

Dehydrogenation of perhydrodibenzyltoluene for hydrogen production: the effect of Mg and Zn dopants on the catalytic activity of Pt/Al₂O₃

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DECLARATION

I, Rudaviro Garidzirai, declare that the dissertation entitled, '***Dehydrogenation of perhydrodibenzyltoluene for hydrogen production: the effect of Mg and Zn dopants on the catalytic activity of Pt/Al₂O₃***' submitted in fulfilment of the requirements for the degree, Master of Engineering in Chemical Engineering, is my own work, which has not been submitted to any institution. All other sources used in this study are acknowledged and referenced accordingly.



Signature

15/11/2021

Date

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Signed at

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- **Garidzirai, R.**, Modisha, P., Shuro, I., Visagie, J., van Helden, P. and Bessarabov, D., 2021. The effect of Mg and Zn dopants on Pt/Al₂O₃ for the dehydrogenation of perhydrodibenzyltoluene. *Catalysts*, 11(4), 490. <https://doi.org/10.3390/catal11040490>

ABSTRACT

Liquid organic hydrogen carriers (LOHC) are hydrocarbon molecules that have the capacity to store and release hydrogen through catalytic hydrogenation and dehydrogenation reactions. The dibenzyltoluene/perhydrodibenzyltoluene (H0-DBT/H18-DBT) system, has been identified as the most promising LOHC molecules for hydrogen storage. However, conventional Pt/Al₂O₃ catalyst used for dehydrogenation of H18-DBT still need to be further improved to obtain high throughput hydrogen production with low deactivation. Modification of Pt/Al₂O₃ is another way of improving the catalytic performance (productivity, degree of dehydrogenation, selectivity and conversion). Therefore, in this contribution the effect of Mg and Zn dopants on the catalytic performance of Pt/Al₂O₃ is investigated for the dehydrogenation of H18-DBT. Firstly, the γ -Al₂O₃ supports were modified with Mg(NO₃).6H₂O and Zn(NO₃).6H₂O precursors to produce Mg-Al₂O₃ and Zn-Al₂O₃ aiming at 3.8 wt % metal loading. Thereafter, the unmodified and modified γ -Al₂O₃ supports were impregnated using H₂PtCl₆.xH₂O to produce Pt/Al₂O₃, Pt/Mg-Al₂O₃ and Pt/Zn-Al₂O₃ aiming at 0.5 wt % Pt loading. The catalysts were characterised using inductively coupled plasma-optical emission spectrometry (ICP-OES), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS), hydrogen temperature programmed reduction (H₂-TPR), ammonia temperature programmed desorption (NH₃-TPD), CO pulse chemisorption, Branuer-Emmett-Teller (BET), X-ray diffraction (XRD) and transmission electron microscopy (TEM). Moreover, the catalysts' performance for dehydrogenation of H18-DBT was evaluated using a batch and fixed bed reactor. The samples resulting from dehydrogenation reaction were analysed using gas chromatography and refractive index techniques.

The initial four dehydrogenation runs (cycles) using a batch reactor at temperatures from 260–300 °C indicated that an increase in temperature increases the performance of all catalysts. Notably, the performance of the catalysts is in the following order: Pt/Mg-Al₂O₃ > Pt/Zn-Al₂O₃ > Pt/Al₂O₃ which suggests that Mg is a suitable and promising dopant. However, all catalysts showed deactivation during the initial four dehydrogenation runs. Furthermore, initial catalysts stability was investigated using a fixed bed reactor at weight hourly space velocity (WHSV) of 0.61 h⁻¹, 22 h time-on-stream and 300 °C. Pt/Mg-Al₂O₃ catalyst showed improved performance when compared to Pt/Al₂O₃ and Pt/Zn-Al₂O₃, and it also showed lower deactivation. The calculated turnover frequencies (TOF) for dehydrogenation of H18-DBT at 300 °C using Pt/Al₂O₃, Pt/Mg-Al₂O₃ and Pt/Zn-Al₂O₃ are: 202, 586 and 269 min⁻¹, respectively. This indicate that Pt/Mg-Al₂O₃ catalyst has the highest amount of active metal sites available for dehydrogenation reaction. This was also confirmed by a high frequency factor (2.3 x 10¹¹) min⁻¹ which suggests high rate of molecular collisions. The dehydrogenation of H18-DBT followed first order reaction kinetics and the obtained activation energy of Pt/Al₂O₃, Pt/Mg-Al₂O₃ and Pt/Zn-Al₂O₃ are 101, 151 and 131 kJ/mol, respectively. In this case, high amount of active sites corresponds to high value of

frequency factor and this is connected to high activation energy. Therefore, lower activation energy for dehydrogenation of H18-DBT will not always produce high reaction rate. Mg lowered the support acidity (as proven by NH_3 -TPD) and the less acidic catalyst is found to be more selective towards the product H0-DBT. Therefore, Mg weakens the adsorption of H0-DBT on Pt surface and promotes H0-DBT desorption. However, the most active catalyst ($\text{Pt/Mg-Al}_2\text{O}_3$) produced high amounts of by-products. This is because more aromatic molecules produced are susceptible to the acidic sites of the support which provides the C–C cracking function.

Keywords: Liquid organic hydrogen carriers; dibenzyltoluene; dehydrogenation; dopants; by-products; $\text{Pt/Al}_2\text{O}_3$ catalyst

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LIST OF ABBREVIATIONS

BET	Brunauer–Emmett–Teller
^{13}C -NMR	Carbon 13 nuclear magnetic resonance
CGH_2	Compressed hydrogen gas
CCH_2	Cryo-compressed hydrogen
CNT	Carbon nanotubes
EDS	Energy-dispersive X-ray spectroscopy
FC	Fuel cell
FCC	Face cubic centered
FFT	Fast Fourier transform
GC	Gas chromatography
GC-MS-SQ	Single quadrupole gas chromatography with mass spectroscopy
H0-DBT	Dibenzyltoluene
^1H -NMR	Proton nuclear magnetic resonance
H18-DBT	Perhydrodibenzyltoluene
H_2 -TPR	Hydrogen temperature programmed reduction
HFR	Hydrogen flow rate
ICP-OES	Inductively coupled plasma optical emission spectrometry
JCPDS	Joint committee on powder diffraction standards
LH_2	Liquefied hydrogen
LOHC	Liquid organic hydrogen carrier
LSHV	Liquid space hourly velocity
M-Hx	Metal hydrides
MSI	Metal support interaction
NH_3 -TPD	Ammonia temperature programmed desorption
PEMFC	Proton exchange membrane fuel cell
PGM	Platinum group metals
PID	Piping and instrumentation diagram

RI	Refractive index
SEM	Scanning electron microscopy
TCD	Thermal conductivity detector
TEM	Transmission electron microscope
XRD	X-ray powder diffraction

NOMENCLATURE

C	Concentration, M
D	Dispersion, %
dod	Degree of dehydrogenation, %
doh	Degree of hydrogenation, %
E _a	Activation energy, kJ/mol
k	Rate constant, min ⁻¹
k ₀	Pre-exponential/frequency factor, min ⁻¹
LHSV	Liquid hourly space velocity, h ⁻¹
Pr	Productivity, gH ₂ /g _{PI} /min
r	Rate of reaction, M min ⁻¹ g _{cat} ⁻¹
S	H0-DBT selectivity, %
TOF	Turn-over frequency, min ⁻¹
WHSV	Weight hourly space velocity, h ⁻¹
wt %	Weight percent
X	H18-DBT conversion, %
ΔH _r ^o	Enthalpy of reaction, kJ/mol-H ₂
ΔX	Deactivation parameter, %
ρ	Density, kg/m ³

CHAPTER 1. INTRODUCTION

1.1 Background

There is a global recognition of a need to reduce greenhouse gas emissions by shifting from the use of fossil-based fuels to renewable energy sources. The intermittency of renewable energy sources (e.g., solar and wind) directly prompts the need to store surplus energy in order to eliminate power fluctuations. Renewable energy sources can be used for the electrolysis of water to produce 'green' hydrogen that can then be stored and utilised for stationary power applications to flatten the fluctuations. Hydrogen is a clean energy carrier, however, it has a low density (0.0813 g/L at STP), making it difficult to store (Fitchner & Idrisova, 2018:275). At STP, a tank of about 11 000 L in volume would be required to store 1 kg of hydrogen (Züttel, 2004:160). This is equivalent to roughly 220 fuel car tanks with a capacity of 50 L each. Therefore, different storage methods have been developed to store considerable amounts of hydrogen gas in practical tank volumes.

Compressed hydrogen gas storage (CGH₂) is a mature technology. It has a volumetric storage capacity in the range 28–40 g/L at pressures of 200–700 bar. However, there are safety concerns at high pressures (700 bar) and the material required to manufacture composite cylinders is costly (Rivard *et al.*, 2019:4). Conventional CGH₂ storage (at 200–300 bar) has low storage density and uses heavy metal cylinders, which makes the transportation of hydrogen inefficient. Liquefied hydrogen (LH₂) has a volumetric storage density of 70 g/L, which is higher than in the case of CGH₂ storage (Zohuri, 2019:124). However, the cryogenic temperatures (-253 °C) need to be maintained in order to keep the hydrogen in liquid state. This process is energy intensive, costly, and there is a problem of hydrogen boil-off losses. Thus, the drawbacks presented by LH₂ and cryo-compressed hydrogen (CCH₂) include the boil-off losses, high energy demand and the cost associated with special tanks that are required to maintain cryogenic temperatures (Moreno-Blanco *et al.*, 2019:1011). The CCH₂ technology combines the attributes of LH₂ and CGH₂. Here, the storage capacity is improved from 70–87 g/L by compressing the liquefied hydrogen to 240 bar at -253 °C.

Hydrogen storage in metal hydrides (M-H_x) also presents challenges. For instance, M-H_x are toxic, heavy, non-reversible, costly, and some materials are scarce (Felderhoff *et al.*, 2007:2644; Mazloomi & Gomes, 2012:3028; Mori & Hirose, 2009:4572; Satyapal *et al.*, 2007:251; Schüth, 2009:157; Züttel, 2004:161). The theoretical volumetric and gravimetric hydrogen storage capacity of M-H_x materials are in the ranges 45–110 g/L and 2–18 wt %, respectively (Aakko-Saksa *et al.*, 2018:813). However, materials with high hydrogen storage capacity (e.g., LiBH₄) require high temperature (>620 °C) and pressure (850 bar) for re-

hydrogenation. For this reason, M-H_x materials, such as NaAlH₄, which desorb hydrogen at low temperatures and pressure (2 bar, 60 °C) are suitable for use in proton exchange membrane fuel cell (PEMFC) applications (Züttel, 2004:168).

Ammonia (NH₃) is also considered to be a potential medium for hydrogen storage and transportation. Its high volumetric and gravimetric hydrogen storage capacity (17.8 wt %, 105 g/L) (Raissi, 2002:4), low storage pressure and long-term stability are some of its beneficial characteristics that make it suitable for this purpose. Despite these excellent characteristics, the toxicity of ammonia cannot be ignored—exposure to 2500 ppm can be fatal within approximately 30 min (Henderson & Haggard, 1943:125). Moreover, ammonia combustion for power generation produces NO_x and the ammonia decomposition for H₂ production requires temperatures >500 °C.

Liquid organic hydrogen carriers (LOHCs) are aromatic and heteroaromatic compounds that can store hydrogen in the presence of a catalyst through a reversible hydrogenation reaction. The well-known LOHC molecules have volumetric and gravimetric hydrogen storage capacity values in the ranges 47–60 g/L and 5.8–7.3 wt %, respectively (Sekine and Higo, 2021:471). LOHC technology enables the storage of hydrogen at ambient conditions for long period of time and without any losses because the hydrogen is chemically bound to the hydrocarbon molecule. LOHC hydrogenation reactions generally take place under conditions between 10 and 50 bar pressure and temperatures in the range 100–240 °C, while the dehydrogenation takes place at ambient pressure and temperatures >200 °C (see Figure 1-1).

Table 1-1 summarises, and compares, properties of different hydrogen storage methods, in line with the DoE targets. It is evident the LOHC technology meets most of the targets for on-board hydrogen storage for fuel cell (FC) vehicles (US Department of Energy, 2017:3). This is because there are also other properties, beside hydrogen storage capacity, that are important and need to be considered. It can be deduced from the table that the common issues in these storage methods is the high energy demand, toxicity and low storage density. The technical issues associated with the LOHC technology is the catalyst performance and thermal management for the release of hydrogen. Table 1-2 tabulates the advantages and disadvantages of various hydrogen storage methods.

Table 1-1. Comparison of different hydrogen storage technologies with the 2025 U.S. DoE technical targets for on-board light-duty vehicles

Parameter	US DoE 2025 targets	CGH ₂	LH ₂	CCH ₂	M-Hx	NH ₃	LOHC
Gravimetric capacity, wt %	5.5	6	7.5	5.4	2–18	17.8	5–7.7
Volumetric capacity, g/L	40	28–40	70	70–87	45–110	105	47–60
Energy density, kWh/kg (kWh/L)	1.8 (1.3)	1.4 (1.3)	3.3 (2.4)	3.3 (2.4)	0.8–1.6 (0.6–1.4)	5.8 (3.6)	1.87 (1.58–2.05)
Leakage/losses (%/day)	<1	<1	1	1	<1	0	0
Transportable	-	Yes	Yes	Yes	Yes	Yes	Yes
Toxicity	-	Low	Low	Low	Low to medium	High	Low to medium
Flammable	-	Yes	Yes	Yes	Yes	Yes	No

^a The following assumptions are made: i) hydrogen capacity of 5.6 kg, ii) targets are for complete systems, iii) all capacities are supplied to the FC system and iv) all targets should be achieved at the end of service life. U.S. DoE, 2017:3; ^b Based on values obtained by (Andrijanovits & Beldjajev, 2012:304); ^c System is based on 700-bar gas cylinder

Table 1-2. Advantages and disadvantages of different hydrogen storage technologies and their respective maturity levels

H ₂ storage technology	Advantages	Disadvantages	Technology status
CGH ₂	Well understood technology and commercially available	Low storage density; high compression energy. Steel cylinders are heavy. Composite cylinders are expensive to construct	Mature
LH ₂	High storage density	Energy intensive liquefaction process; boil-off losses; hydrogen losses	Mature
CCH ₂	High volumetric capacity	High energy demand for both compression and liquefaction. Safety issues	Pre-commercial
M-Hx	High storage density	Unfavourable reversibility, heavy, toxic. Decompose with time. Not readily available, especially complex hydrides	Pre-commercial
Ammonia	Available in abundance and easily liquefiable. High storage capacity	Requires corrosion resistant components. Ammonia is highly toxic	Mature
LOHC	Available in abundance and cost effective. High storage capacity	Thermal management required	Pre-commercial

As already discussed above, the LOHC technology offers numerous advantages over conventional hydrogen storage technologies. Hence, LOHC technology is the main topic of interest in this study. Figure 1-1 illustrates the concept of renewable hydrogen storage and transportation using LOHC technology. Hydrogen is produced from the electrolysis of water using energy from wind or solar photovoltaic modules. Hydrogen is then stored by hydrogenation of LOHCs and transported to end users, where dehydrogenation is performed to release the stored hydrogen. Since the process is reversible and the LOHC is not consumed, the hydrogen-lean LOHC is transported back to the hydrogenation plant for re-hydrogenation. This can be performed for many hydrogenation and dehydrogenation cycles without major decomposition of the LOHC molecule.

Renewable hydrogen is not only used in PEMFCs for power generation but also as a feedstock in the chemical industry, steel production, floating glass manufacturing, hardening of vegetable oils, margarine production, etc. Therefore, renewable sources can be coupled with various end users (e.g., industries, homes, refuelling stations, etc.) via the LOHC technology—aiming at decarbonisation of these sectors.

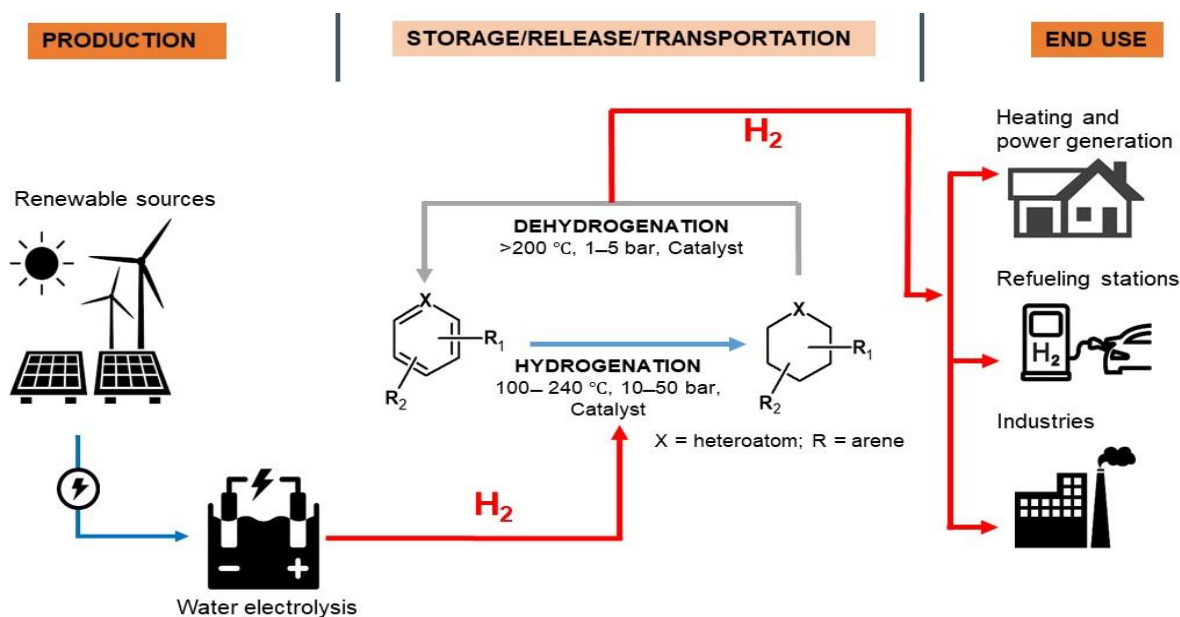


Figure 1-1. LOHC system coupled with renewables for hydrogen storage applications.

1.2 Research motivation

A widely known heat-transfer oil, dibenzyltoluene (H0-DBT), has been extensively studied for hydrogen storage applications due to its unique hydrogen storage properties. Hydrogen is stored by the hydrogenation of H0-DBT to produce the hydrogen-rich molecule perhydrodibenzyltoluene (H18-DBT). This LOHC system is non-flammable, not classified as dangerous goods, available in abundance, remains liquid at sub-zero temperatures, it has a

high storage capacity (6.2 wt %, 57 kg-H₂/m³-H18-DBT) and a high boiling point (380 °C), it is cost effective (3–4€/kg) and compatible with the infrastructure for fuel, etc. (Brückner *et al.*, 2014:232; Modisha *et al.*, 2019:2783).

Nevertheless, further research work is required to develop efficient and stable catalysts for the dehydrogenation of H18-DBT. This is considered important, in efforts to improve the current state-of-the-art catalyst, Pt/Al₂O₃, towards making the LOHC technology increasingly beneficial, and competitive.

1.3 Research problem

The storage of hydrogen remains a challenge for stationary, mobile and transportation (logistics) applications. LOHC technology offers unique hydrogen storage properties, although this technology is not without its own challenges. For example, the most commonly used catalyst (Pt/Al₂O₃) for the dehydrogenation of H18-DBT is prone to deactivation and the formation of by-products. This has a negative impact on the LOHC technology in terms of system reliability and the associated costs of frequent catalyst replacement. The mechanism of deactivation is not fully understood yet—it could possibly be due to the blocking of the catalyst active sites by reactants, products and by-products. The formation of by-products is attributed to possible side reactions, such as C–C cracking/cleavage, due to the acidic nature of the support, and hydrogenolysis on the Pt metal surface. It is therefore envisaged that modification of the support material (Al₂O₃), using alkaline-earth and transition metals (e.g., Mg, Zn, etc.) will reduce the acidity of the Al₂O₃ and subsequently reduce cracking. Mg and Zn dopants are known to have other additional benefits, such as improving the catalyst activity, selectivity and stability (Bai *et al.*, 2009:9885; Ballarini *et al.*, 2012:433; Xue *et al.*, 2012:928; Yu *et al.*, 2007:80).

1.4 Research aim and objectives

In view of the abovementioned, the overall aim of this study is to improve the catalytic performance and stability of the Pt/Al₂O₃ catalyst for the dehydrogenation of H18-DBT in a LOHC system, by modification of the Al₂O₃ support material, using Mg and Zn as dopants.

The specific objectives are the following:

- Preparation of the Mg-Al₂O₃ and Zn-Al₂O₃ by modification of Al₂O₃ support material using incipient wet impregnation method
- Impregnation of the Al₂O₃, Mg-Al₂O₃ and Zn-Al₂O₃ support materials using a Pt precursor, to afford 0.5 wt.% Pt/Al₂O₃, 0.5 wt. % Pt/Mg-Al₂O₃ and 0.5 wt. % Pt/Zn-Al₂O₃

- Evaluation of the catalysts' performance (e.g., productivity, conversion, selectivity) at various reaction temperatures (260–300 °C) for the dehydrogenation of H18-DBT using a batch reactor
- Kinetics study for dehydrogenation H18-DBT using a batch reactor i.e., determination of kinetics parameters such as, rate constant, reaction rate, activation energy and turn-over frequency (TOF)
- Determination of the catalysts' stability for dehydrogenation of H18-DBT using a fixed bed reactor
- Characterisation of the catalysts, before and after the dehydrogenation reaction, to investigate the effect of modification in the physicochemical properties of the catalysts

1.5 Significance of the study

South Africa has the largest (~80%) platinum group metal (PGM) reserves in the world. The majority of these PGM ores are exported at low costs and imported back as finished/processed PGM products at high prices. The use of a PGM catalyst (Pt) in this research and its use in the entire value chain of the hydrogen economy will stimulate the demand of Pt. Moreover, this research work is in-line with a strategy of the South African National Department of Science and Innovation, known as Hydrogen South Africa (HySA). It aligns with the following mandates:

- Stimulation of the demand for PGMs
- Development of a hydrogen fuelling infrastructure as a way of transitioning South Africa into a low-carbon economy (Department of Science and Technology South Africa, 2008:19).

The ability to effectively store and release hydrogen by making use of LOHC technology will surely arouse the need for both government and the private sector to cooperate in this field and, ultimately, the transition to a future low-carbon economy should be realised.

1.6 Dissertation outline

Chapter 1 provides a background on various hydrogen storage technologies, including the associated challenges, as reported in literature. An alternative hydrogen storage method is identified based on its unique properties. The research problem, aims and specific objectives, and significance of the study are clearly presented.

Chapter 2 reviews current literature on the performance of Pt-based catalysts for the dehydrogenation of H18-DBT. Physicochemical properties of the catalysts, as revealed by various characterisation techniques, are also reported.

Chapter 3 provides the experimental details; it describes materials and methods used, and experimental procedures followed for the preparation of catalysts. Operational methods used for the dehydrogenation reaction in the two types of reactors used here (batch and fixed-bed) are also described in detail.

Chapter 4 presents and discusses the results obtained from the catalytic dehydrogenation performance of H18-DBT in both the batch reactor and fixed bed reactor systems, including analysis of the resulting LOHC molecules.

Chapter 5 summarises the key findings of the study, offers recommendations and identifies possible future research areas that should be explored.

CHAPTER 2. LITERATURE REVIEW

This chapter provides a literature review on the performance of Pt-based catalysts under various reaction conditions used for the dehydrogenation of perhydrodibenzyltoluene (H18-DBT). Furthermore, various characterisation tools previously used to determine the physicochemical properties of the Pt-based catalysts are discussed to determine the effect of properties such as surface area, acidity, particle size etc. These properties play a major role in the catalytic dehydrogenation reaction of H18-DBT.

