first step.

Fig. 3-4 shows the effects of the $Pt/H_{18}DBT$ molar ratio and the catalyst structural configuration on the DoD, average H_2 productivity, and product selectivity in the unstirred tank reactor. It is evident from Fig. 3-4a that higher catalyst loadings resulted in increased DoD. As mentioned earlier, the kinetically limited processes (as applicable to the catalytic performance) can be improved by increasing catalyst loading in the reactor [51]. The dehydrogenation of $H_{18}DBT$ includes kinetically limited reactions that require a high catalyst inventory to increase the H_2 yield. The increase in catalyst loading also resulted in a decrease in H_2 productivity (Fig. 3-4a).

Although the H_2 release rate increased with the catalyst amount, the increased H_2 flow did not change to the same extent with the increase in catalyst loading. This can be attributed to the mass transfer resistance at high catalyst loading in a triphasic dehydrogenation process [39]. It can be deduced from Fig. 3-4a that, in the selection of a cost-effective mass of Pt/Al_2O_3 to be deposited on the foam surface, a trade-off should be considered between a high H_2 release rate at high catalyst loading and high H_2 productivity at low catalyst loading.

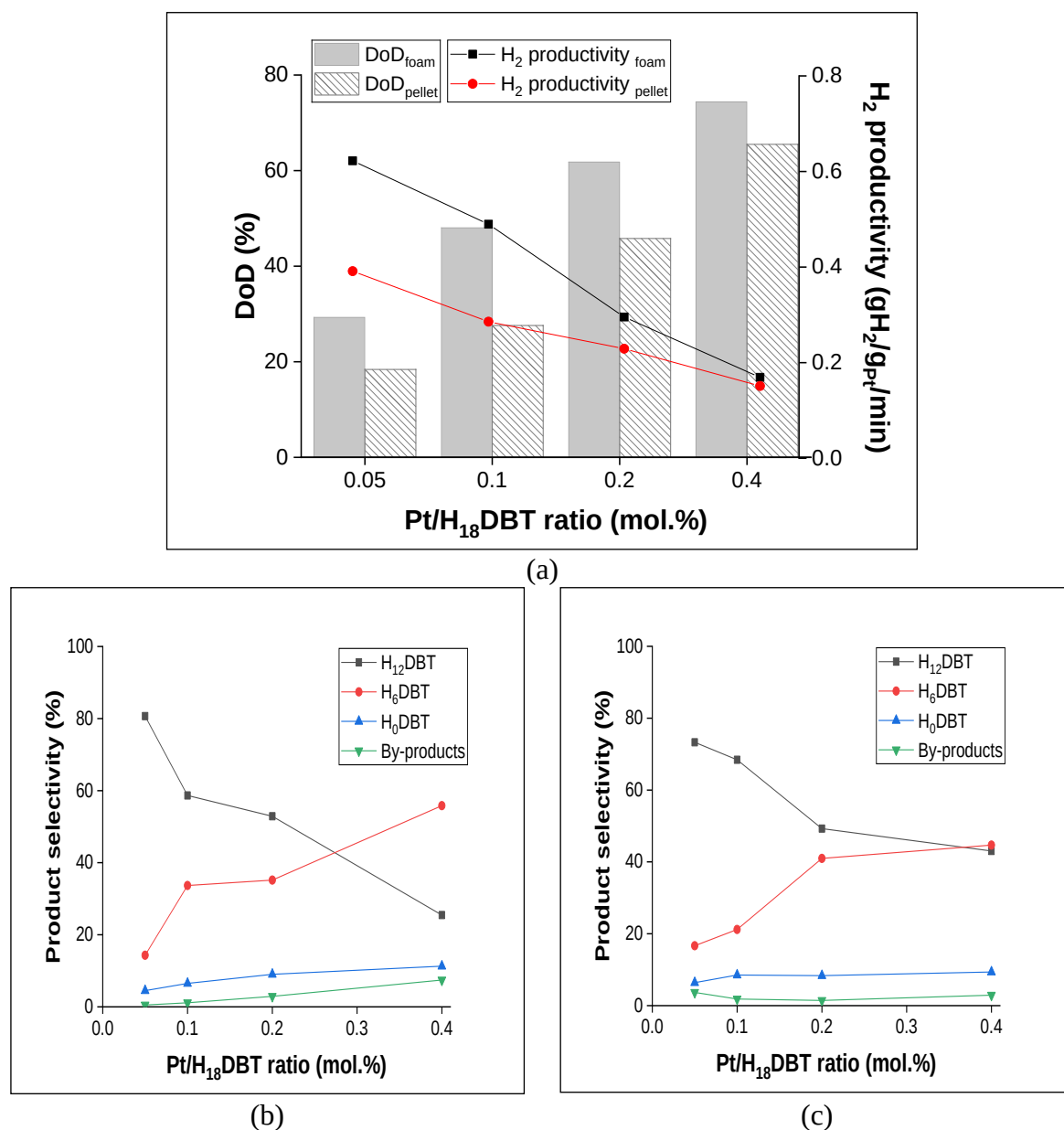


Figure 3-4. Effects of the $Pt/H_{18}DBT$ molar ratio and catalyst configuration on the following: (a) DoD and H_2 productivity; (b) product selectivity in the foam-based reactor; and (c) product selectivity in the pellet-based reactor. LOHC volume, 20 mL; reaction time, 100 min; reaction temperature, 300°C.

The H₁₂DBT selectivity decreased, while that of H₆DBT and H₀DBT increased at higher Pt/H₁₈DBT ratios (Fig. 3-4b,c). The high H₁₂DBT selectivity at a Pt/H₁₈DBT ratio of 0.05 mol.% confirms that the first step of the H₁₈DBT dehydrogenation reaction (Eq. 3-1) occurs much faster than the latter two rate-limiting dehydrogenation steps. In both configurations, as catalyst loading in the reactor is increased, a more significant increase in H₆DBT selectivity—compared to H₀DBT and the by-products—can be observed, while the H₁₂DBT selectivity strongly decreases. This suggests a more rapid conversion from H₁₂DBT into H₆DBT than from H₆DBT into H₀DBT. In both configurations, the H₂ is mostly produced from the first two steps of the H₁₈DBT dehydrogenation reaction. To increase the H₀DBT selectivity, longer residence times will be required or the catalyst properties may need to be optimised using methods such as doping with an appropriate metal or making changes to the morphological support [16,25].

The dehydrogenation of H₁₈DBT at elevated temperatures often results in the formation of by-products generated from the cracking of aromatic molecules. These by-products include benzyltoluene, benzene, toluene, and others [13,52]. The by-product formation was higher on the foam-supported catalyst than on the catalyst pellets. Generally, highly active catalysts tend to generate more by-products [8,13]. Although several of the by-products formed are also LOHCs, their formation alters the properties and affects the life cycle of the original LOHC [19].

3.2.2.2 Effect of reaction temperature on H₁₈DBT dehydrogenation performance

The effect of temperature on the DoD and H₂ selectivity obtained for the two catalytic configurations is shown in Fig. 3-5. A Pt/H₁₈DBT ratio of 0.1 mol.% was selected since it results in a relatively high DoD and H₂ productivity with low by-product formation. Generally, DoD values increase with temperature [53]. Low reaction temperatures result in sluggish H₁₈DBT dehydrogenation reactions. Here, at temperatures of 260–280°C, the catalyst structural configuration did not have a significant effect on dehydrogenation performance.

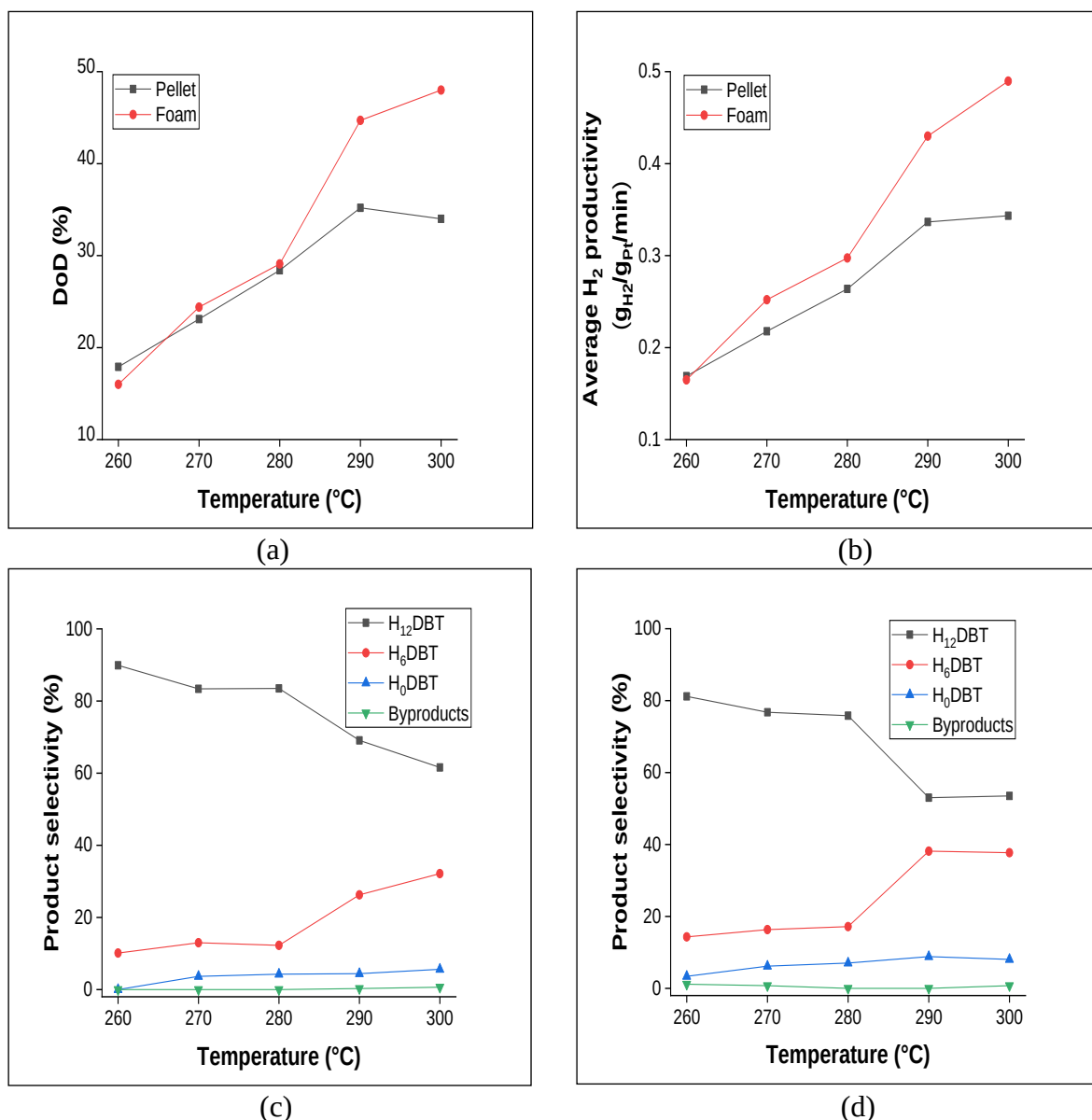


Figure 3-5. Effects of reaction temperature and catalyst configuration on the following: (a) DoD, (b) H₂ productivity, (c) product selectivity in foam-based reactor, and (d) product selectivity in pellet-based reactor. Pt/H₁₈DBT ratio, 0.1 mol.%; LOHC volume, 20 mL; reaction time, 100 min.

At temperatures <280 °C, it is possible that the reaction kinetics control the H₁₈DBT dehydrogenation rate more than diffusion does. As the temperature increases, the Pt/Al₂O₃-coated foam outperformed the Pt/Al₂O₃ pellets more noticeably (Fig. 3-5a,b). This trend could be attributed to a change in regime from kinetic control to diffusion control at temperatures of 280–290 °C. At temperatures of 290–300 °C, the reaction rates increased; therefore, the dehydrogenation process was more controlled by mass transfer than kinetic limitations. It was only in this regime of mass-transfer limitations that the benefits of the foam configuration were more evident.

At all temperatures, H₁₈DBT was mostly dehydrogenated into H₁₂DBT and H₆DBT in both catalytic configurations (Fig. 3-5c,d). Higher temperatures caused the selectivity towards H₁₂DBT to decrease, while that of H₆DBT increased. As the catalyst loading on the foam was constant at all operating conditions, higher temperatures increased the reaction rate of species present in relatively larger amounts on the catalyst surface. Only low amounts of H₀DBT (<10%) resulted from the dehydrogenation process. The H₀DBT selectivity on pellets was slightly higher than that on the foam-supported catalyst. By-product formation was negligible at all temperatures (Fig. 3-5c,d). This was due to the relatively low Pt/H₁₈DBT ratio used in the dehydrogenation tests. For batch processes on foam-supported catalysts, H₂ production rates can be increased and by-product formation minimised by running the dehydrogenation process at relatively elevated temperatures, with low catalyst loading in the reactor.

3.2.2.3 Performance of the foam-based FBR

The benefits of using a catalytically activated foam for the dehydrogenation of H₁₈DBT have been addressed in earlier sections. Further tests were conducted in an effort to better understand the dynamic behaviour of a foam-based H₁₈DBT dehydrogenation system in a bench-scale FBR. The performance of the foam-based reactor in the present study was compared to that of a pellet-based reactor previously used (with similar Pt content and operating conditions) [25].

Fig. 3-6 illustrates the effects of reactor start-up and prolonged exposure on the FBR performance observed for three consecutive 8 h sessions of fresh H₁₈DBT dehydrogenation. During session 1, preheated H₁₈DBT was introduced to the reactor containing freshly coated foams. A pump flow rate of 1.3 mL/min was used to maximise the H₁₈DBT residence time in the reactor. The missing data points within the first 90 min of the catalytic test (Fig. 3-6a) indicate that the first liquid product could only be sampled when the products exited the reactor—90 min after start-up. However, H₂ production commenced as soon as H₁₈DBT reached the catalyst section in the middle of the reactor. The DoD and H₂ release rate steadily decreased within the first 5 h on stream. Unlike in a tank reactor, in an FBR, fresh H₁₈DBT is continuously supplied to the catalyst surface. The decrease in catalytic performance is explained by the slow desorption rate of the dehydrogenation products and by-products adsorbed on the catalyst active sites. The species produced during the process hinder the adsorption of H₁₈DBT on the catalyst surface [21].

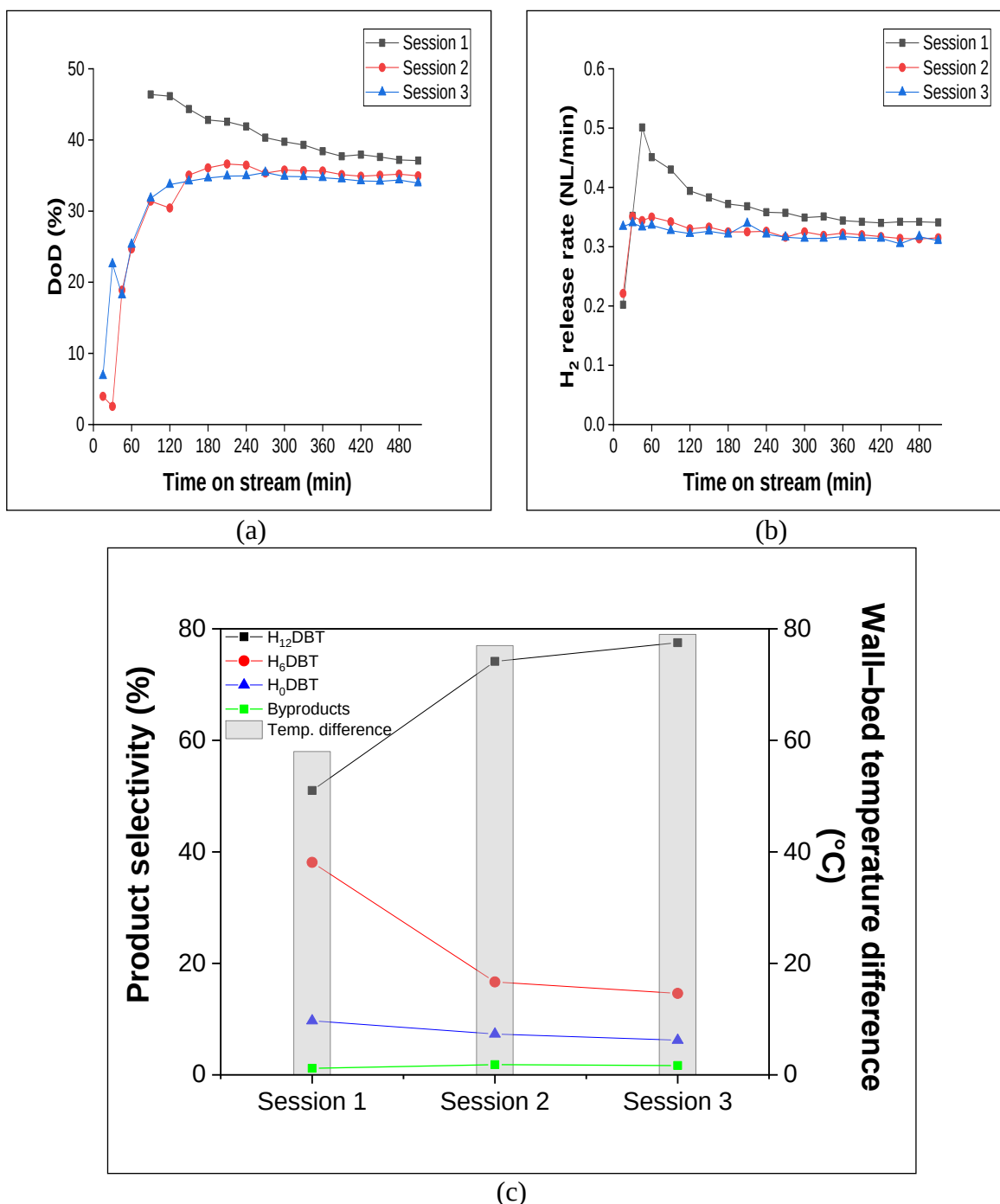


Figure 3-6. Results of three consecutive 8 h dehydrogenation tests: (a) DoD profiles, (b) H₂ release rate profiles, (c) steady-state dehydrogenation product and by-product selectivities, and wall-bed temperature difference. LOHC flow rate, 1.3 mL/min; reaction temperature, 300°C.

This trend has also been reported by Garidzirai et al. [25] (they used 110 g of 0.5 wt.% Pt/Al₂O₃ pellets in a reactor of similar size). Their study revealed that in the packed bed reactor, the H₂ release rate decreased with time—it only stabilised after 12 h on stream. To improve the desorption rate of the products, Müller et al. [30] proposed a process coupling LOHC dehydrogenation with reactive distillation. The difference in boiling points between the fresh

H₁₈DBT and dehydrogenated products could be used to enrich the catalyst bed with H₁₈DBT. Steady-state operations were only achieved after ~5 h on stream. The DoDs and H₂ released were ~38% and 0.34 NL/min, respectively (Fig. 3-6a,b). These values were lower than those obtained by Garidzirai et al. [25] (~55% and 0.42 NL/min, respectively).

This difference in performance was first attributed to the difference in the residence time of the reactant in the catalyst beds. The foams coated with 11 g of 5 wt.% Pt/Al₂O₃ were characterised by higher porosity and a shorter bed length compared to the 110 g of 0.5 wt.% Pt/Al₂O₃ pellets used in the study selected for comparison [25]. The flow through a small and highly porous catalyst bed would result in the decreased residence time of the reactants on the foam-supported catalyst surface. Secondly, the performance decrease could also be due to greater liquid–solid mass transfer resistance in the foam bed than in the pellets. The catalyst preparation method used by Garidzirai et al. [25] also resulted in pellet-based catalysts characterised by an eggshell structure. Their low Pt loading of 0.5 wt.% resulted in a Pt metal dispersion of 38%, which is twice the dispersion obtained for the 5 wt.% Pt/Al₂O₃ used in the present study. The Pt active sites on the coated foam were, therefore, less exposed to the incoming LOHC [8]. As mentioned earlier, the foam-based catalyst bed can be improved by using less porous foam and a coating with lower Pt loading in the catalyst washcoat layer. Nevertheless, the advantage of a foam-based catalytic system could reside in the requirement for less catalytic material (the Al₂O₃ support) and a reduced reactor bed volume.

The results also revealed that, after the reactor start-up, similar reactor stabilisation times were required during dehydrogenation sessions 2 and 3. This indicated that the shutdown and start-up procedures did not have an adverse effect on the catalytic performance. Steady-state H₂ flows were obtained after only 30 min on stream. The shorter stabilisation time can be ascribed to the catalyst surface already being soaked with fresh H₁₈DBT (used for rinsing during the shutdown process in the previous session). After session 1, the steady-state DoD and H₂ flow slightly decreased by less than 3% and 0.02 NL/min, respectively. The performance achieved from sessions 2 to 3 was generally similar. Modisha and Bessarabov [52] observed similar stabilisation during a catalyst reusability test performed in a tank reactor. The activity of a Pt-based catalyst decreased after the first run before stabilising in subsequent runs. The loss of catalytic activity was attributed to the slow desorption rate of the dehydrogenation products and by-products adsorbed on the catalyst surface.

This initial loss of catalytic activity could also explain the selectivity trends seen in Fig. 3-6c. The curve of H₁₈DBT dehydrogenation products reveals that the selectivity towards H₁₂DBT increased by 23.2% between dehydrogenation sessions 1 and 2. Within the same period, the selectivities of H₆DBT and H₀DBT decreased by 21.4% and 3.5%, respectively. H₂ was, therefore, increasingly produced from the dehydrogenation of H₁₈DBT into H₁₂DBT (the fastest step). This decrease in selectivity towards the more fully dehydrogenated products was also observed by Garidzirai et al. [25]. This is an indication of an increase in diffusional resistance, which can be attributed to the strong adsorption of products on the catalyst active sites.

Another consequence of the change in catalytic activity was the increase in heat required to maintain the catalyst bed at the desired reaction temperature of 300°C. The steady-state wall–bed temperature difference increased by 19°C between dehydrogenation sessions 1 and 2 and only by 2°C in session 3 (Fig. 3-6c). The dehydrogenation of H₁₈DBT is an endothermic process. The temperature difference between the reactor wall and the centre of the catalyst bed is justified by the fact that a portion of the energy supplied by the electrical heating jacket is consumed as reaction heat. The additional energy required to maintain a temperature of 300°C during dehydrogenation sessions 2 and 3 could have, therefore, been used to overcome the heat-transfer resistance caused by the strong adsorption of dehydrogenation products on the catalyst surface.

The maximum DoD values achieved during the dehydrogenation of H₁₈DBT in the FBR after 8 h on stream were in the 34–38% range. It was anticipated that an improved DoD would be achieved by recycling the liquid product through the reactor.

Fig. 3-7 summarises the performance of the foam-based FBR obtained after each of the four cycles during the LOHC recycle tests. As the cumulative DoD increased, the H₂ release steadily decreased after each dehydrogenation cycle (Fig. 3-7a). The increase in DoD was expected because, after the first cycle, the liquid product comprised a mixture of different LOHCs that could still be dehydrogenated. The decrease in the H₂ release rate was justified by the slower kinetics of the dehydrogenation of intermediate products (H₁₂DBT and H₆DBT).

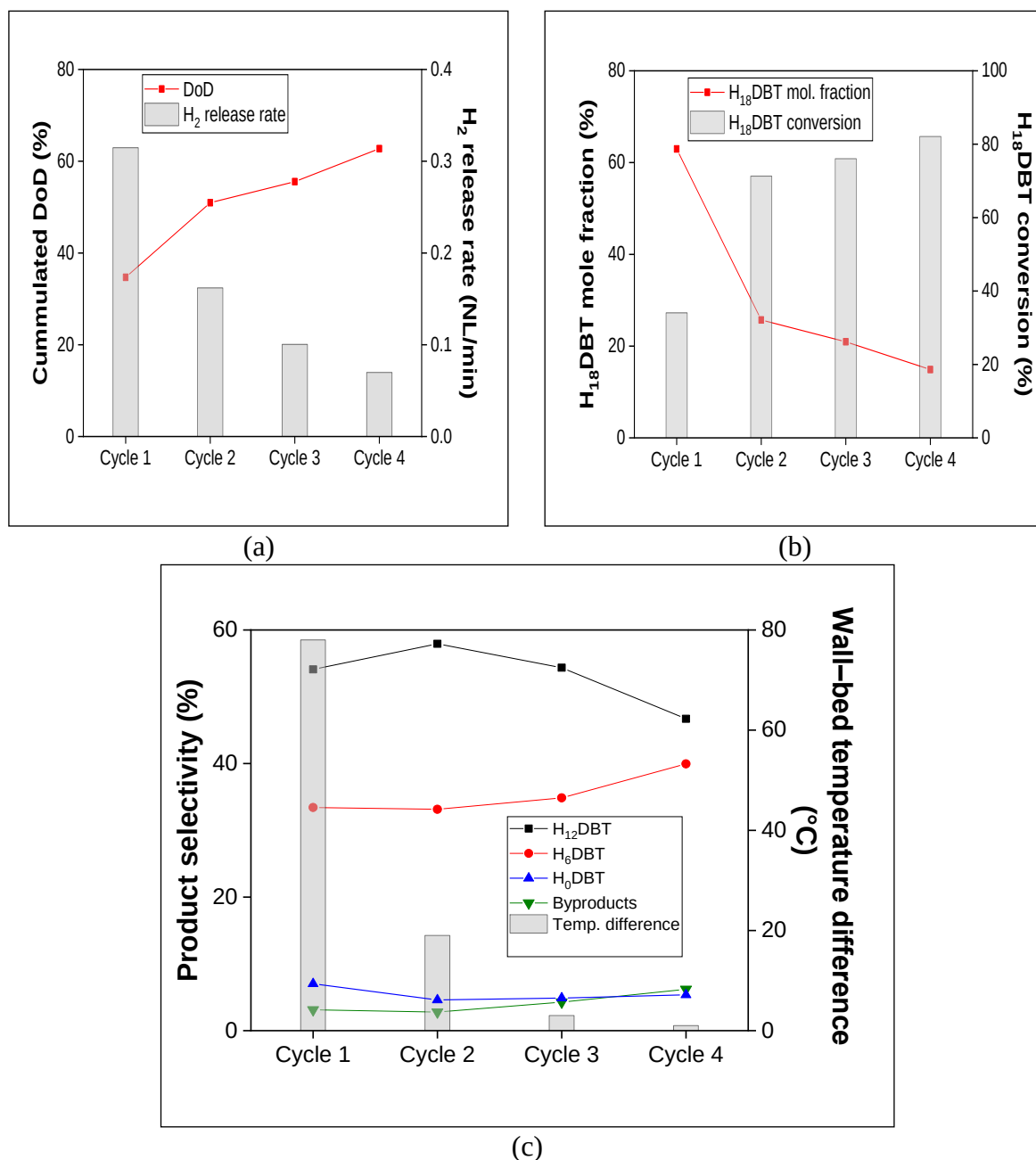


Figure 3-7. Reactor performance during the LOHC recycle tests based on (a) cumulated DoD and H₂ release rate; (b) H₁₈DBT mole fraction and conversion; and (c) product selectivities and temperature difference between the wall and catalyst bed during dehydrogenation experiments.

The H₁₈DBT concentrations generally decreased with the number of cycles (Fig. 3-7b). The conversion of H₁₈DBT doubled from the first to the second dehydrogenation cycle but then increased by only 10.8% from the second to the fourth cycle. This is explained by the fact that during the first few cycles, the concentration of H₁₈DBT was sufficiently high for the molecule to occupy a larger portion of the active sites of the catalyst surface. As the amount of H₁₈DBT decreased, more products were formed, and less H₂ was produced from the first

dehydrogenation step (Eq. 3-1), but more was produced from the second and third steps (Eqs 3-2 and 3-3).

The selectivity towards H_{12} DBT decreased from 54.1% to 46.7%, while the selectivity towards H_6 DBT increased from 33.4% to 40.0% (Fig. 3-7c). It is likely that the dehydrogenation of H_{12} DBT into H_6 DBT occurred at a faster rate than the subsequent dehydrogenation step into H_0 DBT. The selectivity towards H_0 DBT remained <10% after four cycles. Unfortunately, the by-product selectivity also increased with the number of cycles. Multiple cycles are known to increase the tendency towards by-product formation [20]. The formation of by-products reduces the reusability of the LOHC. To prevent excessive by-product formation, further catalyst optimisation or the use of less harsh operating conditions may be required.

The temperature difference between the reactor wall and catalyst bed decreased with the number of cycles of the dehydrogenation product through the reactor (Fig. 3-7c). This suggests that the first step of H_{18} DBT dehydrogenation requires more heat than subsequent steps. It could be argued that a high H_2 release increases heat-transfer resistance at the interface between the LOHC and the catalyst surface. As the H_2 release rate decreases, less heat is required from the heating jacket to maintain the catalyst bed at 300°C. After the fourth cycle, the overall DoD reached a value of 63%. This DoD could also be achieved in a single foam-based FBR containing a longer catalyst bed.

Constant temperature and flow conditions throughout the catalyst bed may not be ideal because of the multiple steps involved in the H_{18} DBT dehydrogenation. It is possible that running dehydrogenation reactors in series could improve the efficiency of the process. Each reactor would need to be set at operating conditions or with a catalyst configuration suited for the specific LOHC mixture to be dehydrogenated.

3.3 Materials and methods

H_0 DBT was obtained from Sasol (Marl, Germany) and further hydrogenated (on site) using a Ni-based catalyst to a degree of hydrogenation (DoH) of ~97%. The 10 PPI (pores per inch) Al foam (porosity ~ 95%) was obtained from Recemat BV (Dodewaard, the Netherlands). The morphological catalyst support (Clariant, Johannesburg, South Africa) consisted of cylindrical γ - Al_2O_3 pellets (length, 2–7 mm; diameter, 1 mm). Hexachloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$), synthesised in-house, was used as the Pt precursor. The gases used for

chemisorption and reactor purging, namely, 10 vol.% CO/He and N₂ (99.999%), respectively, were purchased from Afrox (Johannesburg, South Africa), while H₂ (99.999%) was produced in-house through water electrolysis.

The preparation of the catalyst (5 wt.% Pt/Al₂O₃) and foam coating procedure are illustrated in Fig. 3-8a. The catalyst preparation started with the wet impregnation of Al₂O₃ pellets (150 g) with H₂PtCl₆·6H₂O (19.2 g) following a method reported elsewhere [25,52]. The pellets thus obtained were dried for 4 h in a Labotec EcoTherm digital oven (Labotec, Johannesburg, South Africa) at 120°C. Dried impregnated pellets were subsequently calcined and reduced for 2 h in a stream of air (250 mL/min) and 50 vol.% H₂/N₂, respectively, using a CTF12 horizontal tube furnace (Carbolite Gero, Hope, UK) at 350°C (ramp rate 10°C/min). A portion of the reduced pellets (Fig. 3-8b) was finely crushed into a powder and used to prepare the slurry required to washcoat the Al foam. The slurry consisted of a mixture of Pt/Al₂O₃ powder, polyvinyl alcohol (molar weight 22,000 g/mole) (MCL, Durban, South Africa) as binder, and deionised water. The catalyst, binder, and water were present in a mass ratio of 30:1.5:68.5. The coating procedure commenced with removing organic impurities from the surface of the Al substrate in 99.5 vol.% ethanol (Rochelle Chemicals, Johannesburg, South Africa) for 10 min. The coating process included repetitive steps of dip-coating, dip-blowing (using compressed air), and drying. The procedure was halted when the desired amount of Pt/Al₂O₃ catalyst was coated on the Al foam [42] (Fig. 3-8c). To remove the organic components and activate the foam-supported catalyst, coated foams were calcined in air and reduced in H₂/N₂ as described above. A relatively high Pt loading of 5 wt.% on Al₂O₃ was selected in anticipation of the limited catalyst amounts permissible on the foam struts. It was important to maintain the Pt/H₁₈DBT molar ratios at the desired values while keeping the catalyst inventory on the foam low enough to prevent pore blocking.

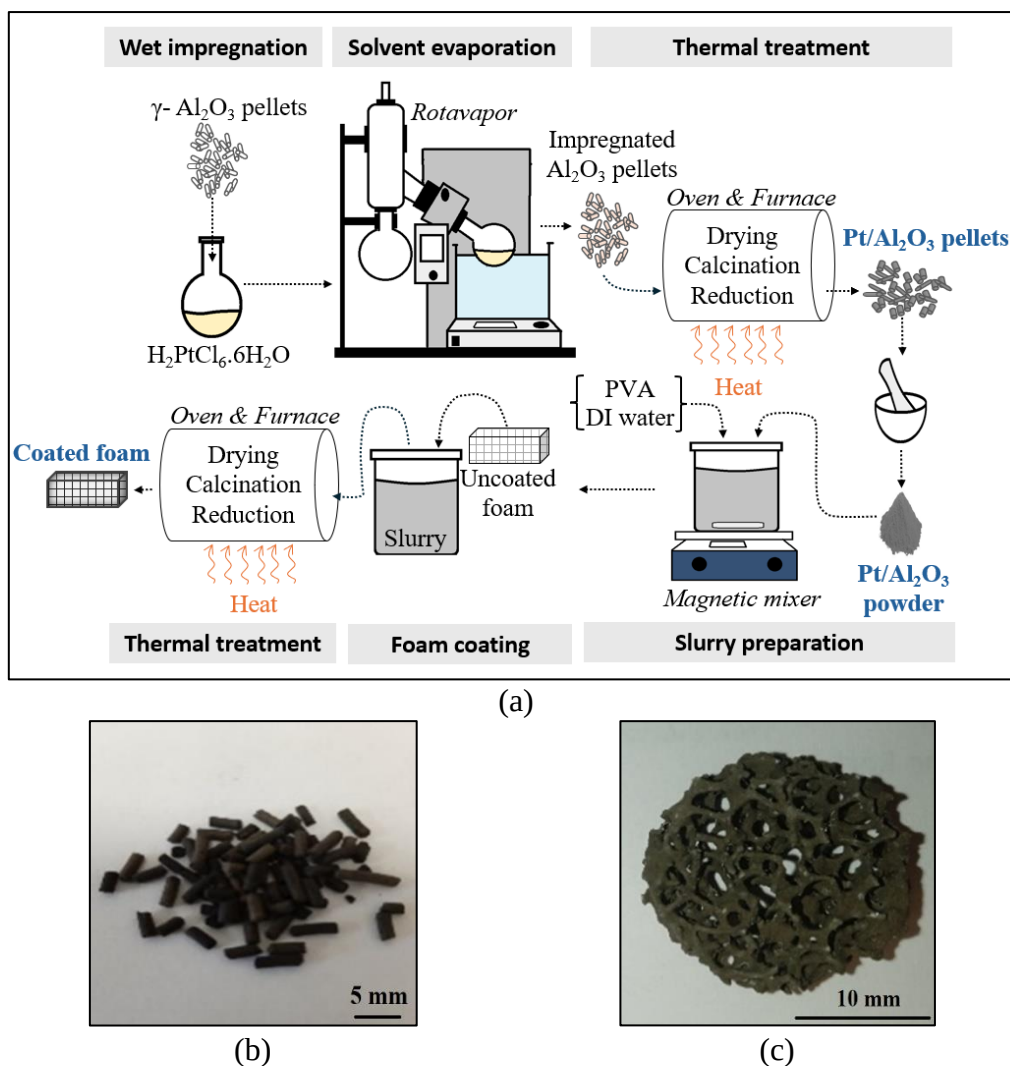


Figure 3-8. Illustrations of (a) catalyst preparation and foam coating procedures; (b) Pt/Al₂O₃ pellets; and (c) Pt/Al₂O₃-coated Al foam.

Selected catalyst characterisation methods were utilised not only to identify the physical and chemical properties of the catalyst used as powder, pellet, or washcoat on the foam but also to identify eventual changes in textural properties due to the catalyst coating process.

A FEI Quanta FEG 250 field emission gun scanning electron microscope (Thermo Fisher Scientific, Waltham, MA, USA) was utilised to characterise the surface morphologies of the foam-supported and pellet-based Pt/Al₂O₃ catalysts. Elemental mapping of the catalyst surface was performed utilising EDS with an X-Max 20 mm² silicon drift detector (Oxford Instruments, Abingdon, UK). SEM images were analysed using the xT Microscope Server and xT Microscope Control software [54]. EDS data were processed using the AZtec software [55].

A high-resolution JEM-2100 transmission electron microscope (JEOL, Tokyo, Japan) was used to estimate the size of Pt nanoparticles from the catalyst samples. Samples of Pt/Al₂O₃ powder

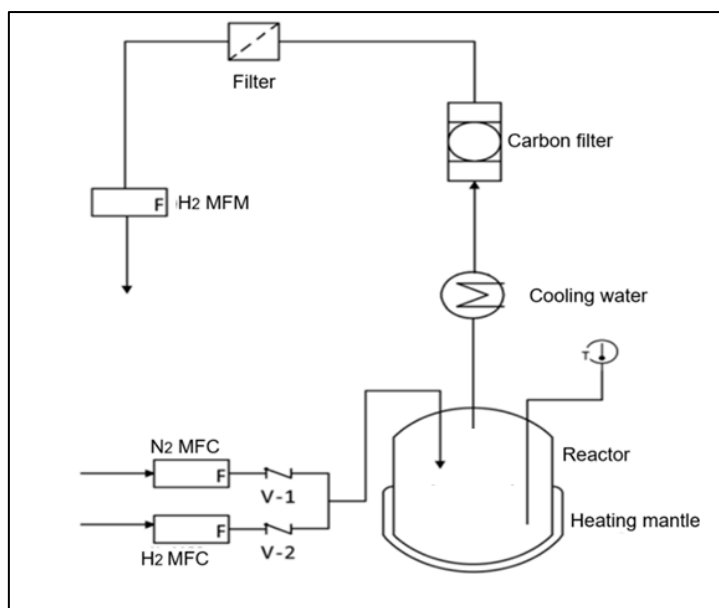
were extracted from the foam washcoat layer and crushed catalyst pellets. The samples were dissolved in ethanol and dispersed on a carbon-coated copper grid for analysis. Mean particle sizes were calculated from TEM images, from 400 particles, using the open-source image processing software, ImageJ [56].

A BELCAT II automated catalyst analyser (Microtrac, Osaka, Japan) was utilised to carry out CO pulse chemisorption on the Pt/Al₂O₃ pellets and coated foams. The analyser was equipped with an electric furnace containing a quartz tube, and He was used as carrier gas. For each test, a catalyst sample (0.1 g) was loaded into the tube and subjected to a pretreatment method: heating in He to 400°C at a ramp rate of 20°C/min, calcination in 10 vol.% O₂/He for 15 min, and reduction in 8 vol.% H₂/He for 20 min. Chemisorption analysis was conducted at 50°C. In total, 10 pulses of 10 vol.% CO/H₂ (50 NmL) were injected into the tube to estimate the Pt metal dispersion, specific surface area, and particle size.

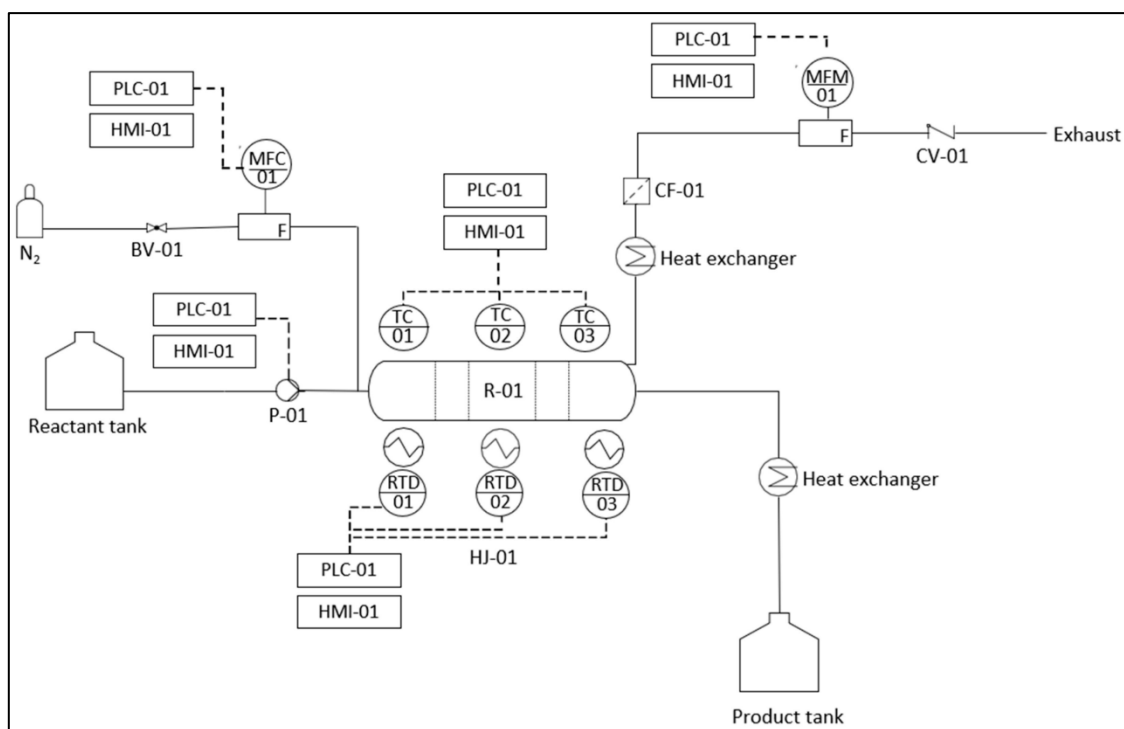
To compare the crystalline structure of the catalysts, XRD analysis of pellet-based and foam-based catalyst powders was carried out using a PANalytical X'Pert PRO X-ray diffractometer (Malvern Panalytical, Malvern, UK). The diffractometer was operated with Cu K α radiation (divergence slit 0.38 nm); the generator voltage was 45 V; and the tube current was 40 mA. Measurements were recorded within an angular range of 5–90°. The diffraction data were recorded at 127 s/step.

To investigate the presence of residual organic compounds in the catalyst after preparation and coating on the foam, TGA was performed using a TGA Q500 V20.13 Build 39 (TA Instruments, New Castle, DE, USA). Catalyst samples (9.5 mg) were heated in 10 vol.% N₂/air from room temperature to 900°C at a constant rate of 10°C/min.

Catalyst activity testing was conducted in two set-ups, as shown in Fig. 3-9. Batch experiments were carried out in an unstirred tank reactor using two different catalyst configurations: Pt/Al₂O₃ pellets and Pt/Al₂O₃-coated foam. The unstirred reactor was mainly selected to avoid damaging the egg-shell structure of the catalyst pellets or to prevent the detachment of the catalyst washcoat layer from the foam substrate. These can result from the frequent collisions between the stirrer and the catalyst. It was anticipated that sufficient mixing would be ensured by the coupling effects of the natural convection within the bulk of the LOHC mixture and the production of H₂ gas at the interface between the catalyst and liquid phases.



(a)



(b)

Figure 3-9. Schematic representation of the two set-ups used for the dehydrogenation of $H_{18}DBT$: (a) tank reactor and (b) FBR [25,52]. Legend. BV: ball valve; CF: carbon filter; CV: control valve; HJ: heating jacket; HMI: human-machine interface; MFC: mass flow controller, MFM: mass flow meter; P: peristaltic pump; PLC: programmable logic controller; RTD: resistance temperature detector; TC: temperature control. [(a) was adapted with permission from Modisha et al. [52], published by the Royal Society of Chemistry, 2020.]

The batch experimental set-up (Fig. 3-9a) comprised a 250 mL three-neck round bottom flask connected to a condenser, carbon filters, and an EL-FLOW mass flow meter (Bronkhorst High-Tech BV, Bronkhorst, The Netherlands). The reaction temperature was set using a heating mantle with a digital feedback controller.

Batch dehydrogenation tests were conducted with H₁₈DBT (20 mL, equivalent to ~0.06 mol H₁₈DBT) using selected operating parameters. The catalytic performance of the Pt/Al₂O₃ pellets and Pt/Al₂O₃-coated foam was compared based on the degree of dehydrogenation (DoD) and H₂ productivities achieved at the same operating conditions.

To investigate the performance of the Pt/Al₂O₃-coated foams in a continuous set-up, dehydrogenation experiments were carried out in an FBR. The reactor (Fig. 3-9b) comprised a horizontal stainless-steel tube (length 900 mm, ID 20 mm) subdivided into three sections: the inlet section, the reaction zone, and the outlet section.

During the reactor start-up, the FBR was heated to a reaction temperature of 300°C. A Medorex TL/150 peristaltic pump (MDX Biotech GmbH, Nörten-Hardenberg, Germany) was used to feed H₁₈DBT to the reactor at a minimum flow rate of 1.3 mL/min. Prior to entering the FBR, the LOHC was heated to ~250°C using an electrical heater to decrease its viscosity and, consequently, the pumping resistance [15]. The inlet section of the FBR further raised the temperature to the reaction temperature. The reaction zone contained a catalyst bed including 10 foam samples (diameter, 20 mm; thickness, 10 mm) coated with a total of 11 g of Pt/Al₂O₃. The inlet and outlet zones were filled with inert material (silica balls and steel wool). A three-phase electrical heating jacket (SAF Wärmetechnik GmbH, Mörlenbach, Germany) was used to control the temperature of the three sections independently. A K-type thermocouple was inserted at the central longitudinal axis of the reactor to measure the temperatures at the three reactor sections. The gas outlet stream was equipped with a carbon filter and condenser, through which the released H₂ passed before reaching an EL-FLOW mass flow meter (Bronkhorst High-Tech BV, Bronkhorst, The Netherlands). The liquid outlet stream comprised a condenser and a LOHC collection tank.

Parameters used in the performance evaluation of the foam-based FBR were set through a Siemens PLC control system. Experimental parameters used during the batch and continuous H₁₈DBT dehydrogenation tests are provided in Table 3-2. Selected experiments were

conducted in triplicate to ensure the reproducibility of the results. Percentage differences were in the order of 5% and 6% for the DoD and H₂ volume released, respectively.

Table 3-2. Experimental parameters used during the batch and continuous H₁₈DBT dehydrogenation tests.

Parameters	Values
Batch experiments	
Pt/H ₁₈ DBT ratio (mol.%)	0.05, 0.1, 0.2, and 0.4
Temperature (°C)	260–300 (10°C increments)
Catalyst configuration	Pt/Al ₂ O ₃ -coated foams and Pt/Al ₂ O ₃ pellets
Reaction time (min)	100
Continuous experiments	
Temperature (°C)	300
Flow rate (mL/min)	1.3
Coated foam bed length (mm)	~100

The Pt/Al₂O₃-coated foams were also tested for three 8 h sessions of continuous operation to assess their ability to maintain a constant catalytic performance during a long-term H₁₈DBT dehydrogenation operation punctuated with start-up and shutdown procedures. Furthermore, tests were conducted by recycling the partially dehydrogenated liquid products three times. The objective of the recycling test was not only to achieve improved DoD and H₂ release but also to understand the effect of recycling on the product composition.

At the conclusion of the experiments, during the reactor shutdown, the electric heaters were switched off, and the reactor was allowed to gradually cool to room temperature. The reactor was purged in a flow of fresh H₁₈DBT to remove the products of dehydrogenation from the catalyst surface. The product gas composition was determined by gas chromatography, using an SRI 8610C GC (SRI Instruments, Menlo Park, CA, USA) instrument equipped with a molecular sieve column (length 0.9 m) and a thermal conductivity detector. The device was calibrated for H₂ and gaseous products most likely to be formed during the dehydrogenation reaction: CH₄, CO, and CO₂ [57]. Analysis of the liquid product was performed using an Agilent 8890 gas chromatograph (Agilent Technologies, Santa Clara, CA, USA) paired with a single quadrupole 5977C mass spectrometer. The system was equipped with a 7693A autosampler and a 30 m HP-5MS UI column (diameter, 0.25 mm; film thickness, 0.25 µm). To

analyse the liquid product, a 20 μL sample of dehydrogenated LOHC was diluted 50 times in a mixture of 11.3 vol.% nonane (internal standard) and hexane.

The dehydrogenation performance was assessed through the following parameters [25,43]:

$$\text{Degree of dehydrogenation (\%)} = \frac{\text{Volume H}_2 \text{ released}}{\text{Volume H}_2 \text{ max}} \times 100 \quad (3-4)$$

$$\text{H}_{18}\text{DBT conversion (\%)} = \frac{\text{mol}_{\text{H}_{18}\text{DBT}_{\text{in}}} - \text{mol}_{\text{H}_{18}\text{DBT}_{\text{out}}}}{\text{mol}_{\text{H}_{18}\text{DBT}_{\text{in}}}} \times 100 \quad (3-5)$$

$$\text{H}_2 \text{ productivity (g}_{\text{H}_2}\text{/g}_{\text{Pt}}\text{/min)} = \frac{\text{mass H}_2 \text{ released}}{\text{mass of Pt} \times \text{reaction time}} \quad (3-6)$$

$$\begin{aligned} \text{Component i selectivity (\%)} \\ = \frac{\text{mol}_i}{\text{mol}_{\text{H}_0\text{DBT}} + \text{mol}_{\text{H}_6\text{DBT}} + \text{mol}_{\text{H}_{12}\text{DBT}} + \text{mol}_{\text{byproducts}}} \times 100 \end{aligned} \quad (3-7)$$

i = H₀DBT, H₆DBT, H₁₂DBT or by-products.

3.4 Conclusions

The findings of this study demonstrated the suitability of a foam coated with 5 wt.% Pt/Al₂O₃ for the dehydrogenation of H₁₈DBT in two different reactor set-ups, an unstirred tank reactor, and an FBR. The results of the catalyst characterisation, including TEM, TGA, XRD, and CO pulse chemisorption, revealed that the properties of the catalyst from the foam washcoat layer and the pellets were similar. Hence, the coating process did not significantly alter the nature of the Pt/Al₂O₃ catalyst. Therefore, the difference in performance between the foam-based and pellet-based systems was attributed to the geometric configuration of the substrates.

Tests carried out in the unstirred tank reactor revealed that the higher surface area of the foam had beneficial effects on the dehydrogenation of H₁₈DBT. Increasing the Pt/H₁₈DBT molar ratio in the reactor from 0.05 to 0.4 resulted in an increase in DoD values from 29 to 74% and 18 to 66% on the Pt/Al₂O₃-coated foams and Pt/Al₂O₃ pellets, respectively. These results demonstrate the importance of increasing the catalyst inventory to overcome limitations due to the sluggish kinetics of the slowest steps of the dehydrogenation of H₁₈DBT. However, the same increase in catalyst loading caused the H₂ productivities to decrease from 0.62 to 0.17

and 0.39 to 0.15 on the foams and pellets, respectively. These lower productivities were attributed to mass-transfer limitations due to the reduced accessibility of the LOHC to the Pt catalyst sites at thicker washcoat layers on the foam surface. The opposite trends of the effect of the Pt/H₁₈DBT molar ratio on DoD and productivity suggest that a trade-off between the two performance criteria should be considered in the selection of optimum catalyst loading on the foam. For the foam-based batch reactor used in this study, a Pt/H₁₈DBT molar ratio of 0.1 mol.% could be considered most suitable, as the DOD and H₂ productivity can be maintained at ~50% and ~0.5 g_{H2}/g_{Pt}/min, respectively.

Continuous dehydrogenation tests were carried out in the foam-based FBR. The prolonged H₁₈DBT dehydrogenation tests carried out in three 8 h sessions revealed that, after an initial decrease in the DoD and H₂ production rate, stable operations could be maintained for >16 h of dehydrogenation, interrupted by shutdown and start-up procedures. However, the maximum DoD achieved at a steady state was 34–38%. This DoD was increased by recycling the liquid product three times into the FBR. However, between the first and fourth LOHC dehydrogenation cycles, a fourfold decrease in H₂ release rate was observed. This was attributed to the increased occurrence of the slower steps of H₁₈DBT dehydrogenation. Nevertheless, after the last dehydrogenation cycle, a DoD of 63% was achieved. The results of the continuous tests suggest that for a foam-based system, a longer catalyst bed consisting of foams with high pore densities with relatively thin catalyst washcoat layers could be beneficial for the H₁₈DBT dehydrogenation process.

Lastly, for all the catalytic tests investigated in this study, the dehydrogenation of H₁₈DBT was characterised by low H₀DBT selectivities, attributed to the low desorption rate of the reaction products.

Recommendations for future studies include focusing on the development of catalysts, as well as the design of reactors, that could lead to the improved dehydrogenation of the intermediates (i.e., H₁₂DBT and H₆DBT) and the desorption of products from the foam surface. Catalyst characterisation methods such as Raman spectroscopy could be performed before and after the reaction to further investigate the reasons for the loss of catalytic activity. Future works could also be directed towards the optimisation of the foam's geometrical properties in view of optimising the thickness of the catalyst washcoat layer. A thinner layer could improve the catalyst adhesion to the foam substrate and increase the mass transfer coefficient during the H₁₈DBT dehydrogenation process. Lastly, the comparison between the performances of foam-

supported and pellet-based catalysts could be conducted in different types of reactors such as stirred tank reactors or vertical FBRs.

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Chapter 4. Passive autocatalytic recombination of hydrogen on a Pt/Al₂O₃-coated metal foam: Experimental evaluation and CFD modelling

Chapter overview (Abstract)

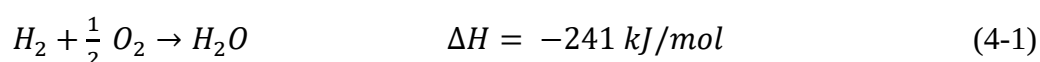
Pt/Al₂O₃-coated Al foams were tested for the passive autocatalytic recombination of H₂. The characterisation of the washcoat surface confirmed the uniform distribution of Pt and Al₂O₃ over the entire washcoat surface. Transmission electron microscopy results revealed a slight increase in particle size from 3.8 to 6.2 nm after prolonged reaction. High H₂ conversions of 57–89% are achieved and the catalyst activity is maintained for >480 h on stream. The performance of the foam-based catalyst bed is similar to that of plates but surpasses that of catalyst pellets. Temperatures recorded at the hottest spots on the foam surface reach a maximum of only 393°C at the highest H₂ inflow. Computational fluid dynamics simulations were performed on the actual foam geometry obtained using computed tomography. The simulations demonstrate the importance of thermal radiation in the model. There is good agreement between results of experimental H₂ conversions and maximum combustion temperatures.

4.1 Introduction

In order to limit the global temperature rise to <1.5°C by 2050, the industrial sector is slowly shifting from fossil fuel to low- or zero-carbon energy sources, such as hydroelectricity, tidal, geothermal, solar and wind energy. Due to the irregular distribution and intermittent nature of several of these sources, causing an imbalance between energy supply and demand, several energy storage technologies are currently being developed. They include flywheels, superconductors, supercapacitors, batteries, compressed air, pumped hydro, phase change materials (latent heat) and chemical storage [1–4]. The chemical storage technique is considered as one of the most realistic options for long-term storage of relatively large amount of energy. This method involves using excess renewable power to produce a chemical compound, known as energy carrier [5]. Green H₂, produced by water electrolysis, has been proposed as a suitable energy carrier due to its high gravimetric energy density (120 MJ/kg), the relative maturity of its production and utilisation technologies [6]. It is also a highly versatile gas; it can be used for energy production in fuel cells or microcombustors, the

reduction of metal ores, and the synthesis of industrial chemical products (ammonia, methane, methanol) and sustainable aviation fuels [7,8].

With such an increasing amount of H₂ being handled in industries of various sizes, there is a clear need for the application of strict safety measures [9]. H₂ leaks in air can pose significant risks of deflagration or detonation in an environment where the gas' self-ignition temperature of ~585°C is reached within its flammability limits (4–75 vol.% H₂ at normal temperature and pressure) [10,11]. Reported methods of H₂ removal include ventilation, deliberate ignition and passive autocatalytic recombination (PAR) [12]. For risk mitigation, ventilation is not always effective due to the high buoyancy of H₂, which can cause the gas to accumulate in dead corners and increase the formation of high-risk zones near the upper sections of confined spaces. On the other hand, deliberate ignition could cause the unintentional formation of NO_x gases as combustion temperatures increase to >800°C [13]. The advantage of PAR technology lies in its ability to prevent the accumulation of H₂. Spontaneous combustion commences at ambient temperature, at low H₂ concentrations (i.e., within the first instants of an accidental leak), without reaching temperatures favourable to the formation of NO_x, and releasing only water as product (Eq. 4-1) [14]. A recombiner can be installed in confined or semi-confined spaces, as well as underground parking, tunnels or mining facilities [15].



Arguably, the most important feature of a recombiner is its catalytic section. Pd and Pt have been reported as two of the most studied PAR catalysts due to their low light-off temperatures and high catalytic activities at temperatures <500°C [16]. However, these noble metal catalysts have a high tendency for sintering at increasing combustion temperatures, resulting in significant loss of catalytic activity. One way to prevent this problem is to use a high-surface morphological support such as alumina, ceria, yttria or zirconia [13,17]. These supports improve the dispersion of active metal nanoparticles (NPs), limit their mobility and prevent their aggregation [11,18]. Du Preez et al.[18] demonstrated the importance of the presence of a morphological support for their Pt sputter-coated on Ti meshes. They showed that the presence of an oxide layer prevented the aggregation of Pt nanoparticles. This high-surface oxide layer improved the catalyst long-term stability.

Another preventive option is making use of high thermal conductivity materials (e.g. metals such as Al, Cu, Ti) as catalyst support structures. They efficiently distribute the heat released

through chemical reaction, thus preventing the occurrence of hot spots at which local aggregation of the NPs could occur [13,14]. Further process intensification could be achieved through the use of porous materials such as open-cell metal foams, which have outstanding heat and mass transport properties [19,20]. These high-surface catalyst support structures facilitate not only mass transport through radial reactant mixing and increased tortuosity, but also heat transport by convection and conduction [21,22].

Experimental studies on catalytic H₂ combustion on foams are reported in literature. A study by Jo et al. [20] offers clear insight into the effects of the inlet H₂ feed rate, the active metal (Pt) content and morphological support (Al₂O₃) loadings on H₂ conversions, and the maximum temperatures obtained during the H₂ combustion process in a tubular reactor. Jin and Kwon [23] investigated the performances of a Pt/Al₂O₃-coated Ni foam and Pt-coated ceramic foam for H₂ combustion at different feed gas flow rates and equivalent ratios (0.5 H₂/O₂ molar ratio). They reported the effects of these operating parameters on the H₂ conversion rates and the maximum temperatures achieved. Furthermore, they discussed the potential effects of the water vapour generated during the process. Fumey et al. [24] developed a H₂-based cooker for domestic applications utilising uncoated and Pt-coated SiC foams as gas diffuser and catalyst bed, respectively, for the combustion of H₂. They reported the effects of the H₂ flow and equivalence ratios on the water heating efficiency of the device. Fernandez et al. [25] conducted H₂ combustion experiments on a clay-bound SiC foam coated with Pt/Al₂O₃-CeO₂. This foam-based catalytic system exhibited a high catalytic performance even at lean H₂/air mixtures and at ambient conditions. Their findings demonstrated the suitability of foam-supported catalysts for H₂ combustion processes.

To further understand the benefits of conducting H₂ combustion processes in foam-based catalytic reactors, particularly in the context of accidental H₂ release, it is considered important to study the difference between different catalyst bed structures. Furthermore, it is important to investigate the effects of prolonged exposure of the catalyst to the reaction medium in order to assess the catalyst durability or resistance to deactivation by sintering [13,14,26].

The PAR process has also been investigated through simulations based on theoretical and analytical knowledge of fluid dynamics and chemical reactions. Computational fluid dynamics (CFD) tools such as Ansys Fluent, COMSOL Multiphysics, STAR-CCM+ or OpenFOAM have been used to simulate the complex chemistry and transport behaviour of the reacting gas in different processes. The focus of the reported H₂ combustion simulations has usually been

on the estimation of temperature, velocity, or gas composition profiles in relatively simple geometries [15,27–33]. For instance, Zaroni et al.[15] developed a CFD model, using COMSOL Multiphysics, to simulate the PAR process on rectangular stainless steel plates. They investigated the effects of inlet flow conditions (H_2 concentration, gas velocity) and plate spacing on the temperature profile along the plate height, the H_2 and CO recombination rates, the surface reaction and the catalyst poisoning by CO. Malakhov et al.[10] used STAR-CCM+ for the CFD simulation of the PAR process in a recombiner consisting of cylindrical ceramic rods. Temperature profiles and H_2 recombination efficiencies were assessed at different H_2 inlet mole fractions. Experimental results were used for model validation. Kim et al.[33] conducted transient CFD simulations in OpenFOAM to study the PAR of H_2 under oxygen (O_2)-rich and O_2 -lean conditions in industrial plate-based recombiners. Their study compared a correlation-based model with a mass-diffusion model and results demonstrated the importance of O_2 diffusion on the H_2 recombination, especially under O_2 -lean conditions.

To simulate more complex fluid behaviours occurring in irregular geometries, an accurate 3D rendering of the solid domain (foam) can be obtained using computed tomography (CT). Here, inaccuracies of the simulation will be only due to the uncertainties related to the differential equations, assumptions and boundary conditions chosen to describe the model [34].

In the present study, a 5 wt.% Pt/ Al_2O_3 catalyst coated on Al foams was tested in a PAR reactor set-up, previously reported by Malakhov et al. [10]. There is currently a need for comparison between different catalyst configurations containing the same amount of Pt/ Al_2O_3 catalyst. Besides, there is no known fully heterogeneous 3D CFD simulation of PAR processes conducted on foam-supported catalysts. The objectives of our study are the following: (1) Characterise Pt/ Al_2O_3 -coated foams and evaluate their catalytic performance in a passive autocatalytic recombiner using steady-state H_2 conversions and coated foam surface temperatures as the main performance criteria. (2) Compare the performance of a recombiner using a Pt/ Al_2O_3 -coated foam, Pt/ Al_2O_3 -coated plates or Pt/ Al_2O_3 pellets in its catalytic section. (3) Carry out a durability test of the foam-supported Pt/ Al_2O_3 catalyst. (4) Carry out a fully heterogeneous CFD modelling of the catalytic H_2 combustion process using accurate 3D geometry of the foam samples in the PAR reactor set-up. The experimental section of this study will give an insight into the difference in performances between geometric configurations of the catalyst bed in the same recombiner. The numerical modelling will provide a deeper

understanding of the flow phenomena and temperature profiles inside a foam-based recombiner.

4.2 Materials and methods

4.2.1 Catalyst preparation and coating procedure

The 5 wt.% Pt/Al₂O₃ catalyst was prepared in-house by the wet impregnation method: 150 g γ -alumina pellets (Sasol, South Africa) were soaked, at ambient temperature, in an aqueous solution containing 19.2 g 38 wt.% hexachloroplatinic acid (H₂PtCl₆) (HySA Infrastructure, South Africa). The water was then removed by evaporation at 60°C and a pressure of 46 mbar in a Büchi Rotavapor® R300 (BÜCHI Labortechnik AG, Switzerland), equipped with an evaporating flask, rotating at a speed of 40 rpm. The H₂PtCl₆-impregnated alumina was subsequently dried in an EcoTherm oven (Labotec, South Africa) at 120°C for ~4 h. Calcination and reduction of the dried pellets was performed at 350°C (ramp rate 10°C/min) over a period of 2 h in a stream of air and 50 vol.% H₂/N₂ (flow rate 250 mL/min), respectively, using a CTF12 horizontal tube furnace (Carbolite Gero, England).

Aluminium foams (Recemat BV, Netherlands) of pore density 10 PPI (pores per inch) and 95% porosity were cut into four blocks (70 mm × 40 mm × 10 mm) and cleaned in 99.5 vol.% ethanol (Rochelle Chemicals, South Africa) for 10 min to remove any organic impurities from the substrate surface. Pt/Al₂O₃ pellets sampled from a batch prepared using the method described above were crushed into fine powder and later used for preparation of the slurry. This slurry consisted of ~30 wt.% of the Pt/Al₂O₃ powder in an aqueous solution containing 1.5 wt.% polyvinyl alcohol (MCL, South Africa) as binder, and 0.1 M HCl as dispersant and etching agent to increase the roughness of the aluminium foam surface [35,36,22]. The mixture was thoroughly homogenised (400 rpm, 60°C, 1 h) using an AccuPlate hotplate stirrer (Labnet International, NJ, USA). The clean and dry foams were then dipped into the slurry. A constant flow of compressed air was used to remove the excess slurry blocking the foam pores. The foam samples were subsequently dried and the process was repeated until the desired amount of catalyst was coated on the foam struts. To stabilise the washcoat layer, the dry coated foams were calcined in air and reduced in 50 vol.% H₂/N₂ (flow rate 250 mL/min) at 350°C in the tube furnace. The same procedure was used to coat the four aluminium plates (70 mm × 40 mm × 2 mm). These were first scraped with sandpaper to increase their surface rugosity and

improve the adhesion of the catalyst. The foam and the plate samples were coated with 3.8 g Pt/Al₂O₃ and their performances compared with that of the same amount of Pt/Al₂O₃ pellets.

4.2.2 Characterisation

The surface morphologies of the Pt/Al₂O₃-coated foams, Pt/Al₂O₃-coated plates and Pt/Al₂O₃ pellets were characterised using a FEI Quanta FEG 250 field emission gun scanning electron microscope (Thermo Fisher Scientific, USA). Elemental mapping of the washcoat surface was performed with energy dispersive X-ray spectroscopy (EDS) using an X-Max SDD 20 mm² detector (Oxford Instruments, England). Scanning electron microscopy (SEM) micrographs were analysed using xT Microscope Server and xT Microscope Control software, while EDS data were processed using AZtec software. Pt NPs were observed via transmission electron microscopy (TEM) using an electron microscope (JEOL JEM 2100, Japan) at 200 kV. Samples were dissolved in ethanol and sonicated for about 30 min then dispersed on a carbon-coated copper grid for analysis. Mean particles sizes were calculated from at least 150 particles obtained from TEM images using the open-source ImageJ program. TEM was performed before and after the long-term utilisation of the Pt/Al₂O₃-coated foam in the PAR process in order to gain insight into the effect of prolonged utilisation on the Pt NPs.

Characteristic dimensions of the coated and uncoated foam samples were determined by CT using the Nikon XT 225 system (Nikon Corporation, Tokyo, Japan) of the Central Analytical Facilities of Stellenbosch University, South Africa [37]. In this process, a voxel size of 55.85 µm was utilised and X-rays were generated at 100 kV and 500 µA. Captured images were analysed with the system-supplied Datos reconstruction software for the reconstruction of the volumetric dataset and the generation of the stereolithography (STL) file. VGSTUDIO MAX 2024.1 (Volume Graphics, Heidelberg, Germany) was used for the visualisation and quantitative analysis of the generated 3D geometry (STL file). From the CT-generated database, the gravimetric surface area, pore density, and the pore and strut diameters of the foam samples were calculated.

4.2.3 Experimental evaluation

Fig. 4-1 shows the two different set-ups in which catalytic H₂ recombination experiments were conducted: first, a passive autocatalytic recombiner [10], for performance evaluation of the Pt/Al₂O₃-coated foams and further comparison with two catalyst structural configurations

previously reported in the literature (plates and pellets) [14,26,38] and, second, a tubular fixed-bed reactor for durability tests on the foam-supported Pt/Al₂O₃ catalyst [26,39].

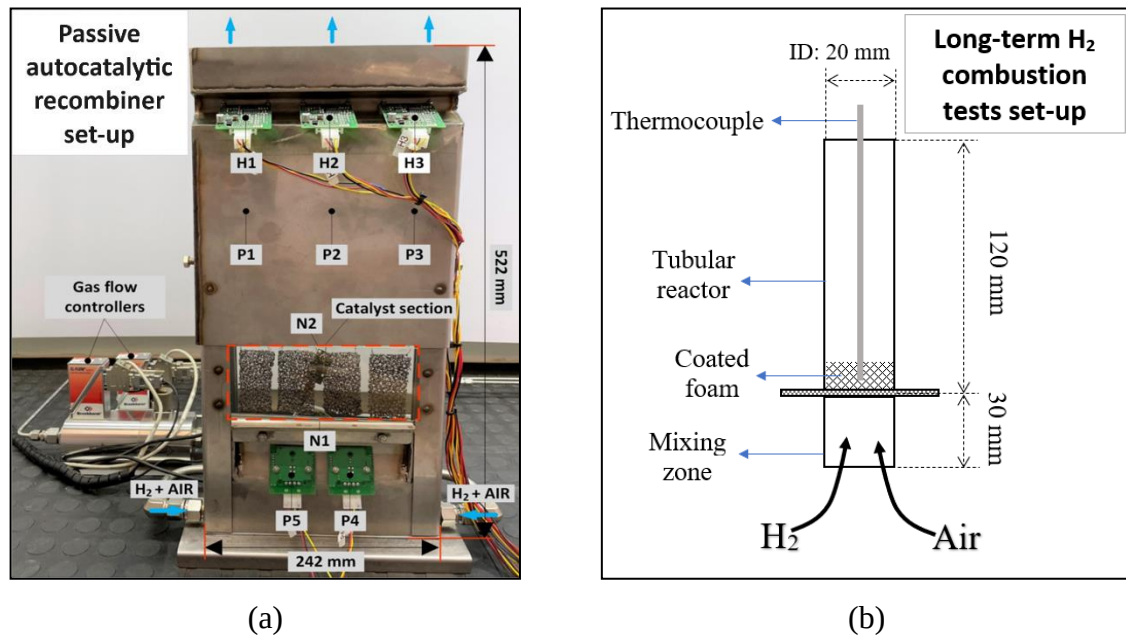


Figure 4-1. (a) Image of the reactor set-up used in the PAR experiments. (b) Schematics of the tubular reactor used for the durability tests. Legend. H1–H3 and P1–P5: H₂ sensors

4.2.3.1 PAR experiments

PAR experiments were conducted in a rectangular recombiner (280 mm × 242 mm × 45.5 mm) that contained the four Pt/Al₂O₃-coated foams (Fig. 4-1a). At the recombiner inlet, 99.9 vol.% H₂ (Hydrogen South Africa Infrastructure, South Africa) and compressed air flow were adjusted using thermal mass flow controllers (EL-FLOW F-201AV, Netherlands). The gas mixtures were then feed to the recombiner inlet (lower section) through a pipe (diameter 10 mm) that distributed premixed mixtures of H₂ and air through 12 holes (diameter 0.5 mm). The mixture was passed through a perforated plate to prevent uneven distribution of the gas at the catalyst region (middle section) where the recombination occurred. The product gas mixture (H₂, O₂, N₂, H₂O) exited the recombiner through its outlet (top section) and was vented to the atmosphere. Three XEN-5320 H₂ sensors (Xensor Integration, Netherlands) were fitted at the recombiner inlet section and three more at the outlet section. The sensor data were recorded every second and then used for calculation of the H₂ conversions at the different flow conditions as given in Table 4-1.

Table 4-1. Operating parameters used during the catalytic activity test in a PAR set-up.

Parameters	Values
H ₂ inlet concentration (vol.%)	2–6 (increments of 1%)
Gas injection velocity (m/s)	2.0, 5.0, 7.5 and 10

Performance assessment was based on the steady-state H₂ conversions and average temperatures recorded on the foam surface at different operating conditions. H₂ conversions were evaluated using Eq. (4-2), in which the number of moles n_{H_2in} was calculated from the gas flow rate, and the inlet and outlet H₂ concentrations. Selected experiments were conducted in triplicate to ensure the repeatability of results. The average deviation in H₂ conversions was ~5%.

$$X_{H_2} = \frac{n_{H_2in} - n_{H_2out}}{n_{H_2in}} \quad (4-2)$$

Surface temperatures were recorded every second using Reveal IR software (Telops, Canada), while temperature profiles were analysed using a high-resolution M100hd IR camera (Telops, Canada) equipped with lenses capable of detecting electromagnetic intensities corresponding to temperatures in the range 0–2500°C.

4.2.3.2 Durability tests

The durability of a foam-supported Pt/Al₂O₃ catalyst was tested in a tubular reactor in which a 10 PPI foam disk (diameter 20 mm, height 10 mm) coated with 0.2 g Pt/Al₂O₃ was placed 3 mm above the inlet nozzle supplying H₂ gas from an electrolyser (Hydrogen South Africa Infrastructure, South Africa) at its maximum release rate of 138 NmL/min. The catalytic H₂ combustion into surrounding air increased the temperature progressively. This increase was recorded every second, over a period of 480 h, using a K-type thermocouple (RS PRO, South Africa).

4.2.4 CFD simulations

The 3D steady-state CFD simulations of the catalyst performance were performed using STAR-CCM+ code supported with thermochemical data and reaction kinetics using the chemistry tool CHEMKIN. The computational domain consisted of the foams and the rectangular casing representing the recombiner's walls. The boundary conditions and

computation domain mesh settings are presented in Fig. 4-2. To capture the real geometric features of the Pt/Al₂O₃-coated foam sample in the numerical study, a STL model was imported into the CFD code. The imported 3D geometry was subjected to re-tessellation and reparation to obtain a continuous surface with no self-intersected faces, edges and vertices. The 3D computational domain was created by inserting the repaired STL model into a rectangular recombining channel that represents an actual experimental channel (Fig. 4-2). Then, 3D foam geometry was duplicated three times in the computational domain and subsequently subtracted from the fluid; then was re-imprinted in order to create an interface between the fluid and solid domains in the simulation. The repaired surface was volume meshed by using the same strategy as reported in previous work [29] (a polyhedral mesh was utilised). Mesh refinement was applied to the recombining inlet and outlet, and around the catalytic section. Mesh independence was reached at a base size of 4 mm and all simulations discussed below were performed using the same base size. The total number of roughly 2 860 000 cells discretises the fluid and solid computational domains. The meshing parameters are summarised in Fig. 4-2.

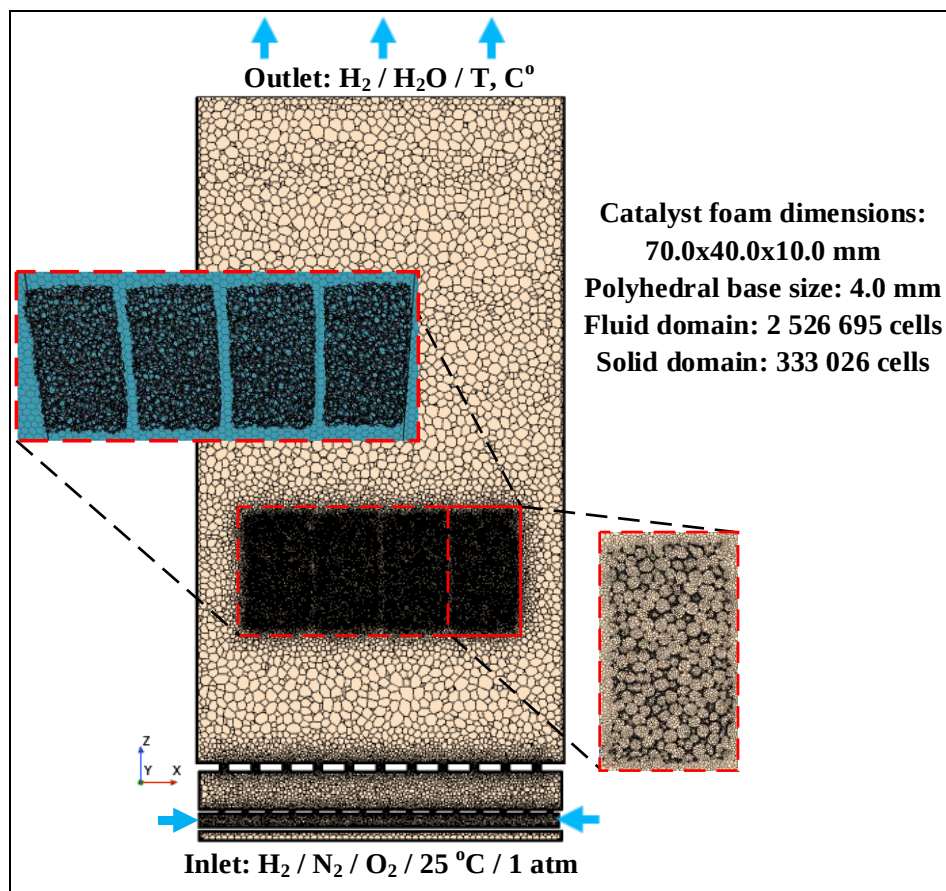


Figure 4-2. Computational domain and boundary conditions of CFD model.

A realisable k-epsilon model with a two-layer approach based on Reynolds-averaged Navier–Stokes equations was used to simulate the turbulent flow inside the channel and through the foam pores [40,41]. A no-slip velocity condition was assumed at the walls and solid domains of the recombiner channel. An experimental inlet mass flow rate of 35.0 ± 0.2 g/min (corresponding to a gas inlet velocity of 10 m/s) and gas mixture composition of 2–6 vol.% were set as the inlet boundary conditions. The governing equations were as follows (3D Cartesian coordinate system) [32,34,42,43].

Conservation of mass:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) = 0 \quad (4-3)$$

where ρ is the density (kg/m³) and $\vec{v}$ is the continuum velocity (m/s).

Conservation of momentum:

$$\frac{\partial(\rho \vec{v})}{\partial t} + \nabla \cdot (\rho \vec{v} \otimes \vec{v}) = -\nabla \cdot \vec{\sigma} \quad (4-4)$$

where $\otimes$ denotes the outer product and $\vec{\sigma}$ is the stress tensor. For a fluid, $\vec{\sigma}$ can be calculated as

$$\vec{\sigma} = -pI + T \quad (4-5)$$

where p is the pressure (Pa), T is the viscous stress tensor, and I is the identity tensor. The viscous stress tensor T can be calculated as

$$T = 2\mu * \frac{1}{2}(\nabla \bar{v} + \nabla \bar{v}^T) - \frac{2}{3}(\mu \nabla * \bar{v})I \quad (4-6)$$

where μ is the dynamic viscosity (Pa.s) and $\bar{v}$ is the mean velocity .

Conservation of species:

$$\frac{\partial \rho Y_i}{\partial t} + \nabla \cdot (\rho U Y_i) = \nabla \cdot \left(J_i + \frac{\mu_t}{Sc_t} \nabla Y_i \right) + S_{Y_i} \quad (4-7)$$

where S_{Y_i} is the mass fraction source term, Y_i is the species mass fraction, U is the total internal energy (J), μ_t is the dynamic viscosity, J_i is the diffusive mass flux (kg/m²/s), and Sc_t is the turbulent Schmidt number. The diffusive flux is calculated based on Fick's law

$$J_i = \rho D_{i,m} \nabla Y_i \quad (4-8)$$

where Y_i is the mass fraction of species i and $D_{i,m}$ is the diffusion coefficient of species i in the mixture (m²/s). The Schmidt number function is available in STAR-CCM+ for specifying molecular diffusivity of components in a mixture and is calculated as

$$Sc_t = \frac{\nu}{D_{i,m}} \quad (4-9)$$

where ν is the kinematic viscosity (m²/s) and $D_{i,m}$ is the diffusion coefficient of species i in the mixture. In this study, a Schmidt number equal to 0.2 was used to influence the molecular diffusion coefficients in order to obtain reasonable accuracy of the computational results [29,44,45].

Conservation of energy:

$$\frac{\partial(\rho E)}{\partial t} + \nabla \cdot (\rho E \vec{v}) = \vec{f}_b \cdot \vec{v} + \nabla \cdot (\vec{v} \times \vec{\sigma}) - \nabla \cdot \vec{q} + S_E \quad (4-10)$$

where E is the total energy per unit mass (J/kg), $\vec{q}$ is the heat flux (W/m²), and S_E is an energy source per unit volume (W/m³).

The applied emissivity of the catalytic surface was $\epsilon_m = 0.9$. The gas mixture (H₂/O₂/N₂) was assumed to be ideal. The components' thermophysical properties were obtained from the CHEMKIN material database. The rate constant was determined using the Arrhenius equation.

$$k_j = AT \exp \left(-\frac{E_a}{R_u T} \right) \quad (4-11)$$

where A is the pre-exponential factor (mol/cm³/K/s), T is the reaction temperature (K) and E_a is the activation energy (J/kmol) and R_u is the universal gas constant (J/kmol/K).

Table 4-2 summarises the detailed surface reaction kinetics mechanism utilised in order to simulate the catalytic H₂ recombination reaction [10,46].

Table 4-2. Heterogeneous mechanism of H₂/O₂ recombination on Pt. (Mechanism taken from a more detailed mechanism of H₂ oxidation on Pt from Deutschmann et al.[47,48])

Reactions	A ^a	E _a ^b	S _{0,i} ^c
1 $H_2 + 2Pt^{(s)} \rightarrow 2H^{(s)}$	0.0	0.0	0.046
2 $2H^{(s)} \rightarrow H_2 + 2Pt^{(s)}$	3.7×10^{21}	6.74×10^7	0.0
3 $O_2 + 2Pt^{(s)} \rightarrow 2O^{(s)}$	1.8×10^{21}	0.0	0.5
4 $O_2 + 2Pt^{(s)} \rightarrow 2O^{(s)}$	0.023	0.0	0.0
5 $2O^{(s)} \rightarrow O_2 + 2Pt^{(s)}$	3.7×10^{21}	2.132×10^8	0.0
6 $H_2O + Pt^{(s)} \rightarrow H_2O^{(s)}$	0.75	0.0	0.0
7 $H_2O^{(s)} \rightarrow H_2O + Pt^{(s)}$	1.0×10^{13}	4.03×10^7	0.0
8 $OH + Pt^{(s)} \rightarrow OH^{(s)}$	1.0	0.0	0.0
9 $OH^{(s)} \rightarrow OH + Pt^{(s)}$	1.0×10^{13}	1.928×10^8	0.0
10 $H^{(s)} + O^{(s)} = OH^{(s)} + Pt^{(s)}$	3.7×10^{21}	1.15×10^7	0.0
11 $H^{(s)} + OH^{(s)} = H_2O^{(s)} + Pt^{(s)}$	3.7×10^{21}	1.74×10^7	0.0
12 $OH^{(s)} + OH^{(s)} \rightarrow H_2O^{(s)} + O^{(s)}$	3.7×10^{21}	4.82×10^7	0.0

^a Pre-exponential factor: A [mol/cm³/K/s],

^b Activation energy: E_a [J/kmol],

^c Sticking coefficient.

The catalytic activity was assumed to occur only on Pt uniformly distributed on the surface of the section of the geometry representing the coated foam. A surface site density of S₀ = 2.7 × 10⁻⁸ kmol/m² was assumed [43]. A catalytic H₂ recombination reaction is associated with high thermal radiation, therefore, the surface-to-surface thermal radiation model was considered in CFD modelling [34]. In this study, the models of gravity force, thermal diffusion and external forces were not considered. The channel walls were assumed to be adiabatic.