2.1 Catalytic dehydrogenation of perhydrodibenzyltoluene

Perhydrodibenzyltoluene (H18-DBT) is the hydrogen-rich molecule obtained after the hydrogenation of dibenzyltoluene (H0-DBT). Both molecules have a low melting point (<-39 °C) and a high boiling point (>370 °C). The former property indicates that both molecules remain liquid at ambient conditions and the latter suggests an advantage of good liquid/gas separation during dehydrogenation, resulting from low vapour pressure (Muller et al., 2015:7974). H18-DBT has a theoretical gravimetric and volumetric hydrogen storage capacity of 6.2 wt % and 56 kg-H₂/m³-H18-DBT, respectively, which is equivalent to an energy density of 2.06 kWh/kg-H18-DBT; see Table 2-1 (Seidel, 2019:14). Based on these values, 1 ml of H18-DBT contains 620 ml of hydrogen gas and, during dehydrogenation, the reactor fills with large volumes of gas, making it difficult to supply the required amount of heat. Therefore, a more efficient catalyst and better heat distribution method are of great importance for this endothermic dehydrogenation reaction. Furthermore, the high viscosity of H0-DBT at 20 °C (434 mPa.s) could result in a problematic pumping issue under extremely cold (weather) conditions.

Table 2-1. Properties of the H0-DBT/H18-DBT LOHC system

Parameter	H18-DBT	H0-DBT
Molar mass, g/mol	290	272
Melting point, °C	<-50	-32 to -39
Boiling point, °C	371	390
Density, kg/m ³ @ 20 °C	911	1040
Flashpoint, °C	161	212
Viscosity, mPa.s @ 20 °C	434	48
Volumetric capacity, g/L	56	
Gravimetric capacity, wt %	6.2	

The dehydrogenation of H18-DBT is a reversible reaction with an enthalpy of reaction (ΔH_r°) equivalent to 65.4 kJ/mol-H₂. Figure 2-1 illustrates the reversible dehydrogenation of H18-

DBT. This reaction commences at temperatures $>270\text{ }^{\circ}\text{C}$ but, for faster reaction kinetics, temperatures $>300\text{ }^{\circ}\text{C}$ are preferred. To this end, Pt-based catalysts (e.g., Pt/ Al_2O_3 , Pt/ TiO_2 , etc.) are found to be more selective for H18-DBT dehydrogenation. Interestingly, hydrogenation and dehydrogenation reactions can take place at the same temperature (e.g., $300\text{ }^{\circ}\text{C}$) using pressure as a variable to switch between reactions (Jorschick *et al.*, 2017:1652). Both hydrogenation and dehydrogenation reactions occur in a 2-in-1 reactor system packed with Pt/ Al_2O_3 catalysts. Therefore, improvement of the current state-of-the-art catalyst (Pt/ Al_2O_3) will be beneficial for the LOHC technology.

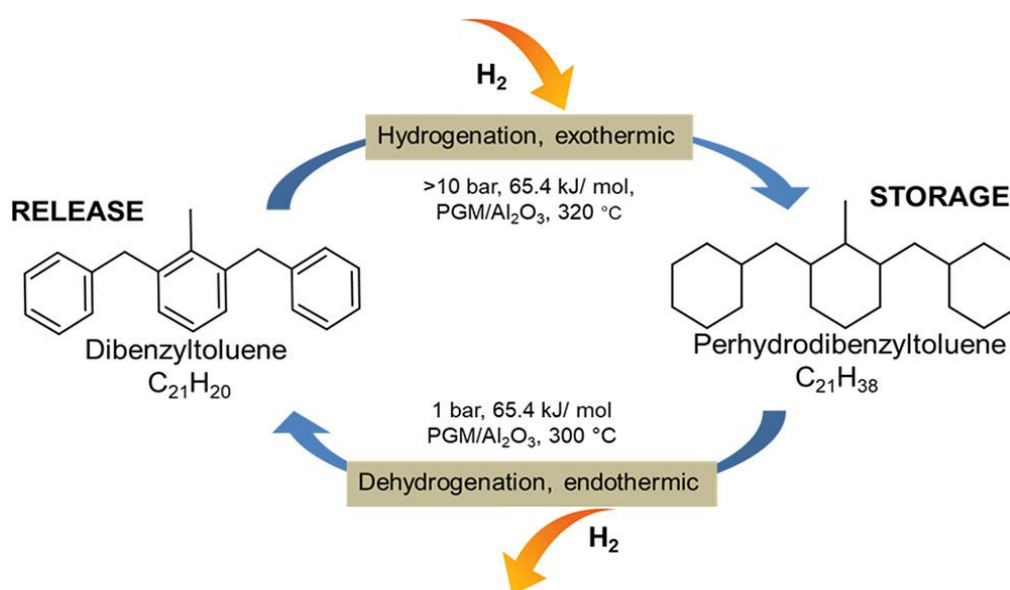


Figure 2-1. Reversible dehydrogenation of H18-DBT. (Modisha *et al.*, 2019:2783)

2.2 Catalyst performance evaluation for H18-DBT dehydrogenation

This section provides an extensive literature review on the performance of different types of catalysts used for the dehydrogenation of H18-DBT. A comparison of reported catalytic performances of various catalysts for the dehydrogenation of H18-DBT is tabulated in Table 2-2.

As mentioned, Pt-based catalysts are, undoubtedly, the most selective catalysts for the release of hydrogen from H18-DBT. The initial catalyst screening tests for dehydrogenation of H18-DBT were conducted by Brückner *et al.* (2014:232). They found that Pt/C (0.015 mol %) was the best catalyst, with a hydrogen yield of 71% after 3.5 h at $270\text{ }^{\circ}\text{C}$, followed by Pt/ Al_2O_3 , Pd/C, Pt/ SiO_2 and Pd/ Al_2O_3 , with yields of 51%, 16%, 10% and 8%, respectively. Results indicated that SiO_2 support and Pd based catalyst are unsuitable for H18-DBT dehydrogenation. The work of Modisha *et al.* (2019:21933) also reiterated that Pt is the best dehydrogenation catalyst for H18-DBT, compared with Pd and Pt-Pd on Al_2O_3 . The 1 wt %

Pt/Al₂O₃ catalyst (0.4 mol %) gave an 82% degree of dehydrogenation (dod) after 1.5 h at 320 °C. The 1 wt % Pt and 1:1 wt % Pt-Pd gave dod values of 11% and 6%, respectively. Indications were that a lower Pt loading is desirable, to maximise catalyst productivity (gH₂/gPt/min) and dispersion. Jorschick *et al.* (2017:1658) therefore studied the dehydrogenation of H18-DBT using 0.3 wt % Pt/Al₂O₃ in a pressure swing reactor. In the first cycle of dehydrogenation, a hydrogen yield and productivity of 81% and 1.2 gH₂/g_{Pt}/min were achieved. However, the catalyst showed declining activity over 13 cycles. To date, several dehydrogenation cycles have been attempted and the presence of by-products observed in each cycle. The liquid-based by-products were also found to be LOHCs, which could subsequently affect the properties (e.g. viscosity, boiling point, etc.) of the parent molecules (Modisha & Bessarabov, 2020:4669). Gaseous by-products such as CH₄, CO and CO₂ have been detected in hydrogen effluent (Bulgarin *et al.*, 2020:720; Modisha *et al.*, 2019:21993; Wunsch *et al.*, 2021:119103). This means that further purification processes are required to ensure that fuel grade hydrogen (>99.97%) is obtained. Bulgarin *et al.* (2020:720) found that by removing water and other impurities from H18-DBT prior to dehydrogenation, the formation of by-products (CH₄ and CO and CO₂) can be reduced. Wunsch *et al.* (2021:119103) used a PdAg membrane to purify hydrogen released from the dehydrogenation of H18-DBT. However, CO and other hydrocarbons deactivated the PdAg membrane. This membrane was regenerated using pure H₂.

The catalyst can be modified to improve its activity and stability, and to reduce the formation of by-products. Recently, Shi *et al.* (2020:10669) modified the surface hydroxyl groups and oxygen vacancies of Al₂O₃ using H₂ and O₂ dielectric barrier discharge plasma. Both treatments led to decreased Pt size and improved Pt dispersion in 3 wt % Pt/Al₂O₃ during H18-DBT dehydrogenation. The best catalyst was the one treated with H₂ since the modification increased surface hydroxyl groups, and improved reactivity and cycling performance. There are a few publications that report on the effect of modifiers/dopants on the dehydrogenation of H18-DBT. Auer *et al.* (2019:3544) investigated the effect of sulphur dopant on the dehydrogenation of H18-DBT using 0.3 wt % Pt/Al₂O₃. The appropriate sulphur loading (0.25 wt %) reduced the formation of by-products and improved catalytic activity from 78% to >90% dod (see Table 2-2). Likewise, Chen *et al.* (2021:6571) loaded 0.25 wt % S on 3 wt % Pt/Al₂O₃ and Pt/TiO₂. Doping with S improved the activity of both catalysts; however, Pt/Al₂O₃ gave more by-products than Pt/TiO₂. Besides sulphur, other dopants have been considered. Seidel (2019:71) studied dopants such as lithium, potassium and caesium, in different ratios, for modification of the Pt/Al₂O₃ catalyst. A dopant to Pt ratio of 5.7 was determined to be the optimum, with lithium being the best dopant (dod = 85%). However, a sulphur loading of 0.5

wt % on Pt/Al₂O₃ gave better performance (dod =95%) compared to undoped Pt/Al₂O₃ with a dod of 81%.

In conclusion, it is evident that Pt-based catalysts with loadings in the range 0.3–3 wt % supported on porous Al₂O₃ are the most suitable for the dehydrogenation of H18-DBT. The best reaction conditions were attained in a batch reactor, at 310 °C and 1 bar, with 0.1 mol % Pt/substrate ratio: dod was 98% and ~3 mol % by-products formed. Al₂O₃ is the dominant support and can achieve even better performance by modification with sulphur. An optimal amount of sulphur blocks the defect sites of Pt responsible for side reactions (by-products) and enhances the desorption of products.

To date, most of the catalysts reported for H18-DBT dehydrogenation reactions are based on fresh catalysts only. Multiple use of the same catalysts for dehydrogenation in batch or fixed bed reactors is rarely reported. Hence, in this study the focus is on using catalysts doped with either Mg or Zn for multiple dehydrogenation cycles to evaluate the performance and stability in a batch reactor. The long-term stability tests are also to be investigated, in a fixed bed reactor.

Table 2-2. Catalytic performance comparison of various catalysts for dehydrogenation of H18-DBT

Authors	Catalyst	Type of reactor	Reaction conditions	Catalytic activity
Modisha <i>et al.</i> (2019: 21932)	1 wt % Pt/Al ₂ O ₃	Batch	T: 320 °C. P: 1 bar; n: 0.4 mol %; t: 90 min	Dod: 82%; Pr: 0.55 gH ₂ /g _{Pt} /min; E _a : 205 kJ/mol
	1 wt % Pd/Al ₂ O ₃			Dod: 11%; Pr: <0.1 g H ₂ /g _{Pt} /min; E _a : 84 kJ/mol
	1:1 wt % Pt-Pd/Al ₂ O ₃			Dod: 6%; Pr: <0.01 g H ₂ /g _{Pt} /min; E _a : 66 kJ/mol
Modisha & Bessarabov (2020:4665)	1 wt % Pt/Al ₂ O ₃	Batch	T: 300 °C; P: 1 bar; n: 0.2 mol %. t: 120 min	Dod: 90%; E _a : 201 kJ/mol; BP: 4.7 mol %
			T: 320 °C; P: 1 bar; n: 0.2 mol %. t: 180 min	Dod: 85%; E _a : 201 kJ/mol; BP: 5.8 mol %
			T: 340 °C; P: 1 bar; n: 0.2 mol %; t: 240 min	Dod: 82%; E _a : 201 kJ/mol; BP: 6.5 mol %
			T: 355 °C; P: 1 bar; n: 0.2 mol %; t: 140 min	Dod: >90%; E _a : 201 kJ/mol; BP: 7.3 mol %

Authors	Catalyst	Type of reactor	Reaction conditions	Catalytic activity
Jorschick <i>et al.</i> (2017:149)	0.3 wt % Pt/Al ₂ O ₃	Batch	T: 290 °C; P: 1.05 bar; n: 0.015 mol %; t: 16 h (20 h)	Dod: 81 (84)%; P: <1.2 gH ₂ /g _{Pt} /min; BP: 6.8 mol %
			T: 290 °C; P: 1.6 bar; n: 0.015 mol %; t: 16 h	Dod: 74; Pr: <1.2 gH ₂ /g _{Pt} /min
			T: 290 °C; P: 2.4 bar; n: 0.015 mol %; t: 16 h	Dod: 58%; Pr: <0.79 gH ₂ /g _{Pt} /min
			T: 290 °C; P: 2.7 bar; n: 0.015 mol %; t: 16 h	Dod: 62%; Pr: <0.49 gH ₂ /g _{Pt} /min
Bulgarin <i>et al.</i> (2020:715)	0.3 wt % Pt/Al ₂ O ₃	Fixed bed	T: 297 °C; P: 1 (2.5) bar ; Flow: 0.25-1 g/min; t: 35 min	Dod: 62% (38%); Pr: <0.49 gH ₂ /g _{Pt} /min; Ea: 117 (149) kJ/mol
Jorschick <i>et al.</i> (2020:14903)	0.3 wt % Pt/Al ₂ O ₃	Batch	T: 260 °C; P: 1 bar; n: 0.05 mol %; t: 23 h	Dod: 58% ; Pr: <0.15 gH ₂ /g _{Pt} /min
Shi <i>et al.</i> (2019: 5348)	5 wt % Pt/Al ₂ O ₃	Batch	T: 270 °C; P: 1 bar; n : 0.3 mol %; t: 180 (300) min	Dod: 55% (56%)
	5 wt % Pt/C		T: 270 °C; P: 1 bar; n: 0.3 mol %; t: 180 (300) min	Dod: 50% (58%)
	5 wt % Pt/SBA-15		T: 270 °C; P: 1 bar; n: 0.3 mol %; t: 180 (300) min	Dod: 29% (34%)
Aakko-Saksa <i>et al.</i> (2020:1658)	1 wt % Pt/γ-Al ₂ O ₃	Batch		Dod: 5%
	1 wt % Pt/C		T: 290 °C; P: 1 bar; n: 0.25 mol %; t: 45 min; 300 rpm	Dod: 80%
	1 wt % Pt/TiO ₂ RP			Dod: 65%
	1 wt % Pt/TiO ₂ AP			Dod: 32%
Lee <i>et al.</i> (2020:13401)	5 wt % Pt/Al ₂ O ₃	Batch	T: 300 °C; P: 1 bar; n: 0.15 mol %; t: 240 min	Dod: 50%
Lee <i>et al.</i> (2021:5526)	5 wt % Pt/Al ₂ O ₃	Batch	T: 300 °C; P: 1 bar; n: 0.15 mol %; t: 150 min	Dod: 4%
	5 wt % Pt/CeO ₂			Dod: 81%
	5 wt % Pt/Al ₂ O ₃	Fixed bed		Dod: 51%

Authors	Catalyst	Type of reactor	Reaction conditions	Catalytic activity
	5 wt % Pt/Al ₂ O ₃		T: 300 °C; P: 1 bar; LSHV: <1h ⁻¹ ; t: 150 min	Dod: 88 %
Shi <i>et al.</i> (2020:10667)	3 wt % Pt/Al ₂ O ₃	Batch	T: 270 °C; P: 1 bar; n: 0.1 mol %; t: 300 min	Dod: 62%; Pr: 40 molH ₂ /mol _{Pt} /min; TOF: 3.9 s ⁻¹
	3 wt % Pt/Al ₂ O ₃ -PL-O ₂			Dod: 65%; Pr: 52 molH ₂ /mol _{Pt} /min; TOF: 3.5 s ⁻¹
	3 wt % Pt/Al ₂ O ₃ -PL-H ₂			Dod: 71%; Pr: 56 molH ₂ /mol _{Pt} /min; TOF: 2.8 s ⁻¹
Peters <i>et al.</i> (2019:13797)	Pt/Al ₂ O ₃	Fixed bed	T: 260–310 °C; P: 1 bar	Ea: 120 kJ/mol; k _o : 125.24 s ⁻¹
Auer <i>et al.</i> (2019:3540)	0.3 wt % Pt/Al ₂ O ₃	Batch	T: 310 °C; P: 0.1 mPa; n: 0.1 mol %; t: 120 min	Dod: 80%; Pr: 0.74 gH ₂ /g _{Pt} /min; BP: 8.3 mol %
	0.3 wt % Pt/Al ₂ O ₃ -0.125 wt % S			Dod: 81%; Pr: 1 gH ₂ /g _{Pt} /min; BP: 5.5 mol %
	0.3 wt % Pt/Al ₂ O ₃ -0.25 wt. % S			Dod: 98%; Pr: 2 gH ₂ /g _{Pt} /min; BP: 3.0 mol %
	0.3 wt % Pt/Al ₂ O ₃ -0.32 wt % S			Dod: 83%; Pr :1 gH ₂ /g _{Pt} /min; BP: 3.2 mol %
Chen <i>et al.</i> (2021:6567)	0.3 wt % Pt/γ-Al ₂ O ₃	Batch	T: 310 °C; P: 1 bar; n: 0.1 mol %; t: 90 min	Dod: 80%; Pr: 1.17 gH ₂ /g _{Pt} /min
	0.3 wt % S (0.185) -Pt/γ-Al ₂ O ₃			Dod: 98%; Pr :1.50 gH ₂ /g _{Pt} /min; BP: 8%
	0.3 wt % Pt/TiO ₂			Dod: 82%; Pr: 0.802 gH ₂ /g _{Pt} /min;
	0.3 wt % S (0.08) -Pt/TiO ₂			Dod: 98%; Pr: 1.37 gH ₂ /g _{Pt} /min; BP: 2.7 %
Chen <i>et al.</i> (2021:6568)	Pt/TiO ₂	Batch	T: 310 °C; P: 1 bar; n: 0.1 mol %; t: 90 min	Dod: 83%
	S (0.1) Pt/TiO ₂			Dod: 85%
	S (0.25) Pt/TiO ₂			Dod: 87%
	S (0.35) Pt/TiO ₂			Dod: 82%

Authors	Catalyst	Type of reactor	Reaction conditions	Catalytic activity
Chen <i>et al.</i> (2021:6569)	Pt/TiO ₂ (S-Pt/TiO ₂)	Batch	T: 270 °C; P: 1 bar; n: 0.1 mol %; t: 90 min; 97 % doh	Dod: ^a 20 (20)%
			T: 280 °C; P: 1 bar; n: 0.1 mol %; t: 90 min; 97 % doh	Dod: ^a 42 (30)%
			T: 290 °C; P: 1 bar; n: 0.1 mol %; t: 90 min; 97 % doh	Dod: ^a 58 (60)%
			T: 300 °C; P: 1 bar; n: 0.1 mol %; t: 90 min; 97 % doh	Dod: ^a 78 (78)%
			T: 310 °C; P: 1 bar; n: 0.1 mol %; t: 90 min; 97 % doh	Dod: ^a 82 (98)%
Kwak <i>et al.</i> (2021:114–124)	0.5 wt % Pt/γ-Al ₂ O ₃	Fixed bed	T: 280 °C; P: 1 bar; n _{H₂} /n _{LOHC} : 0.83 mol %; LSHV: 1.1 mL/mL _{cat} /h	Dod: 38%; Pr: 40 molH ₂ /mol _{met} /min
			T: 300 °C; P: 1 bar; n _{H₂} /n _{LOHC} : 0.83 mol %; LSHV: 1.1 mL/mL _{cat} /h	Dod: 45%; Pr: 50 molH ₂ /mol _{met} /min
			T: 320 °C; P: 1 bar; n _{H₂} /n _{LOHC} : 0.83 mol %; LSHV: 1.1 mL/mL _{cat} /h	Dod: 58%; Pr: 60 molH ₂ /mol _{met} /min
			T: 340 °C; P: 1 bar; n _{H₂} /n _{LOHC} : 0.83 mol %; LSHV: 1.1 mL/mL _{cat} /h	Dod: 62%; Pr: 68 molH ₂ /mol _{met} /min
Ali (2020:817)	2 wt % Pt/Al ₂ O ₃	Batch	T: 290 °C; P: 1 bar; t: 420 min	Dod: 62%
	3 wt % Pt/Al ₂ O ₃			Dod: 65%
	4 wt % Pt/Al ₂ O ₃			Dod: 82%
	5 wt % Pt/Al ₂ O ₃			Dod: 80%
Geißelbrecht (2021:75–76)	0.3 wt % Pt/Al ₂ O ₃	Batch	T: 260 °C; P: 1 bar; t: 1380 min	Dod: 58 %; Pr :0.15 gH ₂ /mol _{Pt} /min
			T: 290 °C; P: 1 bar; t: 1380 min	Pr: 0.9 gH ₂ /mol _{Pt} /min

Authors	Catalyst	Type of reactor	Reaction conditions	Catalytic activity
			T: 310 °C; P: 1 bar; t: 1380 min	Pr: 2.1 gH ₂ /mol _{Pt} /min
Brückner <i>et al.</i> (2014:232–233)	0.5 wt % Pt/Al ₂ O ₃	Batch	T: 270 °C; P: 1 bar; t: 3.5 h; n: 0.15 mol %	Dod: 51%; BP: < 0.01 mol %
	5 wt % Pt/Al ₂ O ₃			Dod: 40%; BP: < 0.01 mol %
	1 wt % Pt/C			Dod: 71%
	5 wt % Pt/C			Dod: 55%
	1 wt % Pt/SiO ₂			Dod: 10%
	5 wt % Pd/C			Dod: 16%
	5 wt % Pd/Al ₂ O ₃			Dod: 8%
Brückner <i>et al.</i> (2014:232–233)	1 wt % Pt/C	Batch	T: 230 °C; P: 1 bar; t: 3.5 h; n: 0.15 mol %	Dod: 16%
			T: 250 °C; P: 1 bar; t: 3.5 h; n: 0.15 mol %	Dod: 36%
			T: 290 °C; P: 1 bar; t: 3.5 h; n: 0.15 mol %	Dod: 98%
	5 wt % Pt/C		T: 230 °C; P: 1 bar; t: 3.5 h; n: 0.15 mol %	Dod: 14%
			T: 250 °C; P: 1 bar; t: 3.5 h; n: 0.15 mol %	Dod: 33%
			T: 290 °C; P: 1 bar; t: 3.5 h; n: 0.15 mol %	Dod: 82%
Seidel (2019:70)	0.3 wt % Pt/Al ₂ O ₃	Batch	T: 310 °C; P: 1 bar; t: 60 min n : 0.1 mol %	Dod: 75%
	0.5 wt % Pt/Al ₂ O ₃			Dod: 61%
	0.6 wt % Pt/Al ₂ O ₃			Dod: 54%
	0.5 wt % Pd/Al ₂ O ₃			Dod: 13%
	0.2: 0.6 (wt:wt %) Pt-Pd/Al ₂ O ₃			Dod: 15%
Seidel (2019:71)	^b 5.7 Cs/Pt on Al ₂ O ₃	Batch		Dod: 40%

Authors	Catalyst	Type of reactor	Reaction conditions	Catalytic activity
	^b 5.7 K/Pt on Al ₂ O ₃		T: 310 °C; P: 1 bar; t: 120 min n: 0.1 mol %	Dod: 80%
	^b 5.7 Li/Pt on Al ₂ O ₃			Dod: 85%
Seidel (2019:85)	0.3 wt % Pt/Al ₂ O ₃	Batch	T: 310 °C; P: 1 bar; t: 120 min n: 0.1 mol %;	Dod: 81%
	(0.25 wt % S) 0.3 wt % Pt/Al ₂ O ₃			Dod: 89%
	(0.5 wt % S) 0.3 wt % Pt/Al ₂ O ₃			Dod: 95%
Seidel (2019:85)	(0.75 wt % S) 0.3 wt % Pt/Al ₂ O ₃	Batch	T: 310 °C; P: 1 bar; t: 120 min n: 0.1 mol %	Dod: 92%
	(1 wt % S) 0.3 wt. % Pt/Al ₂ O ₃			Dod: 87%
	(1.5 wt % S) 0.3 wt % Pt/Al ₂ O ₃			Dod: 88%
	(5 wt % S) 0.3 wt % Pt/Al ₂ O ₃			Dod: 54%

T: dehydrogenation temperature; P: pressure; Pr: productivity; t: reaction time; n: molar ratio of Pt/LOHC; dod: degree of dehydrogenation; BP: by-products; LHSV: liquid hourly space velocity; k₀: frequency or pre-exponential factor; TOF: turn over frequency; PL: plasma treated with O₂ or H₂; RT: rutile phase; AT: anatase phase; ^a dod of Pt/TiO₂ & (S-Pt/TiO₂), respectively; ^b dopant to Pt ratio of 5.7 on 0.3 wt % Pt/Al₂O₃

2.3 Kinetics for dehydrogenation of H18-DBT

Heterogeneous catalysts are preferred for LOHC technology because the reaction mixture is then easily separated from the pelletized catalyst. This enables efficient recycling of the LOHC molecule without the requirement for any further catalyst separation process. The reaction mechanism (sequence of a heterogeneous catalyst) entails a mass transfer of reactants from the bulk fluid to the external surface of the catalyst pellet. This is followed by diffusion of the reactants from the external surface into the pores of the catalyst pellet. Since the reaction occur on the catalytic surface of the pores, it is important that the pore diameter accommodates the size of the reactants and products. A schematic representation of the two-step diffusion process is shown in Figure 2-2.