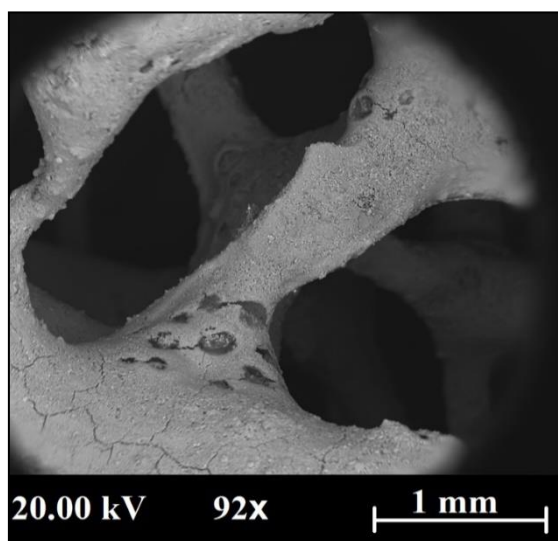
4.3 Results and discussion

4.3.1 Characterisation

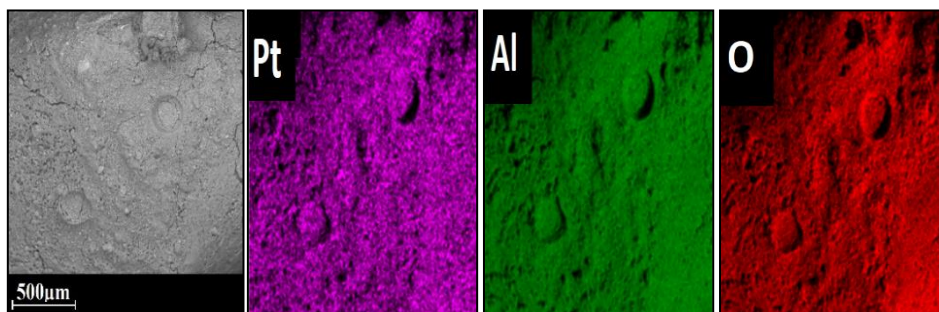
The textural properties related to the Pt/Al₂O₃-coated foams and geometric characteristics of the uncoated and coated foams are now reported and discussed. Their anticipated advantages on catalytic performance in the recombiner are briefly mentioned.

4.3.1.1 Textural properties

Fig. 4-3 shows SEM micrographs of the Pt/Al₂O₃-coated foams and EDS spectra of surfaces. The SEM micrographs of the foam struts confirmed that the Pt/Al₂O₃ catalyst was deposited over the entire surface of the Al foam. The surface of the catalyst layer was generally rugous and cracks were spotted at several struts on the foam (Fig. 4-3a).



(a)



(b)

Figure 4-3. (a) SEM micrograph of the coated foam, (b) EDS maps of the sample surface.

Some surface irregularities could have resulted from the removal of organic species (e.g. polyvinyl alcohol) during the calcination step after catalyst coating. This irregular surface morphology has the benefit of increasing the surface area of the catalyst deposited on the foam; foam-supported catalysts generally have a low gravimetric surface area [49]. The observed disadvantage of cracks in a catalyst washcoat layer is that they constitute weak points from which the catalyst tends to flake off the foam, especially at high catalyst loading or when the catalyst is subjected to intense mechanical or thermal stresses [22,50].

The EDS maps (Fig. 4-3b) confirmed the presence of Pt and Al₂O₃ particles on the entire surface of the catalyst washcoat. An even distribution of Pt on the surface of the washcoat is essential for maintaining high activity of the foam-based catalytic structure because Pt is the active metal in the PAR process. The presence of the morphological support (Al₂O₃) over the surface of the struts was expected as it is the most abundant constituent of the catalyst (~95 wt.%). The high specific surface area of Al₂O₃ is an added advantage in the process. It maintains high dispersion of the Pt NPs over the surface whilst minimizing their agglomeration at prolonged reaction times [13,16].

TEM micrographs of the catalyst powders sampled from the washcoat layers of the foam samples before and after 480 h of reaction are shown in Fig. 4-4. It is evident that long-term exposure to the H₂ combustion process alters the Pt nanoparticle (NP) size. The average size of Pt NPs increased from 3.8 nm to 6.2 nm. Kozhukhova et al. [14] observed a smaller increase in particle size from 3.0 to 3.8 nm on their Pt catalyst supported on anodised Al plates exposed to 530 h combustion at ~160°C. The higher combustion temperatures (~300°C) reached during the long-term test in this study can explain the more pronounced agglomeration of Pt NPs. Nevertheless, the maximum NP size obtained is still within the size range of several catalysts reported in earlier literature, namely 5–20 nm [16,25,51].

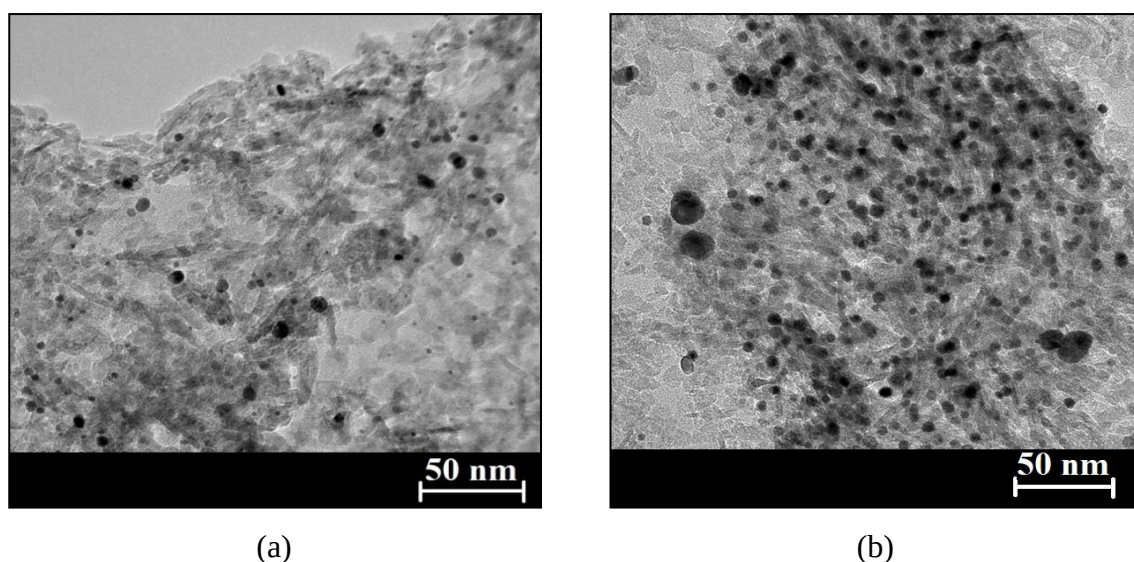


Figure 4-4. TEM micrographs of Pt/Al₂O₃ catalyst extracted from (a) fresh foam and (b) used foam.

The use of Al₂O₃ as morphological support could have prevented excessive sintering of the Pt NPs. In a study of catalytic H₂ combustion on Pt supported directly on stainless steel mesh, Du Preez et al. [39] obtained average Pt NP sizes of up to 120 nm after prolonged H₂ combustion reactions. The higher Pt mobility on the metal surface increases the tendency for agglomeration of Pt NPs, especially at high temperatures (>500°C) or high moisture levels [18].

4.3.1.2 Geometric properties

Table 4-3 presents the geometric parameters calculated using CT results. The results revealed slight differences between the uncoated and coated foam samples. The coating process resulted in a 48% increase in the average strut diameter, which corresponds to an estimated average washcoat thickness of 75 μ m. Such a relatively high value could be expected because 95% of the washcoat consists in the morphological support. Much thinner layers would be achieved if only the active phase (Pt) was deposited directly on the Al foam surface.

Table 4-3. Geometric properties of the 10 PPI Al foam used in this work.

Geometric property	Uncoated foam	Coated foam
Average strut diameter (mm)	0.31	0.46
Average pore diameter (mm)	4.19	3.37
Average pore volume (mm ³)	49.09	34.58
Volumetric surface area (m ² /m ³)	336.02	447.93

Tomograms of the uncoated and Pt/Al₂O₃-coated foam samples are presented in Fig. 4-5. The expected decreases in pore diameter and pore volume are a direct consequence of the increase in strut diameter from the catalyst coating process. In this study, the decrease in pore volume did not result in pore blocking because of the relatively large pores combined with small strut diameters. The 10 PPI foam used in this study has pores sufficiently large to accommodate relatively high catalyst amounts. Foams of higher pore density (e.g. 40 PPI) have the advantage of having a higher volumetric surface area due to the increased number of cells. However, they can easily be blocked during the catalyst coating step. This may result in a significant decrease in porosity and the occurrence of preferential pathways within the catalyst bed during the reaction. An unblocked foam-based catalyst support structure offers the benefit of improving mass transfer because of the high mixing and tortuosity increasing turbulence within the structure. Similarly, heat transfer is also improved by the contribution of conduction, convection and radiation in the heat-transfer mechanism [52].

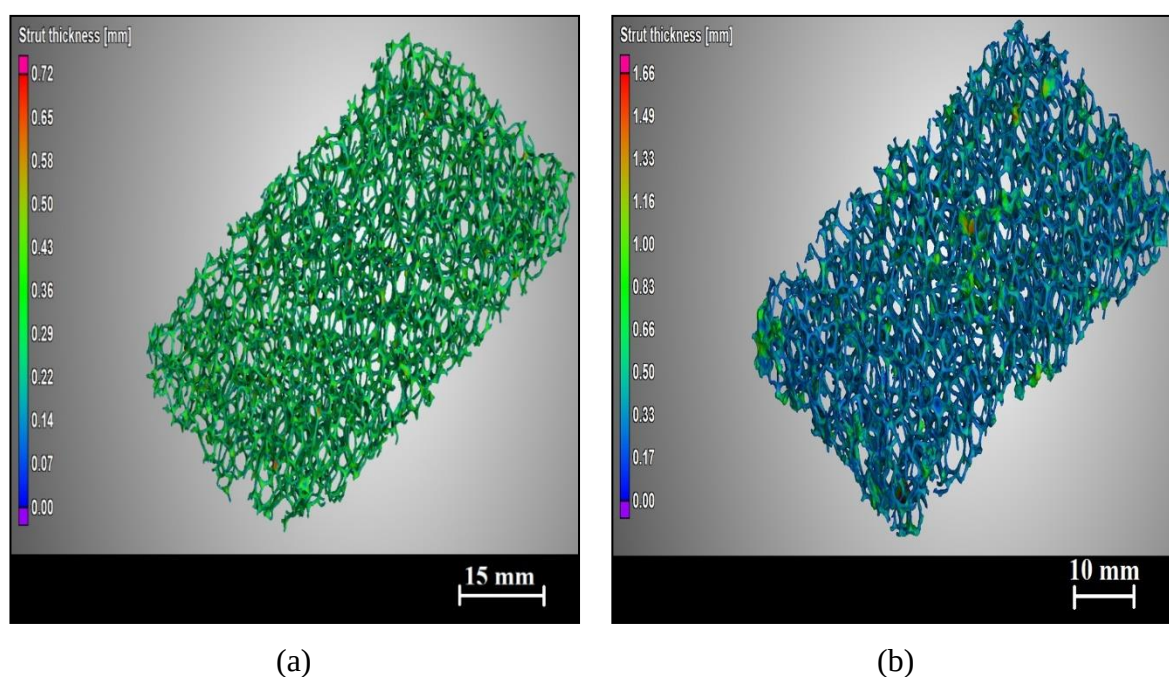


Figure 4-5. Tomograms of 3D structures generated from CT scans of (a) uncoated foam and (b) coated foam.

4.3.2 Catalytic activity tests

The effects of the inlet gas velocity and H₂ inlet concentrations on the performance of the Pt/Al₂O₃-coated foams in the recombiner are now reported. Pt/Al₂O₃-coated aluminium plates and pellet-based catalysts (for which the same amount of Pt/Al₂O₃ was used as on the coated

foams) were also tested, at the same process conditions, for comparison. Average temperatures and temperatures at the hottest spots on the catalyst bed were also recorded to assess the operating conditions that posed the greatest safety risks. It was established that the foam-supported Pt/Al₂O₃ catalyst was able to withstand long-term continuous operation without showing signs of deactivation.

4.3.2.1 Effect of inlet gas velocity and H₂ concentration on the recombiner performance

The effects of the inlet gas velocity and inlet H₂ concentrations on the steady-state recombiner performance are shown in Fig. 4-6. To understand the overall recombination performance as a function of the inlet conditions, the H₂ conversions and surface temperatures were averaged over the four foam samples. During the PAR process, the exothermic H₂ combustion on the Pt/Al₂O₃ catalyst spontaneously commences at ambient temperature. As the reaction proceeds, more catalyst active sites are covered with H₂ and O₂ species, resulting in the occurrence of more H₂ combustion and heat release. This naturally increases the surface temperature of the foam—and the reaction kinetics—resulting in higher H₂ conversions, with further increases in the heat released [53]. Eventually, the combustion process transits from a kinetically controlled to a mass-transfer-controlled regime and a thermodynamic equilibrium is achieved at steady-state conditions [16]. The recombiner performances achieved at these steady-state conditions are strongly dependant on the supply of the gas mixture (reactants and inert N₂) and the reactant consumption rate on the catalyst surface. The process outcome is therefore determined by the competing effects of reaction kinetic rates and mass transfer rate limitations at the gas–solid interface and in the gas phase.

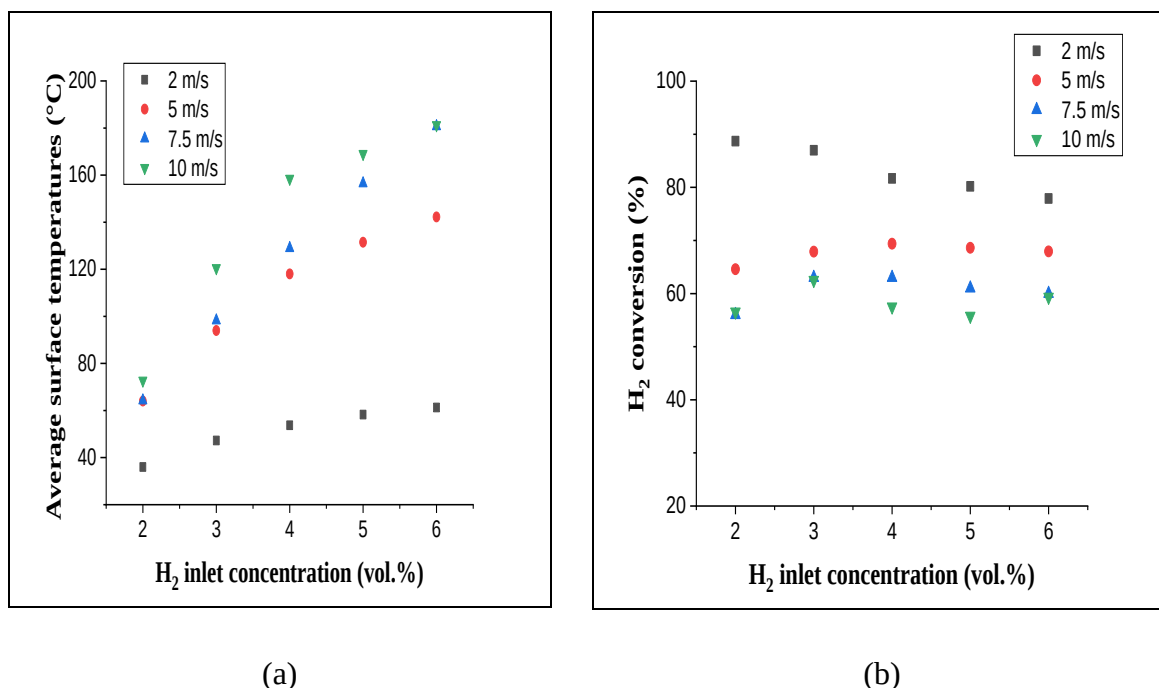


Figure 4-6. Effects of inlet gas velocity and inlet H_2 concentration: (a) on the average surface temperature of the foams and (b) on the H_2 conversions.

Fig. 4-6a shows that the average steady-state surface temperatures of the four coated foam samples generally increases at higher inlet gas velocities. Increasing the surface temperatures causes an increase in the reaction rate [16,53]. However, the increase in combustion rate does not cause an increase in H_2 conversions. From Fig. 4-6b it is evident that an increase in inlet gas velocity results in lower H_2 conversions. This can be attributed to the decrease in residence times on the catalyst surface [20,53]. Shorter residence times result in lower rates of mass transfer of reactants from the bulk of the fluid to the catalyst surface [16]. Consequently, more H_2 and O_2 leave the recombiner unreacted [18]. This, in turn, suggests that limitations in mass transfer rates prevail over kinetic rates at the experimental conditions investigated. Similar trends were also observed in the plate-based and pellet-based recombiners (Fig. B-1, Appendix B1)

It is also evident from Fig. 4-6 that the recombiner performance is differently affected by H_2 concentrations at different inlet gas velocities. At a low gas inlet velocity of 2 m/s, as H_2 inlet concentrations increases from 2 to 6 vol.%, the H_2 conversion decreases from 88.7% to 77.9%, while average steady-state temperatures increase from 36 to 61°C. At higher H_2 inlet concentrations, more H_2 is fed to the foam surface. This results in higher rates of reaction, which then increase the catalyst surface temperature [54]. Despite this, the subsequent increase in combustion rate is not sufficiently high to compensate for the increasing amount of H_2 fed

to the recombiner inlet at higher inlet H₂ concentrations. At higher inlet gas velocities (5–10 m/s), steeper increases in surface temperatures were observed with increasing H₂ inlet concentrations (Fig. 4-6a). Meanwhile, at the same conditions, the H₂ conversions remained almost constant (Fig. 4-6b). At these gas flow rates, the increase in H₂ consumption rates offset the increase in H₂ inflow at higher inlet concentrations.

Moreover, gas–solid and intermolecular gas-phase diffusions could limit the access of the reacting gas to the catalyst active sites [54], as also illustrated in Fig. 4-6. For equivalent amounts of incoming H₂, two different conversions can be obtained depending on the amount of inert gas (N₂) present in the feed. For instance, two gases fed at a velocity of 2 and 5 m/s and containing 5 and 2 vol.% H₂ in air, respectively, introduce H₂ at the same rate in the recombiner but result in different conversions: 80.2 and 57.0%, respectively. Consequently, the recombiner performed better when removing H₂ from slow leaks of relatively high H₂ concentrations than from rapid leaks of low H₂ concentrations.

4.3.2.2 Temperature profiles in the foam-based recombiner

Arguably, one of the greatest practical challenges in a PAR set-up is to establish the optimum location at which maximum H₂ conversion will be achieved, preferably at the lowest temperature possible. Fig. 4-7 reports the average temperatures obtained on each of the four Pt/Al₂O₃-coated foams at different inlet gas flow velocities and H₂ concentrations. The thermograms illustrate the temperature profiles for the four foam samples at selected inlet conditions. There are several possible reasons for the different temperature profiles across the catalyst bed, including an uneven gas distribution inside the recombiner due to different unpredictable flow patterns of the gas entering the reaction zone [10], or a possible higher concentration of the catalytically active metals at one particular spot on the catalyst bed (i.e. a non-uniform catalyst washcoat layer) [14]. This last possibility is unlikely, because the profiles in Fig. 4-7 show that the hottest foams are not the same at the different flow conditions. At inlet gas conditions of 7.5 m/s, the temperature profiles were found to be the most uniform. In the case of accidental leaks in large-scale settings, even gas distribution is very unlikely to occur; hence the recombiner positioning is an important optimisation parameter in the mitigation of risks related to H₂ leaks in confined spaces. Uneven temperature profiles were also observed in the plate-based recombiner (Fig. B-2, Appendix B).

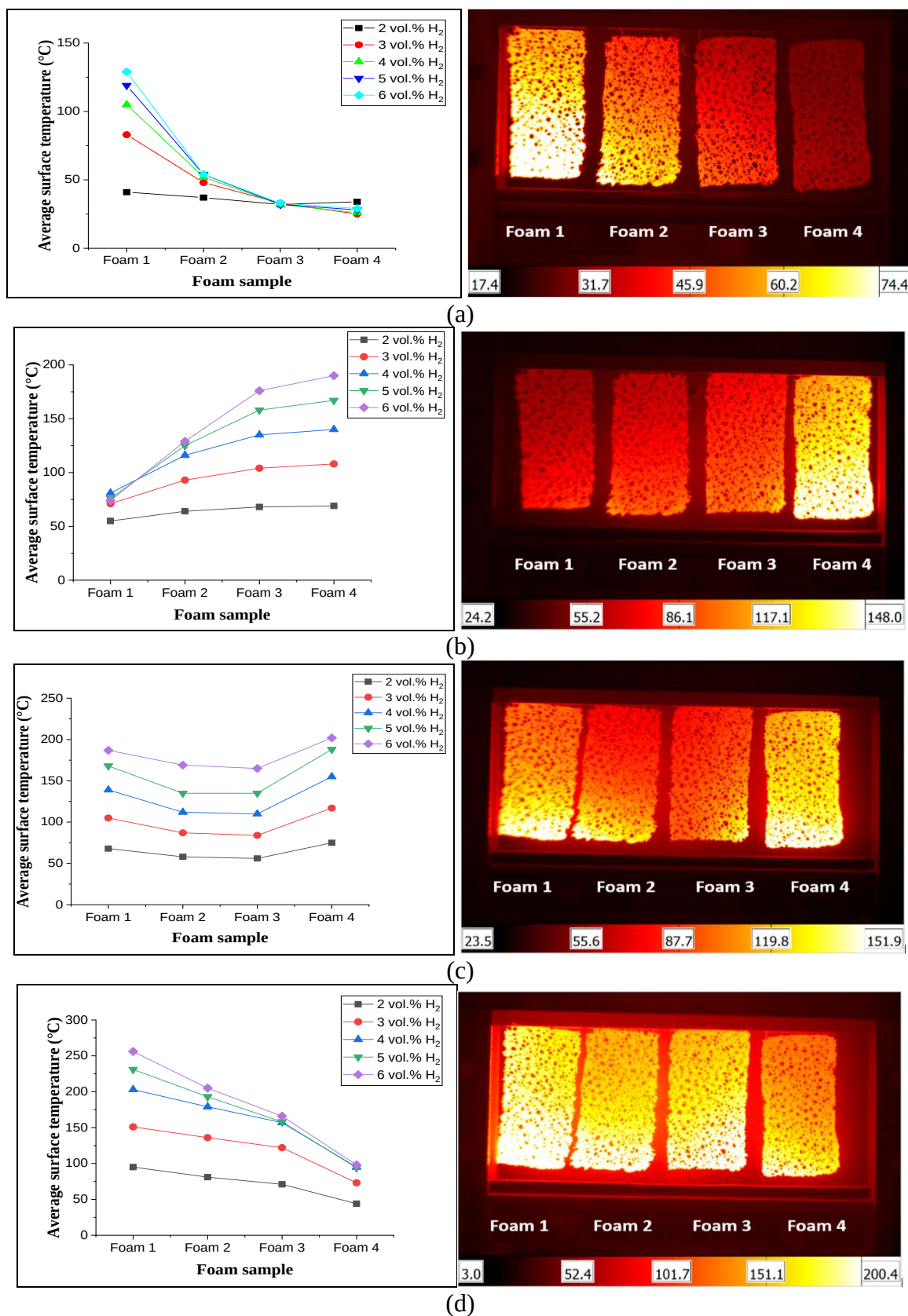


Figure 4-7. Average temperatures obtained at inlet gas velocities of (a) 2 m/s, (b) 5 m/s, (c) 7.5 m/s and (d) 10 m/s, coupled with thermograms, obtained at inlet H_2 concentrations of 3 vol.%.

The highest temperatures were obtained at the base of the foams. A maximum temperature of 393°C was measured on Foam 1 at the highest H₂ inlet concentration and inlet gas velocity. The average surface temperature of Foam 1 was 252°C. This confirms the heat dissipation capability of foam-based catalyst beds, attributed to their high thermal conductivity and high porosity. Heat transfer occurs by conduction through the metal struts as well as convective and radiative heat transfer through the foam's pores [52,53,55]. Relatively large amounts of inert N₂ and unreacted species flow through the foams. These species that enter the recombiner at ambient temperature contribute to cooling the surface of the coated foams. The maximum temperatures obtained on the coated foams were slightly higher than those obtained on the coated plates (Fig. B-3, Appendix B), but they still remained <585°C—the temperature for spontaneous combustion of H₂ within its flammability limits.

4.3.2.3 Effect of configuration of the catalyst region on the recombiner performance

Fig. 4-8 shows the results of a comparison of the performances of the Pt/Al₂O₃-coated foams, coated plates and pellet-based catalysts. Major differences between the three configurations include the volume occupied by the catalyst bed and the exposed catalytic surface area in the recombiner. These differences have an impact on the gas–solid mass transfer rates. The high macro-porosity of the foam-based bed causes it to occupy a larger volume in the recombiner than the plates do, and especially larger than the pellets. This contributes to the higher exposure of H₂ gas on the catalyst surface despite its high dilution in the relatively large amount of N₂ in the incoming gas. For instance, a higher H₂ conversion was achieved in the foam-based catalytic recombiner when a 2 vol.% H₂ gas was fed at a velocity of 2 m/s (Fig. 4-8a). The spontaneous combustion of H₂ at very low concentrations is of great practical importance because a recombiner should be able to prevent accumulation of H₂ by oxidising it within the first instants of slow accidental leaks in confined spaces.

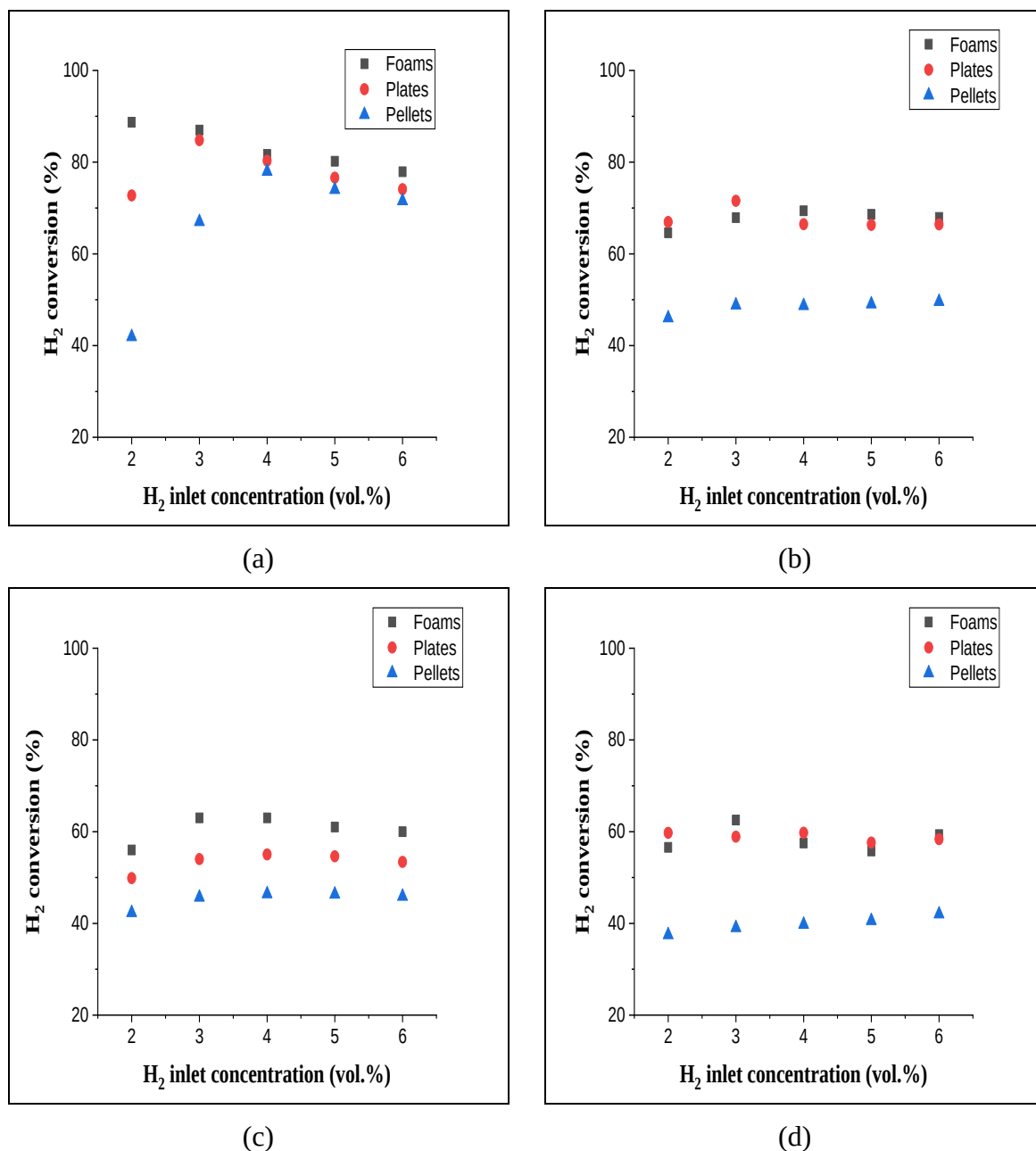


Figure 4-8. Effect of support structure configuration and inlet H_2 concentration on the H_2 conversion at inlet gas velocities of (a) 2 m/s, (b) 5 m/s, (c) 7.5 m/s and (d) 10 m/s.

At the same inlet gas velocity of 2 m/s, and as the H_2 inlet concentrations increases, the performance advantage of the foams is lost. As more H_2 is fed to the recombiner, more H_2 is exposed to the catalyst surface, thus the H_2 conversion on plates and pellets increases, as expected, until the point at which gas–solid mass transfer limitations prohibit higher conversions (Fig. 4-8a). At higher inlet gas flow rates (Fig. 4-8b–d), the pellet-based configuration proves to be less suitable for high-velocity leaks than the foams and plates. The amount of pellets loaded in the recombiner should be increased significantly in order to improve their efficiency. One way to improve the performance of pellets is to use a catalyst of

lower Pt loading (e.g. 0.2 wt.% Pt/Al₂O₃) dispersed on more Al₂O₃ pellets. This increase in dispersion will inevitably require larger amounts of Al₂O₃ to be used in the recombiner.

4.3.2.4 Catalyst durability tests

For safety applications, the recombiner should be equipped with a catalytic system characterised by short initiation times and high stability upon prolonged exposure to streams of H₂ gas. In the present work, the foam-supported Pt/Al₂O₃ catalyst was exposed to a constant H₂ flow of 138 mL/min for 480 h. Fig. 4-9 shows the maximum temperature achieved during the test. On fresh foam-supported Pt/Al₂O₃, H₂ combustion was initiated at ambient temperature (~24°C) after a time of 35 s. The combustion temperature subsequently increased over a period of ~215 s before steady state was achieved (Fig. 4-9a). In an earlier study performed at the same flow conditions [14], H₂ combustion on a Pt catalyst supported on anodised aluminium oxide was initiated within 27 s and stabilised slowly after ~500 s. The rapid heating observed in the present study was attributed to the relatively low amount of material (0.2 g Pt/Al₂O₃ and 0.5 g Al foam) and the high thermal conductivity of the Al foam (237 W/m/K). The catalyst bed could therefore heat up much faster. This can also be seen in the higher combustion temperature achieved (~300°C vs 163°C in [14]) once steady state was reached. Almost constant catalytic activity was maintained for a period of >480 h on stream (Fig. 4-9b). This is a preliminary indication of the stability of the 5 wt.% Pt/Al₂O₃ supported on Al foam.

The fluctuations seen in the temperature profile in Fig. 4-9b were attributed to insufficient thermal insulation, which caused the reactor to be subjected to the environmental fluctuations in the laboratory [13]. Some water vapour condensation was observed around the reactor wall and towards the reactor outlet (these areas were colder than the reactor inlet where the reaction takes place). These droplets caused an increase in relative humidity inside the reactor, even causing some water droplets to fall on the catalyst surface, despite the precaution taken to prevent interference with the catalyst surface.

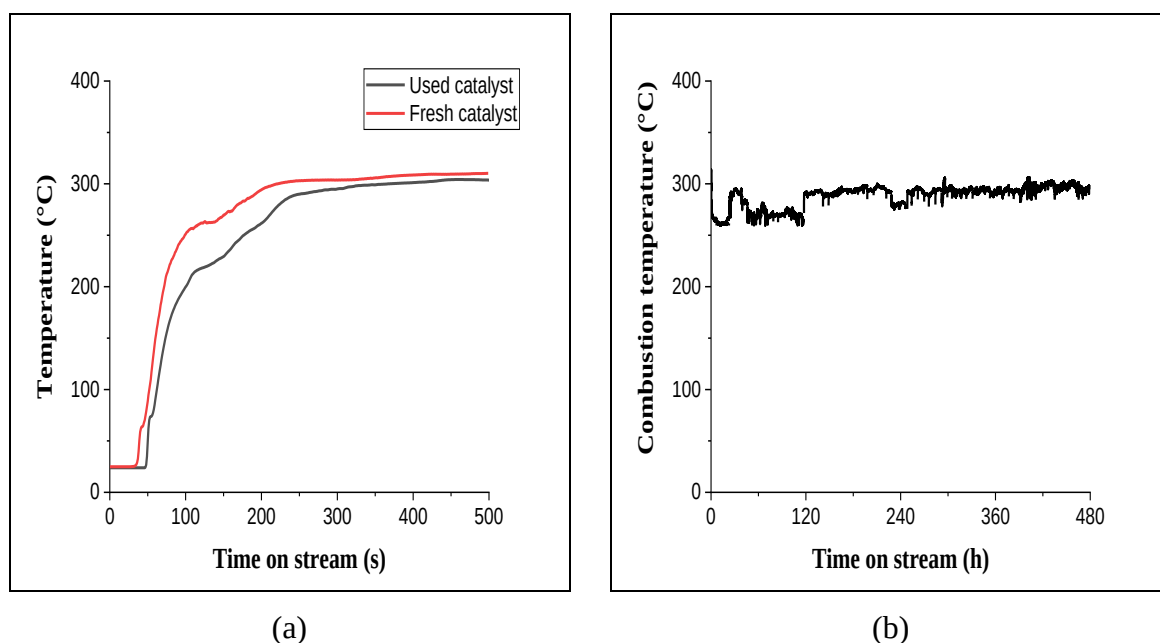


Figure 4-9. Temperature profiles recorded on the surface of a coated foam (a) during the initial 500 s and (b) over a period of 480 h on stream.

The catalyst subjected to the long-term test was allowed to cool to room temperature and was later exposed to the same experimental conditions as the freshly prepared catalyst. The initiation and stabilisation times were increased by ~15 and 95 s, respectively (Fig. 4-9a). This slight change in catalytic behaviour is an indication of possible changes in the textural properties of the catalyst [11]. TEM analysis of the used catalyst revealed an increase in Pt NPs (Fig. 4-4). Nevertheless, the observed maximum temperatures were similar on both the used and fresh catalyst bed.

4.4 CFD modelling results

The catalytic H_2 recombination reaction is highly exothermic. The heat released is transferred through conduction within the struts, convection in the fluid domain and thermal radiation in the foam pores. These three mechanisms of heat transport are included in the conjugated heat transport model [56]. It was found that thermal radiation plays a particularly significant role in the heat transport model. As illustrated in Fig. 4-10, the CFD model validation shows that neglecting the thermal radiation model in CFD simulation of catalytic recombination results in overprediction of the catalyst temperature profile, worsening as the inlet H_2 concentration increases. This has been demonstrated in a plate-type recombiner catalyst by Meynet et al. [57]. Sinn et al. [58] demonstrated similar deviations in their results of a study of combustion on

foam catalysts. The maximum calculated temperature of the catalytic foam was overpredicted by $\sim 120^\circ\text{C}$ at 6 vol.% of inlet H_2 .

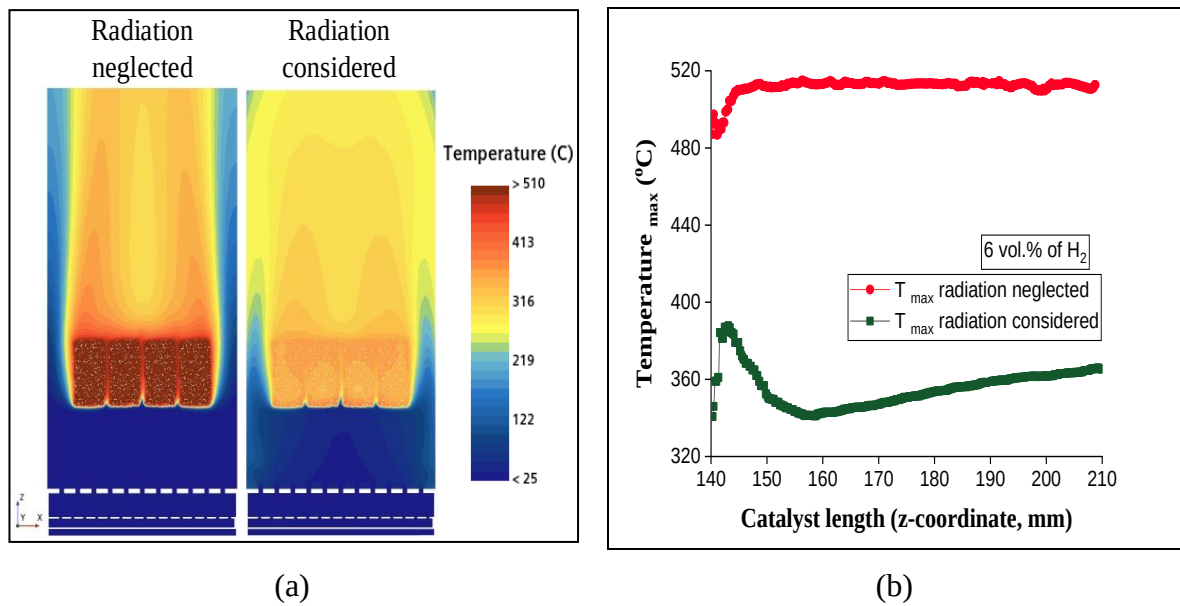


Figure 4-10. Comparison between temperature profiles obtained at an inlet gas flow rate of 35.0 ± 0.2 g/min (inlet velocity ~ 10 m/s) and concentration 6 vol.% H_2 in simulations: (a) including the radiation model and (b) excluding the radiation model.

Fig. 4-11 shows plots of the simulated velocity, H_2 mole fraction, H_2O mole fraction and temperature profiles along the middle of the channel and centre of catalytic foams at 4 vol.% of inlet H_2 . As reported in a previous study by Malakhov et al. [29], at the inlet mass flow rate of 35.0 ± 0.2 g/min the flow velocity is distributed uniformly throughout the recombiner channel and the catalyst area in the middle (Fig. 4-11a,b). Two zones of high turbulence vortex can be seen on the right- and left-hand sides at the bottom of the channel below the catalyst foam. These two turbulent zones cause the flow to decrease, resulting in a slightly lower catalyst temperature of foams 1 and 4 (Fig. 4-11e).

Fig. 4-11c displays the H_2 distribution profile along the recombiner channel, indicating near-complete recombination of H_2 on the catalyst surface and within a small area around the foam. However, a certain amount of H_2 slips away unreacted on the catalyst surface and escapes through the outlet boundary of the channel, resulting in incomplete H_2 conversion.

Fig. 4-11d presents a typical steady-state profile of the H_2O . It demonstrates that ~ 4.04 vol.% of H_2O is generated during the catalytic H_2 recombination reaction at 4 vol.% of inlet H_2 . A similar profile of reaction products has been published by Malakhov et al. [10]. Fig. 4-11e

illustrates the temperature profile along the channel length and the catalyst surface. A maximum catalyst temperature of 293°C was observed at the bottom edge of all four of the foam samples at 4 vol.% of inlet H_2 , corresponding to the position of higher H_2 concentrations and flow rates. The simulated positions and magnitudes of temperature maxima were found to be in good agreement with experimental results.

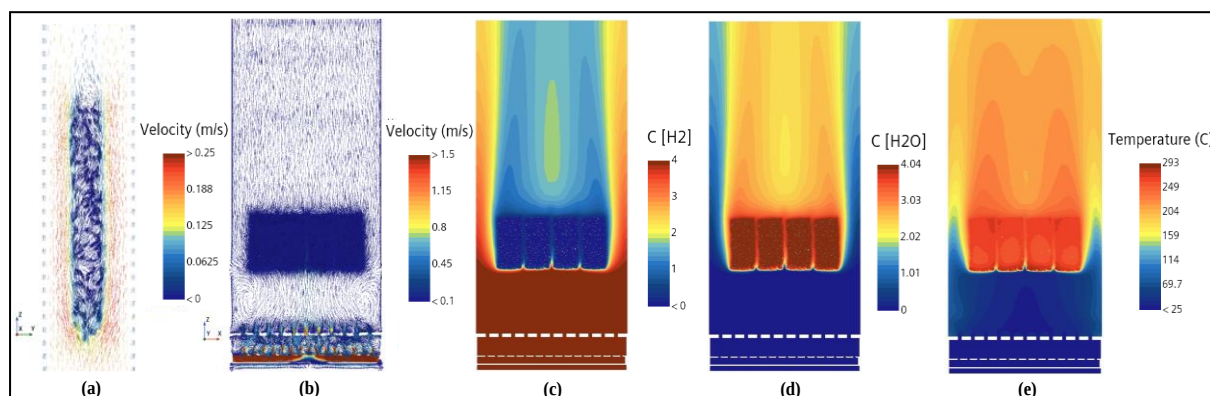


Figure 4-11. Calculated profiles of the velocity, temperature, and concentration of H_2 and H_2O (inlet gas flow rate 35.0 ± 0.2 g/min, inlet H_2 concentration 4 vol.%).

Fig. 4-12 shows the H_2 and H_2O concentration profiles together with a comparison of the simulated and experimental catalyst temperatures along the length of the catalytic foam, obtained at an inlet gas flow rate of 35.0 ± 0.2 g/min and inlet H_2 concentrations of 2 and 4 vol.%. The H_2 profiles demonstrate a near-complete H_2 conversion along the length of the catalytic foam in both cases. The H_2 concentrations at the bottom edge of the foam are about 0.5 and 0.65 vol.%, respectively. These low H_2 concentrations confirm that most H_2 conversion occurs towards the bottom edge of the foam. Therefore, this section heated up faster than the remaining part of the catalytic structure. Nearly complete H_2 conversion was achieved within the first 10 mm from the bottom edge of the foam. At the last few millimetres above the foam, the slight increase in H_2 concentration and temperature are due to the higher velocity of free stream that comes up around the foam (see Fig. 4-11).

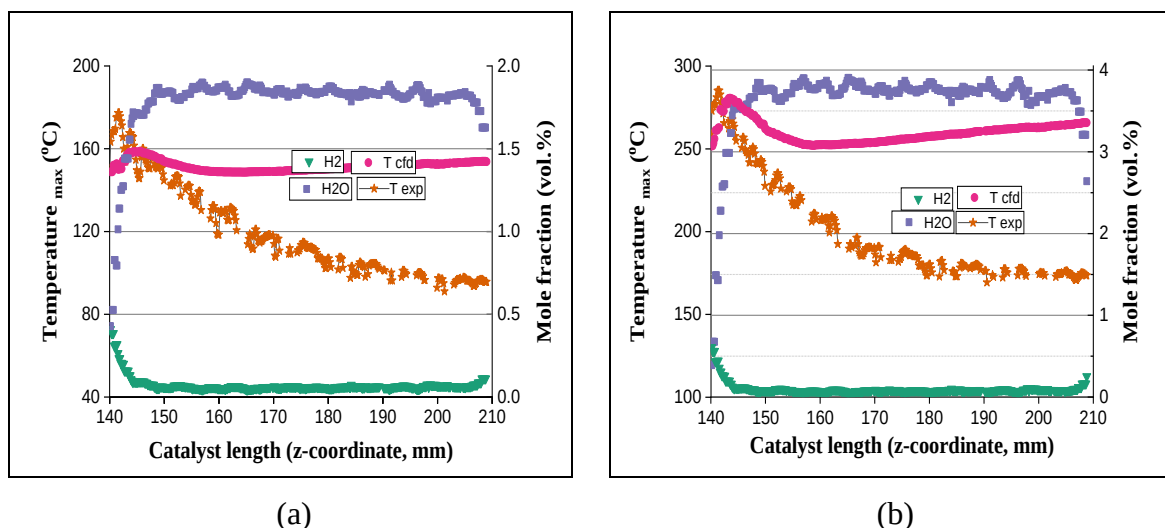


Figure 4-12. H_2 and H_2O mole concentration profiles together with experimental and simulated temperatures obtained at an inlet gas flow rate of 35.0 ± 0.2 g/min and inlet H_2 concentrations of (a) 2 vol.% H_2 and (b) 4 vol.% H_2 .

As mentioned above, at the bottom edge of the foam, the numerically simulated maximum catalyst temperatures are in good agreement with experimental values at all the inlet H_2 concentrations considered here. However, along the foam length, the temperature profiles are systematically different (Fig. 4-13). Both the experimental and simulation profiles decrease after the maximum at the bottom edge until the upper edge of the foam, while the experimental temperature decreases steeply and then stabilises to linear after 30 mm of its length; the numerically simulated temperature slightly decreases for the first 15 mm after the maximum and then increases towards the top edge of the foam without reaching the maximum temperature of the bottom edge. Such a steep down-slope profile indicates heat loss along the catalyst length due to the experimental channel not being truly adiabatic.

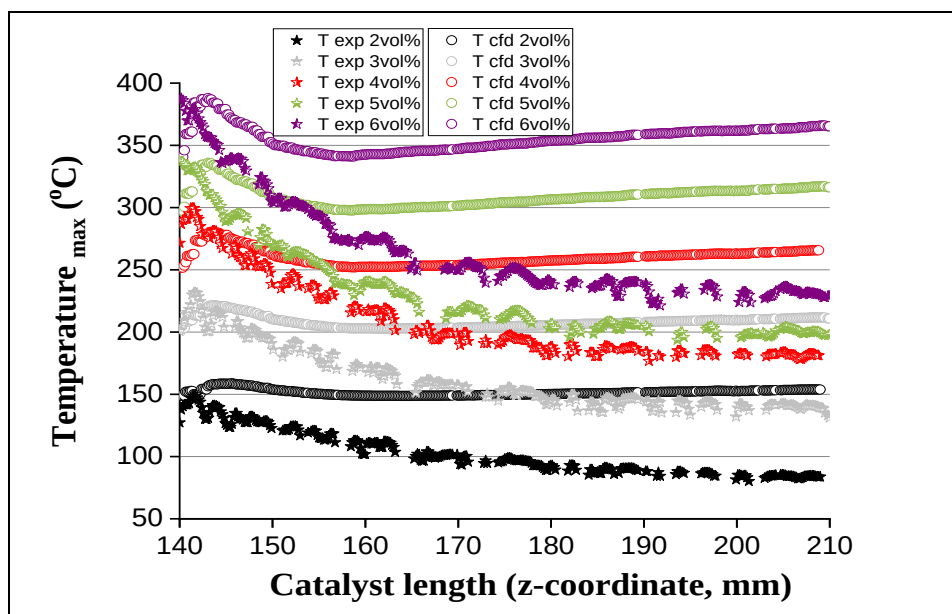


Figure 4-13. Comparison of the experimental and simulation temperature profiles along the foam length (z-coordinate, at an inlet gas flow rate of 35.0 ± 0.2 g/min).

The catalyst demonstrates a lower temperature of $\sim 150^{\circ}\text{C}$ at 2 vol.% of H_2 . The temperature increases as the inlet H_2 concentration increases, resulting in 235°C , 295°C , 340°C and 395°C at 3, 4, 5 and 6 vol.% of inlet H_2 , respectively. It was observed that the deviation between experimental and simulated temperature increased with increasing H_2 concentrations [29]; however, the overall numerically simulated trend demonstrates a reasonable prediction of experiment data.

A comparison of the experimental and simulated H_2 conversions obtained on the foam-based catalyst is displayed in Fig. 4-14, for all considered cases mentioned. Results show that the average experimental and simulated conversions agreed reasonably well. Both cases show that the inlet H_2 concentrations did not significantly affect H_2 conversion.

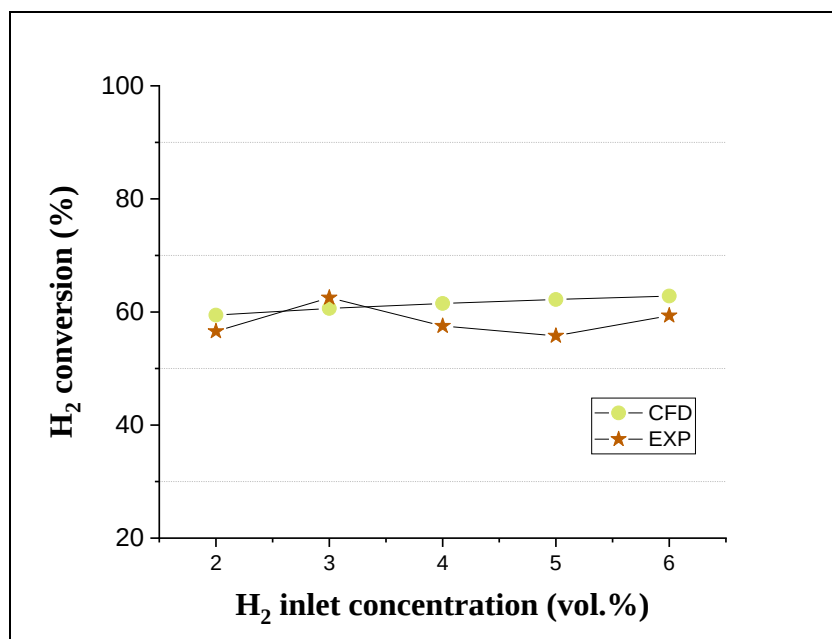


Figure 4-14. Comparison of the experimental and simulated H₂ conversion at an inlet gas flow rate of 35.0 ± 0.2 g/min (inlet gas velocity 10 m/s).

4.5 Conclusions

Catalytic H₂ combustion tests were conducted in a bench-scale passive autocatalytic recombiner containing an in-house prepared catalyst (5 wt.% Pt/Al₂O₃) coated on commercial Al foams. SEM images and EDS spectra of the coated foams revealed a uniform distribution of the catalyst on the entire Al foam surface. This confirms the suitability of slurry coating as catalyst deposition procedure on a metal foam used for PAR. TEM micrographs showed that long-term catalytic activity increased the particle size from 3.8 to 6.2 nm. However, this increase did not negatively impact the catalytic performance. The foam-supported catalyst maintained a constant activity for more than 480 hours on stream.

A comparison between the performances of the foam-, plate-supported and pellet catalysts indicated that the foam-supported catalyst bed has the potential to mitigate risks similar to that achieved with coated plates, and even more so with catalyst pellets, during long periods of exposure to H₂. At the operating conditions investigated in this study, H₂ conversions of 57–89%, 50–87% and 37–78% were obtained on the foam-, plate-supported and pellet catalysts respectively. This suggested that the geometric configuration had a significant effect on the H₂ conversions obtained at different gas flow conditions, i.e. inlet gas velocity, H₂ concentration and gas distribution. The geometric configuration affected the relative importance of kinetic and mass transfer rates on the catalyst surface. Increasing the volumetric surface area of the

catalytic system has the potential to improve the overall H₂ conversion capability of the recombiner.

The uneven temperature profiles observed during the catalytic tests were attributed to the unpredictable gas flow distribution in the recombiner. The profiles revealed the importance of selecting a suitable position for the catalyst bed in the recombiner. Nevertheless, the maximum temperatures obtained at all conditions were much lower than 585°C, temperature at which gas phase combustion can occur.

CFD simulations revealed important insights into the transport phenomena within the Pt/Al₂O₃-coated foams during the PAR process. The simulations demonstrated that neglecting the thermal radiation model can significantly overpredict catalyst temperatures, as evidenced by past studies in plate-type recombiners and on foam-supported catalysts used for CO combustion. The calculated maximum temperatures obtained at the bottom edge of the foams—near the reactor inlet—corresponded well with experimental data. However, evident profile differences were observed elsewhere along the catalyst length. Experimental results indicated a steeper temperature decline compared to simulations, attributed to heat loss under the non-adiabatic experimental conditions. The model also showed that near-complete H₂ conversions were obtained within the catalytic foam region. This suggests that the unconverted H₂ is concentrated in the areas of the recombiner that are not occupied by the foam. Simulated H₂ conversions were also in relatively good agreement with experimental calculations, confirming the validity of the kinetic and transport models used in the calculations.

Overall, this investigation confirms the effectiveness of a foam-supported recombiner for the PAR process. However, some uncertainty remains regarding the benefits of foam-supported catalysts for PAR applications. The following are suggested as topics for further experimental and modelling studies: determinations of the effects of the pore density, the thickness of the washcoat layer, the size and position of the catalytic foam in the recombiner. The numerical study of the PAR could be extended toward understanding the conditions for the onset of the gas-phase H₂ combustion. Additionally, different turbulence models can be tested to investigate the effect of the flow nature on prediction of the catalyst temperature and H₂ conversion.

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Chapter 5. Experimental evaluation of a coated foam catalytic reactor for the direct CO₂-to-methanol synthesis process

Chapter overview (Abstract)

The era of considering carbon dioxide (CO₂) as a waste stream has passed. New methods of utilising CO₂ as a carbon feedstock are currently the focus of extensive research efforts. A fixed-bed reactor containing a commercial Cu/ZnO/Al₂O₃ catalyst washcoated on a Cu foam was used for the synthesis of methanol (MeOH) through direct CO₂ hydrogenation. Catalytic activity tests in this reactor were conducted at reaction pressures of 30 and 50 bar, temperatures in the range 190–250°C, and weight hourly space velocities (WHSV) in the range 1.125–2.925 NL/g_{cat}/h. The best reactor performance was recorded at 50 bar pressure: CO₂ conversion and MeOH selectivity of 27.46% and 82.97%, respectively, were obtained at 240°C and 1.125 NL/g_{cat}/h. Increasing the WHSV to 2.925 NL/g_{cat}/h resulted in a twofold increase in methanol weight time yield (WTY) to 0.18 g_{MeOH}/g_{cat}/h and a decrease in MeOH selectivity to 70.55%. The results presented in this investigation provide insight into the performance of a bench-scale reactor in which mass transfer limitations are non-negligible and demonstrate that metal foams are promising catalyst support structures for CO₂ hydrogenation towards MeOH production.

5.1 Introduction

The increase in anthropogenic carbon dioxide (CO₂) emissions in the last century is a major global concern for environmental and social well-being. Global warming and other climate perturbations urge the industrial sector to consider more sustainable energy alternatives for their fossil fuel-reliant processes. Since the turn of the 21st century, the share of renewable energy sources such as solar and wind power grew exponentially in the sector of electricity generation. This rapid increase in fluctuating power supplied to power grids involved numerous challenges associated with the stability and balance of supply and demand [1].

Chemical energy conversion presents advantages over other energy storage methods, such as hydropower, compressed air energy storage, flywheels and batteries, due to both its long-term storage capability and its potential to trade energy on a global scale [2,3]. In this context, power-to-gas (PtG) and power-to-X (PtX) technologies, which represent the conversion of renewable energy via electrolysis into hydrogen (H₂) and other chemicals such as methane (CH₄) and methanol (MeOH), are opportune. PtG and PtX represent promising solutions for

both the mitigation of global CO₂ emissions and the storage of energy from variable renewable sources during peaks in renewable energy supply. Subsequently, the produced chemicals may be used when the demand for power exceeds the supply capacity [4].

Arguably, one of the sectors hardest to abate from fossil fuel use as primary energy source is the petrochemical industry. MeOH production by means of PtX is considered a topic worthy of investigation, considering the available industrial sources of concentrated CO₂ as feedstock for MeOH production, and MeOH's current global production and demand (MeOH is the second most produced chemical from syngas, at an estimated annual production rate of 110 million tonnes [5]). MeOH has numerous other conversion pathways towards dimethyl ether, formaldehyde and other value-added fuels and chemicals [6].

Industrially, MeOH is produced from carbon monoxide (CO)-based syngas at reaction pressures of 50–100 bar and temperatures of 240–260°C [7]. The alternative direct CO₂ hydrogenation to MeOH process is an exothermic, thermodynamically limited process; it has been investigated at relatively high temperatures (200–300°C) and pressures (5–80 bar) due to the high bond dissociation energy of the stable CO₂ molecule (1072 kJ/mol) [2,8]. The most popular catalysts for MeOH synthesis are the bi-metallic Cu/ZnO catalysts which favour conversion pathways of the hydrogenation of CO₂ to MeOH rather than CH₄ [8]. A proposed dual-site mechanism supposes that Cu sites are responsible for the adsorption and splitting of H₂ into atoms which then transfer to the ZnO sites to hydrogenate CO₂, which is adsorbed in the form of bicarbonate [8]. Cu/ZnO catalysts are usually promoted by a metal oxide (e.g., Al₂O₃ or ZrO₂). Individually, both Cu and ZnO are only slightly active in promoting MeOH production. The synergetic effect obtained from the bi-metallic catalyst, however, is attributed to the stabilisation and dispersion of Cu particles in the presence of ZnO [8]. Kasatkin et al. [9] considered ZnO as a spacer and structure-directing support between Cu particles, affecting the morphology and improving the dispersion of the Cu particles. As a promoter, Al₂O₃ increases the stability of the catalytic pair [8].



In addition to the CO₂ hydrogenation (Eq. 5-1), the endothermic reverse water gas shift (RWGS) reaction (Eq. 5-2) is inevitable in a H₂/CO₂ system if the catalyst selection and process

operation are not ideal. The RWGS reaction decreases the selectivity towards MeOH production via undesired CO formation.

Furthermore, several authors have reported the undesirable effects of CO [10,11] and steam (H₂O) [2,7,12] on the catalytic activity of Cu/ZnO/Al₂O₃ for MeOH synthesis from direct CO₂ hydrogenation. Therefore, the operating conditions and the design of the MeOH synthesis reactor should be carefully chosen so as to maintain the highest possible MeOH selectivity in the process (i.e., to limit the RWGS reaction).

Several studies have focused on the optimisation of process performance by investigating the intrinsic properties of the catalyst [13–15]. For example, Dasireddy and Likoazar [14] compared different synthesis methods, including co-precipitation and ultrasound-assisted catalyst preparation. Qi et al. [15] synthesised a Cu/ZnO-based bi-metallic metal organic framework, which resulted in improved CO₂ conversion, MeOH selectivity and space–time yield when compared to the performance of a conventional Cu/ZnO/Al₂O₃ prepared from Cu and Zn nitrate precursors. Other works have focused on the modification of the Cu/ZnO binary catalyst by the addition of promoters such as Ag, Mg, Cr, or different metal oxide supports such as ZrO₂ or SiO₂ [16–20]. Additionally, these processes were investigated in microreactors in which heat and mass transfer limitations are usually negligible.

To the best of the authors' knowledge, the performance of highly-structured catalyst supports coated with Cu/ZnO/Al₂O₃, and used for direct CO₂-to-MeOH processes, has not been reported yet. A promising option pertaining to the catalyst support is the use of an open-cell metal foam. The latter is a highly porous catalyst support structure that enhances heat and mass transport phenomena due to its high thermal conductivity (commonly Cu or Al sintered metals) and increased mixing potential (high tortuosity) [21–23]. The high thermal conductivity of the metal foam allows for heat transfer to be less dependent on convective effects; instead, it is enhanced by conduction within the metallic matrix, thus limiting hot spots within the reactor, which may be associated with undesired side reactions or catalyst decay [21,23–25]. Radial mass transfer enhances the uniformity of the gas flow pattern, resulting in better accessibility to the completely open-cell foam structure (avoidance of channelled flows) [24,26]. These structures are characterised by a high surface area to volume ratio (>1000 m²/m³) and by better effectiveness factors than conventional catalyst pellets [24,27,28]. In addition, open-cell metal foams are known to be resistant to thermal and mechanical stresses [28].

Open-cell foams have been successfully used in processes including NO_x reduction through NH₃ [24], NH₃ decomposition [29], CO oxidation [26,30], CH₄ steam reforming [23], MeOH steam reforming [31–33] and MeOH synthesis from syngas [21].

This paper aims to expand the knowledge on the typical operations of foam-based intensified reactors to MeOH synthesis from CO₂ waste streams and to demonstrate the performance of a 1.08 L bench-scale reactor by providing suitable steady-state reactor operating conditions for satisfactory CO₂ conversions, MeOH yields and selectivities.

A Cu foam (40 PPI) was used as catalyst support structure for a commercial Cu/ZnO/Al₂O₃ catalyst in a reactor with a designed production capacity of 10 g_{MeOH}/h. During the evaluation of the reactor, the following conditions were used: reaction pressures 30–50 bar, reaction temperatures 190–250°C and space velocities 1.125–2.925 NL/g_{cat}/h. Overall, this investigation supports new information on the process and operation of a catalytic reactor, employing a novel and process-intensifying catalyst support structure for the synthesis of MeOH directly from captured CO₂ and renewable H₂.

5.2 Materials and methods

The following sections provide detailed information on the set-up used during the experimentation (Section 5.2.1); the design of the two-module fixed-bed reactor with structured catalyst support (Section 5.2.2), the characterisation methods used to determine key properties of the catalyst support structure (Section 5.2.3) and the process parameters that were investigated in this study are summarised (Section 5.2.4).

5.2.1 Process flow sheet

The piping and instrument diagram (PID) in Fig. 5-1 illustrates the set-up used during the MeOH synthesis experiments. Two gas feed streams were connected to the reactor inlet. The first supplied, at low pressure, N₂ and H₂, used as purging and reducing fluids, respectively. The second feed stream supplied the reactant mixture: ca. 25 vol.% CO₂ in a balance of H₂ (Afrox, Johannesburg, South Africa). The supply pressure of the reactant mixture was controlled with a KP-series pressure regulator (Swagelok, Johannesburg, South Africa). Both gas streams' flow rates were controlled with respective SLA5800-series thermal mass flow controllers (Brooks Instruments, Hatfield, PA, USA). Directly upstream of the reactor, a gas pre-heater was fitted with a heating cartridge to pre-heat the incoming cold gas stream prior its injection into the modular MeOH synthesis reactor. It was envisioned that a cold gas fed to the

reactor's first module would induce sluggish MeOH reaction kinetics, hence the use of a feed pre-heater (set at the same isothermal temperature condition as the reactor). Downstream of the reactor and after the cold trap, the reactor pressure was controlled using a KPB-series back-pressure regulator (Swagelok, Johannesburg, South Africa).

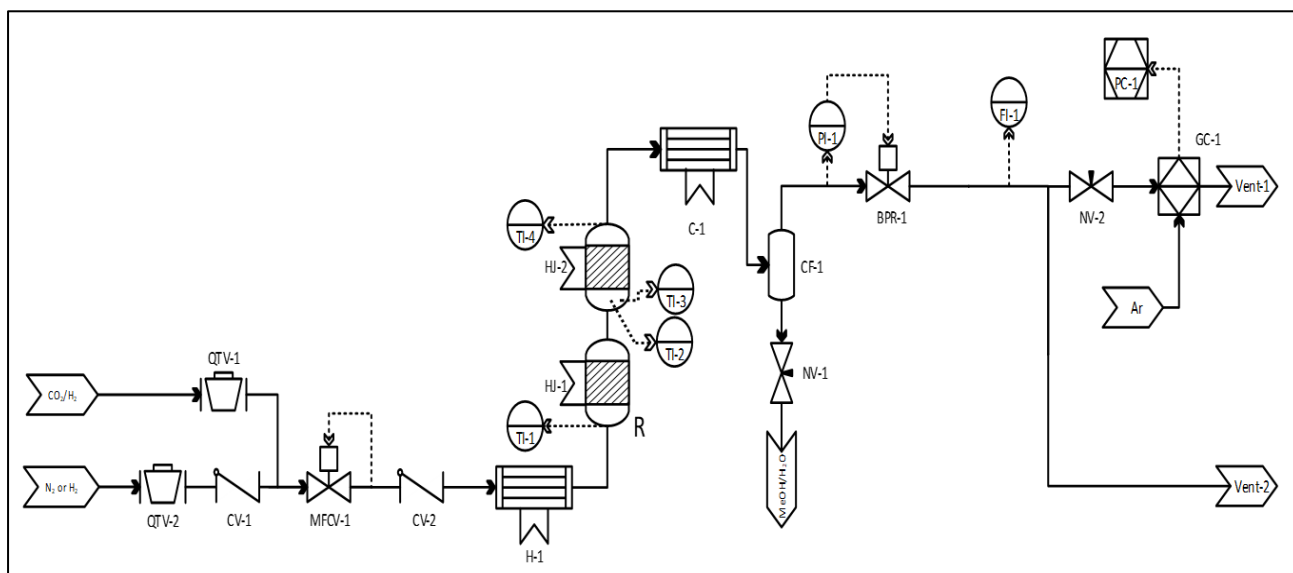


Figure 5-1. PID diagram of the set-up used in the direct CO₂-to-MeOH synthesis process. (BPR: back pressure regulator; C: condenser, CF: auto-draining coalescing filter; CV: check valve; GC: gas chromatograph; FI: flow indicator; H: temperature-controlled heater; HJ: heating jacket; MFCV: mass flow control valve; NV: needle valve; PC: computer; PI: pressure indicator; QTV: quarter-turn valve; R: reactor; TI: temperature indicator).

Sensible and latent heat from the reactor product gas was removed using natural convection over a ¼ inch stainless steel (SS316) pipe coil of 4 m length. Furthermore, the water vapour and MeOH in the product were condensed in a 190 mm shell-and-tube heat exchanger containing a glycol–water coolant (shell-side), the temperature of which was regulated to 10°C, using a chiller (Julabo, Seelbach, Germany). A stainless steel (SS316) coalescing filter (Classic Filters, Rochester, UK) was used to drain the condensate after each experiment.

In this study, the once-through conversion of CO₂ and H₂ was considered (no gas recycling). The flow rate of the product gas was measured with a variable area flow meter (Cole-Parmer, Vernon Hills, IL, USA). The absolute pressure was measured immediately downstream of the variable area flow meter using a high-accuracy digital pressure meter (Wika, Klingenberg, Germany). Both these measurements were used to normalise the product gas flow rate. The product gas composition was quantified with an online SRI 8610C gas chromatograph (SRI Instruments, Torrance, CA, USA) fitted with a HayeSep D column and two molecular sieve 13X columns. The instrument was also fitted with a helium ionisation detector and two thermal

conductivity detectors. The composition of the liquid product (MeOH and H₂O) was determined using a high-performance liquid chromatography instrument (HPLC 1200 instrument; Agilent Technologies, Santa Clara, CA, USA) fitted with refractive index detector and an Aminex HPX-87P column. The weight of the liquid was accurately measured using a high precision balance (Adam Equipment, Johannesburg, South Africa) for subsequent calculations of the MeOH WTY.

5.2.2 Experimental reactor

The MeOH synthesis reactor was designed as a fixed-bed reactor (Fraunhofer IMM, Mainz, Germany) to contain a Cu foam structure, washcoated with 160 g of a commercial Cu/ZnO/Al₂O₃ catalyst supplied by an original equipment manufacturer. Some basic textural properties of the catalyst are summarised in Supplementary Materials (Fig. C-1–C-4, Appendix C). According to the required operating conditions (up to 350°C and 50 bar), the reactor had to be designed regarding the requirements of the European guideline for pressure equipment (Directive 2014/68/EU) [34]. To avoid external inspection leading to higher costs and delays, the reactor was divided into two equal vessels (0.54 L each) connected with a ¼ in stainless steel pipe to reduce the pressurised volume of each module (Figs 5-2a and 5-3a).

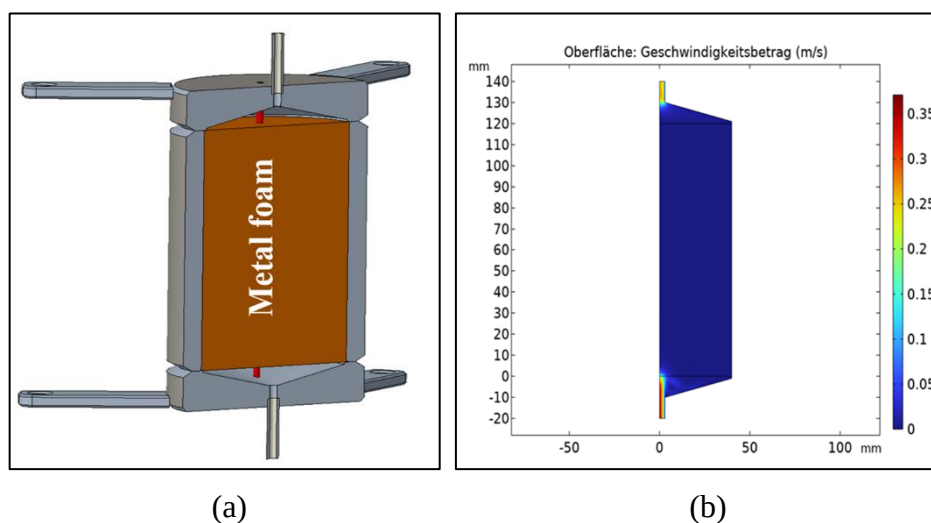


Figure 5-2. Illustration of (a) the longitudinal section a single reactor module and (b) CO₂ flow simulation results (boundary conditions: WHSV = 2.925 NL g⁻¹ h⁻¹, Pressure = 50 bar, Temperature = 250°C).

As a consequence, all realisation steps and the inspection procedure were allowed to be performed in-house. Fig. 5-2a illustrates the longitudinal section of a single reactor module. The inner inlet and outlet sections of each module were devoid of a foam-supported catalyst in

order to maintain homogeneous flow distribution in the catalytic bed. Computational simulation results confirmed the uniformity of flow distribution within the reactor modules (Fig. 5-2b).

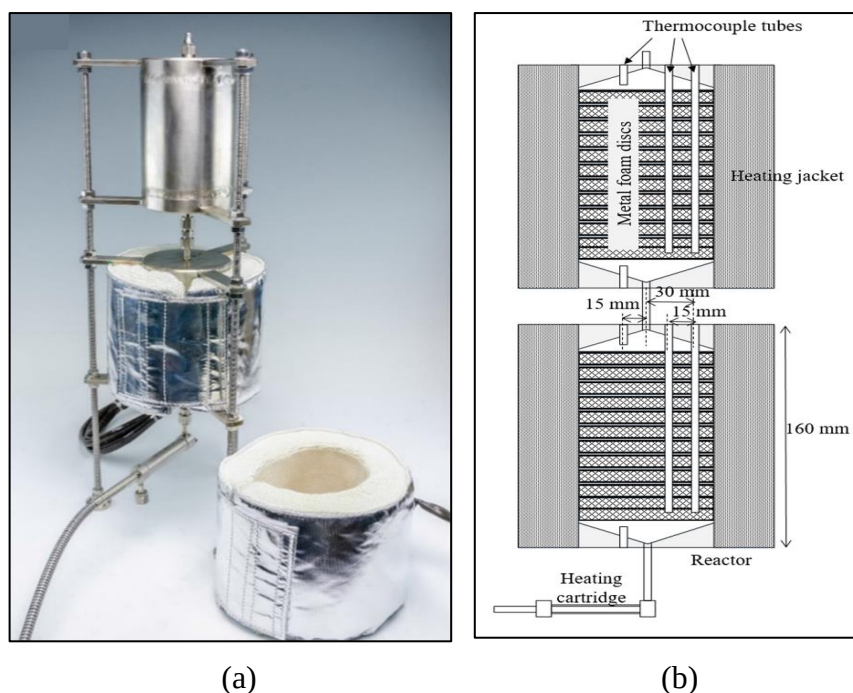


Figure 5-3. (a) The reactor with its two modules. (b) Schematic depicting of the foam arrangement and radially and axially spaced thermocouple ports.

Three radially spaced ports (ID 1.8 mm) for thermocouples were incorporated in the top of each module (Fig. 5-3b). Each module contained 12 washcoated disc-shaped foams (Fig. 5-4c) which fitted tightly to the reactor walls in order to avoid the occurrence of preferential paths and formation of dead zones. The heating cartridge, described in Section 5.2.1 as a feed pre-heater, is visible in Fig. 5-3a. The reactor was operated near-isothermally with two 130 W heating jackets (SAF Wärmetechnik GmbH, Mörlenbach, Germany). The surface temperatures of each reactor module could be measured at the inlet, the outlet and at two other radially spaced positions (Fig. 5-3b) within the reactor.

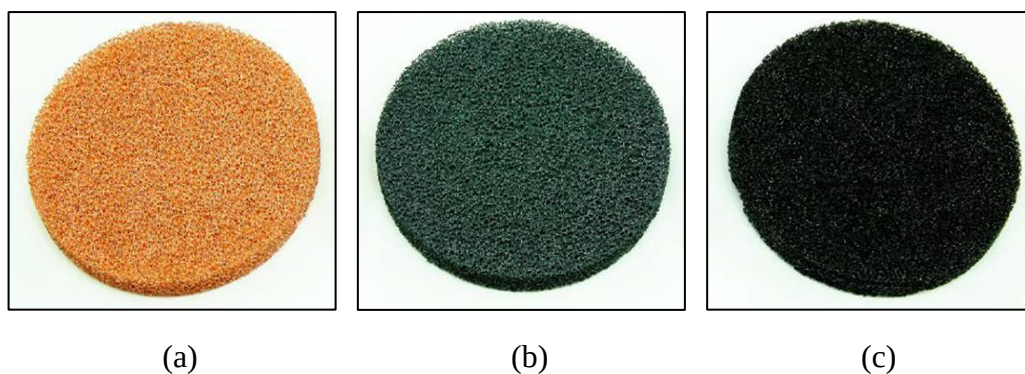


Figure 5-4. Images of Cu foams at different processing steps: (a) original Cu foam; (b) Cu foam after cleaning and annealing and (c) Cu foam after washcoating with the commercial Cu/ZnO/Al₂O₃ catalyst.

5.2.3 Characterisation of the catalyst support structure

In each of the reactor vessels, the catalyst support structure consisted of a set of 12 Cu disc-shaped foams (Fig. 5-4a), prepared using Fraunhofer IMM (Mainz, Germany). Each Cu foam disc was 80 mm in diameter and 10 mm thick. The Cu foams were cleaned with isopropanol in an ultrasonic bath for 30 min. The samples were then annealed at 350°C for 6 h in order to generate an oxide layer and improve the adhesive properties of the Cu foam surface (Fig. 5-4b). The foam structures were coated by applying a suspension of a commercial Cu/ZnO/Al₂O₃ catalyst which was prepared according to a procedure described by O'Connell et al. [35]. The applied catalyst suspension contained a binder (polyvinyl alcohol), deionised water and the commercial catalyst powder (10 wt.%). The coated copper foams (Fig. 5-4c) were dried in air at room temperature in order to remove excess liquid, and ultimately calcined at 350°C for 6 h. The coating process was repeated three times to achieve the desired amount of catalyst. The adhesion of the catalyst washcoat was tested by subjecting the coated foam to a 45 min ultrasound sonication. This operation resulted in a catalyst loss of less than 0.3%.

The gravimetric surface area, pore density, and the pore and strut diameters of an original uncoated and a catalyst washcoated metal foam were determined with computed tomography using a Phoenix Nanotom S system (General Electric Sensing and Inspection Technologies, Wunstorf, Germany) located at the Central Analytical Facilities of Stellenbosch University, South Africa [36]. Both samples were scanned at a voxel size (resolution) of 52 µm. X-rays were generated at 100 kV and 80 µA. A total of 3000 and 3600 images were captured, respectively, during a 360 degree rotation of the samples. These images were used to reconstruct a volumetric dataset with system-supplied Datos reconstruction software.

Visualisation and quantitative analyses were performed in VGSTUDIO MAX 3.5 (Volume Graphics, Heidelberg, Germany).

The morphology of the catalyst and its support structure were observed using scanning electron microscopy (SEM) using a FEI Quanta 250 field emission gun scanning electron microscope (ThermoFisher Scientific, Waltham, MA, USA) and the elemental composition was determined using energy dispersive X-ray spectroscopy (EDS). EDS data analysis was carried out using the Oxford Inca software. To achieve conduction between the sample and the beam of electrons, all samples were coated with carbon, using magnetron sputtering. Subsequently, a resin was used as a suitable material for embedding the samples to be analysed (conditions: 121°C, 290 bar, 20 min), using a PR-10 mounting press (Leco, St Joseph, MI, USA). Line point samples were taken at an equidistance of 40 μm .

5.2.4 Experimental design for the evaluation of the reactor

Prior to the experiments, the catalyst was reduced in a mixture of H_2/N_2 gas at 230°C for 30 min. The reduction temperature was obtained from the H_2 -temperature reduction profile (Fig. C-5, Appendix C). MeOH synthesis was carried out under nearly isothermal and steady-state conditions. A one-factor-at-a-time approach was used to understand each parameter's effect on the performance of the reactor. Table 5-1 summarises the operating conditions in a matrix of seven reactor temperatures, two pressures and three WHSVs. Throughout this study, the WHSV is defined as the ratio of the feed gas flow rate (NL/h) to the catalyst mass (g_{cat}) [8,37]. It should be noted that the highest WHSV (2.925 NL/ g_{cat} /h) was used exclusively for the 50-bar reactor pressure condition, since this reactor pressure was expected to support the highest MeOH synthesis reaction rate (high throughput). CO_2 and H_2 were fed to the reactor in a stoichiometric ratio of 1:3. Each experiment was carried out for 2 h and the product gas was analysed every 15 min. The product gas consisted of a mixture of CO_2 , H_2 and CO. No CH_4 was detected at any of the experimental operating conditions. The liquid product consisted of a mixture of MeOH and H_2O . No other by-product was detected in the chromatographs. The average error on carbon balance for all experiments was <5%.

Table 5-1. Experimental design for the direct CO₂-to-MeOH synthesis process in a foam-based reactor.

Operating parameter	Range
Temperature (°C)	190–250 (in increments of 10°C)
Operating pressure (bar)	30 and 50
WHSV (NL/g _{cat} /h)	1.125, 2.025 and 2.925

The performance of the reactor was assessed considering the CO₂ conversion (Eq. 5-3), MeOH selectivity (Eq. 5-4) and MeOH WTY (Eq. 5-5) [19]. The CO₂ conversion and MeOH selectivity were compared to equilibrium data calculated by simulating a Gibbs reactor in ASPEN Plus v8.6 software (see Section C-6, Appendix C). The non-random two-liquid method fluid property package was used [38]. The reactants were also considered as possible products.

$$X_{\text{CO}_2} = \frac{n_{\text{CO}_2\text{in}} - n_{\text{CO}_2\text{out}}}{n_{\text{CO}_2\text{in}}} \times 100\% \quad (5-3)$$

$$S_{\text{CH}_3\text{OH}} = \frac{n_{\text{CH}_3\text{OH}_{\text{out}}}}{n_{\text{CH}_3\text{OH}_{\text{out}}} + n_{\text{CO}_{\text{out}}}} \times 100\% \quad (5-4)$$

$$\text{WTY}_{\text{CH}_3\text{OH}} = \frac{m_{\text{CH}_3\text{OH}_{\text{out}}}}{m_{\text{catalyst}} \times \text{time on stream}} \quad (5-5)$$

5.3 Results and discussion

5.3.1 Structural properties of the foam

Computed tomography images (Fig. 5-5) show the difference between samples of uncoated and coated foam. It is evident that the coating method resulted in uneven catalyst distribution on the foam. Despite an increase in the average thickness of the struts and the blocking of some of the pores (Fig. 5-5b,c), the open porosity only decreased by 8%; it remained relatively high at 81.6%. This high porosity of foam supports minimises the pressure drop in foam reactors [26,28]. The choice of the coating method is therefore essential in order to achieve high porosity. For example, Ambrosetti et al. [39] found spin coating to be more suitable than dip coating for minimising clogging of their foam samples.

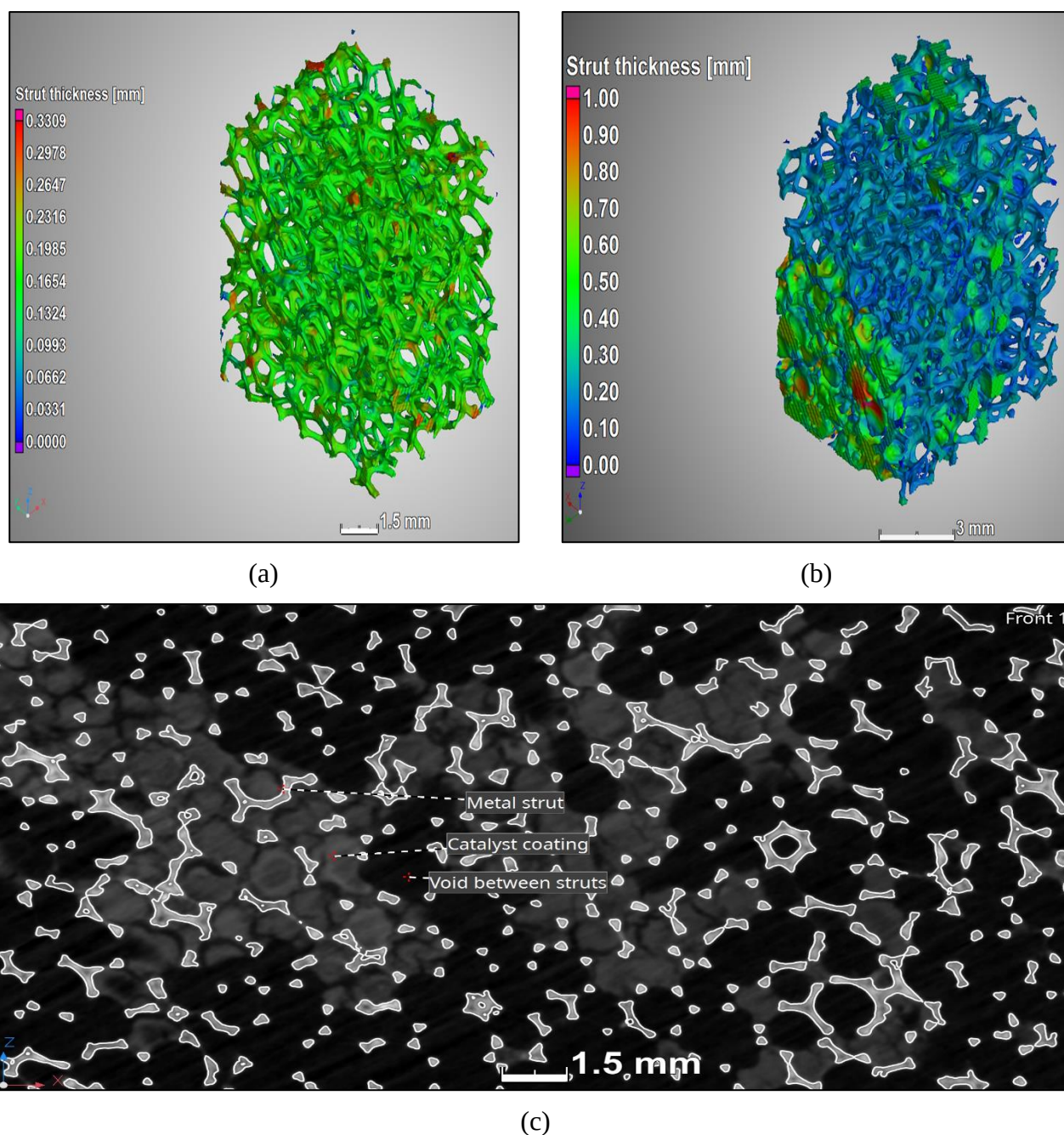


Figure 5-5. Images obtained through computed tomography, illustrating the strut diameters of (a) the uncoated Cu foam, (b) the Cu foam coated with Cu/ZnO/Al₂O₃ and (c) a cross-section of the coated foam with the distribution of the catalyst.