- The reactant, H18-DBT is transported to the boundary of the catalyst (film diffusion).
- After overcoming film diffusion, H18-DBT has to diffuse into the pores where Pt catalyst is located (pore diffusion).

- Once in contact with Pt particles, adsorption of H18-DBT occurs, resulting in a chemical reaction (adsorption and chemical reaction).
- Desorption of the products from the catalyst surface occurs (desorption).
- The products are then transferred from the Pt surface (pore diffusion).
- Products exit the catalyst into the bulk liquid phase (film diffusion).

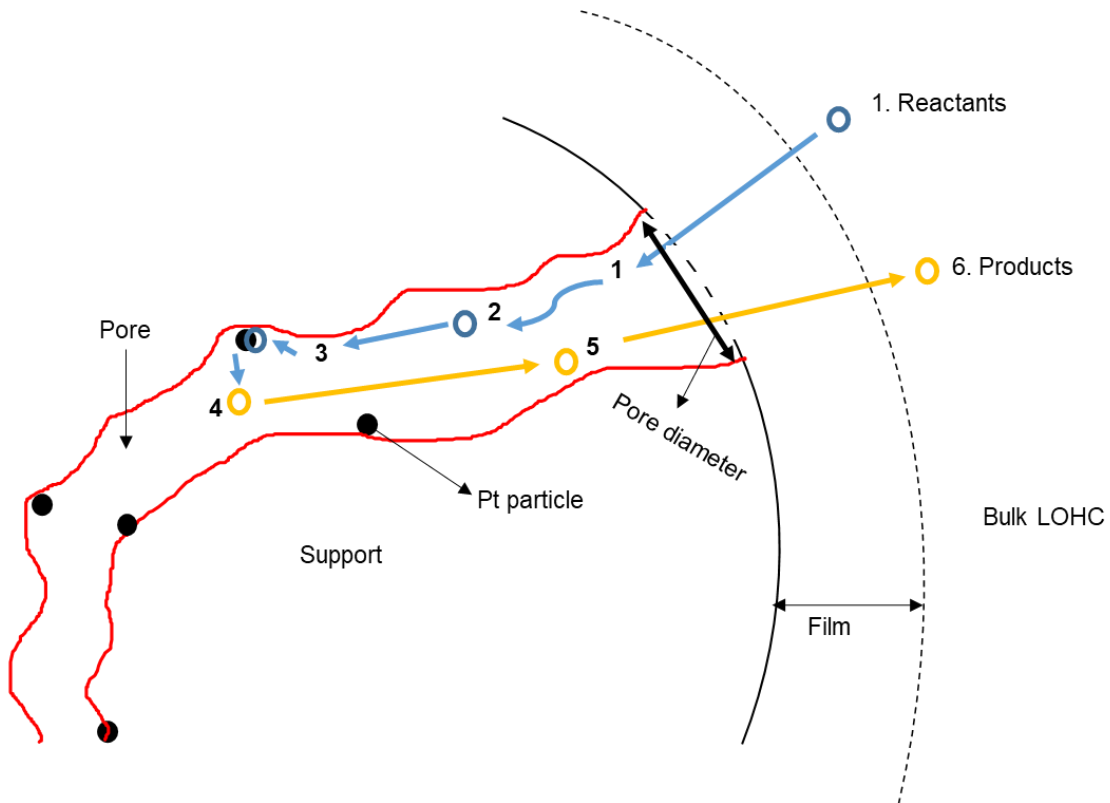


Figure 2-2. Reaction mechanism during the heterogeneous dehydrogenation of H18-DBT. (Hagen, 2015:99)

The rate of reaction (r), which is defined as the change in concentration of the reactants over a period of time, is calculated using equation (2.1)

$$\frac{dC_{\text{H18-DBT}}}{dt}(r) = k.C \quad (2.1)$$

where k is the rate constant and C is the concentration of reactant at time t . The rate constant k is temperature dependent and the relationship is described by Arrhenius using equation (2.2), which can be further simplified to equation (2.3)

$$\ln k = \ln A - \frac{E_a}{RT} \quad (2.2)$$

$$k = Ae^{\frac{-E_a}{RT}} \quad (2.3)$$

where A is the pre-exponential/frequency factor, E_a is the activation energy (J/kmol), R is the universal gas constant (8.314 J/kmol) and T is the temperature in Kelvin.

The frequency factor is an expression of the number of molecular collisions with the correct orientation that should overcome the activation energy barrier. Intrinsic microkinetics refers to the determination of the rate of reaction for a chemical reaction without external influences such as film and pore diffusion, whereas macrokinetics includes them.

Figure 2-3 shows the different kinetic regimes that exist in heterogeneous catalysis. In the kinetic regime, the reaction is slow compared to pore and film diffusion, such that a strong dependence on temperature exists according to the Arrhenius law. In the pore diffusion regime, the rate increases; however, a steep concentration gradient may occur, leading to reactant starvation of the catalyst. Here the reaction is fast, unlike in the pores. In the film diffusion regime, the rate increases slowly and has less dependence on temperature; yet total conversion is achieved anyway (Hagen, 2015:99). Therefore, the slowest reaction proceeds in the kinetic region and relates to the maximum activation energy, whereas the presence of diffusion influences results in low activation energy. Figure 2-4 shows a typical $\ln k$ versus $1/T$ curve, used to determine the activation energy.

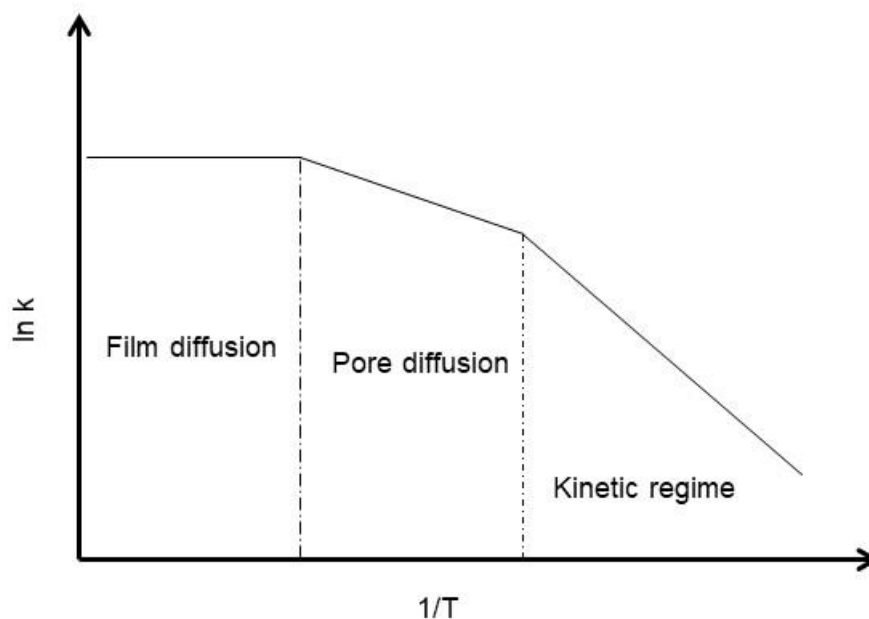


Figure 2-3. The effect of temperature on reaction rate. (Hagen 2015:101)

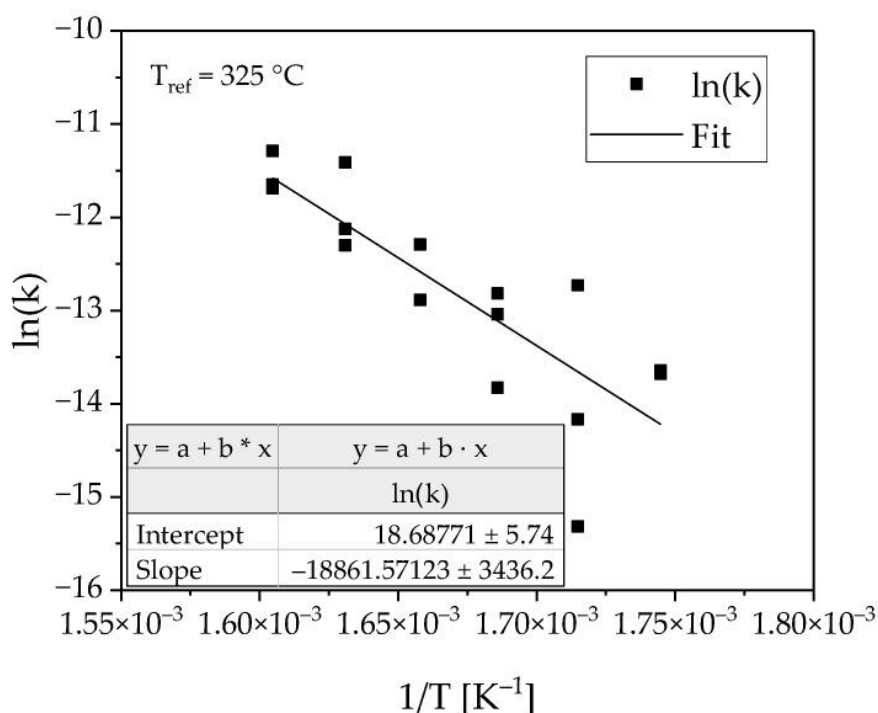


Figure 2-4. Determination of activation energy using Arrhenius equation. (Wunsch et al., 2018:120)

Kinetic studies of the dehydrogenation H18-DBT have been conducted when the hydrogen yield or α was <70% (Auer, 2020:126; Bulgarin et al., 2020:715; Peters et al., 2019:13797; Seidel, 2019:100). According to Preuster, cited by Seidel (2019:98), the back reactions associated with high conversions at temperatures >280 °C do not have a significant effect on modelling the LOHC system. Table 2-3 presents the activation energy recorded by various authors during the H18-DBT dehydrogenation reaction. The activation energies range from 60 to 205 kJ/mol, depending on dehydrogenation conditions; however high activation energies are associated with the absence of mass transfer influences. Both cases, i.e., where mass transfer influences are present and absent, are desirable for reactor design.

Table 2-3. Activation energy for the dehydrogenation of H18-DBT reported by various authors

Catalyst	Conditions	E _a , kJ/mol	Reference
1 wt % Pt/Al ₂ O ₃		205	
1 wt % Pd/Al ₂ O ₃	260–290 °C; 0.4 mol %	84	Modisha <i>et al.</i> (2019:21930)
1 wt % Pt-Pd/Al ₂ O ₃		66	
1 wt % Pt/Al ₂ O ₃	300–355 °C; 0.2 mol %	201	Modisha & Bessarabov (2020:4666)
0.3 wt % Pt/Al ₂ O ₃	280–300 °C, 1 bar (2.5 bar)	117(149)	Bulgarin <i>et al.</i> (2020:715)
0.3 wt % Pt/TiO ₂		145	
0.3 wt % Pt 0,1 wt. % S/TiO ₂	270–310 °C; 0.1 mol %	174	Chen <i>et al.</i> (2021:S5)
Pt/Al ₂ O ₃	260–310 °C	120	Peters <i>et al.</i> (2019:13797)
Pt/Al ₂ O ₃	300–350 °C	156±28,5	Wunsch <i>et al.</i> (2018:119)
0.3 wt % Pt/Al ₂ O ₃ ; d _p ^a :11 nm	280–310 °C; 0.05 mol %	151	
0.3 wt % Pt/Al ₂ O ₃ ; d _p ^a :14 nm	280–310 °C; 0.05 mol %	161	Auer (2019:127)
0.3 wt %Pt/Al ₂ O ₃ ; d _p ^a :18 nm	280–310 °C; 0.05 mol %	169	
0.5 wt % Pt/Al ₂ O ₃		97	
0.3 wt. % Pt/Al ₂ O ₃	270–320 °C; 0.05 mol %	131	Seidel (2019:98)
0.3 wt % Pt 0.14 wt. S/Al ₂ O ₃		143	

^a Pore diameter of alumina

2.4 Catalyst preparation and resulting configurations

The wet impregnation method is the most convenient and cost effective way to prepare catalysts (Munnik *et al.*, 2015:6693). Most Pt/Al₂O₃ catalysts are prepared using the impregnation method (Mehrabadi *et al.*, 2017:9). In principle, impregnation is the contact of a certain volume of precursor solution with a solid support. Incipient or dry impregnation is when the volume of precursor solution is the same as or less than the pore volume of a support, whereas wet impregnation is when an excess amount of solution is used. After impregnation, the supported catalyst is dried, then activated by calcination and reduction. Drying removes excess solvent and aids in the rearrangement of the metal on the support. The rate of drying is well known to influence the distribution of the active metal on the support (see Figure 2-5). For instance, Komiyama (1985:366) reported that a faster drying rate resulted in egg-white (ii)

or egg-yolk type (iii) (also referred to as ‘subsurface impregnation’) distributions for Ni on γ - Al_2O_3 . The former was achieved by the incipient/capillary co-impregnation of the precursor solution with an inorganic or organic acid. Figure 2-5 shows the distribution of the active phase after impregnation, drying and activation. An eggshell type (i) is usually preferred in fast reactions that have diffusion limitations, while a uniform distribution (iv) is preferred for slow reactions to allow reactants sufficient time to reach active centres. Type (iv) is attained by introducing a species that can compete with the active metal for adsorption on the support surface; meanwhile, subsurface configurations (ii & iii) can be achieved by presenting a different species that adsorbs strongly with the support and block the active metal on the catalyst surface. Subsurface configurations are desirable in reactions where the catalyst is prone to irreversible poisoning and in the event that the active metal can be eroded or worn out during stirring/reaction (Pinna, 1998:132).

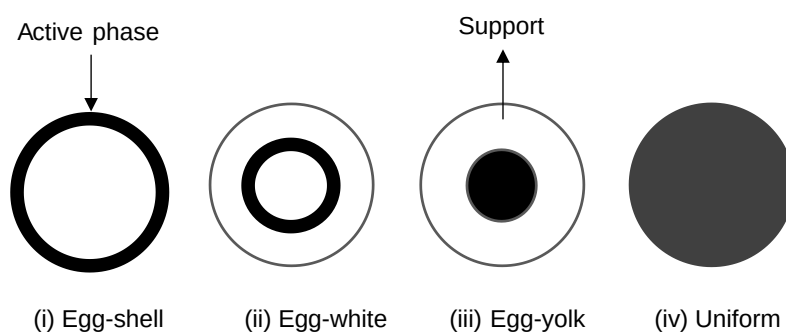


Figure 2-5. The distribution configurations of the active component on support after catalyst preparation. (Pinna, 1998:132)

The activation of the catalyst by calcination and reduction is very important. Calcination removes precursor salts such as chlorides, nitrates and sulphates, and enables the active metal to interact with the support without any competition. It also alters the porosity or textural properties of the support, which is favourable in dehydrogenation reactions. Here, reduction refers to when a reducing agent such as hydrogen is used to activate the active metal on the surface of a catalyst.

2.5 Catalyst characterisation

The characterisation of catalysts reveals information about their physicochemical properties, which play an important role in the catalytic performance. Such information will assist in understanding the catalyst behaviour. Various analytical techniques employed to characterise the catalysts are now discussed.

2.5.1 Brunauer-Emmett-Teller (BET) analysis

The Brunauer–Emmett–Teller (BET) analysis calculates the specific area of catalysts by measuring the volume of a gas adsorbed (usually N₂) at different pressures. This analysis is suitable for microporous (pore diameter <2 nm) and mesoporous (pore diameter 2–50 nm) materials. The BET surface area is then calculated using equation (2.4). Here, V_m is the volume of N₂ adsorbed at STP, P is the pressure at time t and P₀ is the saturation pressure of the adsorbate; and C_{BET} is the BET constant related to the strength of the adsorbate, the adsorbent and the heat of adsorption. BET results are commonly presented in the form of N₂ adsorption–desorption isotherms, as per Figure 2-6. Small pores fill at low relative pressure (P/P₀) while large pores fill at high relative pressure. For mesoporous adsorbents such as γ-Al₂O₃, the pore size should peak in the range 2–50 nm. Pore condensation evidenced by a hysteresis appears anywhere in the range 0.4–0.9 relative pressure. The BET surface area of γ-alumina ranges from 150 to 400 m²/g, depending on the synthesis method, while the pore volume and pore size vary from 0.23 to 0.84 cm³/g and 3 to 50 nm, respectively (Dabbagh *et al.*, 2011:275; Mostafa *et al.*, 2019:5433; Pai *et al.*, 2012:193; Rui *et al.*, 2014:885; Sachse *et al.*, 2017:1516).

$$\text{BET surface area} = \frac{1}{V_m C_{\text{BET}}} + \frac{C_{\text{BET}} - 1}{V_m C_{\text{BET}}} \times \left(\frac{P}{P_0} \right) \quad (2.4)$$

A high surface area for the support is ideal because it ensures a large surface for catalytic activity. Besides a high surface area, the pore structure (pore volume and pore size) is just as important, to facilitate diffusion of reactants and products. The influence of these parameters is immense—a large pore size greatly improves dehydrogenation due to rapid diffusion. For instance, Lee *et al.* (2021:5521) found dehydrogenation of H18-DBT to be more facile with a pore diameter of 12.6 nm than for the support with 4.2 nm. Auer *et al.* (2019:3538) also noted better dehydrogenation of H18-DBT when using a Pt/Al₂O₃ catalyst with a pore diameter of 30 nm.

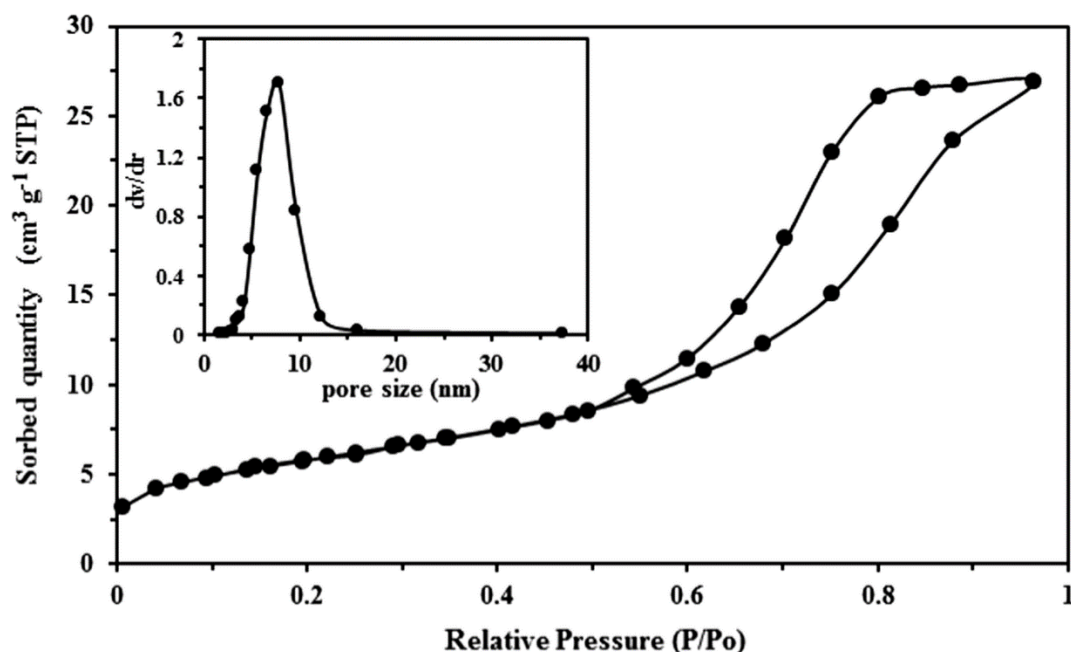


Figure 2-6. Typical N_2 adsorption and desorption isotherms with a pore size distribution curve for mesoporous γ -alumina.(Mostafa *et al.*, 2019:5432)

2.5.2 X-ray diffraction (XRD) and transmission electron microscopy (TEM)

Adsorption is crucial in dehydrogenation reactions since it involves both the physical and chemical adhesion of molecules to the catalyst surface. This then means that the geometry (shape) and size of the Pt nanoparticle determines the type of exposed sites (facets). The greater the number of facets exposed, the higher the surface energy and the more reactive the Pt particle (Huang *et al.*, 2011:11583). This is due to the high density of edges/steps, which serve as active sites for bond breaking (Hagen, 2015:131). For a face centred cubic (FCC) crystalline plane of a Pt nanoparticle, a cubic Pt particle is bound by six atoms at the corners and one atom at the centre of each face. This can result in different forms of facets with low (100, 110, 111) to high (311) index planes. Current research indicates that the development of high-index faceted Pt nanoparticles is beneficial, especially in electrocatalysts. However, maintaining the same facet during synthesis or throughout the reaction presents a challenge (Huang *et al.*, 2011:11579), as it can change or be destroyed when exposed to heat or acidic conditions (Hu *et al.*, 2020:4352).

X-ray powder diffraction (XRD) and transmission electron microscopy (TEM) can be used to detect different Pt and Al_2O_3 phases; see Figure 2-7 and Figure 2.8B. Due to the stability and ease of synthesis of low index facets, Pt (111) is the most detected and studied in the dehydrogenation of aromatics (Amende *et al.*, 2014:1498; Amende *et al.*, 2016:671; Bachmann *et al.*, 2019:144713; Chen *et al.*, 2020:6727; Gleichweit *et al.*, 2015:20300; Ouma,

2018:31902; Ouma, 2019:1035). The Pt (111) used for dehydrogenation of H18-DBT can be fully regenerated at temperatures >400 °C by thermal treatment with oxygen.

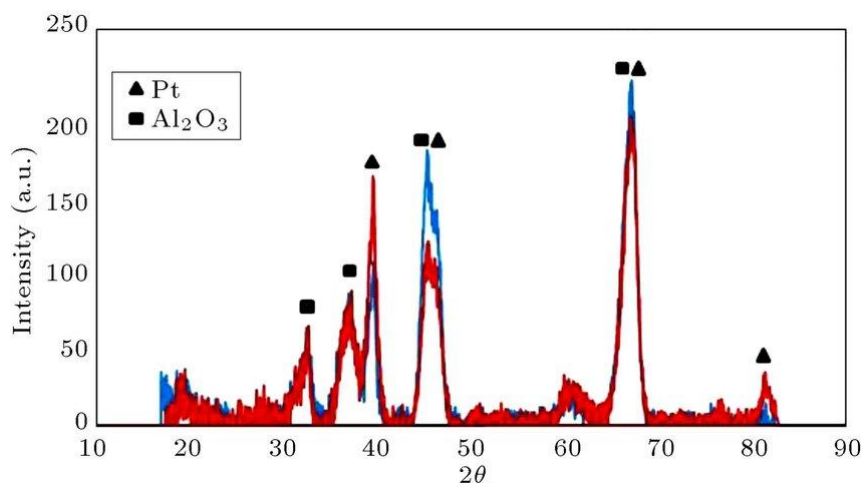


Figure 2-7. XRD pattern indicating peaks for Pt and γ -Al₂O₃ nanoparticles. (Keshavarz & Salabat, 2019:1927)

TEM is used to determine Pt particle size distribution: see Figure 2-8. The resulting histogram obtained by measuring the diameter of particles will give an average particle size. Smaller Pt NPs (<2 nm) have been reported to result in better catalyst performance than bigger particles (>3 nm). This is due to large surface areas and the high Pt dispersions that can be achieved (Kumar *et al.*, 2008:747; Wang *et al.*, 2020:16542; Zhu *et al.*, 2015:6310). For instance, Tuo *et al.* (2018:185) reported that Pt particles size of <2 nm on carbon were effective in the dehydrogenation of decalin than bigger particles (2–4 nm). The reason is that in the presence of small particles, the support effect is more dominant than in the presence of bigger particles, hence catalyst activity is improved. The bottleneck still lies in the optimisation of the particle size because small particles can be highly active, compromising the selectivity of the desired product, while large particles result in low activity with high selectivity (Kumar *et al.*, 2008:750). In this regard, Auer *et al.* (2020:6677) sought to obtain the optimum Pt particle size (~1–5 nm) for the dehydrogenation of H18-DBT using Pt/Al₂O₃ catalysts. The best dehydrogenation performance was obtained when the Pt particles were in the range 1.95–2.7 nm. Interestingly, by-products formation was high with small particles (<2 nm) and low with big particles (>2 nm). Small particles contain low-coordinated surface sites that promote by-product formation. Much research is still needed in order to develop nanoparticles that will favour catalytic activity without compromising on selectivity and by-product formation.

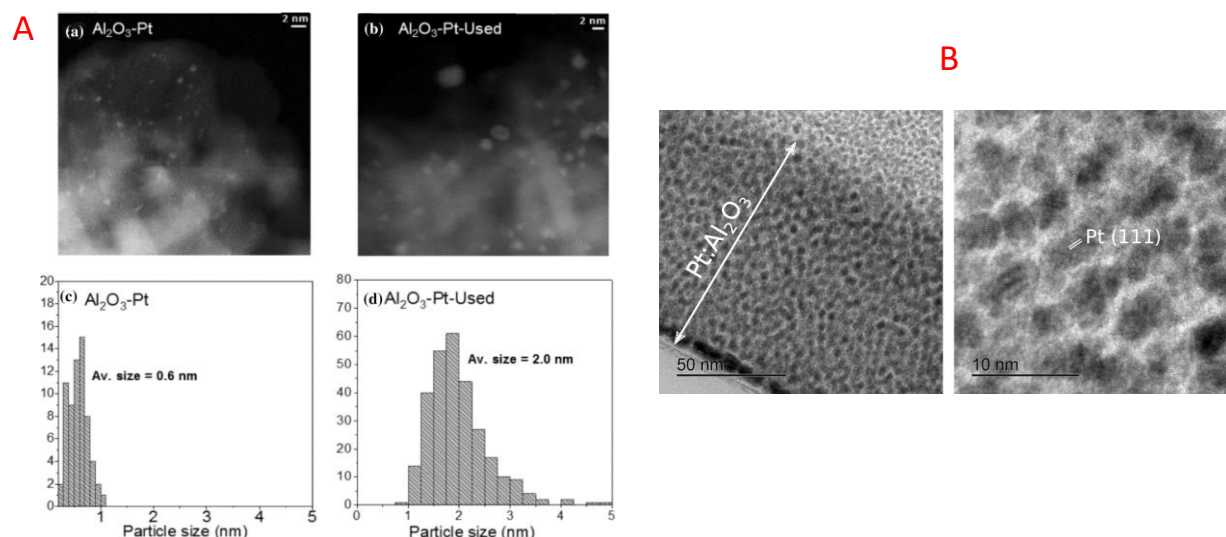


Figure 2-8. TEM images of $\text{Pt}/\text{Al}_2\text{O}_3$, showing (A) Pt size distribution before and after reaction and (B) Pt (111) on Al_2O_3 . (Schwebke *et al.*, 2018:235308-4)

2.5.3 Carbon monoxide (CO) pulse chemisorption

Dispersion is defined as the ratio of the number of free active metal atoms to the total atoms on the surface of a catalyst that can be accessed during the reaction (Hagen, 2015:141). Small particles increase dispersion, while big particles result in small dispersion (Kwak *et al.*, 2021:119285; Tuo *et al.*, 2021:936). The dispersion of Pt on alumina ranges from 15 to 85%, depending on the preparation method (Auer *et al.*, 2019:3543; Chen *et al.*, 2021:6564; Matsushashi *et al.*, 2004:335). It is expected that, with high dispersions, catalyst activity increases; however the support structure/morphology and where the particle is located also play a substantial role—there is not always a direct correlation. For example, Tuo *et al.* (2021:934) treated Pt on carbon nanotube (CNT) surfaces with oxygen and nitrogen for the dehydrogenation of decalin. The treatment improved Pt dispersion in all catalysts, however, the non-treated Pt/CNT ($D = 25\%$) gave better activity ($\sim 420 \text{ mmol H}_2/\text{g}_{\text{Pt}}$) than Pt/CNT-O ($380 \text{ mmol H}_2/\text{g}_{\text{Pt}}$) with a higher dispersion ($D = 31\%$). The decreased performance in the more dispersed catalyst was attributed to the electron-donating property of O_2 , which suppressed electron transfer in Pt, such that adsorption of decalin on the carbon support was compromised. This observation proves that, whereas obtaining higher dispersions is necessary, the surface chemistry cannot be overlooked in the development of a catalyst that will perform well. This is also confirmed by the work recently conducted by Chen *et al.* (2021:6564). Pt/S- TiO_2 (D , 58%) and Pt/ Al_2O_3 (D = 75%) had similar activity; however, Pt/S- TiO_2 was ideal because of the minimum amount of by-products produced (2.7 vs 8 mol %).

The mostly commonly used reactive gas in determining dispersion is H_2 or CO. In the case of CO, the gas is contacted with the surface of a catalyst so that it reacts with the active sites

(chemisorption). The gas is supplied in pulses, where CO is introduced in intervals until the catalyst is fully saturated (see Figure 2-9). The volume of CO chemisorbed is then used to calculate dispersion (D) using equation (2.5) from Lee *et al.* (2021:5522);

$$D = \frac{V_m \times MW_{Pt}}{22414 \times m_{Pt}} \quad (2.5)$$

where V_m is the volume of the adsorbed monolayer, MW_{Pt} is the molar mass of Pt and m_{Pt} is the mass of Pt.

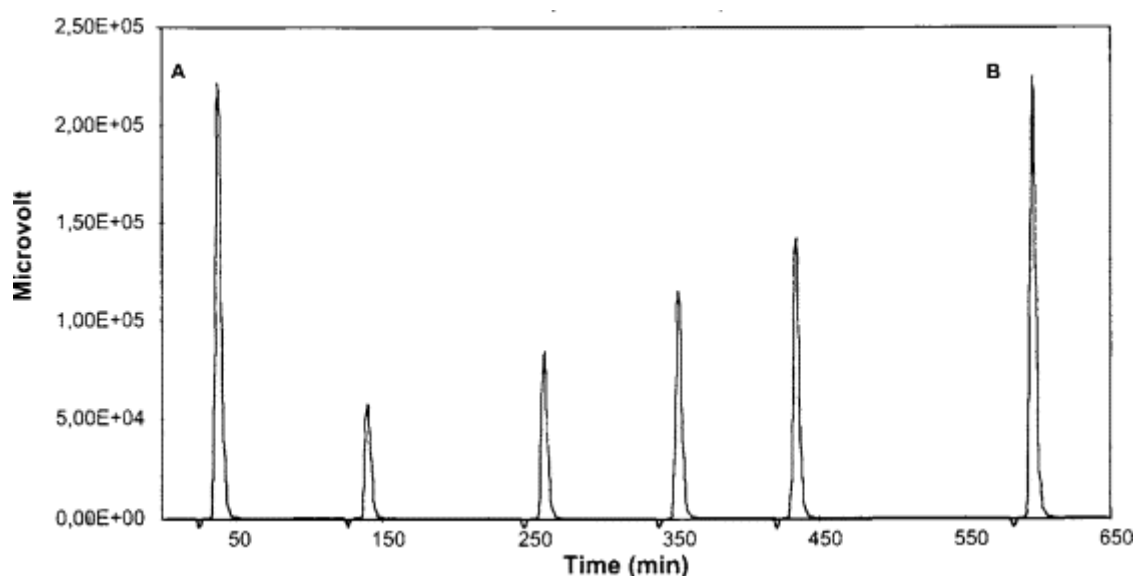


Figure 2-9. Pulse CO chemisorption of Pt/Al₂O₃. (Fadoni & Lucarelli, 2006:26)

2.5.4 Hydrogen temperature programmed reduction (H₂-TPR)

Hydrogen temperature programmed reduction (H₂-TPR) is mostly used to determine the accurate conditions at which metal (Pt) reduction occur in oxides. It also reveals the nature of metal–support interactions (MSIs). When strong MSIs are present, high temperatures are required to reduce or expose the active metal. Basically, a known mass of sample is crushed to fine powder and subjected to H₂ at elevated temperatures. Figure 2-10 shows a typical H₂-TPR of Pt/Al₂O₃. The peaks indicate higher interactions of the catalyst with the reducing agent, or the temperature at which the metal oxide reduce to elemental Pt. The reduction of Pt on alumina has one or two main peaks before 200 °C and the other after 300 °C (Abu-Laban *et al.*, 2017:4; Contreras-Andrade *et al.*, 2009:3838; Luo *et al.*, 2013:1485; Park *et al.*, 2015:2214). The accurate determination of reduction temperature is important and determines the ultimate performance of supported catalysts. Complete reduction ensures, the active metals sites are exposed to the catalyst surface and the more these sites are exposed, the better the chance of improved activity.

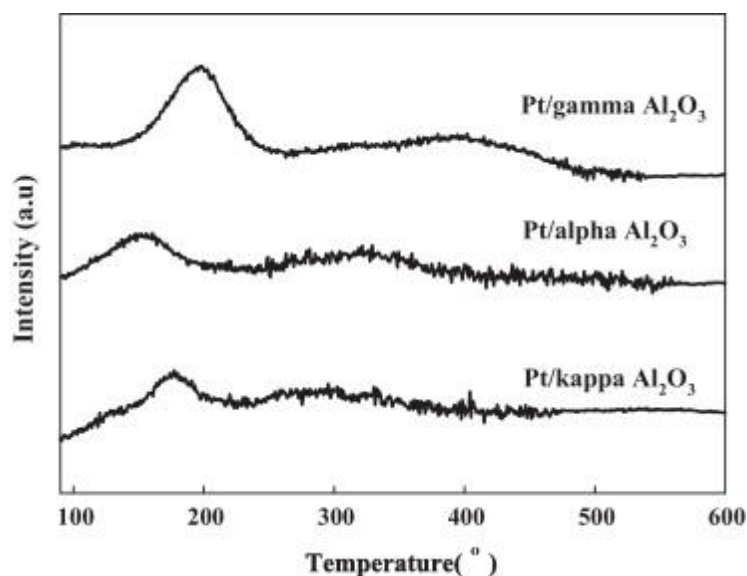


Figure 2-10. H_2 -TPR of Pt/Al_2O_3 showing temperatures at which reduction occurs. (Kim et al., 2012:273)

2.5.5 Acidity

Metal oxide supports such as alumina and zeolites have always been existent as catalysts for isomerisation and hydroforming of hydrocarbons (Benesi & Winkvist, 1979:98). Their acidity is pivotal in catalysis. By general definition, acidity refers to an electron pair acceptor; however, there are two classes of acid sites on oxide surfaces namely: Lewis acid and Bronsted acid (see Figure 2-11). Lewis acids are electron pair acceptors while Bronsted acids are proton donors. γ - Al_2O_3 generally has Lewis acid sites, however, if chloride precursors are used, both Lewis and Bronsted acid sites may be present (Tanaka & Ogasawara, 1970:162).

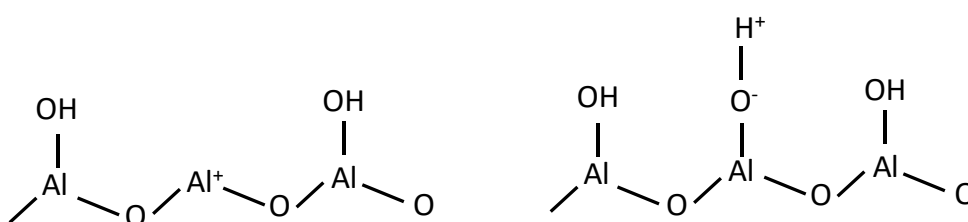


Figure 2-11. Lewis (left) and Bronsted (right) acid sites on Al_2O_3 . (Auer, 2020:6)

It is sometimes necessary to define the type of acid centre but this work only focus on the acid density (number of acidic centres per surface area of sample) and acidic strength with how they affect H18-DBT activity. To analyse the acid density and strength, ammonia temperature programmed desorption (NH_3 -TPD) is widely used (Lee et al., 2016:129; Said & Zaky, 2019:2126; Shi et al., 2017:19845; Thanasilp et al., 2013:52; Stanciulescu et al., 2014:204). Temperature is ramped while NH_3 is contacted with the surface of catalysts. Just like H_2 -TPR

chemisorption, the resulting data from the TCDs are recorded and the graph looks like the one depicted in Figure 2-12. Strong acidic peaks are usually found at high temperatures while weak to medium strength at low temperatures (Gutiérrez-Alejandre *et al.*, 1998:273; Łaniecki *et al.*, 2000:298; Stanislaus *et al.*, 1988:242).

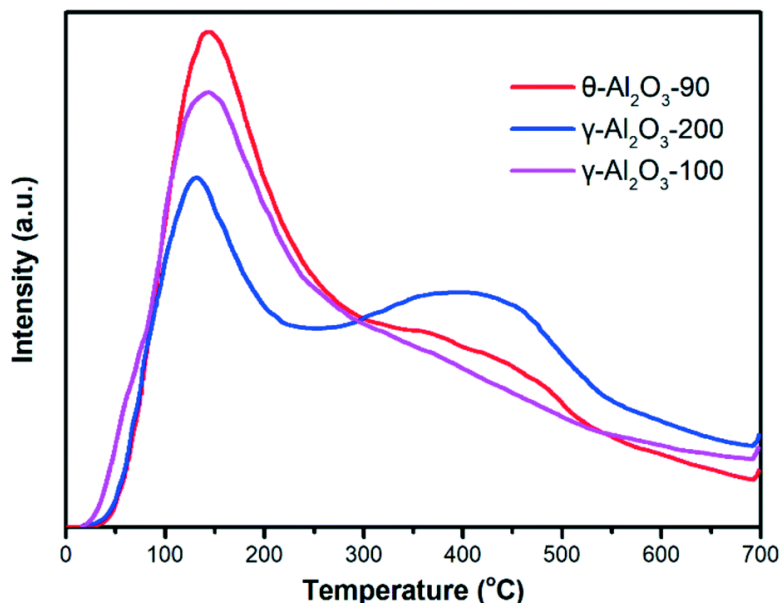


Figure 2-12. NH_3 -TPD analysis of alumina for the determination of acidity. (Wang *et al.*, 2020:3537)

The effect of acidity on dehydrogenation reactions has been extensively studied (Jablonski *et al.*, 1999:189; Rombi *et al.*, 2003:255; Sun *et al.*, 2008:212). Many agree that good regulation of support acidity is beneficial to the activity, selectivity and stability. This is supported by the work of Guenin *et al.* (1987:144), after observing the dehydrogenation of cyclohexane using Pt on non-microporous alumina modified with K and Cl. The reaction was found to be structure insensitive, because poisoning of the catalyst was affected by the support acidity and not variation of the Pt size. Highly acidic Al_2O_3 can lead to coke formation during long chain (C_{16} – C_{19}) paraffin dehydrogenation (He *et al.*, 2014:97). Luo *et al.* (2013:79) found that, the catalyst (Pt/Sn-K/ γ - Al_2O_3) activity for isopentene dehydrogenation, was more dependent on the acidity of the support rather than on the BET surface area. The reason for the better performance of the optimised acidity on an alumina support is best expressed by Regali *et al.* (2014:338); they reported that cracking/coke deposition on the surface of moderate acidity catalysts is suppressed by charge transfer from the modified Pt sites to the support, thereby facilitating desorption of reactants. Therefore, to address the current problems of deactivation of Pt/ Al_2O_3 catalysts used in LOHCs, it may be considered that modifying the Al_2O_3 support with Mg and Zn could aid in altering the acidity and suppressing deactivation.

Modification of the Al₂O₃ support using Mg and Zn has been reported to enhance catalytic performance, strengthen the MSI, change support acidity and improve metal dispersion. For example, Zn modification on both Pt/Al₂O₃ and Pt/ZSM-5 catalysts showed improved catalytic performance for propane dehydrogenation (Ballarini *et al.*, 2012:433; Belskaya *et al.*, 2016:13; Buitrago-Sierra *et al.*, 2012:148; Yu *et al.*, 2007:80; Zhang *et al.*, 2015:352;). Mg-doped Al₂O₃ also has excellent attributes, such as the ability to promote surface diffusion and prevent clustering/sintering by suppressing grain growth (Ballarini *et al.*, 2012:433; Berry & Harmer, 1983:143). Furthermore, it is reported that Mg does not only reduce the acidity of an Al₂O₃ support, but it also lowers the carbon deposition rate, which is known to cause catalyst deactivation (Bai *et al.*, 2009:9885; Xue *et al.*, 2012:928).

2.6 LOHC characterisation

The characterisation of LOHC is essential in order to determine the degree of hydrogenation (doh), H18-DBT concentration, conversion (X), selectivity (S) and by-products. Since the H0-DBT/H18-DBT LOHC system comprises partially hydrogenated intermediates, the determination of doh, and the detection of various intermediates and their isomers, can be challenging when using only basic gas chromatography (GC). Aslam *et al.*, (2016:144) developed a method of separating H0-DBT according to its doh using reversed-phase high performance liquid chromatography. They successfully separated H0-DBT into four stable fractions, with purity >98%. Modisha *et al.* (2018:5636) proposed the use of advanced single quadrupole gas chromatography with mass spectroscopy (GC-MS-QS), which was able to separate and detect the overlapping intermediates and their isomers. Figure 2-13 shows the separated intermediates of reaction mixtures, determined by GC-MS-SQ. The doh obtained from the results was comparable to the values obtained from two dimensional gas chromatography coupled with time of flight mass spectrometry and proton nuclear magnetic resonance (¹H-NMR). Dürr *et al.*, (2021:11) recently used carbon-13 nuclear magnetic resonance and gas chromatography with a flame ionisation detector systems to determine the doh. These techniques are very accurate, and their use can be considered an effective way of determining the doh. The doh determined from GC-MS-SQ can be calculated using equation (2.6) (Müller *et al.*, 2016:22099):

$$\text{doh} = 0.33 x_{\text{H6-DBT}} + 0.67 x_{\text{H12-DBT}} + x_{\text{H18-DBT}} \quad (2.6)$$

Where x is mole fraction

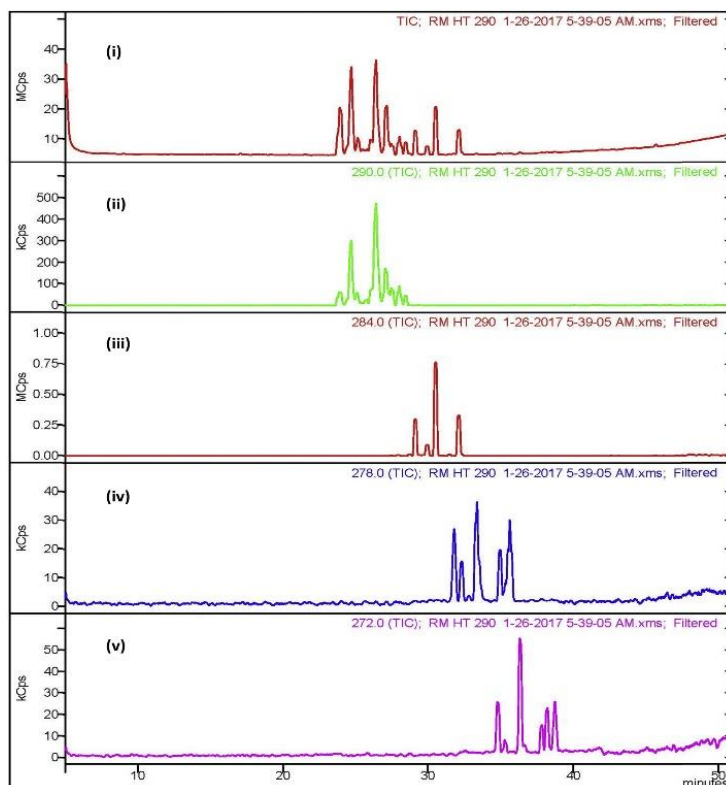


Figure 2-13. Stable intermediates and their isomers obtained during the dehydrogenation of H18-DBT at 290 °C. (Modisha et al., 2018:5631)

Determination of the doh using physical properties such as density and the refractive index (RI) is also ideal because it is cheap, quick, easy and accurate (when calibrated). Müller *et al.* (2016: 22101) reported determination of H0-DBT doh using RI, with a maximum deviation of 0.03%; thus, a calibration curve with a regression value of 0.99997 was obtained (see Figure 2-14). The use of ^1H -NMR, Raman spectroscopy, ultraviolet-visible spectroscopy and viscosity can also be explored.

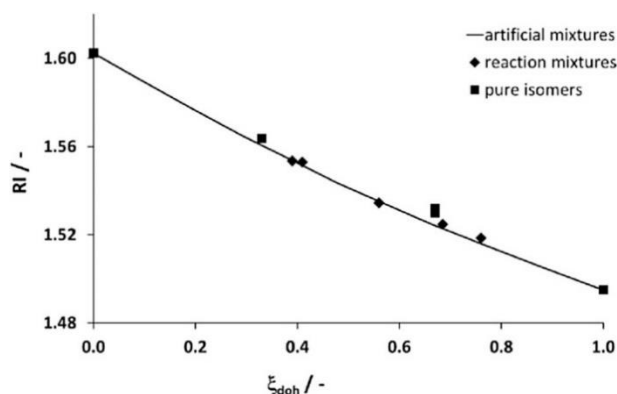


Figure 2-14. The relationship between refractive index and doh at room temperature. (Müller et al., 2016:22101)

The review of catalyst characterisation has highlighted the dependence of the dehydrogenation activity on the physicochemical properties of the catalysts. For the dehydrogenation of H18-DBT, a catalyst that can facilitate the diffusion of reactants and products, is key—therefore, a large pore diameter to accommodate the LOHC molecule is very important. The maximum *d₀* has been obtained when the Pt particle size is in the range 1.95–2.7 nm, with high by-product formation at 1.5 nm. This is because Pt particles have low-coordinated sites that are responsible for by-product formation. Doping with sulphur has been rewarding, since the sites responsible for by-product formation are then suppressed. It was also revealed that the addition of Mg and Zn dopants positively alter physicochemical properties of catalysts such as textural properties, MSI, acidity, Pt size and dispersion; and ultimately improve dehydrogenation performance. Mg-doped Al₂O₃ also has excellent attributes, such as the ability to promote surface diffusion and prevent clustering/sintering by suppressing grain growth. Furthermore, Mg does not only reduce the acidity of an Al₂O₃ support, but it also lowers the carbon deposition rate, which is known to cause catalyst deactivation. Therefore, adding dopants such as Mg and Zn may not only reduce the formation of by-products, but may also improve stability. Further focus needs to be directed at determining the best physicochemical properties of Pt/Al₂O₃ catalysts that result in the most efficient dehydrogenation of H18-DBT, including the optimal Pt size, dispersion, porosity and acidity.

CHAPTER 3. EXPERIMENTAL PROCEDURE

This chapter provides a detailed description of all materials used in this study, followed by the methods used for catalyst preparation and characterisation. Specifications and operational procedures applicable to both the batch and fixed bed reactor systems, as used for the evaluation of catalysts for the dehydrogenation of perhydrodibenzyltoluene, are also provided. Therefore, the following research methodology was used to achieve the specific objectives.

3.1 Materials

Dibenzyltoluene (H0-DBT) was purchased from Sasol (Marl, Germany) and then hydrogenated in-house (using a hydrogenation plant) to produce perhydrodibenzyltoluene (H18-DBT) (99% doh). The spherically shaped γ - Al_2O_3 support pellets (diameter 1–3 mm) were supplied by Sasol (Johannesburg, South Africa). The $\text{Mg-Al}_2\text{O}_3$ and $\text{Zn-Al}_2\text{O}_3$ were prepared by modification of the parent unmodified γ - Al_2O_3 used in this study. Chloroplatinic acid hydrate (38% Pt basis) was purchased from Sigma-Aldrich (Schnelldorf, Germany). Magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98% purity) and zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98% purity) were supplied by Ace Chemicals (Johannesburg, South Africa). The following gases were supplied by Afrox (Johannesburg, South Africa): H_2 (99.999%), N_2 (99.999%), He (99.999%), Ar (99.999%), 10% CO/He , 10% NH_3/He and 10% H_2/Ar . These gases were used for processing the catalysts (calcination and reduction), and to feed the chemisorption equipment used for catalyst characterisation.