Catalytic coating naturally increased the relative density of the foam as more material is added without a noticeable increase in volume. The low relative density of the coated foam (551.35 kg m⁻³) substantiates the ability of foam supports to minimise the weight of the catalyst bed. Catalyst coating increased the surface area to volume ratio by 19.2%. Although the gravimetric surface area is much lower than for conventional catalysts (50–200 m²/g [40]), the high surface-area-to-volume ratio here (2178.1 m²/m³), which compares with that of finely crushed catalysts

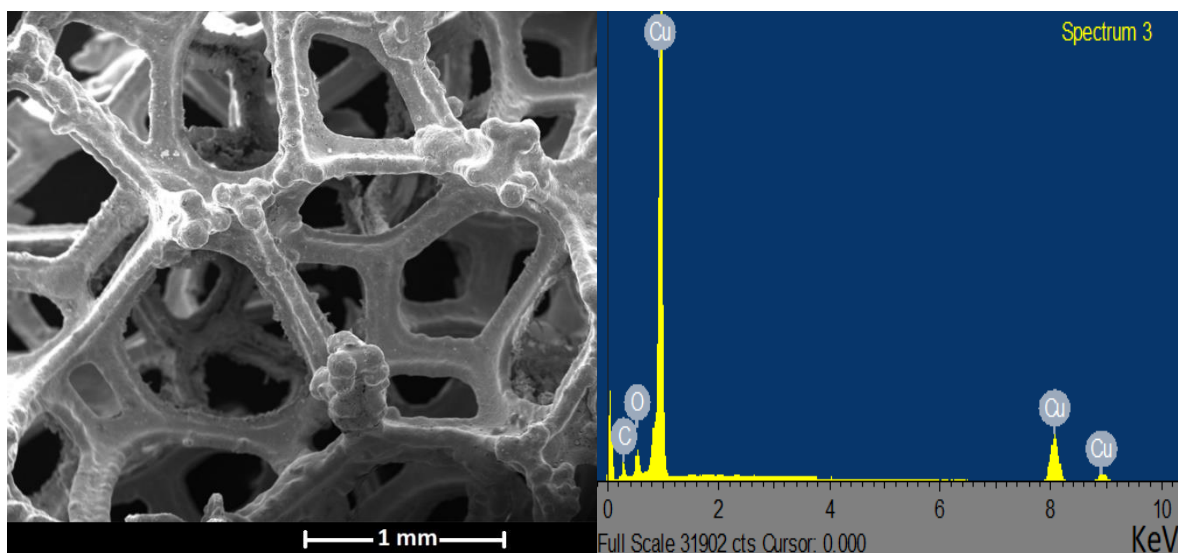
powders, will ensure high performance of the catalytic system. Table 5-2 summarises differences in the geometrical characteristics of the uncoated and coated foam samples.

Table 5-2. Geometrical characteristics of the uncoated and coated foam samples.

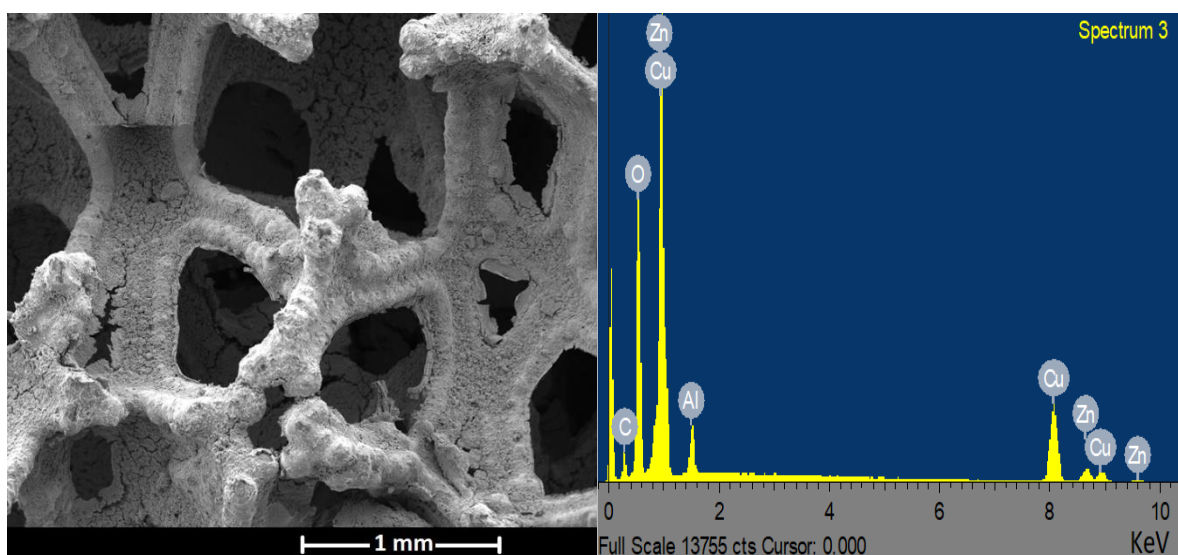
Characteristic	Uncoated foam sample	Coated foam sample
Average pore diameter (mm)	1.61	1.46
Average strut diameter (mm)	0.18	0.34
Gravimetric surface area (m ² /g)	0.0034	0.0041
Open porosity (%)	89.60	81.60
Relative density (kg/m ³)	426.25	551.35
Surface area to volume ratio (m ² /m ³)	1827.2	2178.1

Using ImageJ software, the average pore density was estimated to be 40 PPI, which is similar to the 45 PPI catalyst support structure used by Montebelli et al. [21] for MeOH synthesis from syngas. The pore density of the Cu foam used in our study is not the highest reported in the literature. It is argued that higher pore densities (e.g., 100 PPI) increase the residence time via highly tortuous flows, which then improves mixing and heat transfer of gaseous species [32,41,42]. However, improvements in catalyst coating become more challenging on such foams because of the increased probability of pore blockage [39].

The SEM analysis revealed the monolithic three-dimensional structure of the uncoated Cu foam (Fig. 5-6a). The SEM micrograph shows the irregular and interconnected struts of homogeneous Cu substrate, with clear and unblocked pores. The struts show no apparent cracks. On the other hand, Fig. 5-6b illustrates the coated metal foam structure, in which the washcoat completely covers the struts. The pore diameters are reduced, leading to a decrease in the open porosity (confirmed with computed tomography results). The observed surface roughness of the washcoat is desirable, as it contributes to an increase in the specific surface area of the foam-supported catalyst [43].



(a)



(b)

Figure 5-6. SEM micrographs and EDS spectra of samples: (a) uncoated Cu foam and (b) Cu foam coated with Cu/ZnO/Al₂O₃ catalyst.

5.3.2 Catalytic activity tests

The results reported in this section illustrate the effects of the selected operating parameters (reaction temperature, pressure, WHSV) on the performance of the reactor for CO₂ hydrogenation to MeOH. Figs 5-7 and 5-8 illustrate the respective experimental results at 30 bar (Fig. 5-7) and 50 bar (Fig. 5-8) for the following: (a) CO₂ conversion, (b) MeOH selectivity, (c) MeOH WTY and (d) CO outlet concentration. The CO₂ conversion as well as the MeOH selectivity are compared to equilibrium data calculated using ASPEN Plus v8.6. To ensure

reproducibility of the data, selected experiments were repeated at least five times. The standard deviations of the results calculated for the CO₂ conversion and MeOH selectivity were <3%.

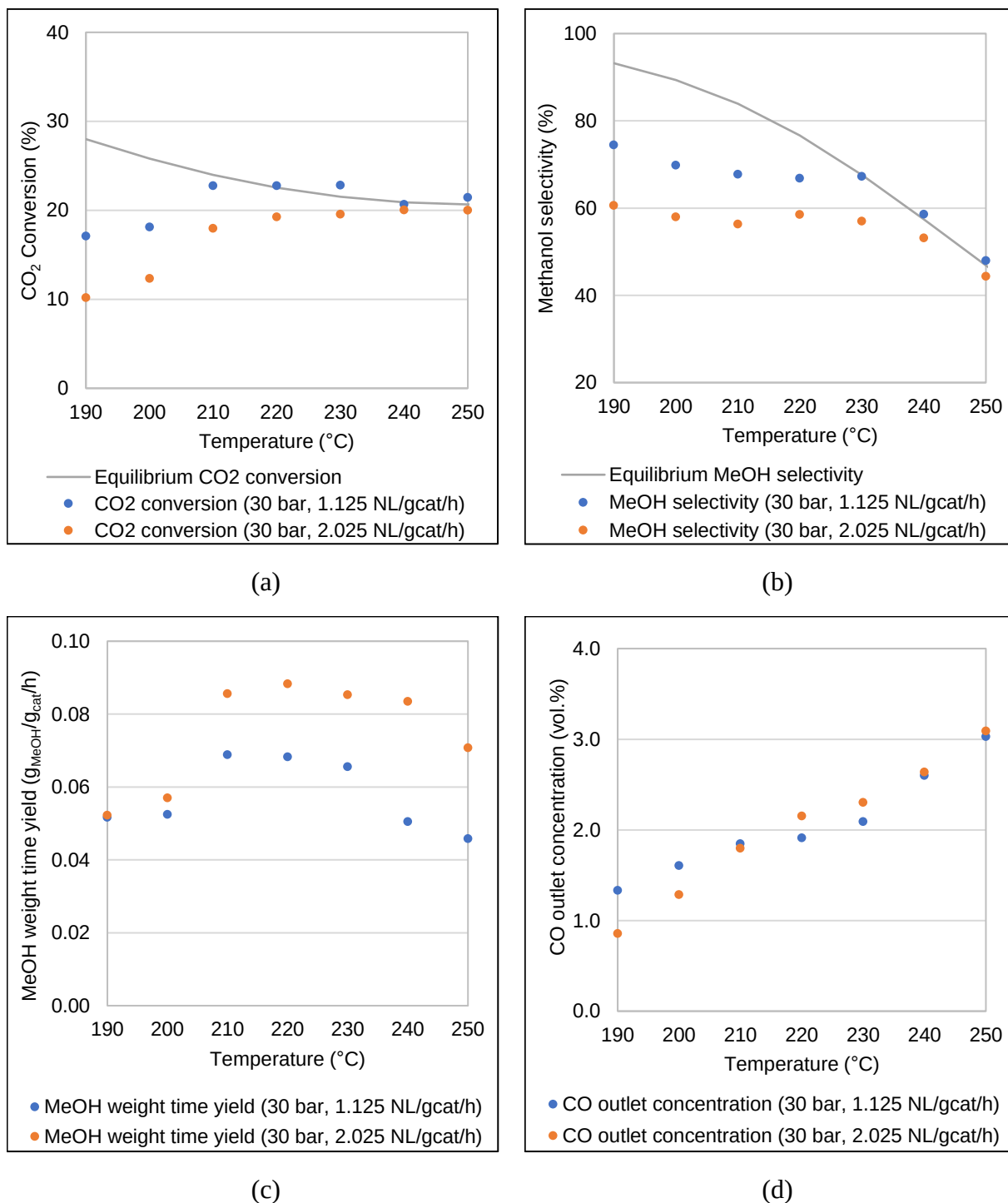
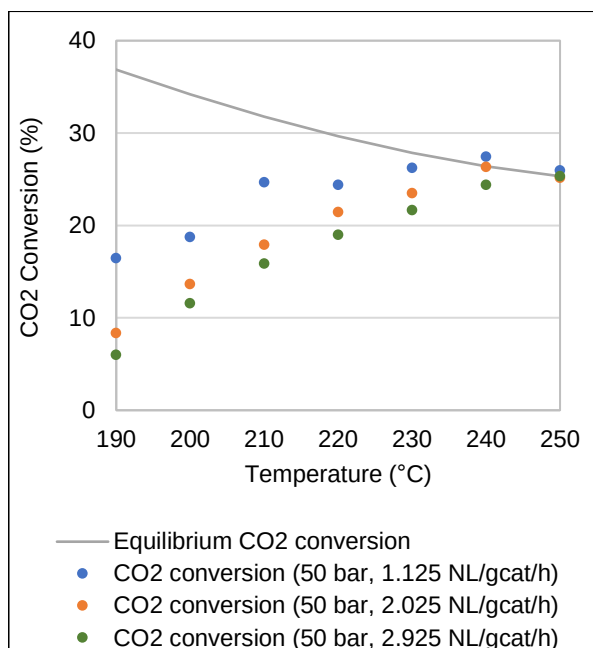
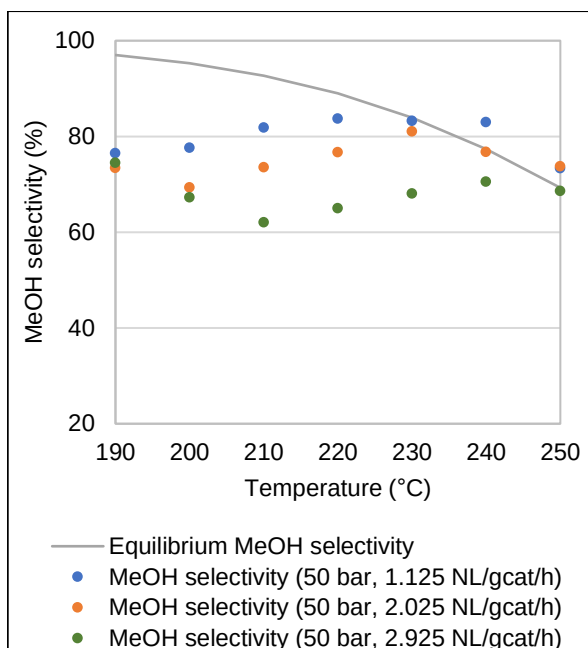


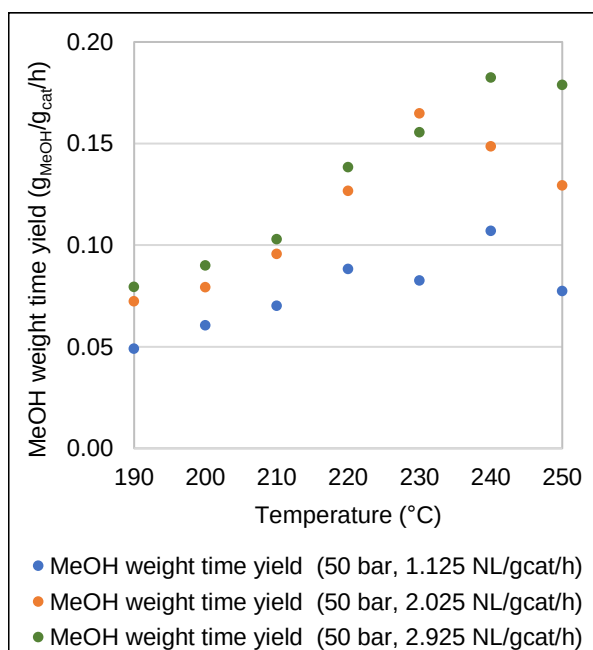
Figure 5-7. Experimental results of the coated foam reactor at 30 bar and temperatures of 190–250°C: (a) CO₂ conversion, (b) MeOH selectivity, (c) MeOH weight time yield and (d) CO outlet concentration.



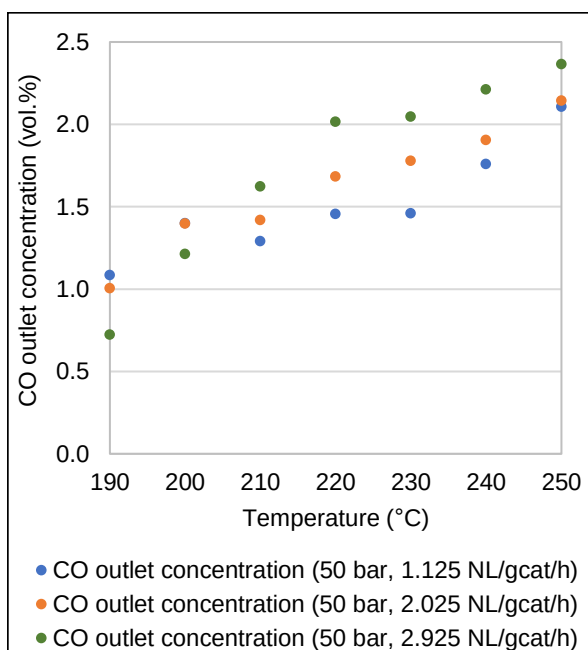
(a)



(b)



(c)



(d)

Figure 5-8. Experimental results for the coated foam reactor at 50 bar and temperatures of 190–250°C: (a) CO₂ conversion, (b) MeOH selectivity, (c) MeOH weight time yield and (d) CO outlet concentration.

Some data points in Figs 7a,b and 8a,b were observed to be above the calculated equilibrium lines. These deviations could be due to the fact that the equilibrium curves were not plotted from experimental data. Additionally, experiments were not conducted under ideal theoretical conditions in which no heat losses or mass transfer limitations are considered.

Despite the low gravimetric surface area of the foam-supported catalyst, the modular MeOH synthesis reactor demonstrated a high catalytic activity for MeOH synthesis through CO₂ hydrogenation at 30 and 50 bar. In the selected temperature range (190–250°C), the thermodynamic equilibrium limited CO₂ conversion to a range decreasing from 28–21% at 30 bar and 37–25% at 50 bar. CO₂ and H₂ were converted to MeOH, CO and H₂O only. In the chosen range of experimental conditions, the commercial Cu/ZnO/Al₂O₃ is only active for CO₂ hydrogenation to MeOH and for the RWGS reaction. No CH₄ or other hydrocarbons were detected.

5.3.2.1 Effect of reaction temperature

CO₂ hydrogenation is an exothermic reaction; it is favoured at low temperatures, as the equilibrium CO₂ conversion curves show (Figs 5-7a and 5-8a). The high stability of the CO₂ molecule is evident in the magnitude of its enthalpy of formation ($\Delta H_{f-298K} = -393.5 \text{ kJ mol}^{-1}$) [13]. The CO₂ conversion increased with an increase in the reaction temperature, from the low point of the temperature range (190°C) until equilibrium CO₂ conversions were reached. For example, at a pressure of 30 bar and a WHSV of 1.125 NL/g_{cat}/h, the CO₂ conversion increased from 17.10% to 22.74% when the reaction temperature was increased from 190 to 220°C. However, a further increase in the reaction temperature to 250°C resulted in a decrease in the CO₂ conversion to 21.44% due to thermodynamic constraints. It is obvious that the low temperature range is kinetically limited, with an increase in the reaction temperature resulting in a faster reaction rate (improved CO₂ conversion), while in the higher temperature range, the CO₂ conversions followed the decreasing trends of the thermodynamic equilibrium.

The molar ratio between MeOH and CO produced was not constant over the temperature range considered. This is confirmed by a variation in MeOH selectivity with temperature for both the reaction pressures investigated (Figs 5-7b and 5-8b). Thermodynamic equilibrium data show that at low temperature the CO production via RWGS is less favoured than MeOH formation. Therefore, with sufficient residence time, it is possible to produce MeOH at low temperature, while minimising CO formation. For example, at both pressures (30 and 50 bar) and for a WHSV of 1.125 NL/g_{cat}/h, the highest selectivities were obtained below the reaction temperature of 230°C.

At higher WHSV, especially at a pressure of 50 bar, it is interesting to note the initial decreasing trend in MeOH selectivity below 210°C, which is then reversed as the temperature increases up to the point at which equilibrium selectivity is reached. CO formation via RWGS has a

higher activation energy than CO₂ hydrogenation to MeOH (110–135 and 38–77 kJ/mol, respectively [44]) and it is thermodynamically favoured at higher temperatures (Eqs 5-1 and 5-2). This could result in higher MeOH/CO product ratios at 190–200°C, which would first decrease with temperature (due to faster increase in CO formation [7]) before increasing with higher MeOH productivities from 210 to 230°C. The subsequent decrease in MeOH selectivity from 230 to 250°C is due to thermodynamic limitations of CO₂ hydrogenation and a simultaneous increase in CO formation via RWGS. It is also possible that, to a lesser extent, increased water formation (Eqs 5-1 and 5-2) with higher reaction temperature inhibits the adsorption of CO₂ on the catalyst surface [7], although experimental validation cannot be provided.

Unlike the formation of CO, the productivity of MeOH (MeOH WTY) follows the CO₂ conversion trends (Figs 5-7c and 5-8c). MeOH formation is also kinetically favoured as the reaction temperature increases, up to the point where thermodynamic limitations begin to dominate CO₂ conversion. Of course, as a secondary carbon-containing product to MeOH, CO formation contributes to the overall CO₂ conversion in a lesser fashion (Figs 5-7d and 5-8d). In this study, it was observed that some CO formation took place due to the RWGS reaction under the reaction conditions investigated (Figs 5-7d and 5-8d). The amount of CO in the product increased monotonously with reaction temperature. CO formation via RWGS has a higher dependency on increases in reaction temperature due to the RWGS reaction's greater activation energy compared with that of MeOH formation [7,44]. The direct CO₂-to-MeOH synthesis process is thus best carried out at moderate reaction temperatures (210–240°C), which favour high MeOH turnover rates to achieve thermodynamic equilibrium, while suppressing undesired CO formation.

5.3.2.2 Effect of weight hourly space velocity

The WHSV is inversely proportional to the residence time of the gaseous reactants in the reactor. In Figs 5-7a,b and 5-8a,b it is clear that a higher WHSV leads to decreased CO₂ conversion and MeOH selectivity. For example, at 50 bar, with an increase in the WHSV from 1.125 to 2.925 NL/g_{cat}/h, the average CO₂ conversion and MeOH selectivity decreased by almost 6% and 12%, respectively. The effects of the WHSV on CO₂ conversions and MeOH selectivities are more noticeable in the temperature range 190–230°C than at the higher temperatures of 240 and 250°C (the equilibrium-controlled region).

Although increases in the WHSV lead to decreases in the CO₂ conversion, the total throughput of the reactor increases, which then correlates with a higher MeOH WTY (Figs 5-7c and 5-8c). At 50 bar, as the WHSV increased from 1.125 to 2.925 NL/g_{cat}/h, the average MeOH WTY increased by 73.41%. CO₂ conversion and an increase in MeOH production rate have been observed to result from an increase in WHSV [7,37]. Despite the increase in MeOH WTY, the increase in WHSV resulted in a decrease in MeOH selectivity. Figs 5-7d and 5-8d show CO outlet concentrations either remaining nearly constant or increasing at higher space velocities. The MeOH selectivity depends on the ratio between the flow rates of CO and MeOH at the reactor outlet (Eq. 5-5). The relationship between the WHSV and the MeOH selectivity is not straightforward because of the unclear interplay between competing reactions (Eqs 5-1 and 5-2) at different reaction conditions. Previous studies show that increasing MeOH selectivities have been associated with increasing WHSV [45,46]. However, Ghosh et al. [37] observed a slight decrease in MeOH selectivity with a nearly threefold increase in WHSV. Bukhtiyarova et al. [7] found that the MeOH selectivity remained almost constant at temperatures of 200°C and between 250–260°C while increasing with a decrease in WHSV between 210 and 240°C. In this case, the increase in selectivity with decreasing WHSV was attributed to the potential of steam—especially when formed in relatively large amount—to decrease CO formation via the water gas shift reaction [7]. Further investigation needs to be conducted in order to understand the impact of the reaction conditions on the kinetics of each of the reactions involved in the process.

It is important to note that the range of space velocities used in this investigation (1.125–2.925 NL/g_{cat}/h) is relatively low compared to similar works in the literature (Table 5-3). The reactor's WHSV can be increased up to a certain point where differential operating conditions are reached, at which point the MeOH WTY will remain constant with further increases in the WHSV [7]. However, operation of the reactor at such high WHSVs is questionable, as the once-through conversion of gaseous substrates is very low and the associated operating costs are high. Therefore, a trade-off is required between a high MeOH WTY and the costs of separation and recycling the unreacted gas to the reactor to maintain a high overall CO₂ conversion.

Table 5-3. Performances of the bench-scale reactor used in this investigation and that of small-scale Cu/ZnO/Al₂O₃-catalysed systems reported in the literature.

Reactor	Catalyst configuration	Experimental conditions	CO ₂ conversion (%)	MeOH selectivity (%)	MeOH WTY (g _{MeOH} /g _{cat} /h)	Ref.
FBR (ID: 10.2 mm)	Catalyst powder diluted in SiO ₂	Catalyst mass: 0.5 g Temperature: 230°C Pressure: 30 bar WHSV: 7.2 NL/g _{cat} /h	19.30	54.70	0.15 **	[4]
FBR (ID: 15 mm; catalyst length: 0.28 cm)	Catalyst powder diluted in SiO ₂	Catalyst mass *: 0.65 g Temperature: 240°C Pressure: 30 bar WHSV *: 9.2 NL/g _{cat} /h	12.00	42.00	0.16 **	[13]
FBR (ID: 13.5 mm; length: 53.3 cm)	Catalyst powder diluted in SiO ₂	Catalyst mass: 1.0 g Temperature: 240°C Pressure: 30 bar WHSV *: 28.46 NL/g _{cat} /h	11.00	45.00	0.77	[7]
FBR (OD: 10 mm)	Bimetallic organic frameworks	Catalyst mass: 0.1 g Temperature: 240°C Pressure: 30 bar WHSV: 14.40 NL/g _{cat} /h	9.10	86.90	0.41	[15]
FBR (ID: 80 mm; length: 16 cm)	Catalyst coated on Cu foam	Catalyst mass: 160 g Temperature: 240°C Pressure: 30 bar WHSV: 2.025 NL/g _{cat} /h	20.04	55.91	0.08	This study
FBR (ID: 80 mm; length: 16 cm)	Catalyst coated on Cu foam	Catalyst mass: 160 g Temperature: 240°C Pressure: 50 bar WHSV: 2.925 NL/g _{cat} /h	24.40	70.55	0.18	This study

FBR: fixed bed reactor.

* Calculated assuming a Cu/ZnO/Al₂O₃ density of 1300 kg/m³.

**Calculated assuming MeOH density of 792 kg/m³.

CO outlet concentrations were barely affected at 30 bar by the WHSV (Fig. 5-7d), while slightly increasing with WHSV at 50 bar (Fig. 5-8d). At the same pressures, the CO₂ conversion and MeOH selectivity were observed to decrease when the WHSV was increased from 1.125 to 2.925 NL/g_{cat}/h (Fig. 5-8a,b), suggesting that the CO₂ hydrogenation to MeOH is more

susceptible to changes in the WHSV than the undesired RWGS reaction [7]. Generally, RWGS is known for being a catalytic reaction associated with millisecond contact time operation—thus emphasising the requirement for highly selective catalysts when CO₂ hydrogenation is the objective.

5.3.2.3 Effect of reaction pressure

The MeOH reactor performance is enhanced by a higher reaction pressure (Figs 5-7 and 5-8). For example, CO₂ conversions, MeOH selectivities and MeOH WTY at 240°C and 1.125 NL/g_{cat}/h were 27.46%, 82.97% and 0.11 g_{MeOH}/g_{cat}/h, respectively, at 50 bar, compared to 20.65%, 58.56% and 0.05 g_{MeOH}/g_{cat}/h at 30 bar. According to Le Chatelier's principle, increasing pressure (50 bar) favours a reaction that proceeds under volume contraction, as in the case in CO₂ hydrogenation to MeOH (Eq. 5-1). In contrast, the RWGS reaction is favoured at the lower pressure condition (30 bar), although Eq. 5-2 shows that no volume contraction or expansion takes place [47]. This can be deduced from Figs 5-7d and 5-8d, which show higher CO outlet concentrations at 30 bar. Trifan et al. [6] also reported that lower reaction pressure assists the RWGS reaction, in comparison to the hydrogenation of CO₂.

Furthermore, Le Chatelier's principle applies to processes that tend towards thermodynamic equilibrium. It is interesting to note that the reaction pressure had a pronounced effect in the equilibrium-controlled region, compared to the kinetically controlled region (Fig. 5-9). For example, at a WHSV of 2.025 NL/g_{cat}/h, the average CO₂ conversions obtained at 190–210°C were 13.31% and 13.48% (50 and 30 bar, respectively) while the average values obtained at 220–250°C were 24.11% and 19.70% (50 and 30 bar, respectively). A similar trend was observed for the MeOH selectivity, WTY and CO outlet concentration. At higher temperatures, the formation of CO approaches the thermodynamic equilibrium, especially at the lower reaction pressure of 30 bar.

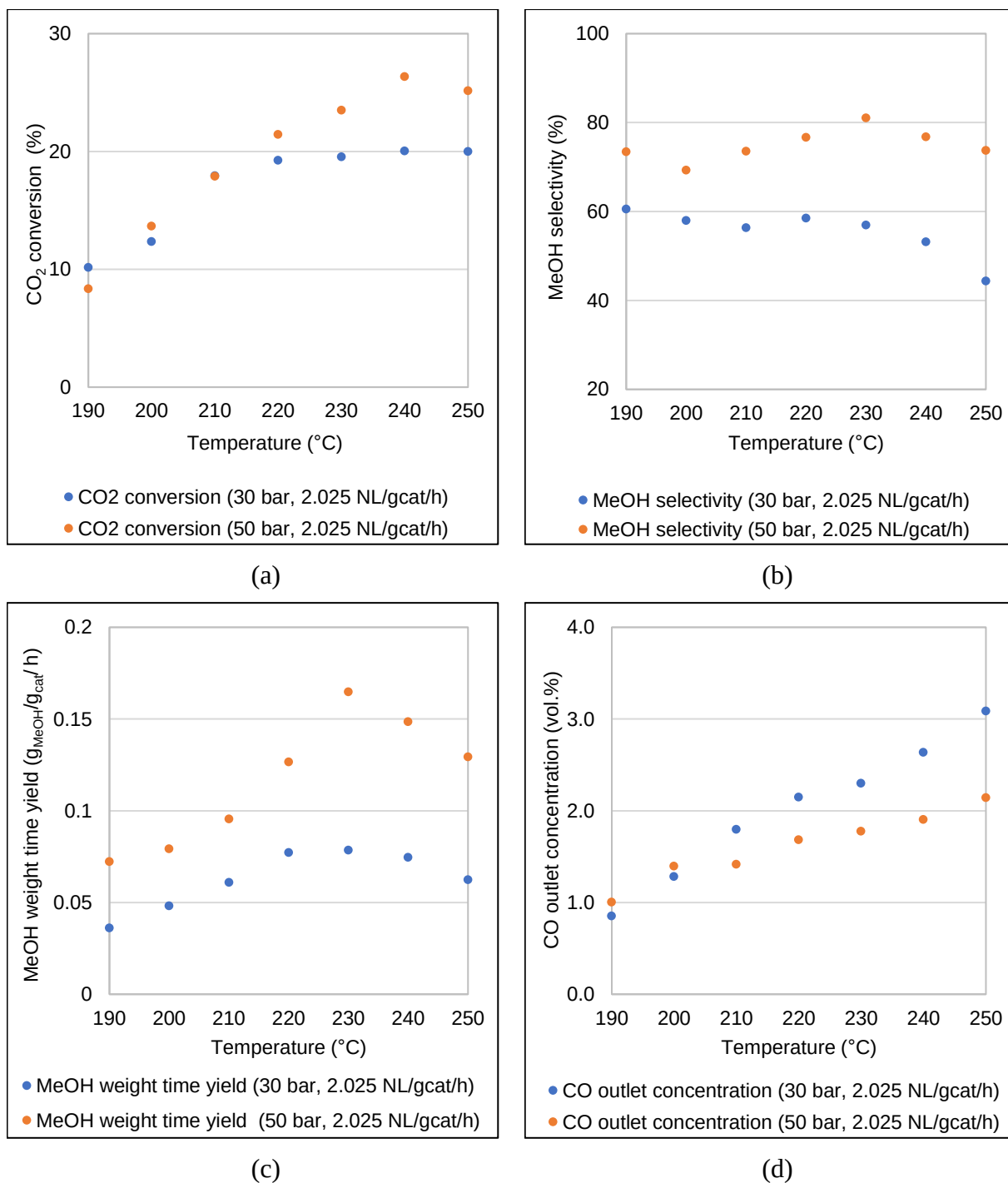


Figure 5-9. Effect of operating pressure on (a) CO₂ conversion, (b) MeOH selectivity, (c) MeOH WTY and (d) CO outlet concentration at temperatures of 190–250°C and a WHSV of 2.025 NL/g_{cat}/h.

5.3.2.4 Measurement of the reactor temperature

Steady state was achieved within the first 5 min of each experiment. Fig. 5-10a shows the reactor temperature measurement points. Throughout the reactor, the nearly isothermal conditions were attributed to rapid dissipation of the net heat of reaction. For all experiments, the maximum difference between the temperatures at the modules inlets (TI-1, TI-2 and TI-3)

was 2°C (Fig. 5-10b). Temperature variation in the radial direction was negligible. The temperatures at levels TI-2 and TI-3 (points radially separated by 15 mm) were found to be nearly equal (maximum difference 1°C) in all experiments conducted in this investigation. The difference between the reactor inlet and outlet temperatures (TI-1 and TI-4) was the highest recorded during all experiments (8–10°C). This difference is due to the rapid heat loss at the outlet (TI-4). It was important to include a feed gas pre-heater at the reactor inlet, ensuring that the gas enters at the desired reaction temperature (TI-1), whereas no special arrangement was required at the reactor outlet.

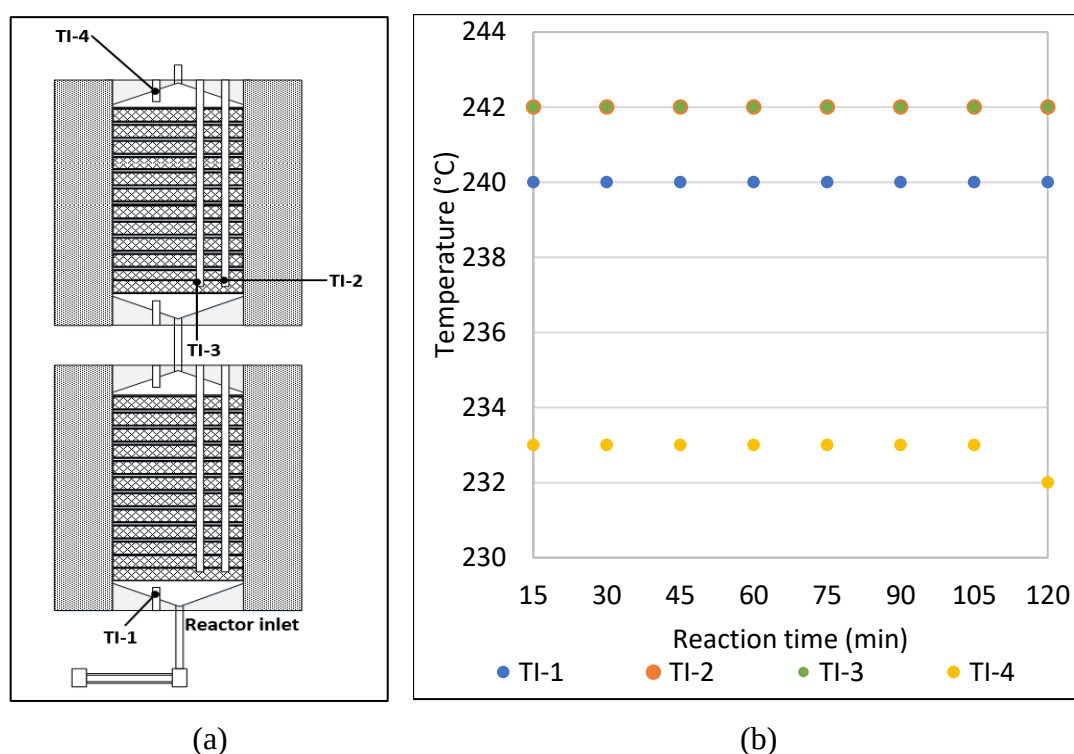


Figure 5-10. (a) Reactor temperature measurement points. (b) Temperature profiles at the selected measurement points at 240°C, 50 bar and WHSV 2.925 NL/g_{cat}/h.

5.4 Selected direct-CO₂-to-methanol synthesis experiments reported in the literature

Reported experimental data on the performance of Cu/ZnO/Al₂O₃ catalysts for direct CO₂-to-MeOH synthesis in open literature are scarce. This synthesis route offers a unique advantage over the traditional syngas route as CO₂ from polluting industries is used for the production of valuable chemicals (carbon recycling). H₂ can be supplied from a non-fossil origin, such as by water electrolysis with renewable energy. Table 5-3 presents results reported in the literature for selected Cu/ZnO/Al₂O₃-catalysed systems and two metal foam reactors created in this

study, as used for CO₂ hydrogenation towards MeOH production, together with the reactor conditions. In all cases, a stoichiometric H₂:CO₂ ratio of 3:1 was used.

A comparison between the performance of the reactor used in this study and microreactors reported in the literature is not simple. Most investigations reported in the literature were conducted at high space velocities, justifying the high MeOH STY achieved. The high space velocities used also suggest that reactions were carried out with negligible mass transfer limitations. Nevertheless, the benefits of the bench-scale reactor include the once-through CO₂ conversions close to equilibrium and high reactor productivity of nearly 15 and 30 g_{MeOH}/h at 30 and 50 bar.

The present investigation is therefore considered a significant contribution in terms of achievable reactor performance with a bench-scale coated foam reactor, supporting a total mass of 160 g of commercial Cu/ZnO/Al₂O₃ catalyst. It demonstrates a direct CO₂-to-MeOH synthesis process that is much closer to what can be expected of significantly larger reactors.

5.5 Conclusions

A coated Cu-foam reactor was evaluated experimentally for the direct CO₂-to-MeOH synthesis process. Despite the low gravimetric surface area of the coated metal foam (0.0041 m²/g), the reactor's performance was satisfactory. The coated metal foam can enhance mass transport through tortuous mixing, providing limited gas diffusional resistance. The coated Cu foam supported nearly isothermal operations through rapid heat dissipation.

A critical evaluation of the reaction temperature, pressure and WHSV provided insight into the kinetic and thermodynamic operating regimes associated with CO₂ hydrogenation towards MeOH production. Generally, the highest CO₂ conversions and MeOH selectivities (up to 27.46% and 83.73%, respectively) were obtained at the highest pressure considered here, 50 bar. Increasing the WHSV resulted in an increase in MeOH yields (up to 0.18 g_{MeOH}/g_{cat}/h) but a decrease in MeOH selectivities. The rate of the CO₂ hydrogenation reaction increased with temperature, but it was limited by the thermodynamic equilibrium. CO formation, as a result of RWGS, also gradually increased with temperature. Noticeably high MeOH selectivities were obtained, especially at temperatures in the range 210–240°C.

Future work could address a comparison of the performance of this foam-based reactor and that of a conventional reactor using the same catalyst at the same operation conditions. Further investigation could also study the feasibility of foam-based reactors, at least at a pilot scale—

comparing reactor performance, and then considering investment and operating costs compared to conventional fixed beds for MeOH synthesis.

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Chapter 6. CFD modelling of a foam-based catalytic reactor used for the direct-CO₂-to-methanol process

Chapter overview

Foam-based reactors are characterised by a complex geometric catalytic structure that enhances heat and mass transport in chemical processes. In this investigation, a simplified pseudo-homogeneous CFD model was developed to simulate the direct-CO₂-to-methanol synthesis in a foam-based reactor consisting of two identical modules. The model, using optimised kinetic rate expressions and effective properties of the system, was successfully validated by experimental findings. The simulated species rate and molar composition profiles revealed the contributions of each of the two reactor modules to the process performance. Lastly, a comparison between the simulated foam-based and a pellet-based reactors indicated that the advantage of the geometric properties of the structured reactor was more apparent at operating conditions at which the process was not limited by thermochemical equilibrium.