3.2 Catalyst preparation

Modified catalyst support materials ($\text{Mg-Al}_2\text{O}_3$ and $\text{Zn-Al}_2\text{O}_3$) were prepared by the incipient wet impregnation method (using $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as precursors). The precursor solution was mixed with the support and stirred for 2 h at 50 °C in a rotary evaporator before introducing a vacuum pressure of 300 mbar. The modified Al_2O_3 samples were dried for 2 h at 100 °C and then calcined for 1 h at 500 °C (temperature ramp rate 2 °C/min) in the presence of NO_2 . The following equations were used in the preparation of 100 g of 3.8 wt % $\text{Mg-Al}_2\text{O}_3$:

$$V_{\text{sol}} (\text{ml}) = \text{Al}_2\text{O}_3 \text{ pore volume} \times \text{impregnation mass (100 g)} \quad (3.1)$$

$$m_{\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}} (\text{g}) = m_{\text{Mg per 100 g}} \times \frac{Mw_{\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}}}{Mw_{\text{Mg}}} \quad (3.2)$$

$$V_{\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}} (\text{ml}) = \frac{m_{\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}}}{\rho_{\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}}} \quad (3.3)$$

$$V_{\text{H}_2\text{O}} (\text{ml}) = V_{\text{sol}} - V_{\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}} \quad (3.4)$$

where V_{sol} is the volume of solution in ml, $V_{\text{H}_2\text{O}}$ is the volume of water to be added, m is the mass in g, M_w is the molecular weight in g/mol and ρ is the density of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in g/cm³.

The Pt based impregnation solution (0.025 M) was prepared by adding chloroplatinic acid hydrate powder to deionised water. The solution was added to each alumina support to produce 0.5 wt % Pt loading. A Büchi rotary evaporator (model R300) supplied by Büchi Labortechnik, Switzerland was used to impregnate pellets. The heating bath was set at 50 °C, while the evaporating flask was under 46 mbar vacuum pressure and rotating at a speed of 40 rpm. An Espec oven (model SU-221) from Espec Corp Japan, was set at 120 °C to dry the pellets over 4 h. Thereafter, pellets were calcined at 350 °C (temperature ramp rate 5 °C/min) in a stream of air (150 mL/min) for 5 h, using a furnace (Carbolite, United Kingdom). The calcined catalysts were reduced in a stream of 10% H_2/Ar (50 mL/min) over periods of 4 h at 350, 400 and 450 °C for Pt/ Al_2O_3 , Pt/Mg- Al_2O_3 and Pt/Zn- Al_2O_3 , respectively. Figure 3-1 shows a schematic representation of the experimental procedure for catalyst preparation.

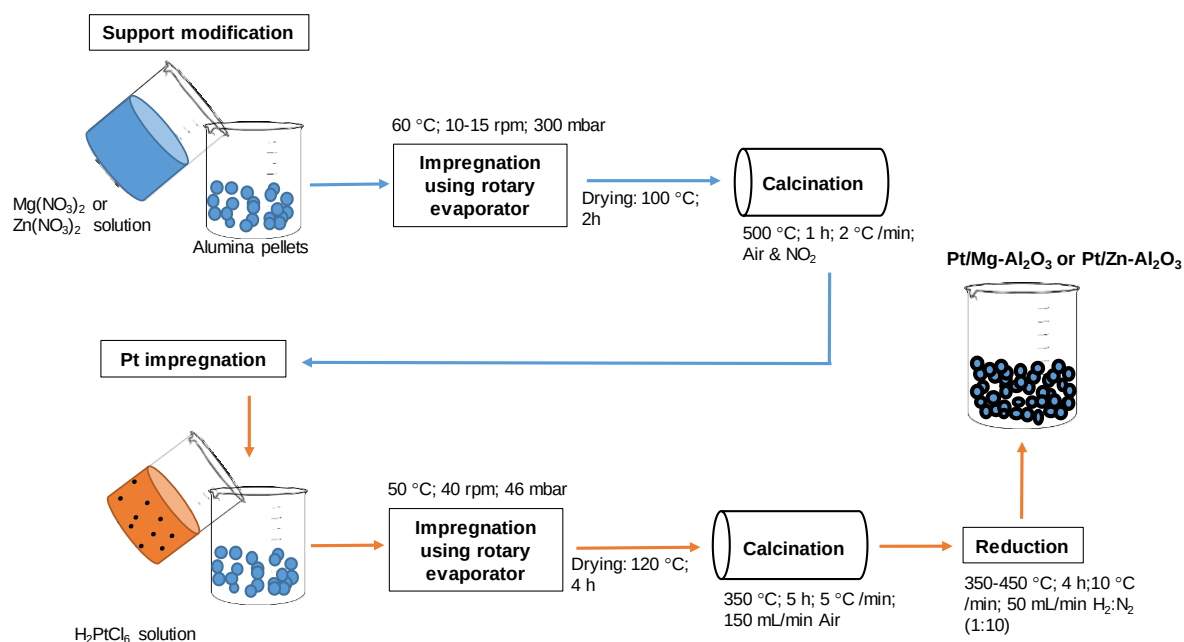


Figure 3-1. Overview of catalyst preparation by the impregnation method.

To prepare 0.5 wt % Pt/ Al_2O_3 catalyst using 38% Pt basis H_2PtCl_6 , the required masses of Pt and Al_2O_3 support were calculated as follows:

for 50 g catalyst with 0.5 wt %:

$$m_{\text{Pt}} (\text{g}) = \frac{\text{Pt loading (wt. \%)}}{100} \times \text{Total mass of catalyst (50 g)} \quad (3.5)$$

$$m_{\text{Al}_2\text{O}_3} (\text{g}) = \text{Total mass of catalyst} - m_{\text{Pt}} \quad (3.6)$$

$$m_{\text{H}_2\text{PtCl}_6} \text{ (g)} = \frac{m_{\text{Pt}}}{C_{\text{Pt in H}_2\text{PtCl}_6}} \quad (3.7)$$

where C_{Pt} is the concentration of Pt in H_2PtCl_6 .

3.3 Catalyst characterisation

3.3.1 Inductively coupled plasma optical emission spectrometry (ICP-OES)

Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to confirm the catalyst loading. Use was made of an Agilent 5110 ICP-OES instrument and the ICP Expert software. Samples were leached for 24 h, using a 1:10 mixture ratio of H_2O_2 :HCl at 60 °C. The leachate was analysed for the presence of Pt, Mg and Zn. The calibration curves for Pt, Mg and Zn are shown in Figure B1–B3 in the appendices.

3.3.2 Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS)

Scanning electron microscopy (SEM) imaging was carried out using an FEI Quanta 250 field emission gun scanning electron microscope, operating at an accelerating voltage of 15 kV. Energy-dispersive X-ray spectroscopy (EDS) line scan analysis was carried out using the Oxford Inca software. The line point samples were taken at an equidistance of 40 microns. All samples were coated with carbon, using magnetron sputtering, to allow conduction between the sample and a beam of electrons from the SEM-EDS instrumentation. To perform an elemental cross-sectional line analysis, the reduced samples were embedded in a resin; see Figure 3-1. This was carried out using a Leco PR-10 Mounting Press at 121 °C and 290 bar, for 20 min. After mounting, the samples were cut to expose the pellets' cross-sectional area; see Figure 3-2.

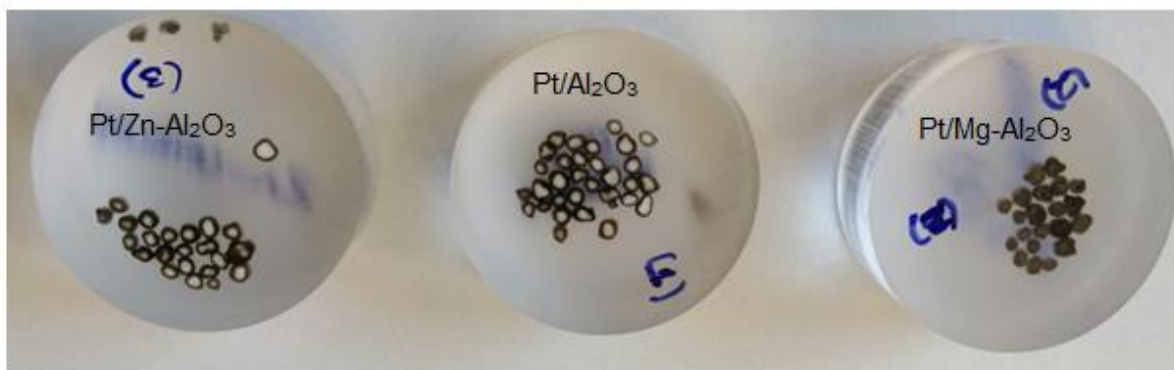


Figure 3-2. Exposed cross-sectional area of catalysts, for SEM-EDS line analysis.

3.3.3 Carbon monoxide (CO) pulse chemisorption

Carbon monoxide (CO) pulse chemisorption experiments were conducted using Micromeritics Auto-Chem II 2910, USA. The quartz U-tube reactor was loaded with 0.6 g of each catalyst. All catalysts samples were reduced before carrying out CO pulse chemisorption experiments. Chemisorption was carried out at 35 °C under a He stream flow rate of 50 ml/min, using a pulsed chemisorption technique (0.5 ml pulses of CO were injected).

3.3.4 Ammonia temperature programmed desorption (NH₃-TPD)

The acidity of support and catalyst samples was measured by NH₃-TPD using a Micromeritics Auto-Chem II 2910 chemisorption analyser. For these experiments, 0.1 g of each catalyst was loaded in a U-type quartz sample tube and 10% NH₃/He gas was used. Samples were pre-treated at 500 °C for 1 h under a He stream (30 ml/min). This was followed by saturation of the sample with NH₃ at 120 °C. Subsequently, the desorption of NH₃ was determined using a TCD, at temperatures ranging from 100 to 900 °C (temperature ramp rate 10 °C/min).

3.3.5 Transmission electron microscopy (TEM)

A transmission electron microscope FEI Tecnai F20 operating at an accelerating voltage of 200 kV was used to determine particle size distribution. Samples were crushed to powder and mixed with ethanol to make a suspension. A mixture was placed in an ultrasonic bath for 30 min at 40 °C. Samples of the mixture were then dropped onto copper grids and analysed for Pt NPs. The particle size was obtained by measuring about 300 particles using Image J software. The histogram of the particle size, for each catalyst, was then fitted using a log-normal distribution curve. The parameters of log-normal distribution (μ -lognormal mean and σ -lognormal standard deviation obtained after fitting the 300 particles) are used to calculate the actual mean (m) and mode (m_o) of each catalyst, using equations (3.8) and (3.9).

$$m = \exp\left(\mu - \frac{\sigma}{2}\right) \quad (3.8)$$

$$m\sigma = \exp\left(\mu - \sigma^2\right) \quad (3.9)$$

3.3.6 Powder X-ray diffraction (XRD)

Powder XRD was performed using a Bruker D8-Advance all-purpose X-ray diffractometer, operated in a locked coupled mode with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 40 mA tube voltage and tube current, respectively. A sample was mounted in the centre of the sample holder on a glass slide and levelled up to the correct height. The measurements were within the range 2θ (0–90°). A position sensitive Lynx-Eye detector was used. Diffraction data were recorded at a speed of 0.5 sec/step, which is equivalent to an effective time of 92 sec/step for a scintillation counter.

3.3.7 Brunauer-Emmett-Teller (BET)

The catalyst's textural properties (surface area, pore volume and diameter) were determined using a Micrometrics instrument (ASAP 2020 V4.01, USA). The sample tube was loaded with 0.3 g sample and degassed at 300 °C for 8 h. The N₂ adsorption/desorption isotherms were then recorded at -196 °C.

3.4 Dehydrogenation activity tests

The dehydrogenation performance was determined in two phases: first in the batch reactor, where the effects of temperature (260–300 °C) and dopants were investigated, and second in a fixed bed reactor, where the catalyst stability was evaluated. Dehydrogenation kinetics were addressed in the batch reactor. The set-up and reaction conditions are described in the following sections.

3.4.1 Dehydrogenation tests: batch reactor

For the dehydrogenation of the H18-DBT (99% doh), a 200-ml three-necked round bottom flask was used as batch reactor. The flask was attached to a condenser with a downstream filter made of glass wool and activated carbon for capturing discharged vapours. A Bronkhorst mass flow meter (EL-Flow F11B-500-AGD-22V; max flow-rate 500 ml/min) was connected to the filter outlet and used to measure the hydrogen flow rate (HFR). The air was removed by purging with N₂ gas. The reactor was heated from the outside by a heating mantle with a digital feedback temperature controller WHM-C10D (Daihan Scientific, Korea), while the cooling condenser was continuously cooled to 10 °C by a cryostat (FED-12, Julabo Labortechnik GmbH, Germany). The temperature and HFR data were logged using LabView software. The

pipng and instrumentation diagram (PID) of the batch dehydrogenation system set-up is shown in Figure 3-3.

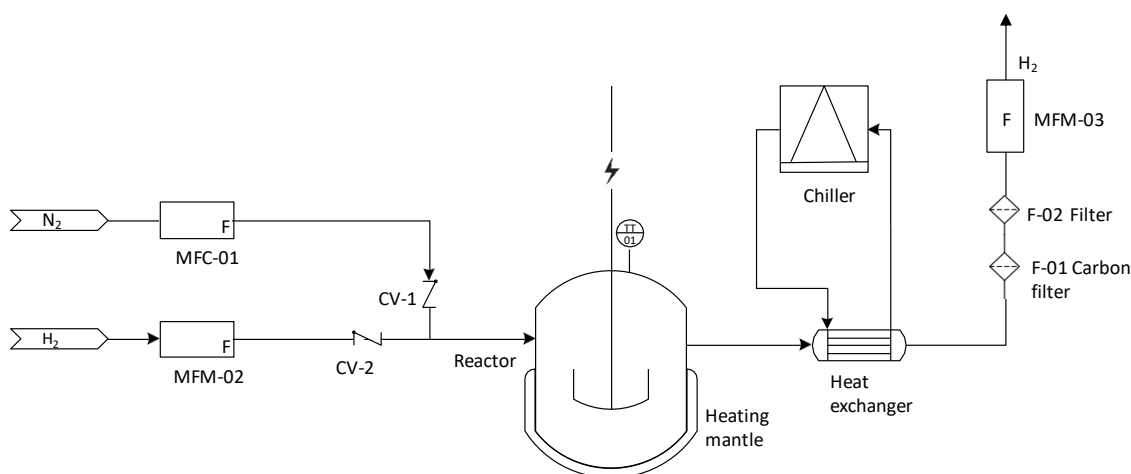


Figure 3-3. PID of a batch reactor dehydrogenation set-up.

The H₂ yield, or dod, obtained from the logged data, was calculated based on the total hydrogen produced vs theoretical hydrogen stored in H18-DBT. This value was confirmed by determining the dod using a refractometer. H₂ yield, productivity (Pr) and concentration (C) were calculated using equations (3.10), (3.11) and (3.12), respectively.

$$\text{H}_2 \text{ yield (\%)} = \frac{\text{Volume of H}_2 \text{ released}}{\text{Theoretical H}_2 \text{ volume}} \times 100 \quad (3.10)$$

$$\text{Pr} = \frac{m_{\text{H}_2}}{m_{\text{Pt}} \cdot t} \quad (3.11)$$

$$C_{\text{H18-DBT}} = \frac{n_{\text{H18-DBT}} \left(1 - \frac{\text{Yield}}{100}\right)}{V_{\text{H18-DBT}}} \quad (3.12)$$

where n and V are the number of moles and volume (ml) of H18-DBT, respectively.

3.4.2 Dehydrogenation tests: fixed bed reactor

A fixed bed reactor was used to study the effect of dopants on the stability of Pt/Al₂O₃. To accomplish this, a hydrogen-rich H18-DBT (>99% doh) was dehydrogenated in a fixed bed reactor made of quartz glass, as shown in the PID diagram shown in Figure 3-4. Prior to dehydrogenation experiments, the system was purged with N₂ gas to remove air from the reactor. A peristaltic pump (Medorex TL/150) was used to pump H18-DBT into the reactor, comprising heating three zones: the preheating zone, reaction zone and cooling zone. Throughout the reactor, a thermocouple was centred horizontally, while an electrical heated

jacket supplied the heat. The spent LOHC molecules from the reactor are cooled then sampled before they enter the product tank. A hydrogen mass flow meter (EL-Flow F11B-500-AGD-22V, Bronkhorst; flow range 0.16–3.5 nL/min; accuracy- 0.5% reading) was connected after a condenser and carbon filter for the measuring the hydrogen flow rate. A Siemens PLC was used to control the dehydrogenation system. For all experiments, a fixed reaction temperature of 300 °C and feed flow of 1.3 mL/min were utilised.

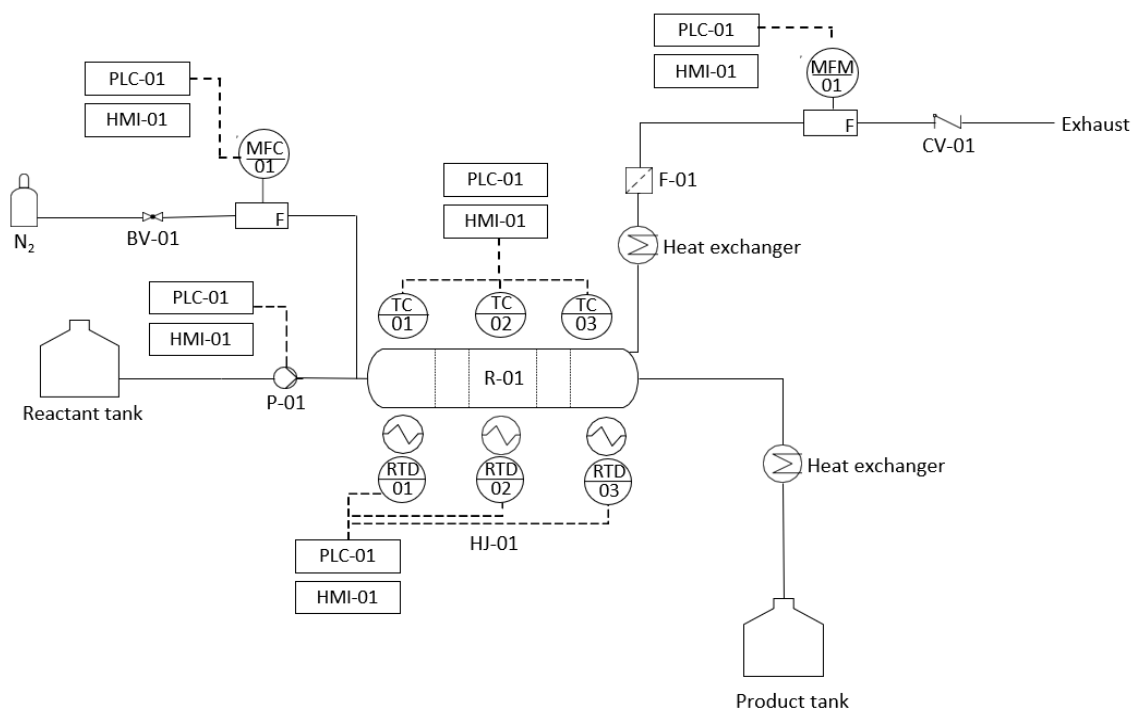


Figure 3-4. PID of the horizontal fixed bed reactor dehydrogenation unit.

3.5 LOHC characterisation

The analysis of liquid carrier molecules was performed using a Scion GC-SQ-MS (Bruker, Malaysia) system. The system was equipped with a CP-8400 autosampler, a GS-Tek GsBP-50+MS column (length 30 m, i.d. 0.25 mm, film thickness 0.25 μ m) and a single quadrupole mass spectrometer. Helium was used as carrier gas. To perform liquid analyses, samples of the reaction mixture were drawn from the reactor and diluted with hexane (1:100 wt/wt); 1 μ l quantities of each sample were injected, at a split ratio of 1:100. The resulting chromatograms were integrated to determine conversion (X), selectivity (S) and by-products, using equations (3.13), (3.14) and (3.15), respectively.

$$X_{\text{H18-DBT}} (\%) = \frac{\text{mol}_{\text{H18-DBT in}} - \text{mol}_{\text{H18-DBT out}}}{\text{mol}_{\text{H18-DBT in}}} \times 100 \quad (3.13)$$

$$S_{H0-DBT}(\%) = \frac{\text{mol}_{H0-DBT}}{\text{mol}_{H0-DBT} + \text{mol}_{H6-DBT} + \text{mol}_{H12-DBT} + \text{mol}_{H18-DBT} + \text{mol}_{\text{by-products}}} \times 100 \quad (3.14)$$

$$\text{By-products (mol \%)} = \frac{\text{peak area of by-products}}{\text{total peak area}} \quad (3.15)$$

CHAPTER 4. RESULTS AND DISCUSSION

This chapter describes, first, the catalytic performances of the catalysts ($\text{Pt}/\text{Al}_2\text{O}_3$, $\text{Pt}/\text{Mg}-\text{Al}_2\text{O}_3$ and $\text{Pt}/\text{Zn}-\text{Al}_2\text{O}_3$), evaluated for the dehydrogenation of perhydrodibenzyltoluene, using batch and fixed bed reactor systems. Then, the results of characterisation of the catalysts, in efforts to determine the effect of catalyst modification on the physicochemical properties of the catalysts, is addressed.

4.1 Catalyst performance evaluation for the dehydrogenation of H18-DBT using a batch reactor

The effect of the dehydrogenation reaction temperature on catalyst performance was evaluated using a batch reactor at temperatures from 260 to 300 °C. The catalysts were subjected to four dehydrogenation cycles (runs); each experimental run was set for a period of 90 min to determine the initial catalytic performance. The four dehydrogenation runs were used to determine the initial stability of the catalysts. In order to determine the reaction kinetics for dehydrogenation of H18-DBT, a stable experimental run is used.

4.1.1 The effect of reaction temperature and dopants on dehydrogenation performance

The effect of reaction temperature on hydrogen flow, productivity and the dod (hydrogen yield) was investigated at temperatures between 260 and 300 °C, for $\text{Pt}/\text{Al}_2\text{O}_3$, $\text{Pt}/\text{Mg}-\text{Al}_2\text{O}_3$ and $\text{Pt}/\text{Zn}-\text{Al}_2\text{O}_3$ catalysts. When the dehydrogenation reaction temperature was increased, the hydrogen flow, productivity and yield increased. This is expected, as an increase in temperature increases the rate of reaction, resulting in high activity. A linear increase was observed for hydrogen flow and productivity for all runs; see Figure 4-1. The activity of the catalysts decreased after the first run, yet some stability was observed between runs 3 and 4. (See also hydrogen flow and yield vs time in Figure A-1). This decrease in activity suggests catalyst deactivation. In run 1, there was no apparent difference in hydrogen flow and productivity between 260 and 280 °C; however, at 290 and 300 °C, slight differences were observed. In runs 2–4, at temperatures 260–290 °C, the activity of all catalysts was similar but the Mg-doped catalyst showed the highest activity at 300 °C. The fresh $\text{Pt}/\text{Mg}-\text{Al}_2\text{O}_3$ catalyst showed a 100% yield at 290 °C, while at the same temperature the $\text{Pt}/\text{Al}_2\text{O}_3$ and $\text{Pt}/\text{Zn}-\text{Al}_2\text{O}_3$ catalysts showed a yield of 78%. $\text{Pt}/\text{Zn}-\text{Al}_2\text{O}_3$ and $\text{Pt}/\text{Al}_2\text{O}_3$ did not provide full dehydrogenation at the temperatures used. After the first run, $\text{Pt}/\text{Mg}-\text{Al}_2\text{O}_3$ still exhibited the highest hydrogen yield of 73%, compared with values of 60% and 50% observed for $\text{Pt}/\text{Zn}-\text{Al}_2\text{O}_3$ and $\text{Pt}/\text{Al}_2\text{O}_3$, respectively.

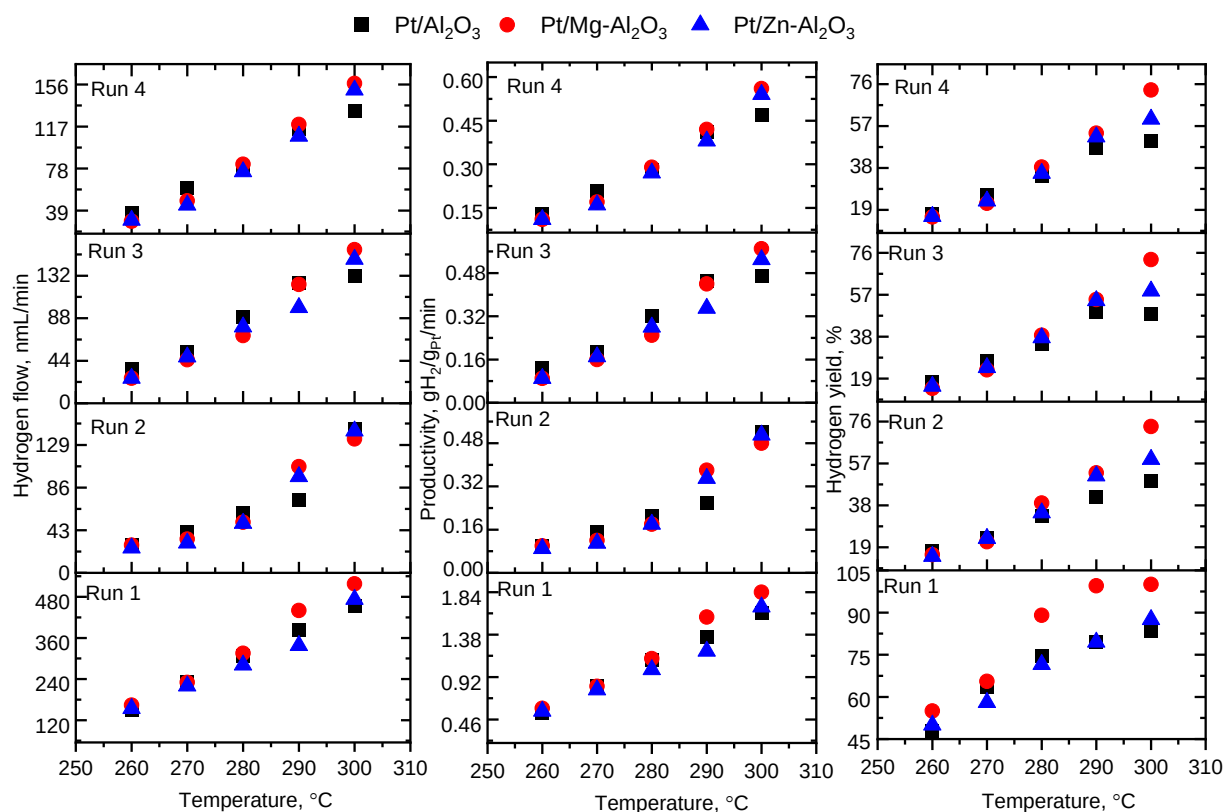


Figure 4-1. The effect of temperature on hydrogen yield and flow. Reaction parameters: H18-DBT, 99% doh; 0.5 wt % Pt; n_{Pt}/n_{LOHC} , 0.2 mol %; temperature, 260–300 °C; time, 90 min.

Figure 4-2 shows a comparison of the activity of our catalysts with literature reports. The unmodified Pt/Al₂O₃ used in this work showed a productivity of 1.62 gH₂/g_{Pt}/min, while other work reported a range of between 0.6 and 1.2 gH₂/g_{Pt}/min. The Mg- and Zn-doped catalysts had productivities of 1.84 and 1.68 gH₂/g_{Pt}/min, respectively. This is comparable with the values obtained by Auer *et al.* (2019:3540) and Chen *et al.* (2021:6568); after doping 0.3 wt % Pt/Al₂O₃ with sulphur, they obtained productivities of 2 and 1.5 gH₂/g_{Pt}/min, respectively. Better productivities were obtained with low Pt loading (0.3 wt %), as reported in literature (Auer *et al.*, 2019:3540; Chen *et al.*, 2021:6568), compared with results recorded in this study with 0.5 wt % Pt. This is because high Pt dispersions are achieved with low Pt loading, which results in better activity. Nonetheless, we consider that the performances recorded in this study are comparable to other performances reported. At this point, Mg appears to be the best dopant for the dehydrogenation of H18-DBT. The better performance of the Pt/Mg-Al₂O₃ catalyst could be due to the lowering of deactivation by Mg dopant as will be revealed in the discussions below.

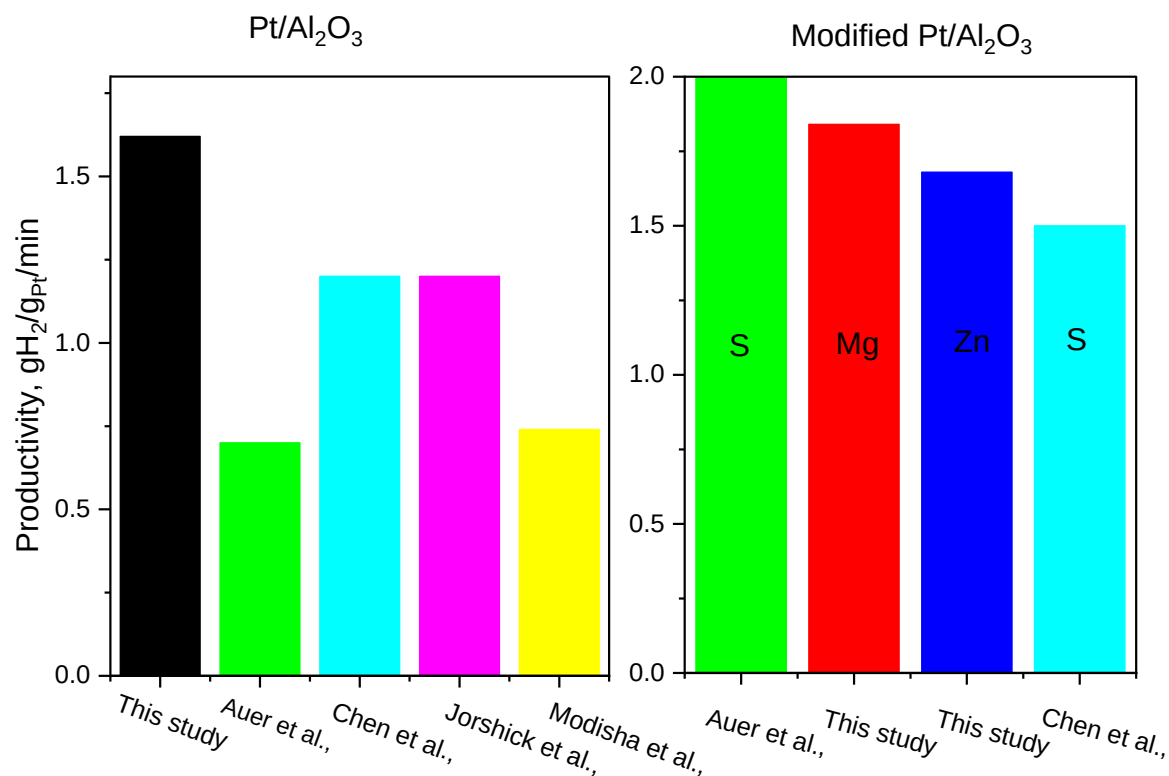


Figure 4-2. Comparison of productivity of different Pt/Al₂O₃ catalysts and their doped counterparts used for H18-DBT dehydrogenation in a batch reactor in this study vs. literature.

The effect of temperature and dopants on the conversion, selectivity and by-product formation were investigated by analyzing the LOHC samples using GC-MS-SQ. Results are presented in Figure 4-3 and Figure 4-4. During the dehydrogenation of H18-DBT, the intermediates H12-DBT and H6-DBT are formed, and they also become dehydrogenated until H0-DBT is the only product present. Therefore, dehydrogenation of H18-DBT follows the order H18-DBT $\rightarrow$ 3H₂ $\rightarrow$ H12-DBT $\rightarrow$ 3H₂ $\rightarrow$ H6-DBT $\rightarrow$ 3H₂ $\rightarrow$ H0-DBT.

The conversion vs. dehydrogenation temperature plots are based on the amount of H18-DBT present after the reaction—Just like activity, conversion, selectivity and by-products increase when the temperature was increased. Fresh and run 4 catalysts had conversions >99.5% and >90%, respectively, at 300 °C, for all catalysts. After fresh runs, conversion decreased significantly (~40% decrease) at 260 °C and 270 °C, but increased again from 280 to 300 °C. Since the dehydrogenation of H18-DBT is highly endothermic, at such low temperatures, the rate of adsorption and desorption processes were compromised, hence the reaction was slow. Although the difference in conversion for all catalysts at the same temperature is less pronounced, the selectivity of the Pt/Mg-Al₂O₃ catalysts is remarkable. At 290 °C, a selectivity of 98% was achieved, compared with 72% and 79% for Pt/Al₂O₃ and Pt/Zn-Al₂O₃, respectively.

After run 4, comparable selectivity for all catalysts was obtained with an apparent difference at 300 °C. At 300 °C, Pt/Al₂O₃ is the least selective catalyst (35%), followed by Pt/Zn-Al₂O₃ and Pt/Mg-Al₂O₃, with 50% and 63%, respectively.

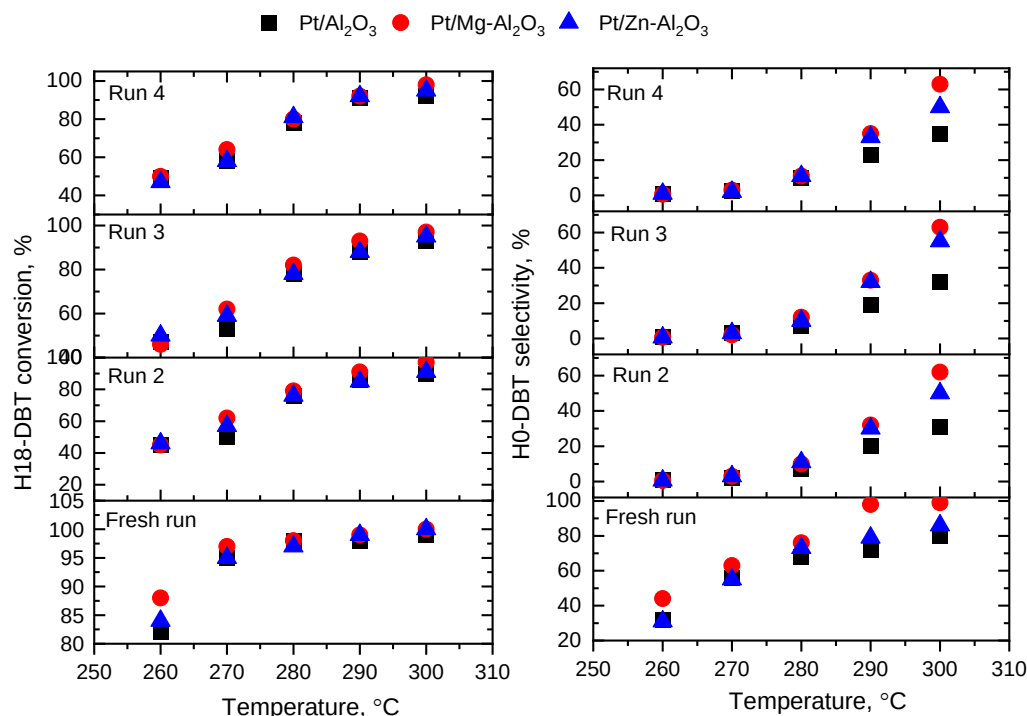


Figure 4-3. H18-DBT conversion and H0-DBT selectivity vs. dehydrogenation. Reaction parameters: H18-DBT, 99% doh; 0.5 wt % Pt; n_{Pt}/n_{LOHC} , 0.2 mol %; temperature, 260–300 °C; reaction time, 90 min.

The amount of by-products formed is directly proportional to the temperature of dehydrogenation and the catalyst activity. The by-products are a combination of high- and low-boiling-point compounds (Modisha *et al.*, 2018:5629). Figure 4-4 shows that the highest amount of by-products (12 mol %) was produced by Mg-doped catalysts, while only 5 and 1.2 mol % were obtained for Pt/Zn-Al₂O₃ and Pt/Al₂O₃, respectively, at 300 °C. After run 4, the amount decreased to 0.68%, 2.1% and 1.9 mol % for Pt/Al₂O₃, Pt/Mg-Al₂O₃ and Pt/Zn-Al₂O₃, respectively. Even in the presence of a high amount of by-products, Pt/Mg-Al₂O₃ performed better than other catalysts.

The deactivation parameter, $\Delta X = (X_i - X_f)/X_i \times 100$, was calculated based on the H18-DBT conversion, to determine the percentage deactivation based on the reaction time of 6 h (four runs of 90 min per run). Figure 4-5 shows the percentage deactivation of the catalysts at 300 °C. The undoped Pt/Al₂O₃ had the highest deactivation of 7.4%, while Zn-doped and Mg-doped had 4.9% and 1.9%, respectively. This suggests that Mg doping suppresses deactivation in a batch reactor, hence leading to an improved performance.

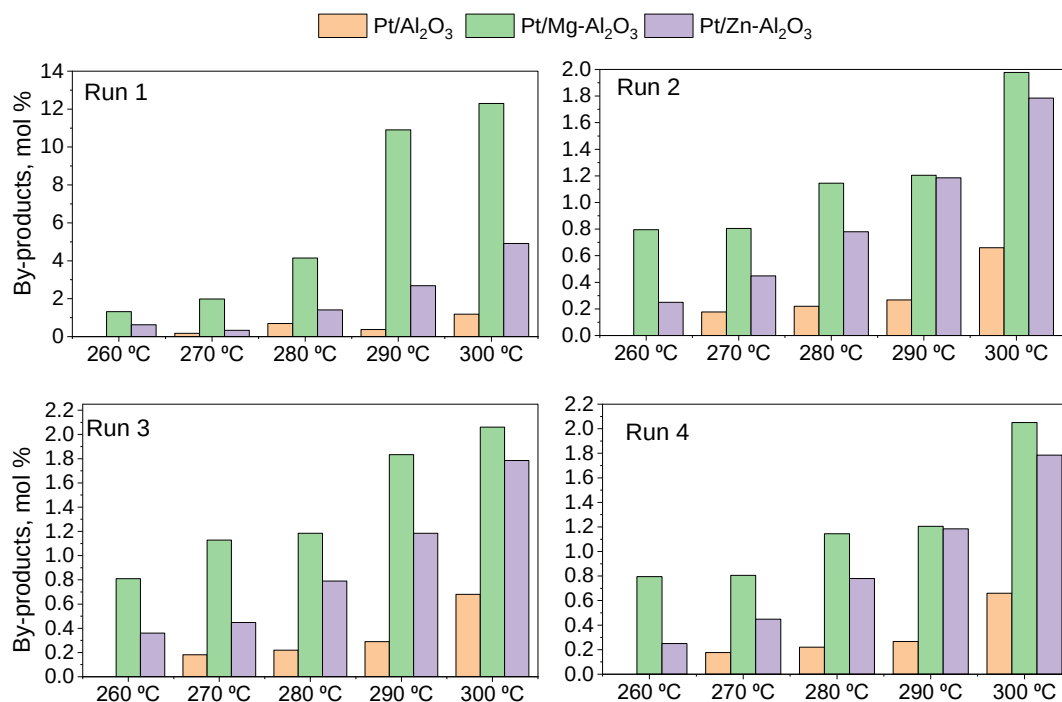


Figure 4-4. By-products formed during the dehydrogenation of H18-DBT in a batch reactor. Reaction parameters: H18-DBT, 99% doh; 0.5 wt % Pt; n_{Pt}/n_{LOHC} , 0.2 mol %; temperature, 260–300 °C; reaction time, 6 h.

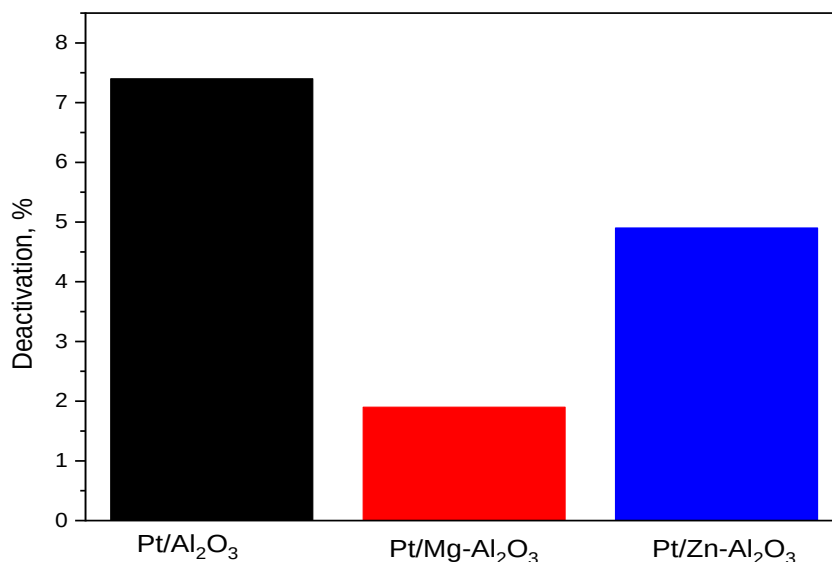


Figure 4-5. The deactivation of catalyst in a batch reactor. Reaction parameters: H18-DBT 99% doh; 0.5 wt % Pt; n_{Pt}/n_{LOHC} , 0.2 mol %; temperature, 300 °C; time, 6 h.

A summary of the performance of catalysts in a batch reactor is presented in Table 4-1. The highest activity for all catalysts was observed at 300 °C. At this temperature, the addition of Mg and Zn dopants significantly increased activity, conversion, selectivity and by-products. For instance, the hydrogen yield from unmodified Pt/Al₂O₃ improved from 82% to 88% (Zn

doped) and 100% (Mg doped). Moreover, full dehydrogenation was achieved within 75 min when using the Mg-doped catalysts, while other catalysts did not give full dehydrogenation within 90 min. A decrease in activity was observed after the first run for all catalysts. The loss of activity can be attributed to catalyst deactivation. The better performance of the Pt/Mg-Al₂O₃ catalysts can be explained by the low deactivation parameter of 1.9%, which suggests that Mg lowered deactivation. Due to the high performance of Pt/Mg-Al₂O₃, a high amount of by-products was observed. Therefore, here, Pt/Mg-Al₂O₃ is considered to be the best catalyst for the dehydrogenation of H18-DBT. To assess the stability of catalysts in dehydrogenation, a fixed bed reactor was used. Results are discussed in Section 4.2.

Table 4-1. Summary of the effect of Mg and Zn dopants on Pt/Al₂O₃ for the H18-DBT dehydrogenation performance at 300 °C in a batch reactor

Catalyst	Y _i (%)	Y _{run 4} (%)	P _i (gH ₂ /g _{Pt} /min)	P _{run 4} (gH ₂ /g _{Pt} /min)	S _i (%)	S _{run 4} (%)	X _i (%)	X _{run 4} (%)	ΔX (%)
Pt/Al ₂ O ₃	82	50	1.62	0.53	80	35	99.3	92	7.4
Pt/Mg-Al ₂ O ₃	100	73	1.84	0.58	99	63	99.9	98	1.9
Pt/Zn-Al ₂ O ₃	88	60	1.68	0.55	86	50	99.9	95	4.9

X_i and X_{run 4} are the initial and final H18-DBT conversion (%), S_i and S_{run 4} are the initial and final H0-DBT selectivity (%), P_i and P_{run 4} are initial and final productivities, Y_i and Y are the initial and final yield (%), ΔX is the deactivation parameter (%).

4.2 Evaluation of catalyst stability during H18-DBT dehydrogenation in a horizontal fixed bed reactor

The effect of Mg and Zn dopants on catalyst stability was then investigated in a horizontal fixed bed reactor. Dehydrogenation experiments were carried out to compare Pt/Al₂O₃, Pt/Zn-Al₂O₃ and Pt/Mg-Al₂O₃ catalysts in reactions that were allowed to run for 22 h at a constant reaction temperature of 300 °C and weight hourly space velocity (WHSV) of 0.61 h⁻¹. Figure 4-6 shows hydrogen yield and HFR vs. catalyst time-on-stream for the dehydrogenation of H18-DBT. The Pt/Mg-Al₂O₃ catalyst had the highest initial HFR of 33 nL/h. Other catalysts (Pt/Al₂O₃ and Pt/Zn-Al₂O₃) had a similar initial HFR, 31 nL/h. For the first 12 h, the HFR was not stable, but after 13 h the catalysts exhibited some stability (particularly Pt/Zn-Al₂O₃). Overall, the Pt/Mg-Al₂O₃ catalyst showed the highest activity and stability for 22 h; the HFR declined from 33 to 26 nL/h. A similar trend is evident in Figure A-2, where catalyst productivity is plotted against time-on-stream. Productivities of ~0.1 gH₂/g_{Pt}/min were observed for all catalysts. Furthermore, when using Pt/Mg-Al₂O₃ the hydrogen yield decreased from 80% to

60%, whereas with Pt/Al₂O₃ and Pt/Zn-Al₂O₃ the hydrogen yield decreased from 72% to 50% and 73% to 51%, respectively. In a batch reactor, all catalyst pellets are immersed in the LOHC, whereas in a horizontal fixed bed, some of the catalyst may have not fully participated in the reaction, hence productivity is low in a fixed bed reactor. Nonetheless, it is clear that doping of Pt/Al₂O₃ with Mg improved stability.

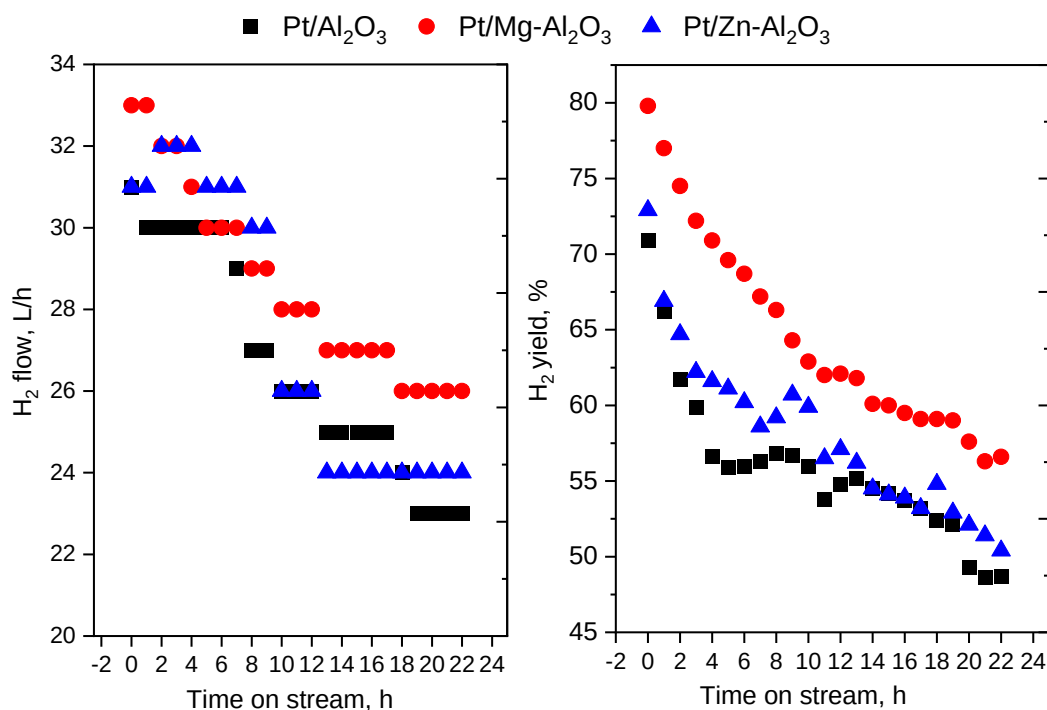


Figure 4-6. Hydrogen yield and flow rate vs. time-on-stream for dehydrogenation of H18-DBT over 22 h. Reaction parameters: Pt loading, 0.5 wt %; H18-DBT doh 99.6%; reaction temperature, 300 °C; feed flow, 1.3 ml/min; catalyst mass, 110 g; WHSV 0.61 h⁻¹.