6.1 Introduction

Direct-CO₂-to-methanol synthesis represents an opportunity for the decarbonisation of the chemical industry and the storage of green hydrogen (H₂) in the form of a more energy dense compound (Dang et al., 2019). The hydrogenation of CO₂ to methanol (MeOH) is an exothermic reaction that proceeds at relatively high temperatures (200–300°C) and elevated pressures (5–100 bar). Due to the occurrence of the competing reverse water gas shift (RWGS) reaction, the CO₂ conversion to MeOH is strongly limited by thermodynamic equilibrium. Hence, due to the relative complexity of the conditions affecting the overall process performance, a suitable catalytic reactor design is crucial.

During the design of catalytic reactors, including MeOH synthesis reactors, specific catalysts have been developed to achieve high conversions, yields and product selectivities (Hettel et al., 2020). Effective catalysts are characterised by high activity and long-term stability over a wide range of operating conditions (Palma et al., 2018). The effects of these conditions on the reactor performance are more predictable at relatively small scales of operation. For large-scale applications, the reactor efficiency is subjected to increased heat and mass transfer limitations

within the catalyst bed (Ferri et al., 2024; Kapteijn and Moulijn, 2022; Weng et al., 2024). To address this issue, there has been increasing interest in the design of process-intensifying technologies such as structured reactors that improve the heat and mass transfer, safety as well as the overall efficiency and catalytic performance in chemical processes (Kapteijn and Moulijn, 2022).

One such technology is the metal foam-based catalytic reactor. At its core, a foam-based reactor typically contains a porous bed composed of highly thermally conductive, reticulated metallic support structure coated with a suitable catalyst. The foam's high porosity improves the reactor's ability to maintain high radial mixing and low pressure drop during catalytic operations (Sinn et al., 2020). The elevated thermal conductivity of metal foams minimises the temperature gradient and hot spot formation within the reactor bed, during endothermic or exothermic reactions (Ding et al., 2010; Dong et al., 2018; Egaña et al., 2018). Foam-based reactors are also characterised by their high surface-to-volume ratios and improved effectiveness factors during catalytic operations (Aguirre et al., 2020). Other practical benefits include their relatively low density and good mechanical strength (Ranut et al., 2014).

The design and optimisation of catalytic reactors generally requires an adequate understanding of the heat and mass transfer phenomena and the chemical reactions occurring on the catalyst surface (Hettel et al., 2020). Due to their intricate geometry and the occurrence of complex transport phenomena in the foam structure, it is difficult to measure local parameters such as temperature, pressure, reactant or product concentrations. With the rapid improvements in computational capabilities over the past few decades, an increasing amount of research relies on numerical modelling and computational fluid dynamics (CFD) simulations to predict, with relatively high accuracy, complex flow fields coupled with transport phenomena (Hettel et al., 2020).

Two approaches are generally used in the simulation of foam-based processes: the heterogeneous and pseudo-homogeneous approaches (Makhania and Upadhyayula, 2022). In the former, fluid and solid phases are considered explicitly as separate entities, with their corresponding properties assigned. The advantage of this method lies in the increased level of accuracy and the detailed information obtained regarding the heat and mass transport in the reactor. On the other hand, the pseudo-homogeneous modelling approach treats all phases as one continuum, characterised by volume-averaged, effective properties (Makhania and Upadhyayula, 2022). Naturally, the heterogeneous modelling approach is more

computationally intensive, therefore it is often conducted on small sections of catalytic reactors. Pseudo-homogeneous modelling is less computationally demanding. Therefore, this approach has been used to simulate larger sections of reactor units at a reasonable level of accuracy for the prediction of temperature and reaction species distribution profiles (Gräf et al., 2016; Guo et al., 2024; Palma et al., 2018; Shigarov et al., 2017).

Recent literature reports some examples of CFD simulation studies of the synthesis of MeOH, mostly from syngas (Hastadi et al., 2024; Izbassarov et al., 2022; Jamshidi et al., 2023; Kyrimis et al., 2021; Mirvakili et al., 2018; Son et al., 2019). For instance, Hastadi et al. (2024) conducted a three-dimensional (3D) particle-resolved simulation of a MeOH synthesis reactor to investigate the effect of five catalyst particle shapes on the pressure drop, temperature and reactant distribution as well as catalyst productivity. This study revealed that those particles whose structure was characterised by an internal void fraction were subjected to lower diffusional limitations than externally shaped particles, resulting in higher production yields per unit catalyst volume. Jamshidi et al. (2023) conducted a two-dimensional (2D) axisymmetric CFD simulation of an industrial tubular reactor used for MeOH production from syngas. After the validation of simulation results with industrial data, the model was used to predict the effects of parameters, including the reactor dimensions, temperature, pressure, feed flow rate and composition. A CFD model of the direct-CO₂-to-methanol synthesis was developed by Izbassarov et al. (2021) who used the heterogeneous approach to simulate a packed bed isothermal and adiabatic reactor. Their results were successfully validated against experimental data published in the literature. The simulations illustrated the effects of catalyst bed configuration, packing density, reaction temperature, space velocity, pressure and CO₂/H₂ ratio on the MeOH and CO production. This study was limited to the one-dimensional and 2D models.

In the present study, a 3D CFD model was developed for the simulation of the direct-CO₂-to-methanol synthesis in a foam reactor previously investigated experimentally (Chapter 5). The objectives of the current investigation include the following: validation of the 3D pseudo-homogeneous CFD model using experimental results reported in Chapter 5, and comparison between the performances of a simulated foam-based reactor and a pellet-based, packed bed reactor (PBR) operated at the same reaction conditions.

6.2 CFD model development

A complete description of the two-module, foam-based reactor is reported in Chapter 5. The 3D model was developed and simulations were conducted using COMSOL Multiphysics v4.4 software. Fig. 6-1 shows the reactor and the computational domain representing the mid-longitudinal section of the modular reactor. Flow and transport properties are assumed to be symmetrically distributed around the central longitudinal plane of the reactor. The domain consisted of a porous region representing the coated foam (highlighted in Fig. 6-1b) and free fluid regions between the foams and towards the inlet and outlet of the reactor.

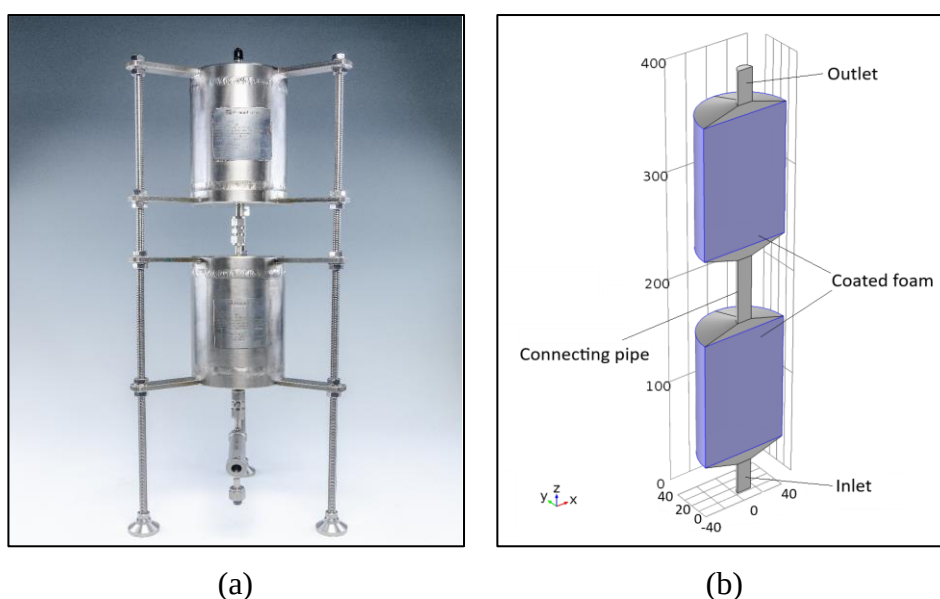


Figure 6-1. (a) Images of the foam reactor used for the direct- CO_2 -to-MeOH synthesis and (b) the corresponding computational domain used in the simulation thereof (porous region highlighted).

The computational domain was discretised in a total of 379017 elements comprising tetrahedral (91.8%), prismatic (8.1%) and pyramidal (0.1%) elements.

The partial differential equations used to describe the reactor included continuity, momentum energy and species conservation equations. Table 6-1 summarises these equations as applied to the porous region (coated foam) and non-porous (free fluid) region. Continuity equations described mass conservation for each region. The species continuity equation accounted for the chemical reactions assumed to occur solely in the coated foam region. Binary diffusion coefficients derived from Fuller–Schettler–Giddings equations were used to describe intermolecular gas-phase diffusion (Fuller et al., 1966). The heat capacity, thermal conductivity and viscosity of each gas species were estimated as functions of the reaction temperature, using

constants obtained from the database of the Chemical Engineering and Materials Research Information Centre (CHERIC, 2024).

Table 6-1. Equations used in the development of the model in COMSOL Multiphysics v4.4.

Governing equation	Mathematical expression
Continuity	Free fluid: $\nabla \cdot (\rho \mathbf{v}) = 0$ Coated foam region: $\nabla \cdot (\epsilon \rho \mathbf{v}) = 0$ Species continuity: $\nabla \cdot (\epsilon \rho \omega_i \mathbf{v}) = \nabla \cdot (\epsilon_p D_{i,j,\text{eff}} \nabla \omega_i) + \sum a_i M_i \rho_s R_i$
Momentum conservation	Free fluid: $\rho(\mathbf{v} \cdot \nabla) \mathbf{v} = \nabla \cdot [-p\mathbf{I} + \mu(\nabla \mathbf{v} + (\nabla \mathbf{v})^T)] + \mathbf{F}$ Coated foam region: $\frac{\rho}{\epsilon} \left(\frac{(\mathbf{v} \cdot \nabla) \mathbf{v}}{\epsilon} \right) = \nabla \cdot \left[-p\mathbf{I} + \frac{\mu}{\epsilon} (\nabla \mathbf{v} + (\nabla \mathbf{v})^T) - \frac{2\mu}{3\epsilon} (\nabla \cdot \mathbf{v})\mathbf{I} \right] - \left(\mu \kappa^{-1} + \frac{\rho \nabla \cdot \mathbf{v}}{\epsilon^2} \right) \mathbf{v} + \mathbf{F}$
Energy conservation	Free fluid: $\rho C_p \mathbf{v} \cdot \nabla T = \nabla \cdot (k_{\text{eff}} \nabla T)$ Coated foam region $\rho \epsilon C_p \mathbf{v} \cdot \nabla T = \nabla \cdot (k_{\text{eff}} \nabla T) + H_r$

Momentum conservation equations include Navier–Stokes and Brinkman–Forchheimer-extended Darcy equations to describe the flow in the free fluid region and within the coated foam, respectively. Throughout the simulation, the gas flow is assumed steady state and laminar (low Reynolds number), through a catalyst bed of uniform porosity in which heat losses were neglected (Behloul et al., 2021).

Due to the simplified nature of the pseudo-homogeneous model, heat transfer was limited to conduction and convection. To estimate the overall gas mixture density, viscosity, thermal conductivity and heat capacity, the respective properties of each species were mixture-averaged (Izbassarov et al., 2022). A local thermal equilibrium was assumed between the coated foam and the gas phase (Izbassarov et al., 2022).

The two reactions governing the consumption and generation of chemical species during the simulations were the CO₂ hydrogenation to MeOH (Eq. 6-1) and the RWGS (Eq. 6-2). In this

model, MeOH is assumed to be produced from the hydrogenation of CO₂, the CO hydrogenation to MeOH was therefore considered negligible (Kubota et al., 2001; Kyrimis et al., 2021).



Kinetic rate expressions and constants used in the simulations were adapted from the work of Son et al. (2019) who used kinetic rates proposed by Graaf et al. (1988). Most of the values of the kinetic parameters were kept the same except the equilibrium constants and the pre-exponential factors of the CO₂ hydrogenation and RWGS rate equations, $K_{P,RWGS}$ and $K_{P,M}$, k_{MS} and k_{RWGS} , respectively. COMSOL Multiphysics' Nelder–Mead optimisation algorithm based on a least-square objective function was used in the estimation of the new values of these kinetic parameters. The kinetic rate of the CO₂ hydrogenation to MeOH and the RWGS are expressed in Eqs 6-3 and 6-4 (Son et al., 2019).

$$r_{MS} = \frac{k_{MS}K_{CO_2} \left[f_{CO_2} f_{H_2}^{1.5} - \frac{f_{H_2O} f_{CH_3OH}}{K_{P,MS} f_{H_2}^{1.5}} \right]}{(1 + K_{CO_2} f_{CO_2})(1 + K_{H_2}^{0.5} f_{H_2}^{0.5} + K_{H_2O} f_{H_2O})} \quad (6-3)$$

$$r_{RWGS} = \frac{k_{RWGS}K_{CO_2} \left[f_{CO_2} f_{H_2} - \frac{f_{CO} f_{H_2O}}{K_{P,RWGS}} \right]}{(1 + K_{CO_2} f_{CO_2})(1 + K_{H_2}^{0.5} f_{H_2}^{0.5} + K_{H_2O} f_{H_2O})} \quad (6-4)$$

Fugacity coefficients were assumed to be equal to 1 since the fluid was considered an ideal gas mixture of H₂, CO₂, MeOH, H₂O and CO (products) (Izbassarov et al., 2021; Leonzio and Foscolo, 2020). Besides, CO or CO₂ methanation reactions were neglected based on the analysis of the product obtained during the experiments (Chapter 5). All chemical reactions were simulated assuming negligible catalyst deactivation (Leonzio and Foscolo, 2020). Table 6-2 summarises the expressions of reaction rate parameters used in the present study.

Table 6-2. Kinetic reaction rate parameters used in the simulation

Parameter	Expression
k_{MS} (mol/kg _{cat} /s/MPa ^{1.5})*	$5.00 \times 10^8 \exp\left(-\frac{68252}{RT}\right)$
k_{RWGS} (mol/kg _{cat} /s/MPa ^{1.5})*	$4.50 \times 10^{15} \exp\left(-\frac{126573}{RT}\right)$
K_{CO_2} (1/MPa)	$1.02 \times 10^{-6} \exp\left(\frac{67439}{RT}\right)$
K_{H_2} (1/MPa)	$2.71 \times 10^2 \exp\left(-\frac{6291}{RT}\right)$
K_{H_2O} (1/MPa)	$3.80 \times 10^{-10} \exp\left(\frac{80876}{RT}\right)$
$K_{P, RWGS}$ (-)*	$10^{-\frac{2090}{T}+1.50}$
$K_{P, MS}$ (-)*	$10^{\frac{2097}{T}-8.33}$

* Values adjusted through parametric optimisation. Others are as reported by Son et al. (2019).

The direct-CO₂-to-MeOH process in the foam-based reactor was simulated using the same conditions as used experimentally (Table 6-3). The experimental feed gas compositions and flow rates were assigned to the reactor inlet. The feed was also assumed to be preheated to the reaction temperature. The reaction temperature was imposed on the side walls of the two modules to simulate the heat supply from the heating jackets. The remaining reactor walls were set to be thermally insulated. The experimental pressure conditions were set to the reactor outlet. A no-slip condition was imposed at the gas–solid interfaces in the reactor (Izbassarov et al., 2022).

Table 6-3. Reaction conditions used in the simulation

Operating parameter	Value
H ₂ /CO ₂ molar ratio (-)	3/1
Weight hourly space velocity (WHSV) (NL/g _{cat} /h)	1.125, 2.025 and 2.925
Reaction temperature (°C)	200–250 (increments of 10°C)
Reaction pressure (bar)	30 and 50

Similar to the experimental investigation, the performance criteria used in this section included the CO₂ conversion (Eq. 6-5), MeOH selectivity (Eq. 6-6), CO outlet concentration and MeOH weight time yield (WTY) (Eq. 6-7).

$$X_{\text{CO}_2} = \frac{n_{\text{CO}_2\text{in}} - n_{\text{CO}_2\text{out}}}{n_{\text{CO}_2\text{in}}} \times 100\% \quad (6-5)$$

$$S_{\text{MeOH}} = \frac{n_{\text{CH}_3\text{OH}_{\text{out}}}}{n_{\text{CH}_3\text{OH}_{\text{out}}} + n_{\text{CO}_{\text{out}}}} \times 100\% \quad (6-6)$$

$$\text{MeOH WTY} = \frac{m_{\text{CH}_3\text{OH}_{\text{out}}}}{m_{\text{catalyst}} \times \text{time on stream}} \quad (6-7)$$

6.3 Simulation results

This section summarises the results obtained during the 3D CFD simulation of the direct-CO₂-to-MeOH process in pseudo foam-based reactor and PBR. First, the kinetic model was validated using experimental CO₂ conversions, MeOH selectivities, CO outlet concentrations and MeOH WTY obtained in the foam-based reactor at operating conditions reported in Table 6-3. The validated model was then used to evaluate the effects of the operating conditions on the CO₂, MeOH and CO longitudinal mole fraction profiles in the foam-based reactor. Lastly, the model was used as a tool to compare the general performance of the foam-based reactor and PBR.

6.3.1 Model validation

Fig. 6-2 shows a comparison between the experimental and simulated results for selected operating conditions. The effects of reaction temperature and pressure on the simulated performance of the reactor were generally in agreement with the experimental observations. To obtain these results, it was necessary to fine-tune selected kinetic parameters. The CO₂ conversions and selectivities (Fig. 6-2a,b) depended on the production of MeOH and CO (Fig. 6-2c,d). Kinetic rate parameters reported by Son et al. (2019) resulted in insignificant MeOH or CO production rates. Their simulated reactor was much larger than the one modelled in the present study (production capacities: 50 vs 0.72 kg/day). Optimising the pre-exponential constants was required to adjust the magnitude of the reaction rates in order to obtain satisfactory conversions and selectivities. The reported pre-exponential constants of the kinetic rate of reactions (6-1) and (6-2) were increased by factors of 223 and 38793, respectively. The reported equilibrium constant of the RWGS reaction was increased by a factor of 3296. This parameter governs the transition from the RWGS to the water gas shift (WGS) reaction as H₂O

and CO accumulate in the reactor, forming more CO₂ (decreasing CO₂ conversion) with increasing temperatures (Kubota et al., 2001).

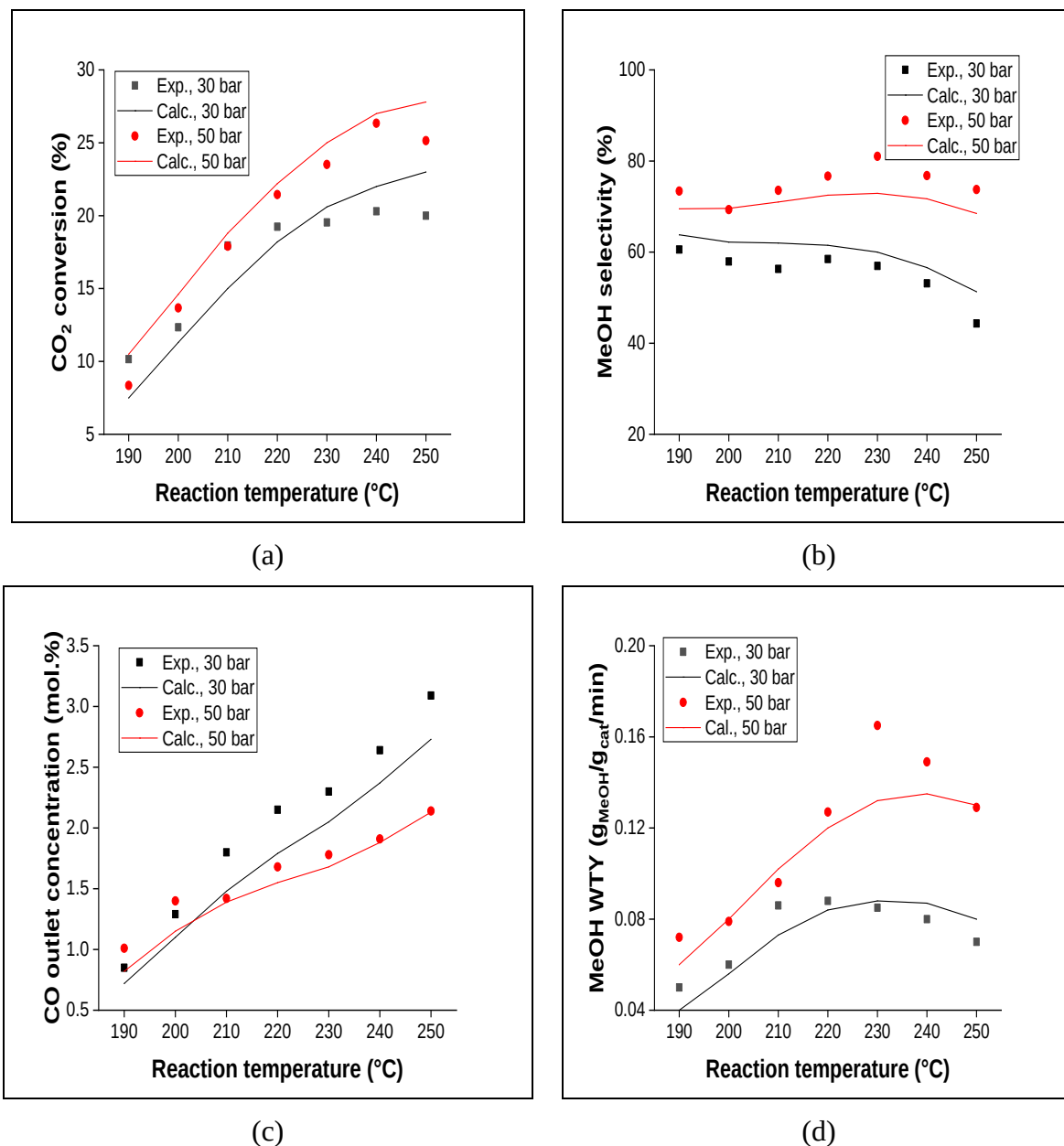


Figure 6-2. Comparison of experimental and simulated data for (a) CO₂ conversions, (b) MeOH selectivities, (c) CO outlet concentrations and (d) MeOH WTY, obtained at a WHSV of 2.025 NL/g_{cat}/h

As stated earlier (Section 6.2), in this model, CO hydrogenation to MeOH is assumed to be negligible. Therefore, the optimisation of the kinetic parameters can also be considered a way to incorporate the eventual effects of the neglected equations in the process. The estimation of these lumped parameters resulted in fewer equations used in the simulation, a more simplified model and consequently, less computational time required.

Furthermore, the validity of the model was tested using the parity plots shown in Fig. 6-3. The plots were generated using the experimental and simulated results obtained at all the operating conditions reported in Table 6-3. Despite the non-linearity of the data, the estimated coefficients of determination were all > 0.95 . The deviations between the experimental and simulated results were mostly within the 15% limits. These deviations could be improved by optimising more kinetic parameters such as the equilibrium constants or activation energies of each of the reactions involved in the process. This will naturally require a more computationally intensive optimisation procedure.

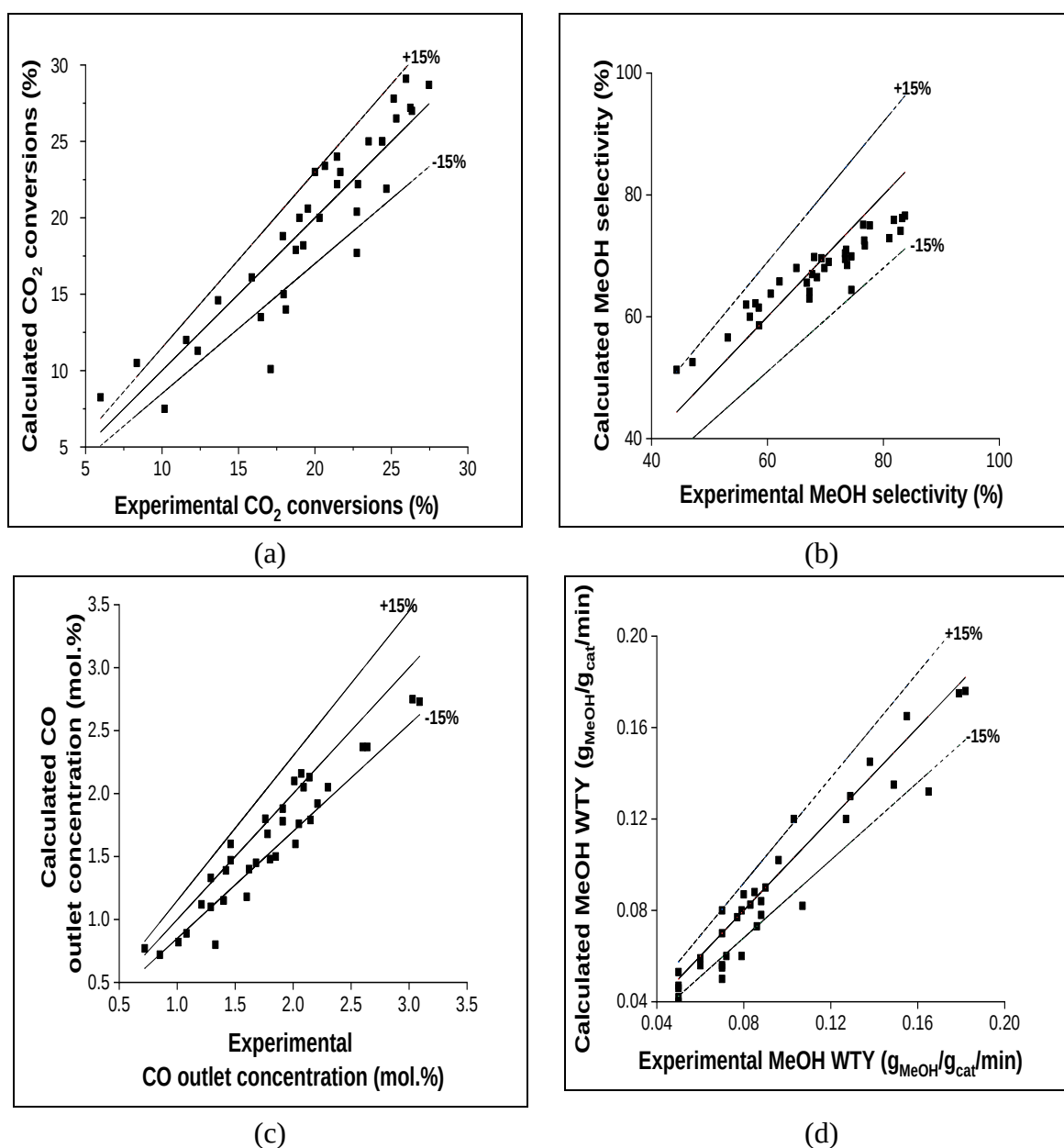


Figure 6-3. Parity plots of (a) CO₂ conversions, (b) MeOH selectivities, (c) CO outlet concentrations and (d) MeOH WTY, obtained at operating conditions investigated experimentally and in the CFD simulations

The satisfactory linear relationship between the data and relatively small number of large deviations indicates that the simplified kinetic model used in the present study could be successfully used in reactor design to predict the kinetic performance at different process conditions (Kubota et al., 2001).

6.3.2 Simulation of flow, velocity and temperature profiles

Although the pseudo-homogeneous model does not provide detailed flow patterns and velocity profiles, it can be used to estimate overall flow characteristics within a significant portion of the reactor volume. Streamlines shown in Fig. 6-4a confirm the uniform gas distribution within the reactor (no dead volume). This was anticipated because the system is highly pressurised (30 and 50 bar) and the inlet flow rates are relatively low (3.0–7.8 NL/min).

An example of the velocity profile obtained during the simulation of the foam-based reactor is shown in Fig. 6-4b. The highest velocity magnitudes are observed in the inlet, connecting and outlet pipes. These sections are the only ‘free fluid’ regions of the computational domain. The flow of the gas mixture is not affected by any solid material, except the reactor wall, at which the no-slip condition applies. The velocity is almost zero ($\sim 0.36 \times 10^{-3}$ m/s) throughout the porous phase (coated foam) because the no-slip condition also applies to the boundary between the solid foam and the gas phase. Simulated velocity profiles show the highest velocities towards the zones of least flow resistance (Izbassarov et al., 2021).

The temperature profile in the reactor (adiabatic system) is shown in Fig. 6-4c. The temperature difference between the heated reactor wall and the centre of the catalyst bed was insignificant. Nearly isothermal conditions were also obtained during the experimental evaluation of the reactor. The negligible change in temperature could be explained by the facts that the simulations/experiments were conducted at relatively low inlet gas flow and that two competing reactions—one endothermic and the other exothermic—occur simultaneously in the reactor (Leonzio and Foscolo, 2020). The resulting temperature profile would therefore depend on the relative amounts of MeOH and CO produced from CO₂ conversion in each of the two modules (Izbassarov et al., 2021). Lastly, this ideal isothermal situation could also originate from the characteristic of the pseudo-homogeneous model itself. The pseudo-homogeneous model is intrinsically biased towards uniform flow and material distribution in the simulation domain. The system is considered as one entity characterised by effective properties which are averaged from the constituents of the fluid and solid domains. Therefore, considering the

experimental and simulation results, the foam-based reactor can be considered isothermal in an overall performance evaluation.

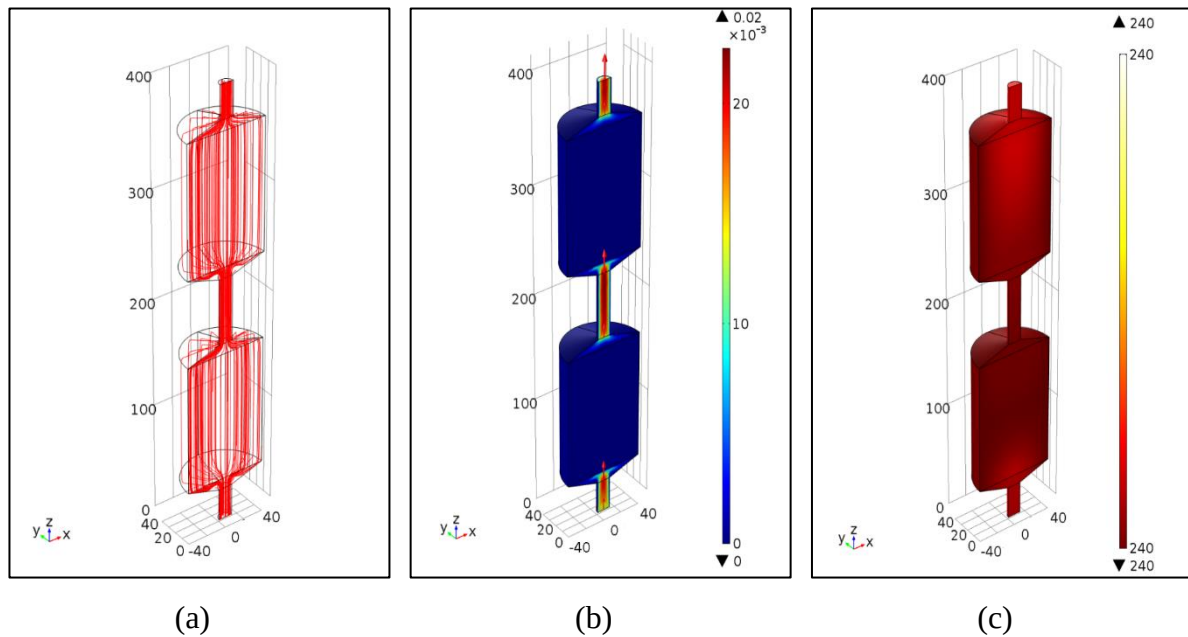


Figure 6-4. Flow profiles in the reactor: (a) gas streamlines, (b) velocity and (c) temperature profiles simulated at a WHSV of 2.025 NL/g_{cat}/h, temperature of 240°C and pressure of 50 bar

6.3.3 Consumption/production rate profiles

The following are evident from the different rate profiles depicted in Fig. 6-5: (1) the reaction occurs solely in the porous section of the reactor (from 40–160 and 240–360 mm) and (2) the rate of consumption/formation of species is higher in the first module (bottom) than in the second. The rate of consumption of the reacting species (Fig. 6-5a) and the rate of formation of product species (Fig. 6-5b) are correlated by stoichiometric coefficients of the CO₂ hydrogenation and RWGS reactions (Eqs 6-1 and 6-2).

In the first module (from 40 to 160 mm), the decrease in species consumption/production rates is attributed to the equilibrium limitation of the RWGS reaction (Eq. 6-2). Both chemical reactions (Eqs 6-1 and 6-2) occur simultaneously as the gas reaches the catalyst bed in the first module. As reaction proceeds, more CO and H₂O are produced, gradually shifting the equilibrium towards the WGS reaction (Le Chatelier principle). This decreases the rate of consumption of CO₂ and the rates of production of CO and H₂O (Fig. 6-5b). The occurrence of the WGS reaction at 240°C is illustrated in Fig. 6-5b by the negative rate of CO formation (Leonzio and Foscolo, 2020). Based on Eq. 6-3, the MeOH production rate is also affected by the formation of products. Nevertheless, the MeOH formation rate is less disturbed by

fluctuations in gas composition than the rates of formation/consumption of the other species present in the reactor.

These rate profiles could be used as a guide for the selection of the suitable reactor size or the optimum reaction conditions. These parameters should promote a high CO₂ conversion to MeOH while minimising CO formation.

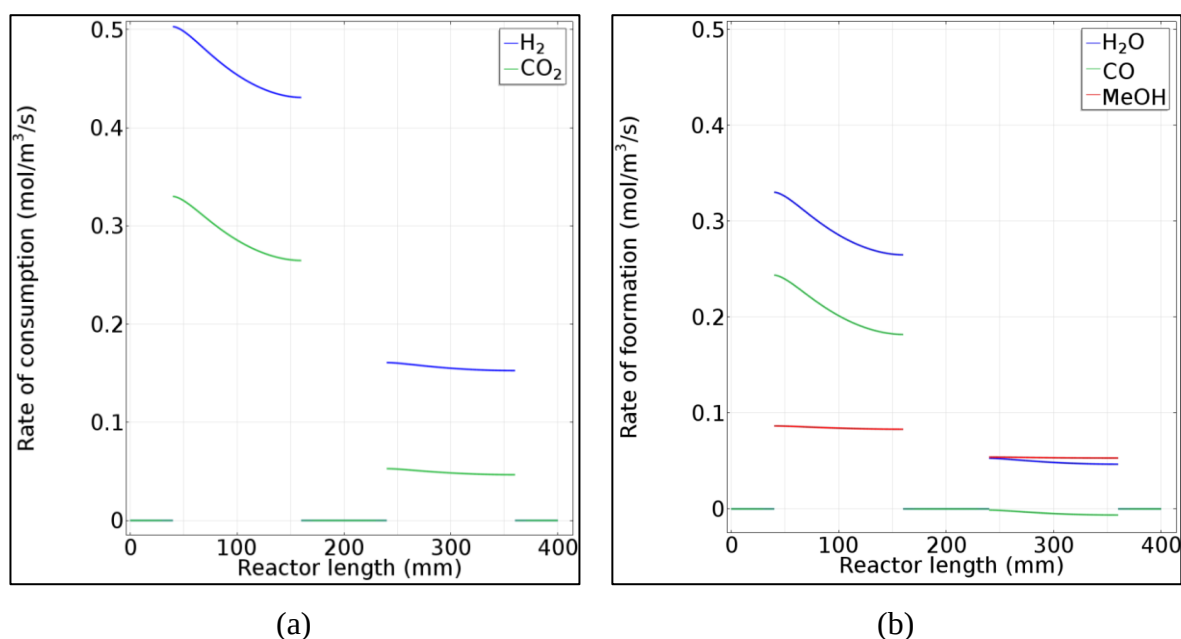


Figure 6-5. Rates of (a) consumption of H₂ and CO₂ and (b) formation of CO, H₂O and MeOH at a temperature of 240°C, pressure of 50 bar and WHSV of 2.025 NL/g_{cat}/h.

6.3.4 Effects of operating parameters on molar fraction profiles

Mole fractions were plotted against the length of the central longitudinal axis of the reactor, going from the inlet pipe to the outlet pipe (from 0 to 400 mm). A concentration gradient can be observed at the inlet section of the two modules (Fig. 6-6). These sections are devoid of any catalytically active component. As seen in Fig. 6-5, no reaction occurs in the inlet and connecting pipes (from 0 to 40 and 160 to 240 mm, respectively). The change in molar composition was attributed to intermolecular gas diffusion. A concentration difference exists between the inlet of the reactor modules and the entrance of the foam (catalyst bed). At steady-state conditions, a concentration gradient can therefore be expected between regions characterised by different species compositions. Diffusion also plays a role in the two catalyst beds. These sections are characterised by a high porosity, relatively high temperatures and a low gas velocity gradient in the direction of flow. The rather flat mole fraction profiles obtained

in the foam sections could be the result of high species mixing (convection) combined with intermolecular diffusion in gas phase.

The effects of temperature, pressure and WHSV on the composition profiles of MeOH and CO are shown in Fig. 6-6. The overall trends agree with experimental findings reported earlier (Chapter 5). In general, in the temperature, WHSV and pressure ranges investigated in the present study, higher temperatures increase CO₂ conversion to MeOH and CO due to increased reaction kinetics (Izbassarov et al., 2022) (Fig. 6-6a,c). Increasing the pressure results in improved MeOH yields and lower CO production because of the effect of H₂O on the RWGS equilibrium (Fig. 6-6b,d) (Arab et al., 2014). A high WHSV value leads to decreased MeOH production due to lower residence times but it barely affects the CO formation because of equilibrium limitations of the RWGS.

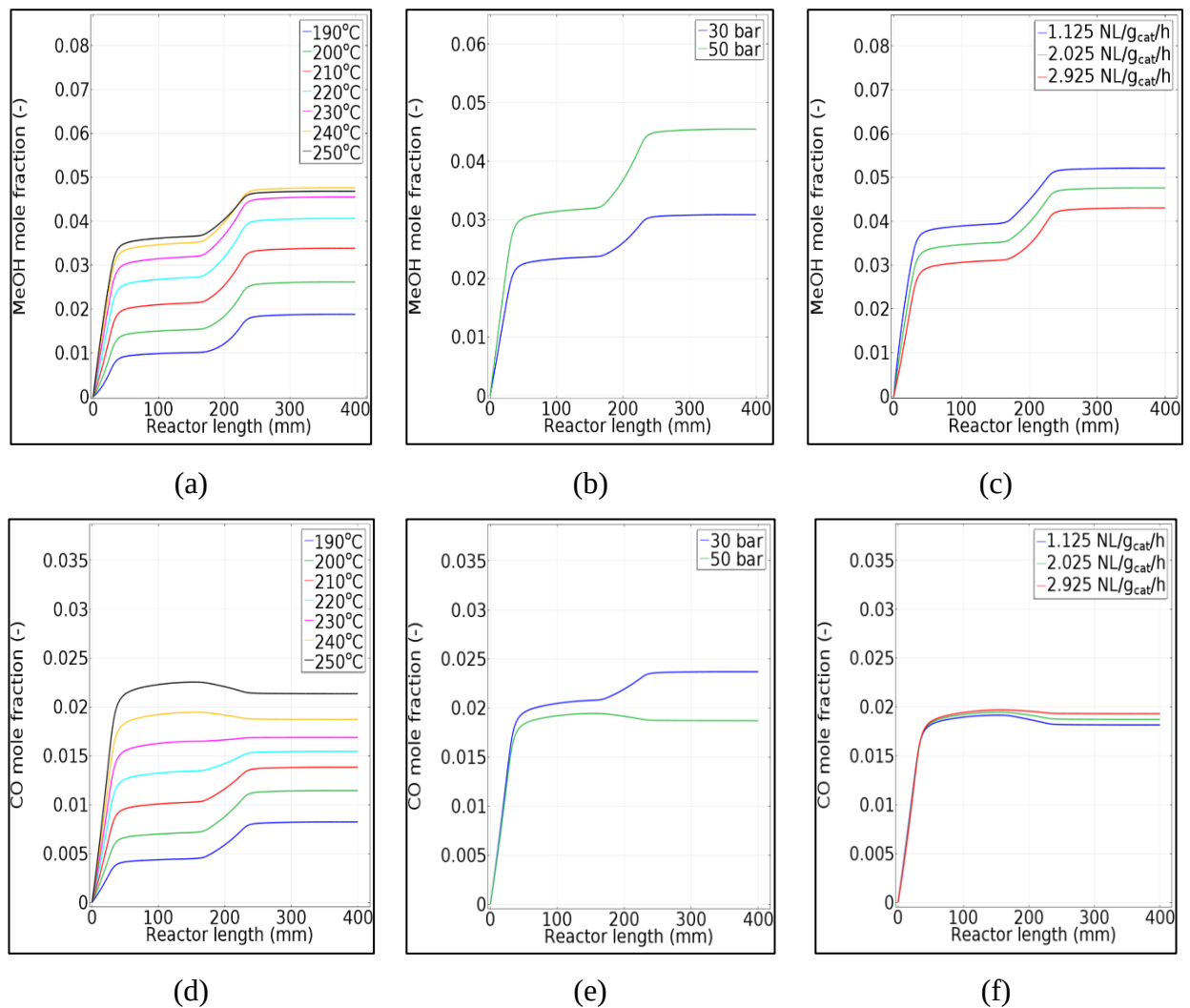


Figure 6-6. Effects of (a) temperature, (b) pressure and (c) WHSV on the MeOH mole fraction and effects of (c) temperature, (d) pressure and (f) WHSV on the CO mole fraction in the reactor. WHSV 2.025 NL/g_{cat}/h in a, b, d, e. Pressure of 50 bar in a, c, d, f

It can also be deduced from Fig. 6-6, that the two reactor modules contributed significantly to the overall performance of the system. MeOH formation increased from the first module to the next at all simulated operating conditions (Fig. 6-6a–c). This could be explained by the reaction rate profiles in Fig. 6-5b, which show that the rate of MeOH production does not decrease to a large extent from the first reactor module to the second. The CO mole fraction profiles varied according to the operating condition investigated (Fig. 6-6d–f). At low temperatures (190–220°C), CO formation increased as the gas mixture passed from the first to the second module (Fig. 6-6d). At these temperature conditions, the equilibrium H_2 , CO_2 , CO and H_2O compositions were not reached within the total length of the reactor. At higher temperatures, the CO mole fraction remained nearly constant (230°C) or decreased (240–250°C). At these conditions, H_2O produced from CO_2 hydrogenation to MeOH shifts the equilibrium to higher consumption of CO in the reactor. This could also explain the decrease in the CO mole fraction in the second reactor module at higher pressure (Fig. 6-6e) and higher WHSV (Fig. 6-6f).

6.3.5 Comparison between simulated foam-based reactor and PBR

To understand the benefit of the foam used as catalyst support structure in the direct- CO_2 -to-MeOH process, a pseudo-homogeneous model of a modular PBR was developed and used for comparison.

6.3.5.1. PBR model

The method used in the development of the PBR model was similar to the procedure described in Section 6.2. Just like the foam-based reactor, the PBR also consisted in two identical modules connected by a middle pipe. However, a few changes had to be made to the reactor properties. First, the catalyst bed porosity was set to 0.41, which is about half of the porosity of the foam-based bed simulated as described in earlier sections of this chapter. This value corresponds to the porosity of a typical packed bed filled with spherical catalyst pellets of diameter < 0.15 times lower than the reactor diameter (Arab et al., 2014). Since the total amount of catalyst was the same in both reactors (160 g Cu/Zn/ Al_2O_3), the total catalyst bed length of the PBR modules was reduced to 110 mm, i.e. half that of the foam-based bed. Second, the properties (e.g. thermal conductivity, heat capacity) of the PBR only accounted for the catalyst, i.e. the contribution of the Cu structure was ignored. Leonzio and Foscolo (2020) used a similar method to compare the temperature distribution in a structured reactor and a PBR. The 2D

pseudo-homogeneous reactor models of the two reactors used in their study were distinguished through their respective thermal conductivities.

6.3.5.2. Overall performance comparison between the foam-based reactor and the PBR

Fig. 6-7 shows the predicted performance of a PBR compared with results of a simulated foam-based reactor.

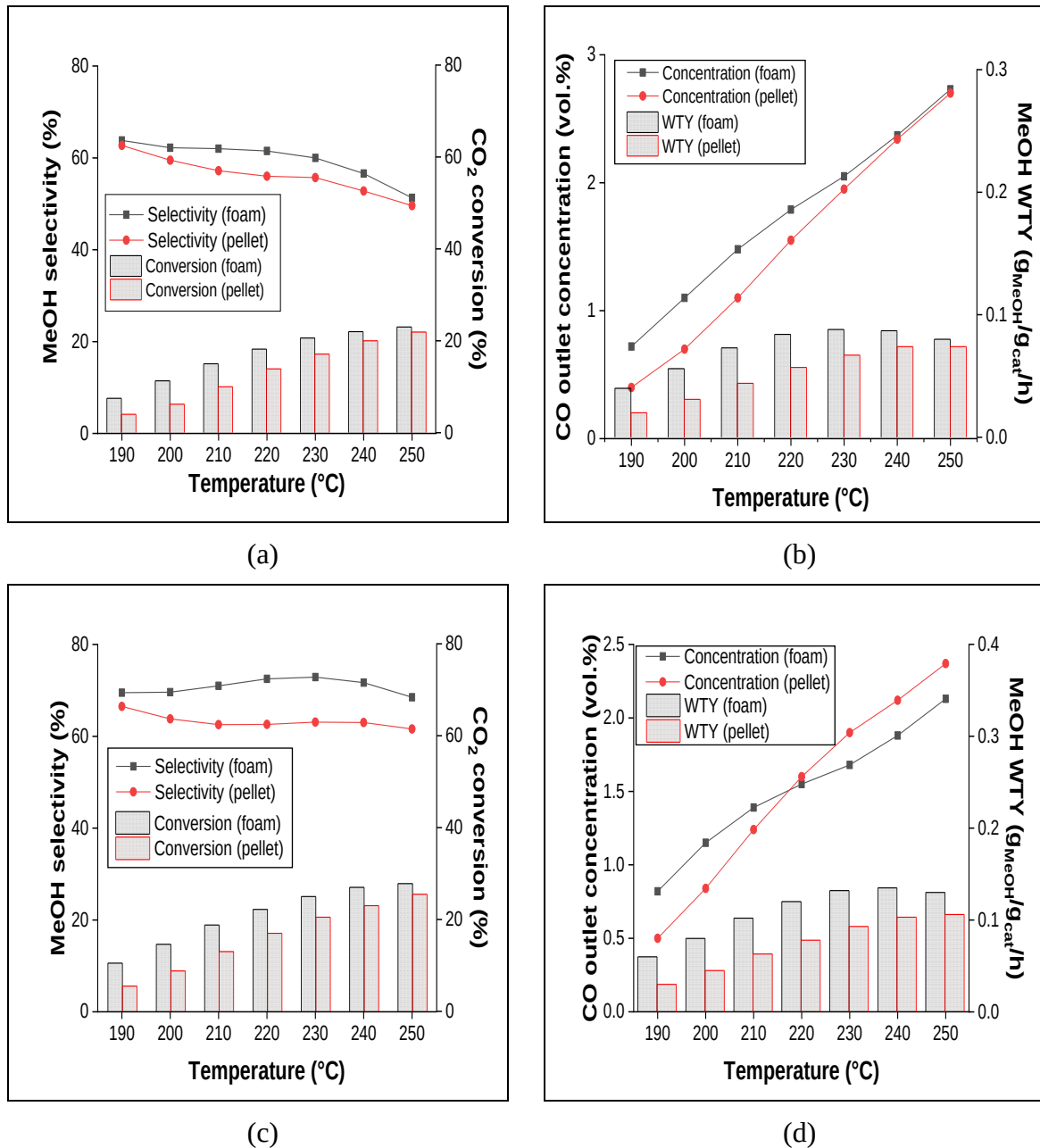


Figure 6-7. Performance comparison between foam-based reactor and PBR: (a) CO₂ conversions and MeOH selectivity at 30 bar, (b) CO outlet concentration and MeOH WTY at 30 bar, (c) CO₂ conversions and MeOH selectivity at 50 bar, (d) CO outlet concentration and MeOH WTY at 50 bar.

Generally, the foam-based reactor slightly outperformed the PBR at 30 bar (Fig. 6-7a,b) and 50 bar (Fig. 6-7c,d). This can be attributed to the better contact between the reacting species and the catalyst on the solid foam favoured by the high porosity and increased length of the catalyst bed. The ratio of the CO₂ conversions obtained in the foam-based reactor and PBR decreased from 2 to 1.1 and 2 to 1.05 at 30 and 50 bar, respectively, as the temperature increased from 190 to 250°C (Fig. 6-7a,c). These results suggest that the advantage of a high-porosity or residence time within the catalytic foam-based bed are better reflected at the process conditions resulting in performances being less affected by thermochemical equilibrium limitations (i.e. under kinetically controlled regimes). These limitations cause the CO₂ conversion to MeOH to decrease with reaction temperature. Therefore, compared to the PBR, the foam-based reactor could be more beneficial at low temperature conditions.

MeOH selectivities were also affected by differences in the geometric configurations of the foam-based reactor and PBR. The difference in selectivities between the two reactor configurations increased as the pressure changed from 30 to 50 bar (Fig. 6-7a,c). This can be explained by the CO outlet concentration and MeOH WTY results, as depicted in Fig. 6-7b,d. The CO production and MeOH yield both increased with increasing CO₂ conversions but the MeOH/CO ratio increased more significantly in the foam-based reactor than in the PBR. Additionally, at 50 bar, higher outlet CO concentrations were attained in the PBR than in the foam-based reactor at temperatures of 220–250°C. At the same conditions, the MeOH yield remained lower in the PBR than in the foam-based reactor. This increase in CO production prevented further increase in MeOH selectivity in the PBR. The higher CO outlet concentrations observed in the PBR at temperatures > 220°C is because the amount of H₂O produced from the conversion of CO₂ in the pellets was not sufficient to promote the commencement of the CO conversion through the WGS reaction. This is also a direct consequence of the lower contact time between the reactants and catalyst in the PBR. The temperature profiles obtained for the PBR (not shown) were not different to the profiles for the foam-based reactor (Fig. 6-4c). Therefore, in the present study, the difference in the performances of the foam-based reactor and PBR is not attributed to temperature profiles, contrarily to the simulation results of Leonzio and Foscolo (2020) for instance. The small dimensions of the PBR and its relatively low MeOH and CO throughput could be the reason of the uniform temperature profile obtained for the catalyst bed.

6.4 Conclusions

In this investigation, a pseudo-homogeneous CFD model was developed to simulate the direct- CO_2 -to-MeOH in a modular foam-based reactor. Kinetic expressions used in the model were obtained by simplifying expressions and optimising constant parameters proposed in the literature. The satisfactory linear fit between experimental and modelling results not only demonstrated the suitability of the adapted kinetics but also showed the ability of the model to be used as a performance prediction tool in the preliminary design of a foam-based reactors.

The contribution of the two reactor modules was also assessed by analysing the species consumption/formation rate profiles and molar composition profiles inside the reactor. It was expected that the thermochemical equilibrium would affect the process by limiting the CO_2 conversion, the production of MeOH or CO. The overall performance could also be related to the geometry of the reactor. In this regard, suitable operating conditions can be selected to maximise the performance of a reactor characterised by a specific geometric configuration.

Lastly, by adjusting the geometric and physical properties of the computational domain, a PBR was also simulated. Its performance was compared to that of the foam-based reactor. Generally, better CO_2 conversions and MeOH selectivities were obtained on the foam-based reactor. The slightly lower performance of the PBR was mainly attributed to the difference in geometric features of the system, namely the porosity and reactor length.

This study can be considered as a first—and simplified—step in an attempt to model a foam-based reactor and eventually compare it with a reactor of a different configuration. Recommendations for further studies should be directed at improving the model by using more accurate kinetic data applied to a fully heterogeneous simulation of the reactor. In this way, diffusion limitations as applicable to heat transfer and mass flow profiles could be better simulated. For optimisation purposes, further studies could also make use of the current model to compare different foam-based reactor designs, such as a single-module reactor or reactors of different dimensions (i.e. diameter, length) with the current design.

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Chapter 7. General conclusions and recommendations

Chapter overview

This chapter summarises the main conclusions obtained in the different experimental and modelling sections of this thesis. The chapter also summarises the main contributions of the current investigation to the scientific knowledge base. Finally, a few recommendations are listed for future studies.

7.1 Conclusions from this study

In the transition to a more sustainable world, renewable energy sources are expected to play a significant role in the energy supply. Through the technological advancements achieved over the past decades, the cost of production of renewable energy from variable sources (e.g. solar and wind energy) has been steadily decreasing. This represents a great opportunity, especially for the African continent endowed with large reserves of natural resources as well as vast regions of solar irradiation and high wind potential. Hydrogen (H_2) is expected to be a major component in the renewable energy sector thanks to its potential as an energy carrier and an essential feedstock to produce speciality chemicals. However, there are some practical challenges intrinsically associated to the conversion of renewable power to H_2 or chemicals of higher energy density. These include the storage of H_2 and the prevention of risks associated with accidental H_2 released especially in confined spaces. Several technologies have been developed to solve these problems. Reactors have been designed for the safe H_2 storage in and release from liquid organic H_2 carriers (LOHCs). Passive autocatalytic recombiners have been utilised to prevent leaked H_2 gas from dangerously accumulating to concentrations comprised within its flammability limits. However, these technologies are subjected to limitations, notably in the transport of heat and mass within the reactor. These transport limitation issues can be mitigated through the design of process-intensifying, high surface area catalytic structures.

In this investigation, metal foams were explored as surface extended catalyst support structures used for process intensification in the dehydrogenation of perhydro-dibenzyltoluene (H_{18} DBT), the passive autocatalytic recombination of H_2 and the direct- CO_2 -to-methanol (MeOH) synthesis. In general, utilising a foam-supported catalyst instead of a pellet-based or a plate-based catalyst did not result in a decrease in the catalytic performance in the range of operation conditions explored for each process. The advantage of performance of the coated foams over

that of other catalyst configurations depended on the relative importance of kinetic or diffusion limitations in the selected biphasic or triphasic chemical processes. The conclusions that follow could therefore serve as a guide to assess the relevance of coating a catalyst on a surface-extended support structure such as the metal foam.

- I. The dehydrogenation of $H_{18}DBT$ was conducted on a 5 wt.% Pt/Al_2O_3 catalyst in the form of pellets or coated on an aluminium (Al) foam. The dehydrogenation experiments were conducted in an unstirred tank reactor to compare the two catalytic configurations. The foam's geometric properties (high volumetric surface area and porosity) enhanced the dehydrogenation step characterised by the fastest kinetics but mainly limited by interphase diffusion. However, the foam-based catalytic configuration had less benefits when the dehydrogenation process reached steps in which the kinetics were much slower. Moreover, the beneficial effect of the foam geometry decreased with increasing catalyst loadings. With higher loadings, the diffusional path from the bulk of the liquid phase and the catalyst active site increased, thus slowing the diffusion. Catalyst durability tests and liquid product recycling tests were conducted in a fixed bed reactor (FBR). Typically, Pt-based catalysts undergo an initial loss in activity. This was also observed for the foam-supported Pt/Al_2O_3 catalyst which started exhibiting a stable behaviour from ~5 h on stream. When comparing the foam-based and the pellet-based FBRs, one of the perceived disadvantages of the foam-based FBR is its low catalyst inventory which leads to low contact time between the liquid and the catalyst at a given $H_{18}DBT$ inlet flow rate. This resulted in decreased degree of dehydrogenation (DoD) achieved in a single pass of $H_{18}DBT$ through the reactor. The DoD was increased by recycling the LOHC products three times in the reactor. As the number of cycles increased, a significant drop in H_2 release was observed. The lower H_2 production rate was attributed to the occurrence of the slowest steps of the $H_{18}DBT$ dehydrogenation reaction, i.e. the dehydrogenation of intermediates such as $H_{12}DBT$ or H_6DBT .
- II. The passive autocatalytic recombination (PAR) of H_2 was conducted in an in-house developed recombiner fitted with a catalytic bed consisting of either of the following configurations: Pt/Al_2O_3 pellets, Pt/Al_2O_3 catalyst coated on Al plates or Pt/Al_2O_3 coated on Al foams. The H_2 conversions observed in the foam-based recombiner were similar to those obtained on the plate-based but higher than those achieved on the pellet-based recombiner. The differences between the gas–solid interphase areas of the foam, plates and pellets were considered as the main reasons for the performance disparities

between the foam-based or plate-based and the pellet-based recombiners. As H_2 combustions are characterised with fast kinetics, a high volumetric surface area played an important role in the conversion of H_2 , especially as the inlet gas velocity increased. It is possible that the difference between total surface areas of the foam-based and plate-based catalyst beds was not high enough to cause variations in diffusional limitations that could induce significant disparities in H_2 conversions. Therefore, using a simple plate-based recombiner could suffice in achieving acceptable H_2 conversions in the recombiner.

The temperature profiles obtained during experiments were an indication of the uneven distribution of the H_2 flow through the recombiner's catalyst section. This unpredictable gas behaviour suggests that recombiners should be placed at strategic positions where the probability of H_2 flow is the highest. Nevertheless, the foam-based recombiner demonstrated a satisfactory heat dissipation capability through convection, diffusion and radiation. This prevented the maximum temperature achieved during experiments to reach the minimum temperature for spontaneous gas-phase combustion (i.e. 585°C). A 3D heterogeneous CFD simulation of the PAR of H_2 in the foam-based recombiner successfully predicted H_2 conversions and maximum temperatures obtained on the coated foams. This numerical tool can therefore be used for the design or optimisation of the geometric features in foam-based recombiners, including the size, position and pore density of the foams.

- III. A commercial $\text{Cu/ZnO/Al}_2\text{O}_3$ catalyst was coated on a copper foam and experimentally tested for the direct- CO_2 -to-MeOH process in a bench-scale, two-module FBR. The process was investigated at different temperature, pressure and space velocity conditions. Typically, the effects of the reactor operating conditions followed the general behaviour of a conventional MeOH synthesis reactor. Generally, the thermodynamic equilibrium limited the beneficial effects of increased temperatures on the process performance. An increase in reaction temperature generally increased the CO_2 hydrogenation kinetics. Simultaneously, temperature also increased reverse water gas shift kinetics, which caused a decrease in MeOH selectivity. The CO_2 conversions and MeOH selectivities and weight time yields (WTY) increased at higher pressures because of the equilibrium shift towards higher CO_2 conversions. At higher space velocities, the MeOH production increased while the CO_2 conversions and MeOH selectivities decreased. This was attributed to low residence time of reactants in the foam bed as well as the difference in kinetics between the reverse water gas shift and

CO₂ hydrogenation to MeOH reactions. Temperature profiles within the reactor demonstrated that the operations were conducted under nearly isothermal conditions. These experiments demonstrated the suitability of the foam-based reactor in the process of direct MeOH synthesis from CO₂ and green H₂.

- IV. A 3D pseudo-homogeneous CFD model was developed to simulate the experimental results obtained for the direct-CO₂-to-MeOH synthesis studied in the previous chapter. In this modelling approach, kinetic equations were simplified by neglecting the CO direct conversion to MeOH. Selected kinetic rate parameters were optimised using the Nelder-Mead algorithm. The model was successfully validated using experimental CO₂ conversions, MeOH selectivities, WTY and CO outlet concentrations. The results demonstrated the suitability of a model using simplified kinetics and geometric features in the prediction of the overall performance of the direct-CO₂-to-MeOH synthesis structured reactor. The model was further used as a prediction tool, to simulate the performance of a pellet-based modular reactor. The simulations showed that the foam-based reactor outperformed the pellet-based reactor thanks to their difference in geometric characteristics, including the porosity and catalyst bed length. These geometric properties resulted in higher reactant residence times in the foam-based reactor than the pellet-based reactor.

7.2 Contributions of this work to the current knowledge base

Foam-supported catalyst structures have demonstrated their ability to enhance H₂ processes characterised by fast kinetics and significant diffusion limitations. Kinetically limited processes can be improved by using large amounts of catalyst. Foam-based systems are usually more limited in their catalyst inventory compared to conventional pellet-based systems for instance. This makes them less suited for kinetically limited applications. However, when diffusion limitations are the main issue, foam-supported catalysts present an opportunity for the improvement of the catalytic activity through a more effective use of the catalyst active sites.

The following points summarise the contributions from each of the experimental or modelling section of this research project.

- I. To the best of the author's knowledge, no H₁₈DBT dehydrogenation was previously performed on a foam as catalyst support structure. These experiments revealed that the

metal foam was a suitable Pt/Al₂O₃ catalyst support structure for the unstirred dehydrogenation of H₁₈DBT. It was also evident that the performance of the foam-supported catalysts surpassed that of the pellets, especially at low catalyst loadings, which resulted in thin washcoat layer and therefore, small diffusional paths. The results confirmed the process-intensifying characteristic of the coated foam which ensures sufficient contact between the catalyst and the LOHC.

Besides, the H₁₈DBT recycle tests in the FBR revealed the effect of consecutive dehydrogenations of the liquid product on the H₂ released and cumulated DoD at the end of each cycle.

- II. During the PAR process, the performance of the foam-based recombiner was compared to that of plate-based and pellet-based recombiners using the same amount of Pt/Al₂O₃ catalyst in order to understand the effect of the geometric configuration of the catalyst bed. Although the H₂ recombination reaction on Pt-based catalysts is characterised by spontaneous, fast kinetics, the experiments revealed the importance of high surface support in the PAR process.

Additionally, a 3D heterogeneous CFD simulation was conducted as an attempt to understand the detailed flow patterns, concentration and temperature profiles inside the foam-based recombiner at different operating conditions.

- III. The study of the direct-CO₂-to-MeOH synthesis in a bench-scale foam-based reactor expanded the current knowledge on the application of process-intensifying reactors in chemical processes. The experiment results demonstrated the ability of the coated foam to be considered as suitable catalyst bed for the direct CO₂ hydrogenation to MeOH. The results also revealed the ability the metal foam to maintain a uniform temperature profile inside the catalyst bed.

- IV. The numerical study of the direct-CO₂-to-MeOH synthesis in the foam-based reactor resulted in the development and validation of a 3D pseudo-homogeneous CFD model that included simplified and optimised kinetic rate expressions. This model was used to assess the contribution of each of the two reactor modules to the overall process performance. The validated model was also utilised for the comparison study between a foam-based and pellet-based reactors. This model can be considered for further optimisation of the geometric characteristics in the design of direct-CO₂-to-MeOH synthesis reactor on a similar catalyst.

7.3 Recommendations for future studies

This study was limited to a simple analysis of the performance of the foam-based catalytic structure in selected H_2 applications. There is a vast opportunity to delve deeper into each of the topics explored in the present study. The following paragraphs will summarise suggestions for future studies.

In this work, diffusion and kinetics limitations were perceived as important factors in the determination of the advantage of coating a catalyst on foam structures used in specific chemical processes. There is therefore a need to design a more quantitative technique, based on dimensionless ratios (e.g. Damköhler number or Thiele modulus) to assess the suitability of the foam as catalyst support structures for a given process.

The characteristics of the foam-supported catalyst not only depend on the procedure used during the manufacture of the foam but also the method used for catalyst deposition. In our investigation, the foam geometric properties (e.g. porosity, pore density) were kept constant for each of the selected processes. It would be interesting to explore the effect of a change in the foam geometric properties on the catalytic performance of a system. The foam coating method was limited to dip-coating of ready-made catalysts. The experimental investigation on the foam as catalyst support structures could be extended to studies on the use of different coating methods and their effects on process performances.

The numerical simulations were conducted at macroscale level, to predict the overall reactor performance. In order to fully describe foam-based process reported in this study, future works could focus on using heterogeneous simulations for the detailed quantification of heat and mass transfer coefficients at microscale level.

Appendix A. Supplementary materials – LOHC dehydrogenation on metal foams

A.1 Catalyst surface composition

Table A-1 provides the surface composition of the foam-supported and pellet-based Pt/Al₂O₃ catalysts as obtained from the EDS analysis. More Pt is present on the surface of the pellet than on the surface of the coated foam (7.43 vs 5.26 %). The higher Pt content on the surface of the pellet could have originated from the preparation method (wet impregnation of Al₂O₃ pellets), which gives the pellets an eggshell structure. More Pt is present on the surface than in the core of the catalyst pellet.

Table A-1. Elemental composition of the catalyst surface (EDS analysis).

Element	O	Al	S	Cl	K	Ca	Fe	Rh	Pt
Foam	43.01	50.61	0.0	0.86	0.05	0.21	0.0	0.0	5.26
Pellets	43.66	44.81	0.12	3.07	0.38	0.09	0.1	0.33	7.43

A.2 Results of liquid and gas analysis

Fig. A-1 illustrates the structures of some of the compounds detected during the analysis of low-boilers, liquid by-products of H₁₈DBT dehydrogenation. The by-products are mainly the results of the cracking of the LOHC molecules present in the dehydrogenated liquid. High-boilers (molar mass > 268 g/mol) were also detected; however, their structures were not elucidated with absolute certainty from the available database.

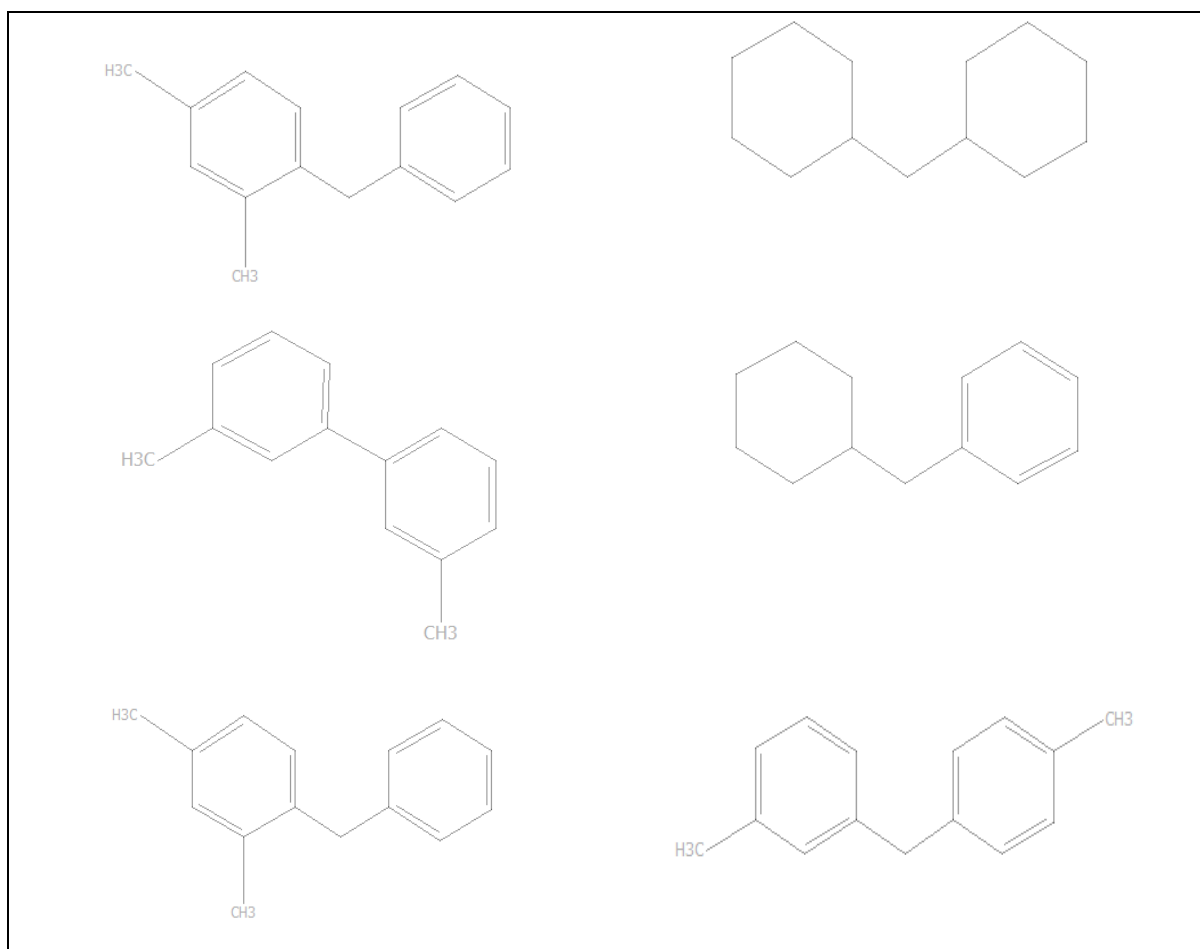


Figure A-1. Structures of low-boilers, by-products produced during the dehydrogenation of H₁₈DBT.

Chromatograms obtained during the analysis of the gas products obtained during the dehydrogenation of H₁₈DBT in the foam-based and pellet-based reactors are shown in Fig. A-2. During H₁₈DBT dehydrogenation on the foam-supported or pellet-based catalysts, only H₂ was detected as a product of the reaction. No CO, CO₂, or CH₄ was detected. The small N₂ peak in Fig. A-2a was caused by air contamination during the handling of the gas sampling bag.

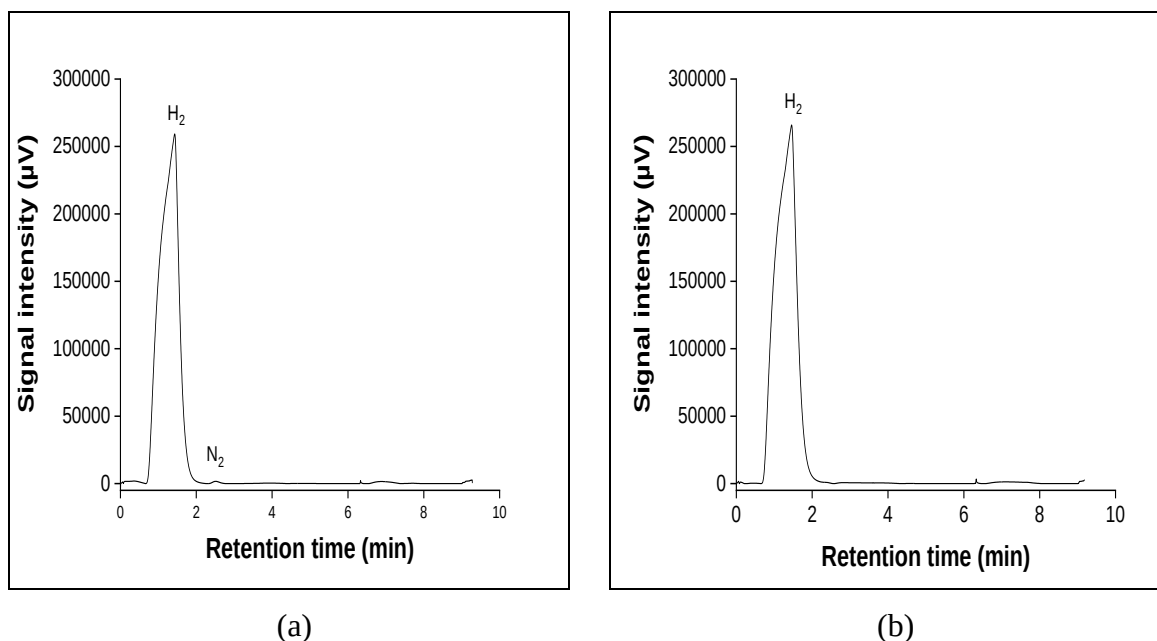


Figure A-2. Chromatograms from analysis of the gas products obtained during the dehydrogenation of H₁₈DBT at 300°C and a Pt/H₁₈DBT ratio of 0.4 mol.%: (a) foam-based reactor; (b) pellet-based reactor.

A.3 Comparison between the catalytic performance of the foam-supported and powder-based Pt/Al₂O₃

Fig. A-3 shows the H₂ release rates on the foam-supported and powder-based Pt/Al₂O₃ catalyst. CO pulse chemisorption tests revealed that the Pt/Al₂O₃ powder had higher metal dispersion and a higher Pt surface area (19% and 46 m²/g on the coated foam and 28% and 69 m²/g on the powder). The initial H₂ release in the powder-based reactor was higher than, or similar to, that in the foam-based reactor. Due to the transition between reaction steps in the dehydrogenation process, the H₂ release decreases in both the foam- and powder-based reactors; however, this occurs more rapidly in the latter. Noting the fact that the reactors were not stirred, the foam support structure has the advantage of occupying a greater volume than the catalyst powder or pellets in the LOHC. This causes it to be exposed to more unreacted H₁₈DBT, which, by nature, is slightly less dense than dehydrogenated H₀DBT. Therefore, after the initial rapid H₂ release, as the gas evolution subsides, less mixing occurs within the liquid phase, causing the powder

to settle at the bottom of the reactor, while the foam remains exposed to unreacted, less dense $H_{18}DBT$.

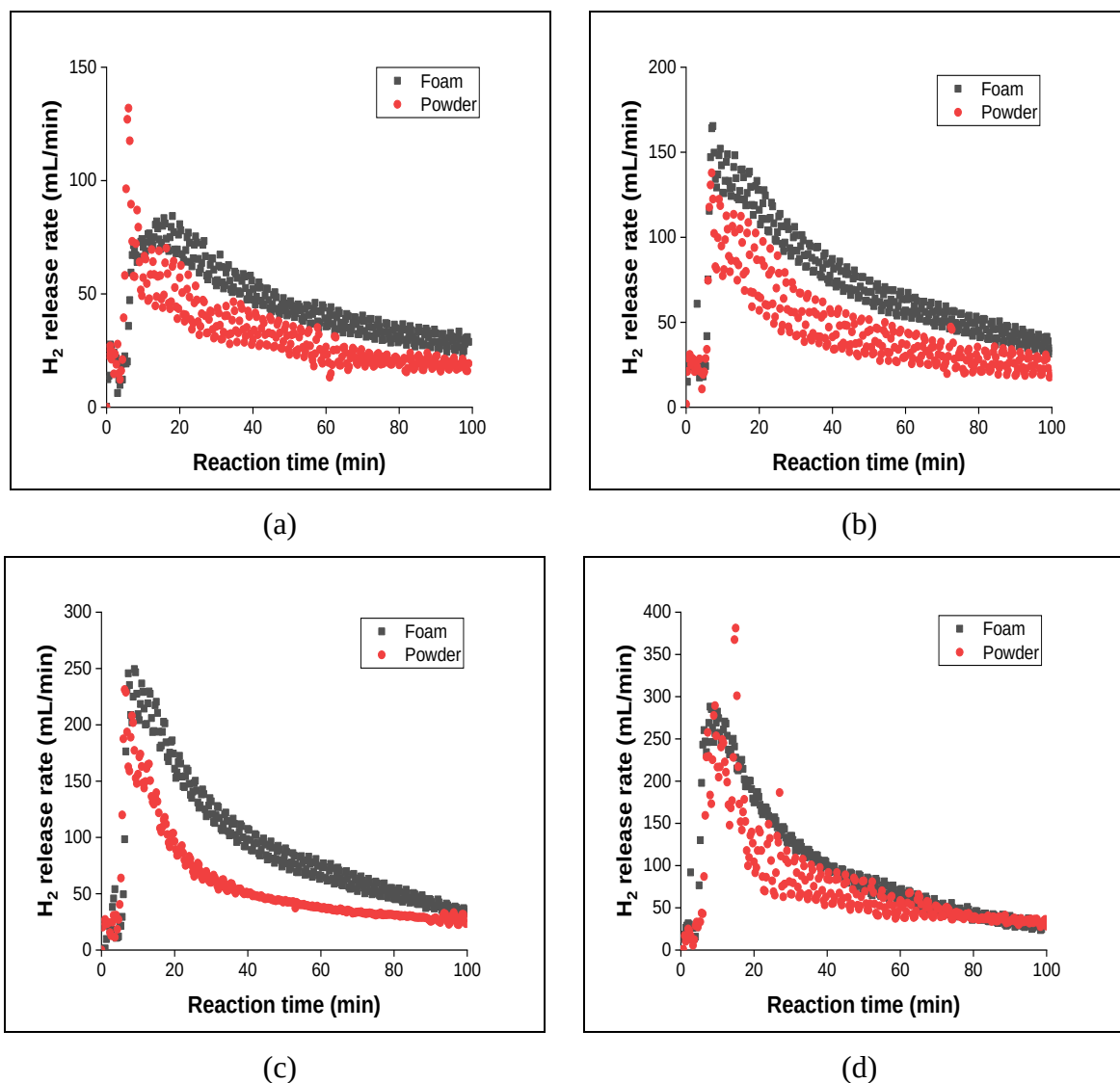


Figure A-3. Evolution of release rate with reaction time at various Pt/LOHC mol. ratios: (a) 0.05, (b) 0.1, (c) 0.2, and (d) 0.4 mol.%. ($H_{18}DBT$ volume, 20 mL; reaction time, 100 min; reaction temperature, 300°C.)

Appendix B. Supplementary materials – PAR on surface-extended catalysts

B.1 Effect of gas flow conditions H_2 conversions achieved in the plate-based and pellet-based recombiners

Fig. B-1 shows the H_2 conversions obtained on the plate-based and pellet-based recombiners at different inlet gas velocities and H_2 concentrations. The effect of the inlet gas velocity and H_2 concentration on the H_2 conversions on the Pt/ Al_2O_3 -coated plates and Pt/ Al_2O_3 pellets show similar trends to those observed on the metal foam. Increasing the H_2 inlet concentration has a very limited effect on the H_2 conversion. This could be due to an increase in the diffusion layer as more H_2 is fed to the reactor inlet.

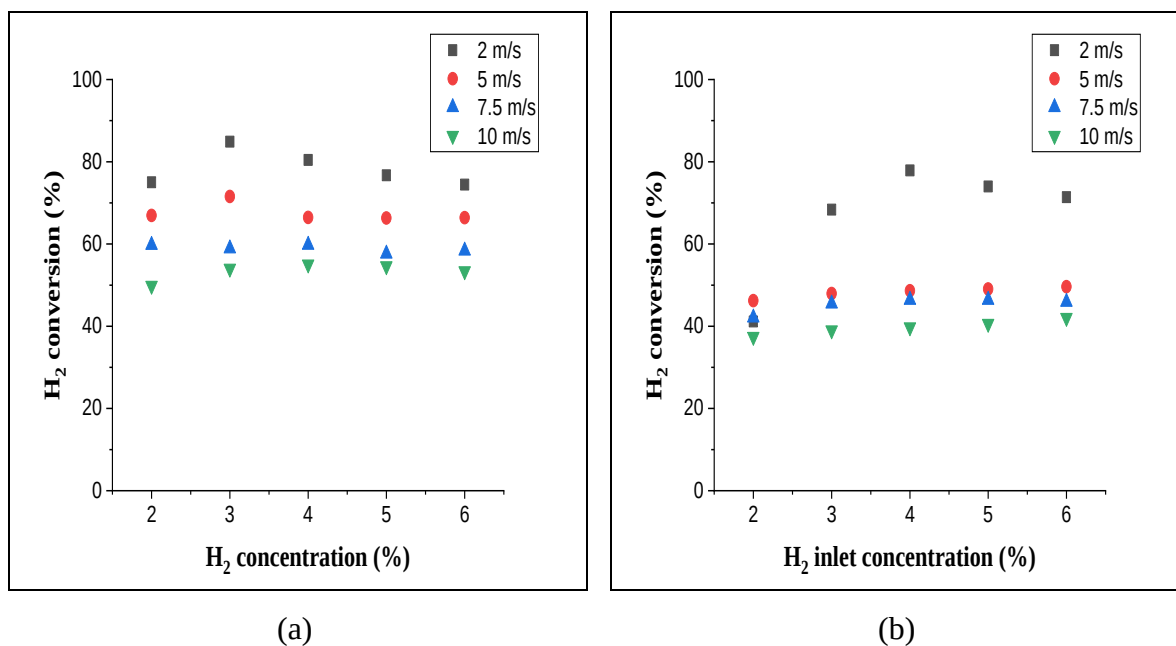


Figure B-1. Effect of inlet gas velocity and H_2 concentration on H_2 conversions obtained (a) on plates and (b) on pellets.

B.2 Temperature profiles in the plate-based recombiner

Fig. B-2 shows the mean temperatures obtained on the four Pt/Al₂O₃-coated plates at different inlet gas velocities and inlet H₂ concentrations.

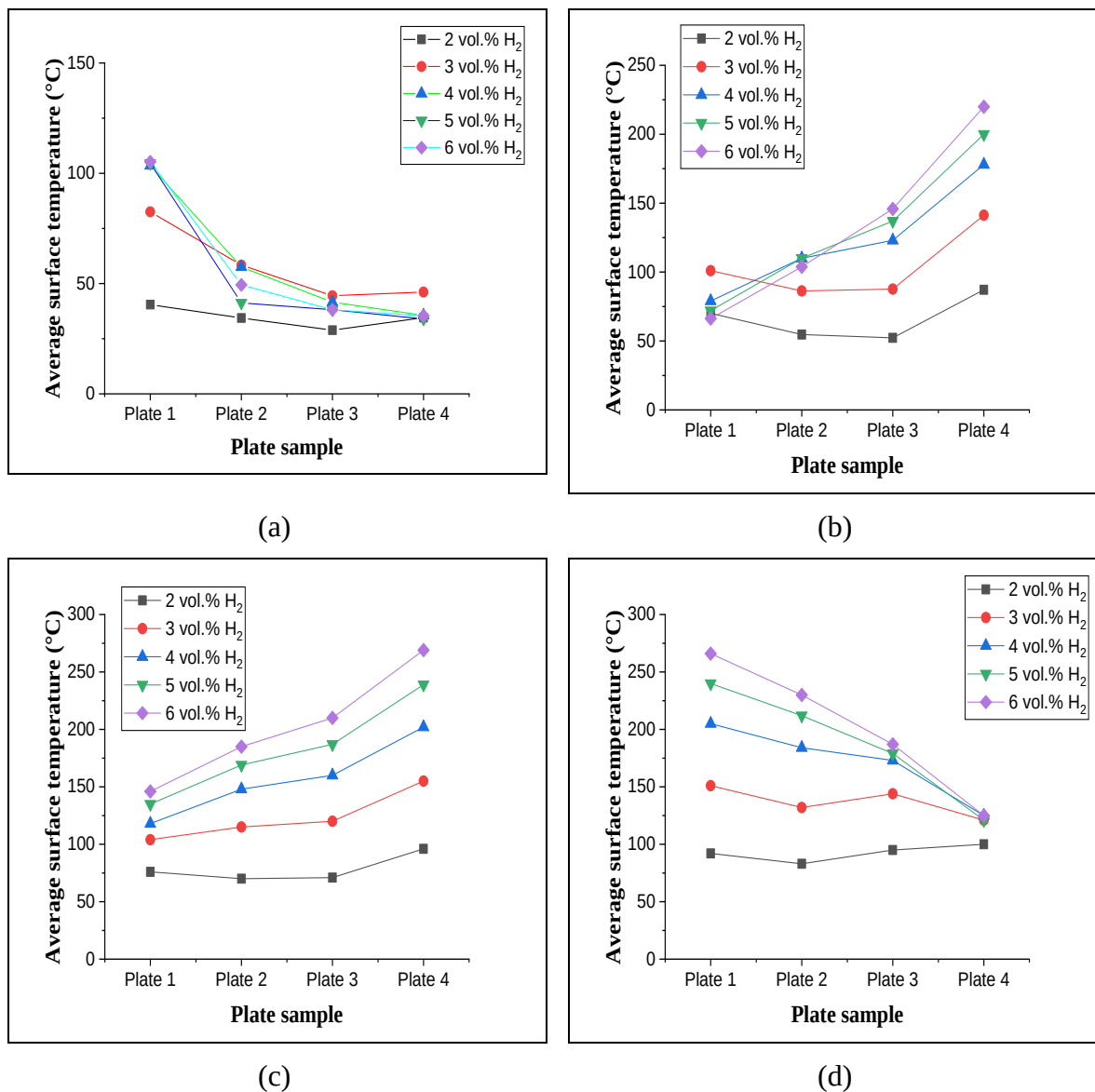


Figure B-2. Average temperatures on plates at (a) 2 m/s, (b) 5 m/s, (c) 7.5 m/s and (d) 10 m/s gas inlet velocities.