Figure 4-7 displays the H18-DBT conversion using Pt/Al₂O₃, Pt/Mg-Al₂O₃ and Pt/Zn-Al₂O₃ catalysts. The Pt/Mg-Al₂O₃ catalyst had the highest initial conversion of 99%, followed by the Pt/Zn-Al₂O₃ and Pt/Al₂O₃ catalysts, with 97% and 96%, respectively. After 22 h, Pt/Mg-Al₂O₃ exhibited a stable conversion of 92%, whilst the other catalysts exhibited slightly lower conversions. Mg is known to increase the rate of Al₂O₃ grain densification by raising the diffusion coefficient (Berry & Harmer, 1986:147). The larger the grain size, the lower the pore reduction and this minimizes pore diffusion limitations. Hence, an improved H0-DBT conversion was observed. As shown in Figure 4-7, the conversion difference between Pt/Al₂O₃ and Pt/Zn-Al₂O₃ catalyst is insignificant.

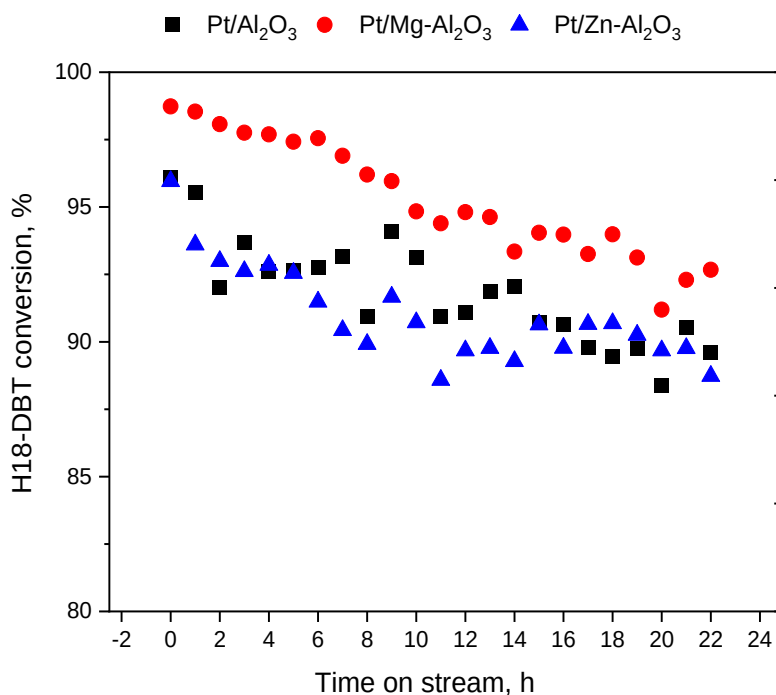


Figure 4-7. Conversion of H18-DBT vs. time-on-stream over 22 h of dehydrogenation. Reaction parameters: Pt loading 0.5 wt %; H18-DBT doh 99.6%; reaction temperature, 300 °C; feed flow, 1.3 ml/min; catalyst mass, 110 g; weight hourly space velocity, 0.61 h⁻¹.

The initial selectivity of Pt/Mg-Al₂O₃, Pt/Zn-Al₂O₃ and Pt/Al₂O₃ towards H0-DBT was 78%, 75% and 71%, respectively; see Figure 4-8. Pt/Al₂O₃ was the least selective catalyst with a final selectivity of 45%, whereas Pt/Mg-Al₂O₃ was the most selective catalyst, with a final selectivity of 57%, after 22 h. The high selectivity could be an effect of Mg weakening the adsorption of H0-DBT on the Pt surface and promoting the H0-DBT desorption. It appeared that a less acidic catalyst favoured dehydrogenation and increased selectivity, compared with highly acidic supports. Strong acidic sites of the support facilitate C–C breaking; as a result, carbon becomes deposited on the catalyst surface (Zhang *et al.*, 2011:1637). Thus, the high selectivity could be attributed to an effect of Mg on the adsorption of H0-DBT on the Pt surface and promoting the H0-DBT desorption. Figure 4-8 also shows the selectivity of catalysts towards other intermediates: H12-DBT and H6-DBT. All catalysts showed a decline in selectivity towards H0-DBT and an increase towards the H6-DBT and H12-DBT intermediates. The decline in selectivity over time is due to the deactivation of catalysts. Pt/Al₂O₃ selectivity towards H6-DBT increased from 24% to 39%, while that of H12-DBT increased from 5% to 10%. This indicates that, over time, the catalyst active sites are compromised by deactivation, and H6-DBT and H12-DBT intermediates become difficult to dehydrogenate.

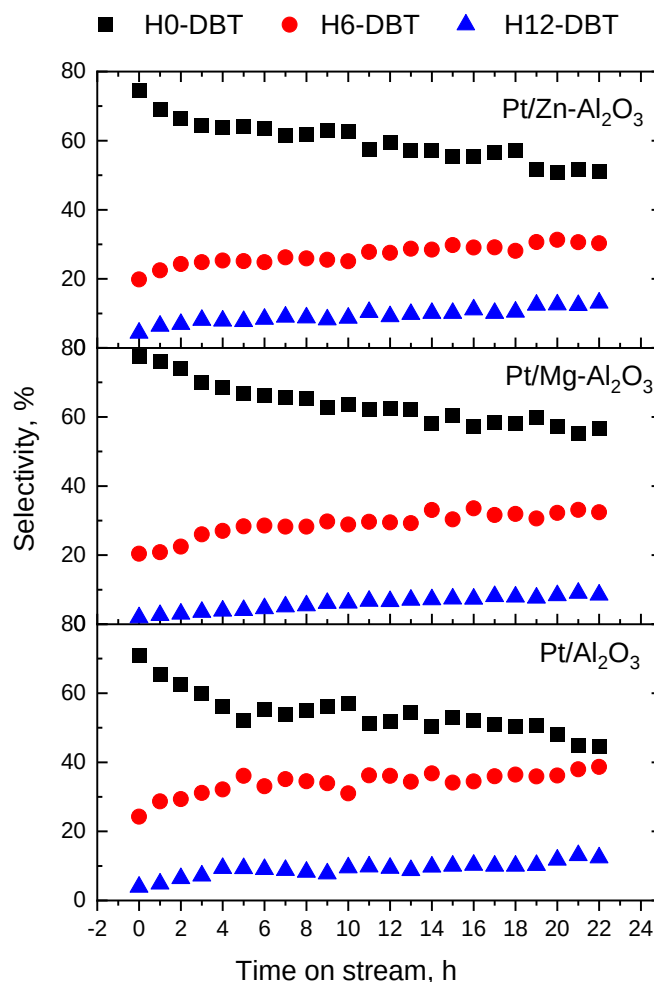


Figure 4-8. Selectivity of the catalysts to H0-DBT, H6-DBT and H12-DBT over 22 h time-on-stream. Reaction parameters: Pt loading, 0.5 wt %; H18-DBT, doh 99.6%; reaction temperature, 300 °C; feed flow, 1.3 ml/min; catalyst mass, 110 g; weight hourly space velocity, 0.61 h⁻¹.

Figure 4-9 shows by-products formed during the dehydrogenation of H18-DBT. The amount of by-products was high during the first 1 h of the experiment, then decreased with time. The higher the catalytic activity, the more by-products were produced. Pt/Mg-Al₂O₃ showed the highest initial concentration of by-products (6.8 mol %), followed by Pt/Zn-Al₂O₃ (5.3 mol %) and Pt/Al₂O₃ (4.2 mol %). After 22 h, Pt/Mg-Al₂O₃ still produced the highest concentration of by-products (3.2 mol %). Even though Pt/Mg-Al₂O₃ is less acidic, a highly active catalyst produces more by-products because the Pt active sites could promote C–C cleavage by hydrogenolysis. Bocanegra *et al.* (2004:22) have reported that Pt/MgAl₂O₄ has a higher hydrogenolytic capacity than Pt/Zn-Al₂O₄. In addition, more aromatic molecules produced as a result of high activity are susceptible to the acidic sites of the support which provides the C–C cracking function. Therefore, catalysts that exhibited improved catalytic activity contributed to the most by-products.

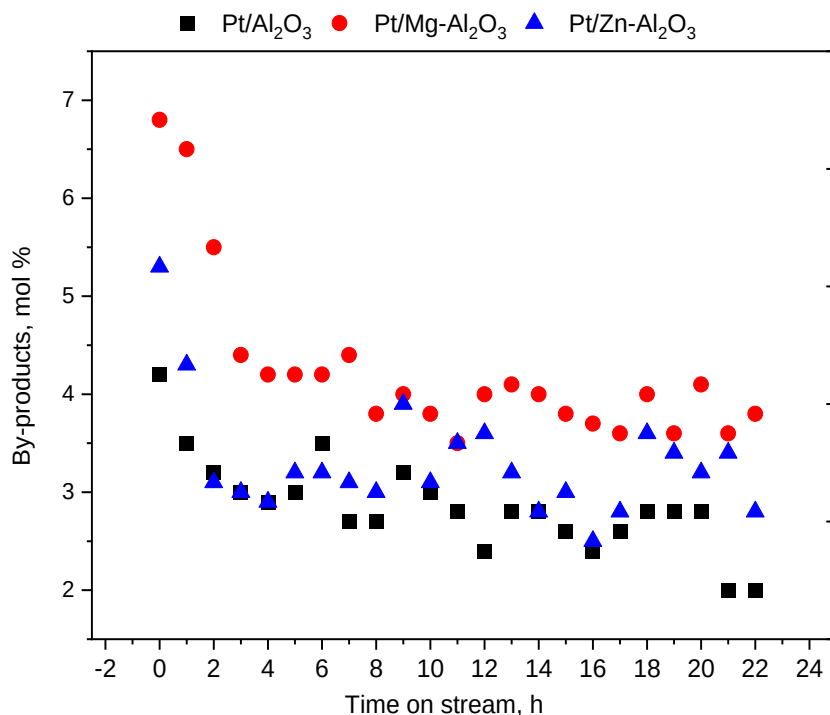


Figure 4-9. Amount of by-products obtained over 22 h of catalyst time-on-stream. Reaction parameters: Pt loading, 0.5 wt %; H18-DBT, doh 99.6%; reaction temperature, 300 °C; feed flow, 1.3 ml/min; catalyst mass, 110 g; weight hourly space velocity, 0.61 h⁻¹.

Table 4-2 summarises the performance of the catalysts used here for the dehydrogenation of H18-DBT in a fixed bed reactor. The addition of Mg improved the activity and stability of Pt/Al₂O₃ catalysts. Pt/Mg-Al₂O₃ catalyst has the lowest deactivation parameter ($\Delta X = 6.1\%$) compared with Pt/Al₂O₃ ($\Delta X = 7.2\%$) and Pt/Zn-Al₂O₃ ($\Delta X = 7.3\%$). Optimizing the Mg loading could lower the deactivation parameter and thus improve the catalyst stability further. Bai *et al.* (2009:9889) reported the same phenomena for Mg-doped PtSnNa/ZSM-5; the deactivation parameter decreased from 10% to 7%.

Table 4-2. Summary of catalysts performance for the dehydrogenation of H18-DBT in a fixed bed reactor at 300 °C for 22 h time on stream

Catalyst	X _i	X _f	S _i	S _f	Y _i	Y _f	ΔX
Pt/Al ₂ O ₃	97	90	71	45	72	49	7.2
Pt/Mg-Al ₂ O ₃	99	93	77	57	80	60	6.1
Pt/Zn-Al ₂ O ₃	96	89	74	51	73	51	7.3

X_i and X_f is the initial and final conversion (%), S_i and S_f is the initial and final selectivity (%), Y_i and Y_f is the initial and final yield (%), ΔX is the deactivation parameter (%)

4.3 Kinetics study of the dehydrogenation of H18-DBT

This subsection addresses the reaction kinetics for dehydrogenation of H18-DBT using a batch reactor. The effects of temperature on the kinetics parameters (e.g., reaction rate, rate constant, TOF, etc) was investigated. The experiments were conducted at dehydrogenation temperatures in the range 260–290 °C, so that the hydrogen yield was <70%. This is to avoid back-reactions that occur at high conversions (Wunsch *et al.*, 2018:120).

As is evident in Figure 4-10, for all catalysts, the concentration of H18-DBT decreased with time. The decrease in H18-DBT concentration is a function of temperature. Hence, the concentration gradient becomes steeper with an increase in temperature. At 300 °C, a H18-DBT concentration of 0.84 M was observed for Pt/Mg-Al₂O₃, while Pt/Zn-Al₂O₃ and Pt/Al₂O₃ had final concentrations of 1.30 and 1.42 M, respectively.

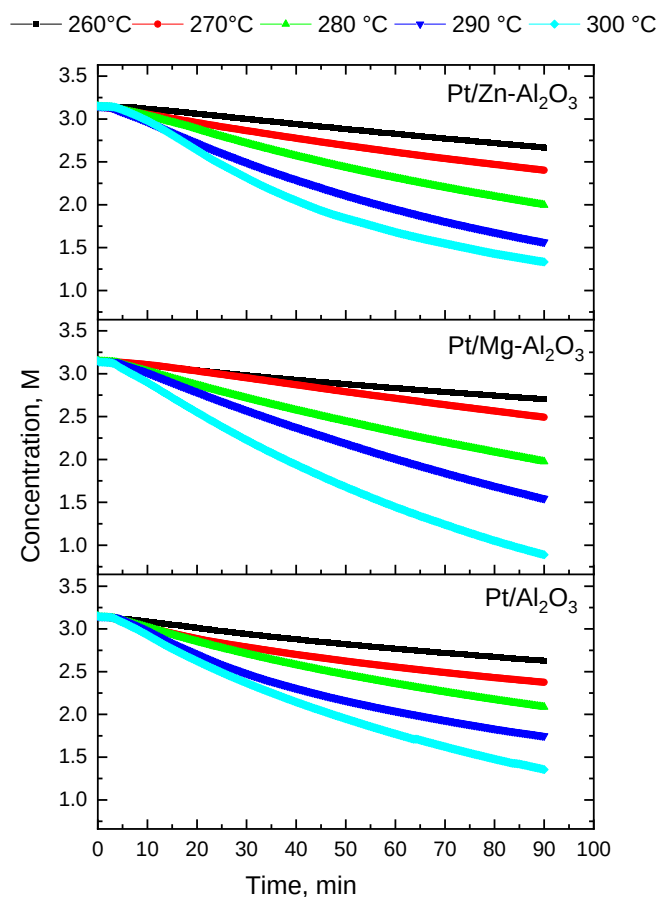


Figure 4-10. The change in concentration of H18-DBT versus time for Pt/Al₂O₃ catalysts in a batch reactor. Reaction parameters: H18-DBT, 99% doh; 0.5 wt % Pt; n_{Pt}/n_{LOHC} , 0.2 mol %; temperature, 260–300 °C; reaction time, 90 min.

4.3.1 Determination of reaction order, rate constants, initial rates of reaction and turn-over frequencies

From the equation (3.12), the rate constants (k), initial rate of reactions (r) and turnover frequencies (TOFs) can be calculated using the equations below (4.1 and 4.2), as reported by Sotoodeh (2011:170). The TOF is defined as the number of reactant molecules converted by each Pt molecule per unit time.

$$r = k \times C_0 \quad (4.1)$$

$$\text{TOF} = \frac{k \times \text{Mwt}_{\text{Pt}} \times C_0}{M_{\text{Pt}} \times D} \quad (4.2)$$

Here, k is the rate constant, C_0 is the initial concentration of H18-DBT, Mwt_{Pt} is the molecular mass of Pt, M_{Pt} is the Pt loading and D is the Pt dispersion.

The dehydrogenation kinetics of H18-DBT followed first-order reaction kinetics, as seen by the linear fit of $\ln(C/C_0)$ vs. time in Figure 4-11. This is in accordance with literature (Modisha *et al.*, 2019:21930). Rate constants were obtained from the slopes of the respective graphs and used to calculate the rate of reaction and TOFs, with results tabulated in Table 4-3. Clearly, activity increases with an increase in temperature. This is due to the collision of molecules induced by high temperatures, which increases the reaction rate. Undoped Pt/ Al_2O_3 showed higher rate constants at low temperatures (260 and 270 °C) than Pt/Mg- Al_2O_3 and Pt/Zn- Al_2O_3 . At 260 °C, Pt/ Al_2O_3 gave a rate constant of 0.00180 min^{-1} , while Pt/Mg- Al_2O_3 and Pt/Zn- Al_2O_3 gave 0.00140 and 0.00170 min^{-1} , respectively. However, at temperature >280 °C, this changed drastically; the activity of the doped catalysts, particularly with Mg, increased from 0.0049 to 0.0137 min^{-1} . The TOF followed a similar trend. A high TOF value indicates a high activity due to increased amount of available active site for the reaction. A Mg-doped catalyst had the highest activity, TOF 586 min^{-1} , which is more than two times greater than that achieved with a Zn-doped catalyst (269 min^{-1}) and almost three times greater than that with an undoped catalyst (202 min^{-1}) (calculated for dehydrogenation reactions at 300 °C).

Shi *et al.* (2020:10667) recorded TOF values in the range $168\text{--}234 \text{ min}^{-1}$ at 270 °C, which are three times greater than the values $70\text{--}103 \text{ min}^{-1}$ recorded in this study (at the same temperature); see Table 4-3. This may be explained by the fact that they used a high Pt loading of 3 wt % whereas in the present study only 0.5 wt % loading was used. The presence of more Pt particles per surface area tends to produce more hydrogen and increase the catalytic activity.

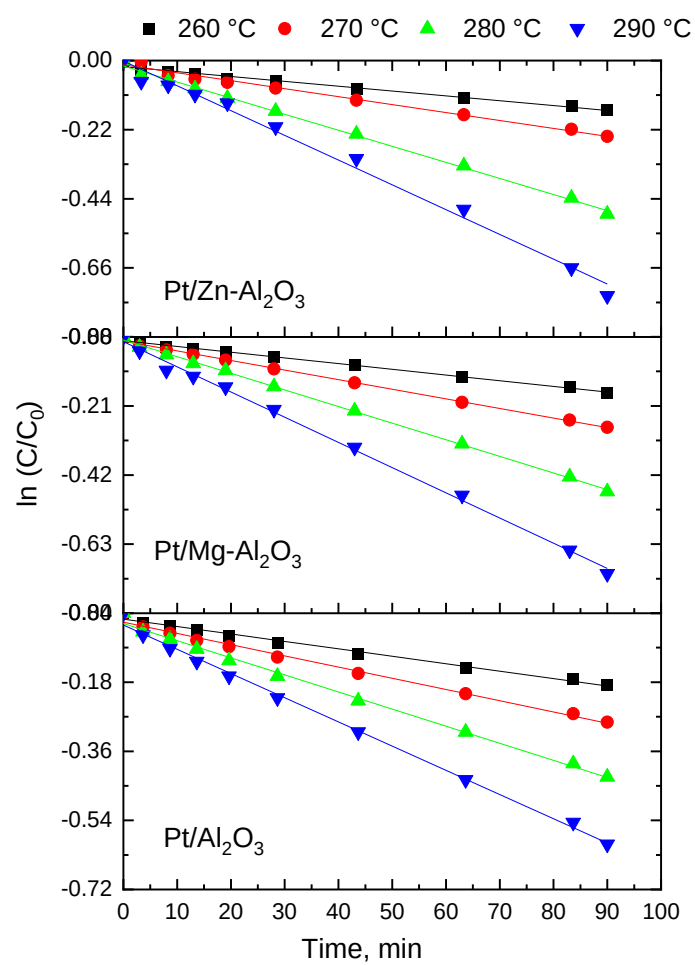


Figure 4-11. First-order reaction kinetics of Pt/Al₂O₃ catalysts during H18-DBT dehydrogenation between 260 and 290 °C.

Table 4-3. Rate constants, initial rates of reaction, TOFs, H₂ recovery, H18-DBT conversion and H0-DBT selectivity of H18-DBT dehydrogenation using Pt/Al₂O₃, Pt/Mg-Al₂O₃ and Pt/Zn-Al₂O₃ catalysts between 260 and 300 °C

Catalyst	Temp, °C	k, min ⁻¹	Initial rate of reaction, M min ⁻¹ g _{cat} ⁻¹	TOF, min ⁻¹
Pt/Al ₂ O ₃	260	0,00180	0,02352	47
	270	0,00270	0,03696	70
	280	0,00420	0,05376	109
	290	0,00600	0,08064	155
	300	0,00780	0,09702	202
Pt/Mg-Al ₂ O ₃	260	0,00140	0,01806	61
	270	0,00240	0,03150	103
	280	0,00490	0,06258	209
	290	0,00830	0,09996	355
	300	0,01370	0,17640	586
Pt/Zn-Al ₂ O ₃	260	0,00170	0,02016	49
	270	0,00280	0,03318	81
	280	0,00490	0,05999	142
	290	0,00800	0,09576	231
	300	0,00930	0,10836	269

4.3.2 Determination of activation energies and pre-exponential factor for dehydrogenation of H18-DBT

The activation energy of the catalysts was calculated using the Arrhenius model, where the graph of $\ln k$ vs $1/T$ is plotted; see Figure 4-12. The slope of the graph provided activation energies of 102, 130 and 151 kJ/mol for Pt/Al₂O₃, Pt/Zn-Al₂O₃ and Pt/Mg-Al₂O₃, respectively; see Table 4-4. The regression was found to be >0.99 for all catalysts. Pt/Al₂O₃ had a lower activation energy, which means that external mass influences were high at the selected temperatures (260–290 °C) compared to other catalysts. The frequency or pre-exponential factor, which indicates the number of collisions that overcame the H18-DBT activation energy per minute, was low, with lower activation energies. Therefore, the higher the frequency factor, the more reactive the catalyst, and the better the performance and the higher the activation energy. In this case, high amount of active sites corresponds to high value of frequency factor and this is connected to high activation energy. The low activation energy for dehydrogenation of H18-DBT will not always produce high reaction rate. A similar trend was observed by Seidel

(2019:98); the dehydrogenation of H18-DBT at 270–320 °C with 0.5 wt % Pt/Al₂O₃; 0.3 wt % Pt/Al₂O₃ and 0.3 wt % Pt/Al₂O₃ (0.14 wt % S) gave activation energies of 97, 131 and 143 kJ/mol, respectively. High activation energies (131 and 143 kJ/mol) for catalysts with large pore diameter (24.6 nm) were obtained (compared with 97 kJ/mol for a pore diameter 3.2 nm). Therefore, the addition of Mg and Zn dopants reduced the diffusion barrier, as evidenced by the low activation energy (102 kJ/mol) of the undoped catalyst. Mg also increase basic surface OH groups on catalysts which enhances fast kinetics as evidenced by the work of Kim *et al.* (2021:119889). The Ru/MgO catalysts had better activity and kinetics compared to Ru/Al₂O₃ during hydrogenation of benzyltoluene owing to the low surface acidity of MgO support. This then confirms the higher catalytic activity of the Mg-doped catalyst compared with other catalysts considered here.

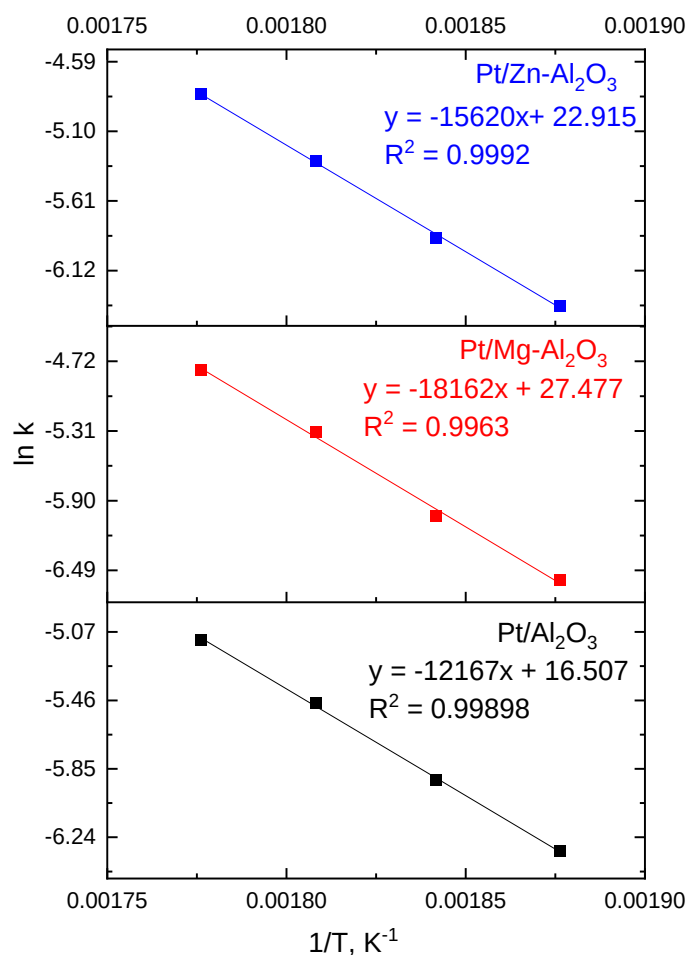


Figure 4-12. Arrhenius plot for the dehydrogenation of H18-DBT between 260 and 290 °C.