As was observed for the foam-based recombiner, the temperatures obtained on the four plates are not uniform. The flow dynamics inside the bench-scale recombiner are not straightforward and can be affected by several factors, including the turbulence inside device, the different heating rates – and H₂ conversion rates – on each of the plates.

B.3 Maximum temperatures measured in the foam-based and plate-based recombiners

Fig. B-3 shows the maximum temperatures obtained on the foam and plates at a gas inlet velocity of 10 m/s, the gas velocity at which the highest temperatures were obtained in this investigation. The temperatures on the foams are 17–29% higher than those on the plates. It is anticipated that the foam-based catalyst bed would heat up more than the plate-based bed because less material is used in the foam-based recombiner. However, it was observed that the average temperatures on the foam surfaces were similar to, or lower than, temperatures on the plates. This is an indication of the rapid heat dissipation potential offered by the foam-based system.

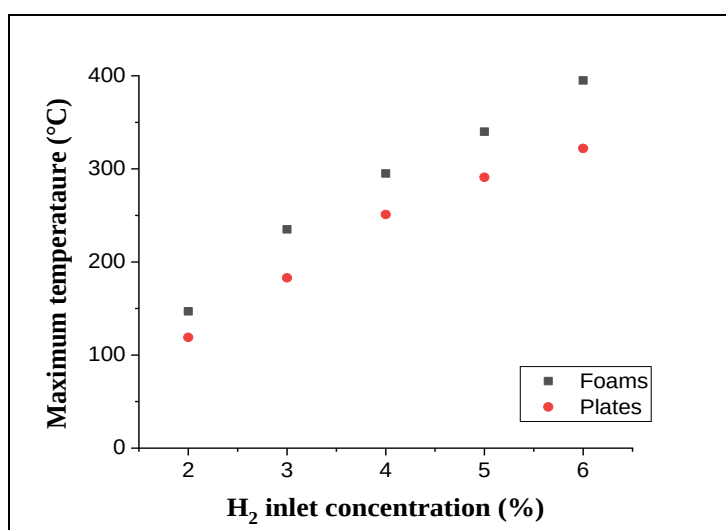


Figure B-3. Temperatures at the hottest spots recorded at a gas inlet velocity of 10 m/s in the foam-based recombiner.

Appendix C. Supplementary materials – Direct CO₂-to-methanol synthesis on metal foam

Nomenclature	
f	Fugacity, mol/m ³
G	Gibbs free energy, J/mol
N_{ij}	Number of moles of component i in reaction j
R_{const}	Ideal gas constant, J/K/mol
T	Temperature, K
Greek symbols	
μ_i	Chemical potential of component i , J/mol
Superscript	
^{o}	Standard state

The citations used in this section follow the style and numbering used in Chapter 5. The references are included in the ‘References’ section, at the end of Chapter 5.

C.1 Scanning electron microscopy–Energy dense X-Ray spectroscopy of the Cu/ZnO/Al₂O₃ catalyst

SEM-EDS results confirmed the presence of Cu, Zn, Al and O in the catalyst. The SEM micrograph (Fig. C-1a) shows a catalyst consisting of a large number of isolated and agglomerated globular catalyst particles. The EDS maps (Fig. C-1b) show a very homogeneous distribution of Cu, Zn and Al in the catalyst, which is expected to result in beneficial interactions between well-mixed and uniformly spread nanoparticles, especially Cu and ZnO.

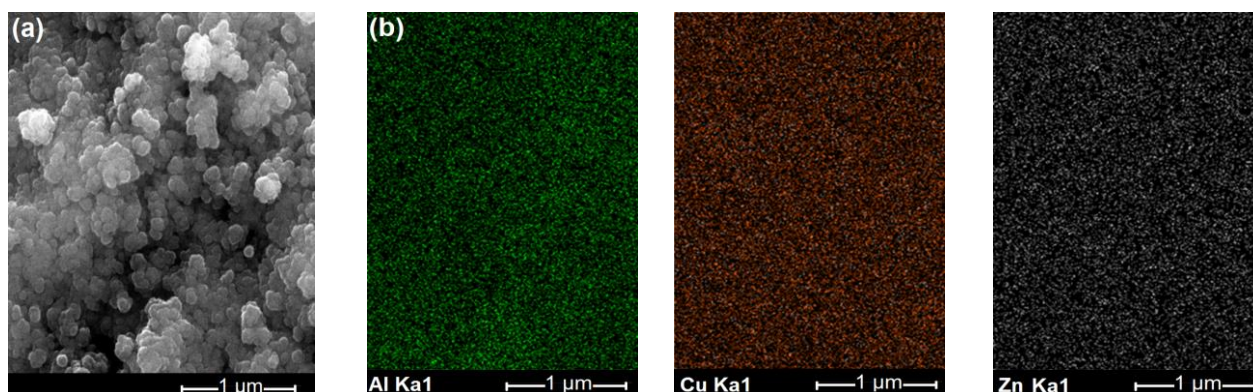


Figure C-1. Commercial Cu/ZnO/Al₂O₃ catalyst: (a) morphology displayed on the SEM micrograph and (b) EDS maps of elemental distribution: Al (green), Cu (red) and Zn (black).

C.2 N₂ adsorption/desorption profile of the Cu/ZnO/Al₂O₃ catalyst

The N₂ adsorption/desorption profile of the catalyst (Fig. C-2) corresponds to a Type IV isotherm with a H1 hysteresis loop, which is a characteristic of catalysts with a mesoporous structure [48].

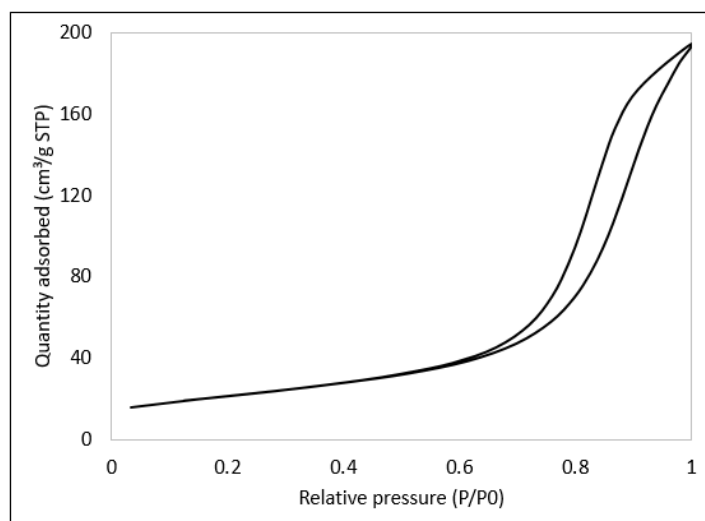


Figure C-2. Isothermal (-196°C) linear plot of the N₂ adsorption/desorption on the Cu/ZnO/Al₂O₃ catalyst.

C.3 X-ray diffractogram of the Cu/ZnO/Al₂O₃ catalyst

The XRD diffractogram of the catalyst (Fig. C-3) confirmed the presence of CuO and ZnO. Al₂O₃ peaks were not visible, probably because of their low content or amorphous nature.

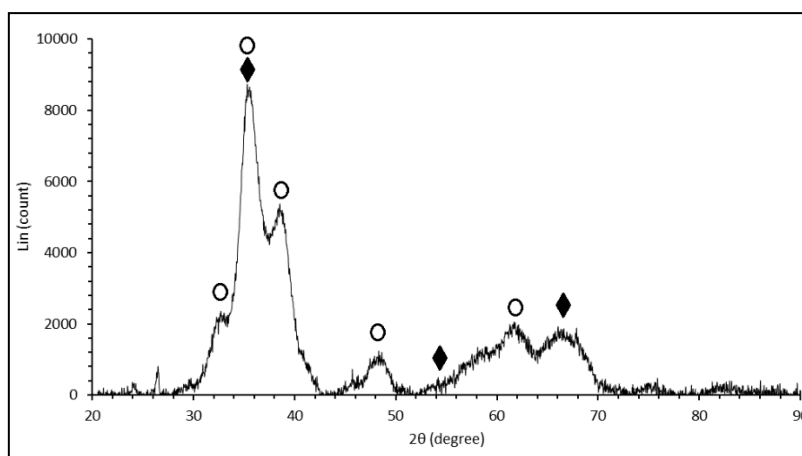


Figure C-3. XRD diffractogram of the Cu/ZnO/Al₂O₃ catalyst showing typical CuO (◆) and ZnO (○) peak positions as reported in the literature [14,18,39].

C.4 Transmission electron microscopy of the Cu/ZnO/Al₂O₃ catalyst

The TEM micrographs (Fig. C-4) reveal that the catalyst components (Cu, ZnO and Al₂O₃) are hardly distinguishable. Furthermore, the fact that the particles are not well shaped can also denote a low level of crystallinity of the catalyst components [9], TEM micrographs suggest an intimate contact between Cu and ZnO particles. This has been reported to enhance the catalytic performance of Cu/ZnO/Al₂O₃ [9,14].

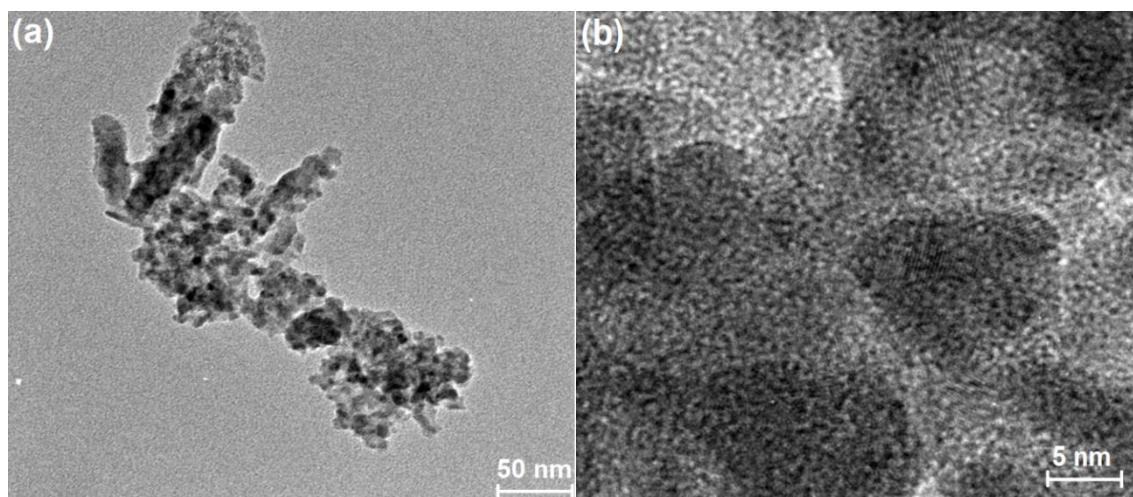


Figure C-4. Cu/ZnO/Al₂O₃ catalyst: (a) low-magnification and (b) high-magnification TEM micrographs.

C.5 Catalyst temperature programmed reduction profile

H₂ temperature programmed reduction profile (Fig. C-5) was used for the determination of the Cu/ZnO/Al₂O₃ catalyst reduction temperature. A reduction temperature of 230°C was used in the reduction of the catalyst prior to experiments.

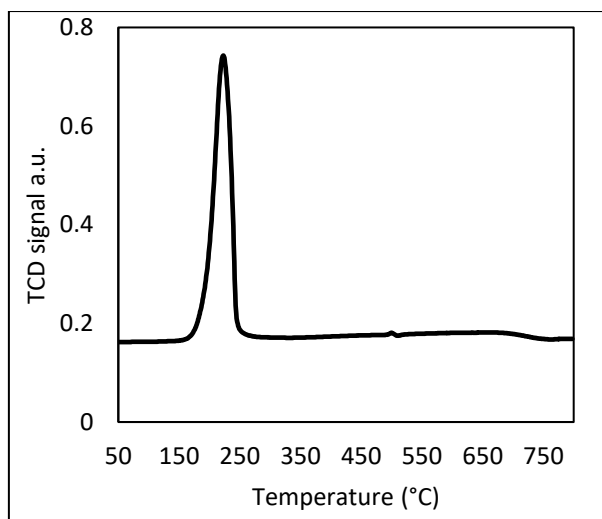


Figure C-5. H_2 -TPR profile of the Cu/ZnO/Al₂O₃ catalyst.

C.6 Equilibrium calculations

Equilibrium calculations were performed using ASPEN v8.6 Gibbs equilibrium reactor (RGibbs). In order to simulate the direct CO₂-to-MeOH process, and generate the equilibrium CO₂ conversion and methanol selectivity curves, the feed composition was set to 75% H₂ and 25% CO₂, and the products were set to include CO, H₂O, the unreacted CO₂ and H₂. The RGibbs works on the principle of Gibbs free energy minimisation, which is a non-stoichiometric method, assuming that a system of n components involved in r reactions is thermodynamically favoured when the change in Gibbs dG free energy is minimum [49,50].

$$dG = \sum_{i=1}^n \sum_{j=1}^r \mu_i dN_{ij} = 0.$$

In Eq. B1, the chemical potential μ_i of component i is calculated by

$$\mu_i = R_{const} T \left[G_i^0 + \ln \left(\frac{f_i}{f_i^0} \right) \right].$$

Neither methane nor other hydrocarbons were part of the product gas. Hence, the CO₂ hydrogenation to MeOH and reverse water gas shift were the only possible reactions in the system.

C.7 Long-term catalytic activity test: an initial observation

The direct-CO₂-to-MeOH catalytic activity tests were extended to a durability study to observe the stability of the performance of the commercial Cu/ZnO/Al₂O₃ catalyst after its initial exposure (> 70 h) to different operating conditions in the foam-based reactor. The Long-term

test was conducted for ~110 hours, at an inlet gas flow rate of 2 NL/min, a pressure of 30 bar and a temperature of 230°C. It was observed that the catalyst exhibited a relatively stable performance during the entire test period (Fig. C-6). This is not unexpected for commercial Cu/ZnO/Al₂O₃ catalysts, which have often demonstrated highly stable catalytic performance for extended reaction times [7,21].

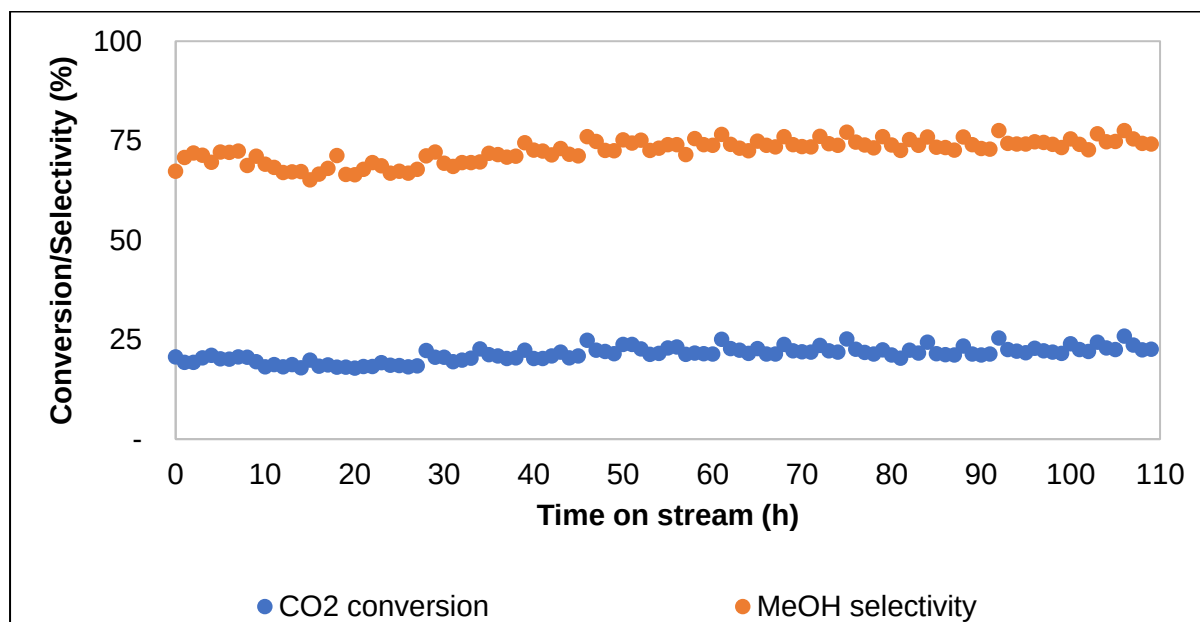


Figure C-6. Preliminary direct CO₂-to-MeOH synthesis durability test performed at a pressure of 30 bar, a temperature of 230°C and a flow of 2 NL/min.

This observation is only a preliminary conclusion which suggests a relatively high stability in the performance of the commercial foam-supported Cu/ZnO/Al₂O₃ used in this study. Nevertheless, longer tests (several more days) are required to confirm this initial observation.

Appendix D. Statement from co-authors

STATEMENT FROM CO-AUTHORS

To whom it may concern

I, *Nicolaas Engelbrecht*, hereby give Kyatsinge Cédric Musavuli consent to use the publication listed below, of which I am co-author, in the thesis entitled “*Surface extended catalyst support structures for hydrogen energy applications*”. The thesis is submitted for the degree *Doctor Philosophiae in Chemical Engineering* at the Potchefstroom campus of the North-West University, South Africa.

Musavuli, K.C., Engelbrecht, N., Everson, R.C., Modisha, P., Kolb, G., Zapf, R., Hofmann, C., Bessarabov, D. 2023. Experimental Evaluation of a Coated Foam Catalytic Reactor for the Direct CO₂-to-Methanol Synthesis Process. *ChemEngineering*, 7(5), 16.

As a current *Postdoctoral fellow at Aarhus University, Denmark*, my involvement in the research paper was to *design, procure components for, and oversee the assembly of the balance-of-plant around the methanol synthesis reactor. I was also involved in providing feedback on the revised draft of the manuscript before publication in the journal: ChemEngineering.*

Nicolaas Engelbrecht

Signature

15/10/2024

Date

STATEMENT FROM CO-AUTHORS

To whom it may concern

I, Dr. Gunther Kolb, hereby give Kyatsinge Cédric Musavuli consent to use the publication listed below, of which I am co-author, in the thesis entitled “*Surface extended catalyst support structures for hydrogen energy applications*”. The thesis is submitted for the degree *Doctor Philosophiae in Chemical Engineering* at the Potchefstroom campus of the North-West University, South Africa.

Musavuli, K.C., Engelbrecht, N., Everson, R.C., Modisha, P., Kolb, G., Zapf, R., Hofmann, C., Bessarabov, D. 2023. Experimental Evaluation of a Coated Foam Catalytic Reactor for the Direct CO₂-to-Methanol Synthesis Process. *ChemEngineering*, 7(5), 16.

As the Head of the Energy Division at Fraunhofer Institute of Microengineering and Microsystems, my involvement in the research paper was to provide resources, reading and editing.

Gunther
Kolb

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von Gunther Kolb
Datum: 2024.10.24
11:53:12 +02'00'

Signature

22nd October 2024

Date

STATEMENT FROM CO-AUTHORS

To whom it may concern

I, Christian Hofmann, hereby give Kyatsinge Cédric Musavuli consent to use the publication listed below, of which I am co-author, in the thesis entitled “*Surface extended catalyst support structures for hydrogen energy applications*”. The thesis is submitted for the degree *Doctor Philosophiae in Chemical Engineering* at the Potchefstroom campus of the North-West University, South Africa.

Musavuli, K.C., Engelbrecht, N., Everson, R.C., Modisha, P., Kolb, G., Zapf, R., Hofmann, C., Bessarabov, D. 2023. Experimental Evaluation of a Coated Foam Catalytic Reactor for the Direct CO₂-to-Methanol Synthesis Process. *ChemEngineering*, 7(5), 16.

As head of the group Reformer- and reactor technology at Fraunhofer-IMM, my involvement in the research paper was reactor design and reactor realization.

Christian
Hofmann

Signature

Digital unterschrieben
von Christian Hofmann
Datum: 2024.10.22
10:55:54 +02'00'

22nd October 2024

Date

STATEMENT FROM CO-AUTHORS

To whom it may concern

I, Dr. Ralf Zapf, hereby give Kyatsinge Cédric Musavuli consent to use the publication listed below, of which I am co-author, in the thesis entitled “*Surface extended catalyst support structures for hydrogen energy applications*”. The thesis is submitted for the degree *Doctor Philosophiae in Chemical Engineering* at the Potchefstroom campus of the North-West University, South Africa.

Musavuli, K.C., Engelbrecht, N., Everson, R.C., Modisha, P., Kolb, G., Zapf, R., Hofmann, C., Bessarabov, D. 2023. Experimental Evaluation of a Coated Foam Catalytic Reactor for the Direct CO₂-to-Methanol Synthesis Process. *ChemEngineering*, 7(5), 16.

As a specialist for catalyst coating at Fraunhofer Institute for Microengineering and Microsystems, my involvement in the research paper was to coat the copper foam with the commercial Cu/ZnO/Al₂O₃ catalyst.

Ralf
Zapf

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unterscriben von
Ralf Zapf
Datum: 2024.11.04
12:43:48 +01'00'

Signature

22nd October 2024

Date

STATEMENT FROM CO-AUTHORS

To whom it may concern

I, **DG Bessarabov**, hereby give Kyatsinge Cédric Musavuli consent to use the publications listed below, of which I am a co-author, in the thesis entitled “*Surface extended catalyst support structures for hydrogen energy applications*”. The thesis is submitted for the degree *Doctor Philosophiae in Chemical Engineering* at the Potchefstroom campus of the North-West University, South Africa.

Musavuli, K.C., Engelbrecht, N., Everson, R.C., Modisha, P., Kolb, G., Zapf, R., Hofmann, C., Bessarabov, D. 2023. Experimental Evaluation of a Coated Foam Catalytic Reactor for the Direct CO₂-to-Methanol Synthesis Process. *ChemEngineering*, 7(5):16.

Musavuli, K.C. Malakhov, A., Everson, R.C., Kozhukhova, A., Modisha P. and Bessarabov, D. 2024. Passive autocatalytic recombination of hydrogen on a Pt/Al₂O₃-coated metal foam: Experimental evaluation and CFD modelling. *International Journal of Hydrogen energy*, 94:1374–1388.

Musavuli, K.C., Modisha, P., Everson, R.C., Malakhov, A. and Bessarabov, D. 2025. Metal Foam as Surface-Extended Catalyst Support Structure for Process Intensification in the Dehydrogenation of Perhydro-Dibenzyltoluene on a Pt/Al₂O₃ Catalyst. *Catalysts*, 15(1):44

As a Professor at North-West University (Potchefstroom Campus), Faculty of Engineering, South Africa, and Director of HySA Infrastructure (CoC), Faculty of Engineering, North-West University (Potchefstroom Campus), South Africa, my involvement in the research paper was project conceptualization and supervision, funding acquisition, manuscript reviewing and editing. I was also involved in providing feedback on the revised draft of the manuscript before publication.



Signature

05 February 2025

Date

STATEMENT FROM CO-AUTHORS

To whom it may concern

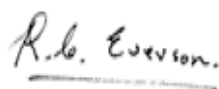
I, Prof. R.C. Everson, hereby give Kyatsinge Cédric Musavuli consent to use the publication listed below, of which I am a co-author, in the thesis entitled "*Surface extended catalyst support structures for hydrogen energy applications*". The thesis is submitted for the degree *Doctor Philosophiae in Chemical Engineering* at the Potchefstroom campus of the North-West University, South Africa.

Musavuli, K.C., Engelbrecht, N., Everson, R.C., Modisha, P., Kolb, G., Zapf, R., Hofmann, C., Bessarabov, D. 2023. Experimental Evaluation of a Coated Foam Catalytic Reactor for the Direct CO₂-to-Methanol Synthesis Process. *ChemEngineering*, 7(5):16.

Musavuli, K.C. Malakhov, A., Everson, R.C., Kozhukhova, A., Modisha P. and Bessarabov, D. 2024. Passive autocatalytic recombination of hydrogen on a Pt/Al₂O₃-coated metal foam: Experimental evaluation and CFD modelling. *International Journal of Hydrogen energy*, 94:1374–1388.

Musavuli, K.C., Modisha, P., Everson, R.C., Malakhov, A. and Bessarabov, D. 2025. Metal Foam as Surface-Extended Catalyst Support Structure for Process Intensification in the Dehydrogenation of Perhydro-Dibenzyltoluene on a Pt/Al₂O₃ Catalyst. *Catalysts*, 15(1):44

As a Professor at the School of Chemical and Minerals Engineering, North-West University, I hereby give permission to Kyatsinge Musavuli to submit the works which I co-authored toward the publication of his thesis. My contribution to the work was as the main supervisor involving conceptionalization, guidance and evaluation towards his studies from which the publications originated and in proofreading the work.



Signature

3rd February 2025

Date

STATEMENT FROM CO-AUTHORS

To whom it may concern

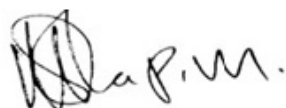
I, Phillimon Modisha, hereby give Kyatsinge Cédric Musavuli consent to use the publications listed below, of which I am a co-author, in the thesis entitled “*Surface extended catalyst support structures for hydrogen energy applications*”. The thesis is submitted for the degree *Doctor Philosophiae in Chemical Engineering* at the Potchefstroom campus of the North-West University, South Africa.

Musavuli, K.C., Engelbrecht, N., Everson, R.C., Modisha, P., Kolb, G., Zapf, R., Hofmann, C., Bessarabov, D. 2023. Experimental Evaluation of a Coated Foam Catalytic Reactor for the Direct CO₂-to-Methanol Synthesis Process. *ChemEngineering*, 7(5):16.

Musavuli, K.C. Malakhov, A., Everson, R.C., Kozhukhova, A., Modisha P. and Bessarabov, D. 2024. Passive autocatalytic recombination of hydrogen on a Pt/Al₂O₃-coated metal foam: Experimental evaluation and CFD modelling. *International Journal of Hydrogen energy*, 94:1374–1388.

Musavuli, K.C., Modisha, P., Everson, R.C., Malakhov, A. and Bessarabov, D. 2025. Metal Foam as Surface-Extended Catalyst Support Structure for Process Intensification in the Dehydrogenation of Perhydro-Dibenzyltoluene on a Pt/Al₂O₃ Catalyst. *Catalysts*, 15(1):44

As Associate Professor, my involvement in the research paper was to conceptualize and review/edit.



Signature

2025/02/03

Date

STATEMENT FROM CO-AUTHORS

To whom it may concern

I, **AA Malakhov**, hereby give Kyatsinge Cédric Musavuli consent to use the publications listed below, of which I am a co-author, in the thesis entitled “*Surface extended catalyst support structures for hydrogen energy applications*”. The thesis is submitted for the degree *Doctor Philosophiae in Chemical Engineering* at the Potchefstroom campus of the North-West University, South Africa.

1. Musavuli, K.C., Malakhov, A., Everson, R.C., Kozhukhova, A., Modisha P. and Bessarabov, D. 2024. Passive autocatalytic recombination of hydrogen on a Pt/Al₂O₃-coated metal foam: Experimental evaluation and CFD modelling. *International Journal of Hydrogen energy*, 94:1374–1388.
2. Musavuli, K.C., Modisha, P., Everson, R.C., Malakhov, A. and Bessarabov, D. 2025. Metal Foam as Surface-Extended Catalyst Support Structure for Process Intensification in the Dehydrogenation of Perhydro-Dibenzyltoluene on a Pt/Al₂O₃ Catalyst. *Catalysts*, 15(1):44

As a Post-Doctoral Research Fellow at HySA Infrastructure, North-West University, South Africa, my involvement in the research paper 1 was to design a CFD model of the catalytic hydrogen recombination of a foam-based catalyst and numerical analysis of the catalyst performance for PAR and compare calculated results with experimental data. I was also involved in providing feedback on the revised draft of the manuscript before publication in the International Journal of Hydrogen Energy.

As a Post-Doctoral Research Fellow at HySA Infrastructure, North-West University, South Africa, my involvement in the research paper 2 was to investigate performance of Pt/Al₂O₃ catalyst coated on aluminium (Al) foam in a tank reactor and an FBR for process intensification in the dehydrogenation of perhydro-dibenzyltoluene. I was also involved in providing feedback on the revised draft of the manuscript before publication in the Catalysts journal.

Malakhov AA

03 February 2025

Signature

Date

STATEMENT FROM CO-AUTHORS

To whom it may concern

I, **Alina Kozhukhova**, hereby give Kyatsinge Cédric Musavuli consent to use the publications listed below, of which I am a co-author, in the thesis entitled “*Surface extended catalyst support structures for hydrogen energy applications*”. The thesis is submitted for the degree *Doctor Philosophiae in Chemical Engineering* at the Potchefstroom campus of the North-West University, South Africa.

Kyatsinge Cédric Musavuli, Alexander Malakhov, Raymond Cecil Everson, Alina Kozhukhova, Phillimon Modisha and Dmitri Bessarabov. 2024. Passive autocatalytic recombination of hydrogen on a Pt/Al₂O₃-coated metal foam: Experimental evaluation and CFD modelling. *International Journal of Hydrogen Energy*, 94,1374–1388.

As **Postdoctoral Researcher at North-West University**, my involvement in the research paper was **Writing – Review and Editing**.



Signature

18th November 2024

Date

Appendix E. Research articles and conferences related to this study

This section lists the research papers (front pages attached) and conferences attended in which the results obtained in this project were presented.

E.1 Published articles

Musavuli, K.C., Modisha, P.; Everson, R.C.; Malakhov, A.; Bessarabov, D. 2025. Metal foam as surface-extended catalyst support structure for process intensification in the dehydrogenation of perhydro-dibenzyltoluene on a Pt/Al₂O₃ catalyst. *Catalysts*, 15(1):44.

Musavuli, K.C., Malakhov, A., Everson, R.C., Kozhukhova, A., Modisha, P. and Bessarabov, D. 2024. Passive autocatalytic recombination of hydrogen on a Pt/Al₂O₃-coated metal foam: Experimental evaluation and CFD modelling. *International Journal of Hydrogen energy*, 94:1374–1388.

Musavuli, K.C., Engelbrecht, N., Everson, R.C., Modisha, P., Kolb, G., Zapf, R., Hofmann, C., Bessarabov, D. 2023. Experimental evaluation of a coated foam catalytic reactor for the direct CO₂-to-methanol synthesis process. *ChemEngineering*, 7(5):16.

E.2 Conferences attended

Musavuli, K. C., Engelbrecht, N., Everson, R. C., Modisha, P., Kolb, G., Zapf, R., Hofmann, C. & Bessarabov, D. 2023. Experimental Evaluation of a Coated Foam Catalytic Reactor for the Direct CO₂-to-Methanol Synthesis Process [Oral presentation]. Syngas Convention 4, 2–5 April 2023, Cape Town, South Africa.

Musavuli, K. C., Engelbrecht, N., Everson, R. C., Modisha, P., Kolb, G., Zapf, R., Hofmann, C. & Bessarabov, D. 2023. Experimental Evaluation of a Coated Foam Catalytic Reactor for the Direct CO₂-to-Methanol Synthesis Process [Poster presentation]. International Partnership for Hydrogen and Fuel Cells in the Economy, 24–25 April 2023, Pretoria, South Africa.

Musavuli K.C., Modisha P., Everson R.C. & Bessarabov D. 2023. Experimental evaluation of a foam-based packed bed reactor for the catalytic dehydrogenation of perhydro-dibenzyltoluene. [Poster presentation]. Catalysis society of South Africa (CATSA), 5–8 November 2023, Mossel Bay, South Africa.

Article

Metal Foam as Surface-Extended Catalyst Support Structure for Process Intensification in the Dehydrogenation of Perhydro-Dibenzyltoluene on a Pt/Al₂O₃ Catalyst

Kyatsinge Cedric Musavuli ¹, Phillimon Modisha ¹, Raymond Cecil Everson ², Alexander Malakhov ¹
and Dmitri Bessarabov ^{1,*}

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Abstract: Dibenzyltoluene/perhydro-dibenzyltoluene (H₀DBT/H₁₈DBT) is considered a promising liquid organic hydrogen carrier (LOHC) pair for the storage and transportation of green hydrogen (H₂). However, at the point of use, the catalytic dehydrogenation of H₁₈DBT is still limited by mass transport limitations. To address this issue, the dehydrogenation of H₁₈DBT was successfully conducted on Pt/Al₂O₃-coated foams in both an unstirred tank reactor and a fixed-bed reactor (FBR). A performance comparison between coated foams and pellets in the tank reactor revealed that H₂ productivities were 12–59% higher in the foam-based reactor than in the pellet-based reactor. Since the textural properties of the foam-supported and pellet-based catalysts were similar, the higher degree of dehydrogenation (DoD) and H₂ productivity achieved by the former were attributed to the geometric properties of the foam structure. Long-term tests performed in the FBR demonstrated the ability of the coated foams to maintain steady activity for >16 h on stream. However, the single-pass DoDs achieved were 34–38%. By recycling the partially dehydrogenated products three times into the FBR, the DoD improved to 63%. The results of this study demonstrated the capabilities of the coated foams in the process intensification of LOHC dehydrogenation reactors.

Keywords: hydrogen storage; LOHC; perhydro-dibenzyltoluene; metal foam; process intensification



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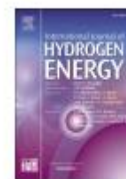
1. Introduction

In recent decades, green hydrogen (H₂) has been considered a very attractive energy carrier. It is a gas of high energy density (120 MJ/kg) that can be converted into energy through environmentally friendly processes [1]. H₂ also has the potential to minimise the gap between energy supply and demand caused by the fluctuating nature of widely used renewable energy sources such as wind and solar power [2–4]. Due to the low density of H₂ at normal temperature and pressure conditions and its tendency to diffuse through metals, establishing an energy distribution system partly relying on the storage of excess renewable energy in the form of green H₂ presents several practical challenges. For instance, the current methods of H₂ storage and transportation are energy-intensive, relatively unsafe; and, therefore, costly [5,6]. Compressed and liquid H₂ requires harsh conditions such as



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journal homepage: www.elsevier.com/locate/hjePassive autocatalytic recombination of hydrogen on a Pt/Al₂O₃-coated metal foam: Experimental evaluation and CFD modellingKyatsinge Cédric Musavuli^a, Alexander Malakhov^a, Raymond Cecil Everson^b, Alina Kozhukhova^a, Phillimon Modisha^a, Dmitri Bessarabov^{a,*}^a HySA Infrastructure Centre of Competence, Faculty of Engineering, North-West University, Private Bag X6001, Potchefstroom, 2531, South Africa^b Centre of Excellence in Carbon-based Fuels, School of Chemical and Minerals Engineering, Faculty of Engineering, North-West University, Private Bag X6001, Potchefstroom, 2531, South Africa

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ABSTRACT

Pt/Al₂O₃-coated Al foams were tested for the passive autocatalytic recombination of H₂. The characterisation of the washcoat surface confirmed the uniform distribution of Pt and Al₂O₃ over the entire washcoat surface. Transmission electron microscopy results revealed a slight increase in particle size from 3.8 to 6.2 nm after prolonged reaction. High H₂ conversions of 57–89% are achieved and the catalyst activity is maintained for >480 h on stream. The performance of the foam-based catalyst bed is similar to that of plates but surpasses that of catalyst pellets. Temperatures recorded at the hottest spots on the foam surface reach a maximum of only 393 °C at the highest H₂ inflow. Computational fluid dynamics simulations were performed on the actual foam geometry obtained using computed tomography. The simulations demonstrate the importance of thermal radiation in the model. There is good agreement between results of experimental H₂ conversions and maximum combustion temperatures.

1. Introduction

In order to limit the global temperature rise to <1.5 °C by 2050, the industrial sector is slowly shifting from fossil fuel to low- or zero-carbon energy sources, such as hydroelectricity, tidal, geothermal, solar and wind energy. Due to the irregular distribution and intermittent nature of several of these sources, causing an imbalance between energy supply and demand, several energy storage technologies are currently being developed. They include flywheels, superconductors, supercapacitors, batteries, compressed air, pumped hydro, phase change materials (latent heat) and chemical storage [1–4]. The chemical storage technique is considered as one of the most realistic options for long-term storage of relatively large amount of energy. This method consists using excess renewable power to produce a chemical compound, known as energy carrier [5]. Green H₂, produced by water electrolysis, has been proposed as a suitable energy carrier due to its high gravimetric energy density (120 MJ/kg), the relative maturity of its production and utilisation technologies [6]. It is also a highly versatile gas; it can be used for energy production in fuel cells or microcombustors, the reduction of metal ores, and the synthesis of industrial chemical products (ammonia, methane,

methanol) and sustainable aviation fuels [7,8].

With such an increasing amount of H₂ being handled in industries of various sizes, there is a clear need for the application of strict safety measures [9]. H₂ leaks in air can pose significant risks of deflagration or detonation in an environment where the gas' self-ignition temperature of ~585 °C is reached within its flammability limits (4–75 vol% H₂ at normal temperature and pressure) [10,11]. Reported methods of H₂ removal include ventilation, deliberate ignition and passive autocatalytic recombination (PAR) [12]. For risk mitigation, ventilation is not always effective due to the high buoyancy of H₂, which can cause the gas to accumulate in dead corners and increase the formation of high-risk zones near the upper sections of confined spaces. On the other hand, deliberate ignition could cause the unintentional formation of NO_x gases as combustion temperatures increase to >800 °C [13]. The advantage of PAR technology lies in its ability to prevent the accumulation of H₂. Spontaneous combustion commences at ambient temperature, at low H₂ concentrations (i.e., within the first instants of an accidental leak), without reaching temperatures favourable to the formation of NO_x, and releasing only water as product (Eq. (1)) [14]. A recombiner can be installed in confined or semi-confined spaces, as well as underground

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Article

Experimental Evaluation of a Coated Foam Catalytic Reactor for the Direct CO₂-to-Methanol Synthesis Process

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Abstract: The era of considering carbon dioxide (CO₂) as a waste stream has passed. New methods of utilising CO₂ as a carbon feedstock are currently the focus of extensive research efforts. A fixed-bed reactor containing a commercial Cu/ZnO/Al₂O₃ catalyst washcoated on a Cu foam was used for the synthesis of methanol through direct CO₂ hydrogenation. Catalytic activity tests in this reactor were conducted at reaction pressures of 30 and 50 bar, temperatures in the range 190–250 °C, and weight hourly space velocities (WHSV) in the range 1.125–2.925 NL g_{cat}^{−1} h^{−1}. The best reactor performance was recorded at 50 bar pressure: CO₂ conversion and methanol selectivity of 27.46% and 82.97%, respectively, were obtained at 240 °C and 1.125 NL g_{cat}^{−1} h^{−1}. Increasing the WHSV to 2.925 NL g_{cat}^{−1} h^{−1} resulted in a twofold increase in methanol weight time yield (WTY) to 0.18 g_{MeOH} g_{cat}^{−1} h^{−1} and a decrease in methanol selectivity to 70.55%. The results presented in this investigation provide insight into the performance of a bench-scale reactor in which mass transfer limitations are non-negligible and demonstrate that metal foams are promising catalyst support structures for CO₂ hydrogenation towards methanol production.

Keywords: CO₂ utilisation; direct CO₂ hydrogenation; metal foam; methanol synthesis; power-to-X



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1. Introduction

The increase in anthropogenic carbon dioxide (CO₂) emissions in the last century is a major global concern for environmental and social well-being. Global warming and other climate perturbations urge the industrial sector to consider more sustainable energy alternatives for their fossil fuel-reliant processes. Since the turn of the 21st century, the share of renewable energy sources such as solar and wind power grew exponentially in the sector of electricity generation. This rapid increase in fluctuating power supplied to power grids involved numerous challenges associated with the stability and balance of supply and demand [1].

Chemical energy conversion presents advantages over other energy storage methods, such as hydropower, compressed air energy storage, flywheels and batteries, due to both its long-term storage capability and its potential to trade energy on a global scale [2,3]. In this context, power-to-gas (PtG) and power-to-X (PtX) technologies, which represent the conversion of renewable energy via electrolysis into hydrogen (H₂) and other chemicals such as methane (CH₄) and methanol (MeOH), are opportune. PtG and PtX represent promising solutions for both the mitigation of global CO₂ emissions and the storage of energy from variable renewable sources during peaks in renewable energy supply. Subsequently, the produced chemicals may be used when the demand for power exceeds the supply capacity [4].