Table 4-4. Frequency factor and activation energy of Pt/Al₂O₃ catalysts

Catalyst	k ₀ (min ⁻¹)	E _a (kJ/mol)
Pt/Al ₂ O ₃	1.77E+07	102
Pt/Mg-Al ₂ O ₃	2.30E+11	151
Pt/Zn-Al ₂ O ₃	1.15E+10	130

k₀ is the pre-exponential factor

4.4 Summary of H18-DBT dehydrogenation activity in a batch and horizontal fixed bed reactor

Table 4-5 gives a summary of the performance of the catalysts in the batch and fixed bed reactors. Initial dehydrogenation tests using a batch reactor aided in evaluating catalyst performance and selecting a suitable temperature for the dehydrogenation reaction. The performance at 300 °C was found to be the best because of the high activity. Overall, catalyst behaviour was correctly predicted in the batch reactor; the Mg-doped catalyst performed well in both batch and fixed bed reactors. Due to the long residence time in the batch system, a high yield, productivity, conversion and selectivity were observed. However, this comes at the expense of very high by-product formation (12 mol %) compared to horizontal fixed bed reactor (7.3%). For H₂ application in FCs, a fixed bed reactor would be the best option because hydrogen flow is continuous, and by-products are reduced. The deactivation noted in both reactors may be due to a reduced reaction surface area, due to catalyst poisoning, which was minimized by Mg dopants. The superior activity of Mg-doped catalysts in both reactors was attributed to the following.

- The suppression of the diffusion barrier in Mg-doped catalysts minimized pore diffusion during H18-DBT dehydrogenation.

The H18-DBT kinetics revealed that the addition of dopants increased the activation term, which is related to the absence of diffusion limitations.

Table 4-5. Summary of the dehydrogenation performance of H18-DBT in a batch and horizontal fixed bed reactor at 300 °C

Parameter	Batch reactor		Fixed bed reactor	
Pt/Al ₂ O ₃	Run 1	Run 4	Initial	Final
H ₂ flow, nL/h	27	8.5	31	24
Productivity, gH ₂ /g _{Pt} /min	1.63	0.51	0.1	0.06
H ₂ yield, %	82	50.2	72	49
H0-DBT selectivity, %	86	33	71	45
H18-DBT conversion, %	> 99	92	97	90
By-products, mol %	1.2	0.68	4.2	2
Deactivation (ΔX), %	7.7		7.2	
Pt/Mg-Al ₂ O ₃				
H ₂ flow, nL/h	29	10.2	33	26
Productivity, gH ₂ /g _{Pt} /min	1.73	0.61	0.1	0.07
H ₂ yield, %	100	73,3	80	60
H0-DBT selectivity, %	97	63	77	57
H18-DBT conversion, %	>99	97	99	93
By-products, mol %	12.3	2.1	6.8	3.2
Deactivation, %	2.7		6.1	
Pt/Zn-Al ₂ O ₃				
H ₂ flow, nL/h	26	9.5	31	23
Productivity, gH ₂ /g _{Pt} /min	1.54	0.57	0.1	0.06
H ₂ yield, %	87.5	60.1	73	51
H0-DBT selectivity, %	86	52	74	51
H18-DBT conversion, %	>99	94	96	89
By-products, mol %	4.9	1.9	5.3	2.8
Deactivation, %	6		7.3	

4.5 Catalyst characterisation

Pt/Al₂O₃ catalysts were characterised, by various methods, to determine attributes that contributed to the dehydrogenation performance of H18-DBT. A detailed discussion of results obtained from characterisation of the catalysts follows.

4.5.1 Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

The target Pt loading for all catalysts was 0.5 wt % Pt. The actual loadings confirmed by ICP-OES for Pt/Al₂O₃, Pt/Mg-Al₂O₃ and Pt/Zn-Al₂O₃ were 0.48, 0.49 and 0.48 wt %, respectively (values given are the averages of three ICP tests done, for each catalyst, on different days). Standard errors were no greater than 0.01, indicating that the impregnation experiments were

reproducible here. See Table 4-6. The target loading of Mg and Zn was 3.8 wt %. The actual loadings were 3.89 and 3.44 wt %, respectively.

Table 4-6. Metal loadings and elemental composition of the catalysts determined using ICP-OES

Catalyst	Target Pt loading (wt %)	Actual loading (wt %)		
		Pt	Mg	Zn
Pt/Al ₂ O ₃	0.5	0.48 ± 0.010	-	-
Pt/Mg-Al ₂ O ₃	0.5	0.49 ± 0.007	3.89	-
Pt/Zn-Al ₂ O ₃	0.5	0.48 ± 0.001	-	3.44

4.5.2 Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS)

SEM-EDS confirmed the presence of Pt, Mg and Zn in the reduced catalysts; see Figure 4-13. Elemental line analysis indicated that the Mg-doped catalyst had the highest amount of Pt distributed throughout the pellet (uniform distribution). The Zn-doped and undoped catalysts were of the eggshell type, where there is much Pt on the edges and little inside (<0.1% Pt) the catalysts. This is consistent with the image in Figure 3-2. Mg promoted the diffusion of the precursor solution during impregnation; hence Pt is distributed throughout the support.

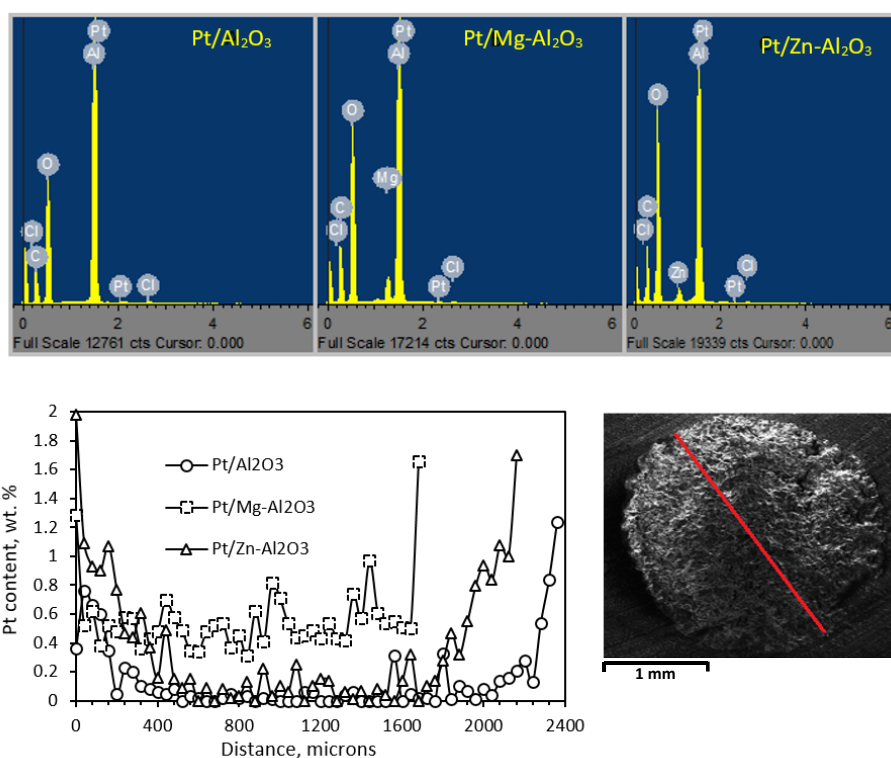


Figure 4-13. Elemental line scan analysis showing Pt distribution at 40-micron equidistance.

4.5.3 Hydrogen temperature programmed reduction (H₂-TPR)

H₂-TPR profiles showed broad and intense peaks at temperatures between 100 and 200 °C and small peaks at temperatures between 300 and 500 °C; see Figure 4-14. The first broad peaks were due to the reduction of PtO and PtO₂ species, weakly bonded to the surface of the support (Park *et al.*, 2015:2214). The second peak indicated strong support interaction with Pt, possibly leading to the formation of PtAl₂O₄ spinel species (formed during impregnation and calcination), which are difficult to reduce. It is interesting to note that the second peaks of the Mg- and Zn-doped Pt/Al₂O₃ shifted to higher temperatures, indicating the presence of stronger interactions with the support than in the case of non-doped Pt/Al₂O₃. Therefore, doped catalysts have stronger MSIs than non-doped Pt/Al₂O₃. This is known to prevent the sintering of particles. Furthermore, Kumar *et al.* (2004:221) ascribe the increase or shift in reduction temperature of an Mg-doped catalyst to the weak electronegative bond between Mg and O₂ in MgO, which causes the oxygen to preferably bond with Pt. Another possible reason is the formation of Mg and Zn aluminates, which increases the reduction temperature.

The following hydrogen consumptions for Pt/Al₂O₃, Pt/Mg-Al₂O₃ and Pt/Zn-Al₂O₃ were observed: 34, 64 and 55 µmol/g, respectively. The hydrogen consumption of 34 µmol/g for Pt/Al₂O₃ is close to the theoretical value (30.3 µmol/g) reported for the complete reduction of Pt⁴⁺ to Pt⁰ (Prestvik *et al.*, 1998:121). However, the consumption of Pt/Mg-Al₂O₃ and Pt/Zn-Al₂O₃ is higher than the stoichiometric value for reducing all platinum species. This increment could possibly be due to the reduction of impurities on the support (Martins *et al.*, 2017:2017:5).

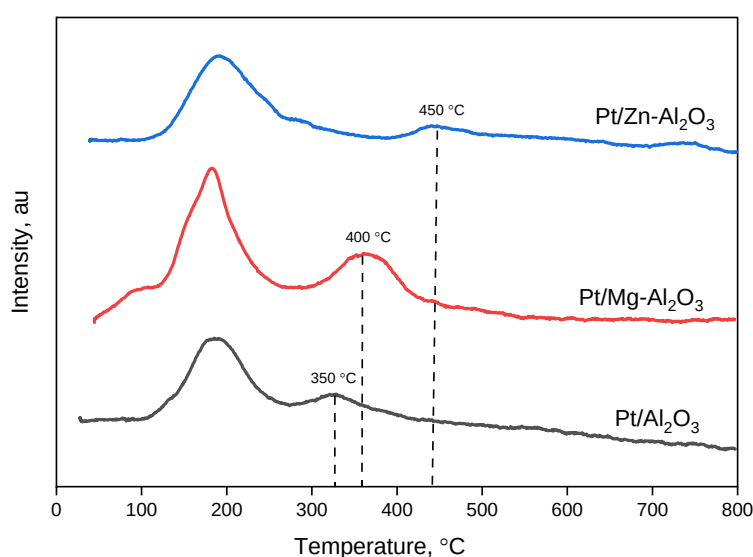


Figure 4-14. H₂-TPR profiles of the calcined catalysts.

4.5.4 Carbon monoxide (CO) pulse chemisorption

The addition of Mg and Zn dopants decreased the dispersion of Pt particles. See Table 4-7. A decrease in the metallic surface area and the formation of strongly bonded Pt complexes with doped Mg and Zn support may contribute to this. Strong MSIs make it difficult for CO to absorb onto Pt due to fewer exposed active sites. However, several reports describe an increase in dispersion upon Mg doping (Ballarini *et al.*, 2012:10; Kumar *et al.*, 2004:220). A low dispersion of 34% for Pt/Mg-Al₂O₃ compared with 38% for Pt/Al₂O₃ can be ascribed to alteration of the adsorptive properties of Pt/Mg-Al₂O₃ when Pt reacts with the basic sites of Mg (Escobar *et al.*, 2017:200; Martins *et al.*, 2017:4). Pt/Zn-Al₂O₃ has the lowest Pt dispersion, 23%, which is relatively close to values reported in literature (Bensaddik *et al.*, 1998:267; Belskaya *et al.*, 2016:18). This low dispersion could be due to the formation of Pt-Zn alloys and strong interactions that may not be active in CO chemisorption (Belskaya *et al.*, 2016:9). The elemental line scan in Figure 4-13 showed high Pt distribution throughout the Mg-doped catalyst (not an eggshell type) as opposed to the surface dispersion of Pt shown in Table 4-7.

Table 4-7. H₂-TPR and CO pulse chemisorption results of the catalysts

Catalyst	Pt dispersion, %	Active particle diameter, nm	Metallic surface area, m ² /g _{sample}	H ₂ consumption, μmol/g
Pt/Al ₂ O ₃	38	3.0	0.47	34
Pt/Mg-Al ₂ O ₃	34	3.3	0.42	64
Pt/Zn-Al ₂ O ₃	23	5.0	0.28	55

4.5.5 Ammonia temperature programmed desorption (NH₃-TPD)

The NH₃-TPD results are shown in Figure 4-15, including desorption profiles (solid lines) and their respective deconvoluted peaks (dotted lines) for the Al₂O₃ supports and Pt/Al₂O₃ catalysts. The first peak was at 200–250 °C and the second at 550–700 °C. These peaks are ascribed to the desorption of NH₃ due to weak/intermediate acidic sites and strong acidic sites, appearing in the regions of 200–400 °C and 400–550 °C, respectively, for γ-Al₂O₃ (Berteau & Delmon, 1989:273; Gutiérrez-Alejandre *et al.*, 1998:273; Shi *et al.*, 2017:19845; Stanislaus *et al.*, 1988:241).

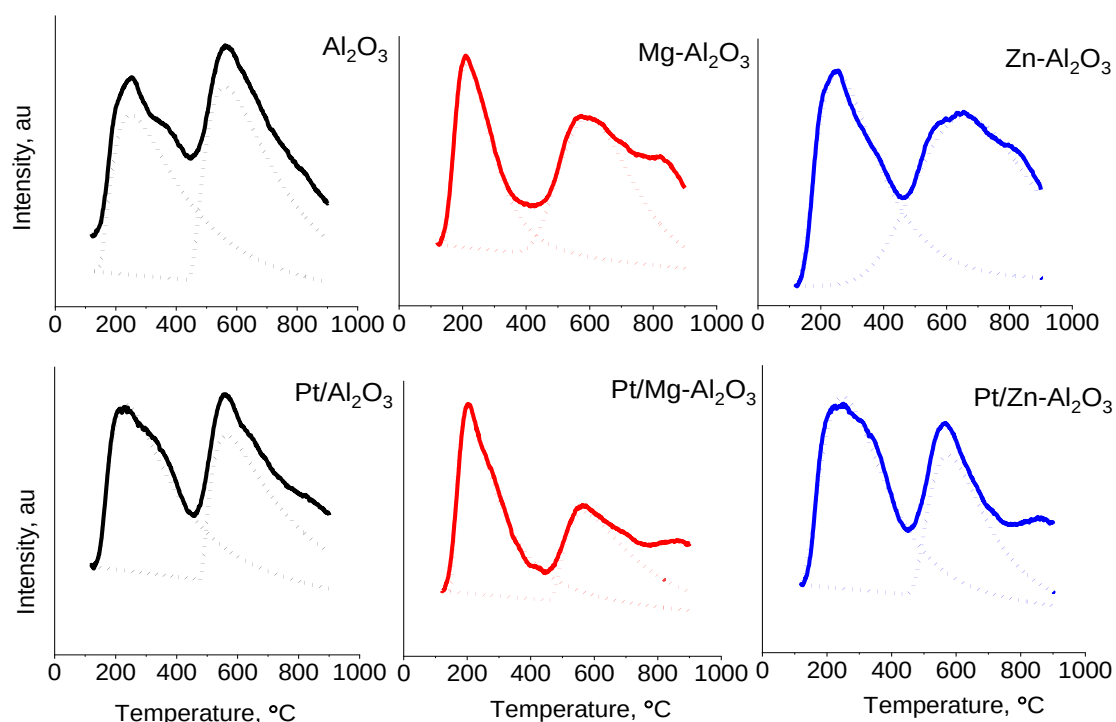


Figure 4-15. NH_3 -TPD profiles of Al_2O_3 supports and $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts.

Values for the acidity of supports and catalysts as determined by NH_3 -TPD are tabulated in Table 4-8. Mg doping decreased the total acidity of Al_2O_3 from 0.63 to 0.40 mmol NH_3/g , while Zn doping slightly increased it to 0.68 mmol NH_3/g . The order of the total acidity of supports was $\text{Zn-Al}_2\text{O}_3 > \text{Al}_2\text{O}_3 > \text{Mg-Al}_2\text{O}_3$. The addition of Mg decreased the total acidity of alumina by 37%, whereas the addition Zn increased it by 8%. Mg is inherently basic and leads to a decrease in the strength of acidic sites. The strong acidic sites inhibit desorption of products, hence the ability of Mg to decrease these sites led to improved selectivity to H0-DBT and the ultimate enhanced performance. The increased acidity in Zn-doped alumina is due to the substitution of proton sites on the Al_2O_3 framework with the doping Zn species, leading the regeneration of new proton sites on the support (Karnjanakom *et al.* 2016:240).

Table 4-8. Acidity of supports and catalysts, determined by NH_3 -TPD

Catalyst/support	Temperature, °C		Total acidity, mmol $\text{NH}_3/\text{g}_{\text{cat}}$	Peak fraction	
	A	B		A	B
Al_2O_3	251	562	0.63	0.45	0.55
$\text{Mg-Al}_2\text{O}_3$	214	597	0.40	0.43	0.57
$\text{Zn-Al}_2\text{O}_3$	252	659	0.68	0.44	0.56
$\text{Pt/Al}_2\text{O}_3$	236	566	0.48	0.52	0.48
$\text{Pt/Mg-Al}_2\text{O}_3$	202	565	0.41	0.56	0.44
$\text{Pt/Zn-Al}_2\text{O}_3$	250	575	0.49	0.60	0.40

A: first peak, B: second peak

4.5.6 X-Ray Diffraction (XRD)

Broad XRD peaks of pure alumina were detected at 32.5, 37.0, 38.9, 45.0 and 67.5°. There was no difference observed between doped, undoped or Pt loaded catalysts. This is because Pt, Mg and Zn particles are small and highly dispersed in the bulk alumina phase, therefore undetectable by XRD. The positions at which the Pt peaks should be observed are shown as vertical black dotted lines in Figure 4-16. The Pt loading was too low to be detected by XRD. For the Mg- and Zn-doped catalysts, there was no clear evidence of the existence of Mg and Zn oxides or aluminates ($\text{MgAl}_2\text{O}_4/\text{ZnAl}_2\text{O}_4$) because their main peaks overlap with those of alumina (Bai *et al.*, 2015:182; Buitrago-Sierra *et al.*, 2012:150; Zhang *et al.*, 2019:86).

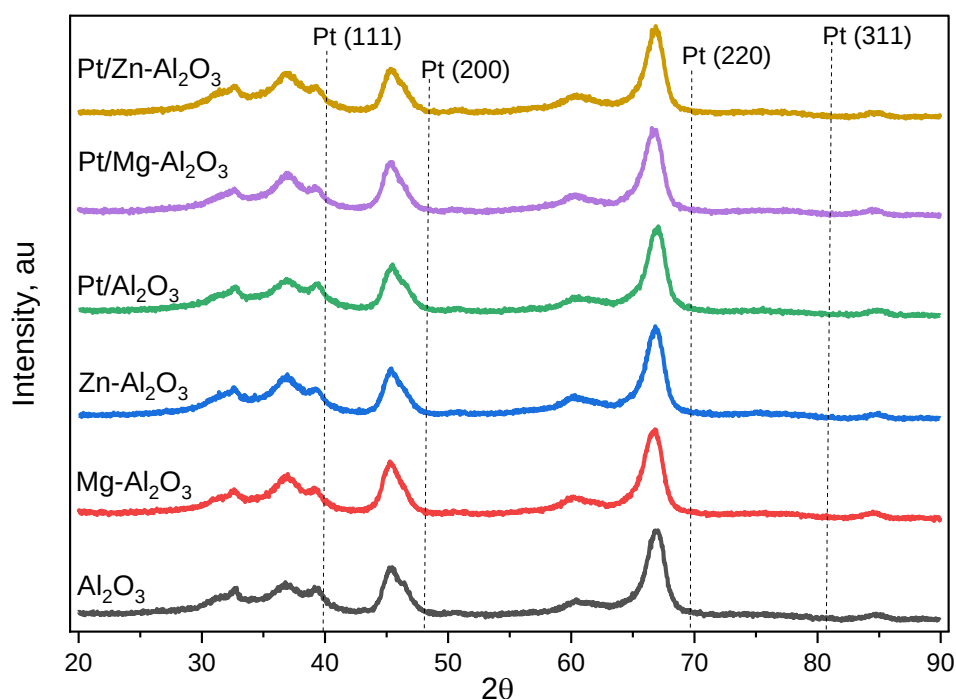


Figure 4-16. XRD patterns of catalysts and alumina supports.

4.5.7 Transmission Electron Microscopy (TEM)

TEM images revealed the presence of Pt NPs, as indicated by dark dispersed spherical particles; see Figure 4-17(a–c). The measured d-spacing between the lattice fringes of the Pt/Al₂O₃ particles was 2.07 Å and 2.4 Å. These d-spacing values correspond to the (200) and (111) family of planes, respectively. Furthermore, we obtained a d-spacing of 2.4 Å for Pt/Mg-Al₂O₃ catalyst. Miyazawa *et al.* (2017:3) measured a d-spacing of 2.3 Å, corresponding to the (111) plane. For the Pt/Zn-Al₂O₃ catalyst, d-spacing values of 2.11 and 2.12 Å were obtained. These d-spacing values correspond to the d-spacing reported by the Joint Committee on Powder Diffraction Standards (JCPDS) for FCC Pt. Table 4-9 summarises the measured d-values from fast Fourier transform (FFT) analysis, the family of planes, which correspond to these spacing, and the error for the values reported in the literature.

Table 4-9. d-spacing values from FFT measurements and JCPDS

hkl values	Measured d value, Å	JCPDS d value, Å	Error, %
111	2.123	2.26	6
200	2.11	1.96	8
	2.07		5.6

The mean particle size of the fresh catalysts was in the range 1.54–1.72 nm fs, and 2.1–2.24 nm and 2.14–2.80 nm for catalysts that sustained 6 h and 22 h of dehydrogenation at 300 °C, respectively; see Figure 4-17 and Table 4-10. However, Pt particles were not observed in the Pt/Zn-Al₂O₃ sample; it is possible that Zn affects nucleation and growth of particles, as reported by Belskaya *et al.* (2016:22). Figure 4-18 shows the Pt size distribution before and after dehydrogenation for 6 and 22 h. The slight increase in particle size after 6 and 22 h of reaction is negligible and cannot be linked to Pt sintering, since it occurs at temperatures >300 °C. The discrepancy in results of the particle size obtained from CO chemisorption and TEM has been reported elsewhere (Kirilin *et al.*, 2014:389; Modisha *et al.*, 2019:21932).

Table 4-10. Log-normal distribution parameters, mean and mode of Pt nanoparticles obtained by TEM before and after 6 h and 22 h dehydrogenation reactions.

Catalyst	μ	σ	m	mode
Before reaction				
Pt/Al ₂ O ₃	0.50	0.30	1.72	1.51
Pt/Mg-Al ₂ O ₃	0.52	0.18	1.70	1.62
Pt/Zn-Al ₂ O ₃	0.41	0.21	1.54	1.44
After 6 h dehydrogenation				
Pt/Al ₂ O ₃	0.78	0.21	2.24	2.10
Pt/Mg-Al ₂ O ₃	0.71	0.24	2.09	1.92
Pt/Zn-Al ₂ O ₃	0.15	0.20	-	-
After 22 h dehydrogenation				
Pt/Al ₂ O ₃	1.00	0.24	2.80	2.57
Pt/Mg-Al ₂ O ₃	0.73	0.25	2.14	1.93
Pt/Zn-Al ₂ O ₃	-	-	-	-

μ is the lognormal mean; σ is the lognormal standard deviation; m is the actual mean particle size

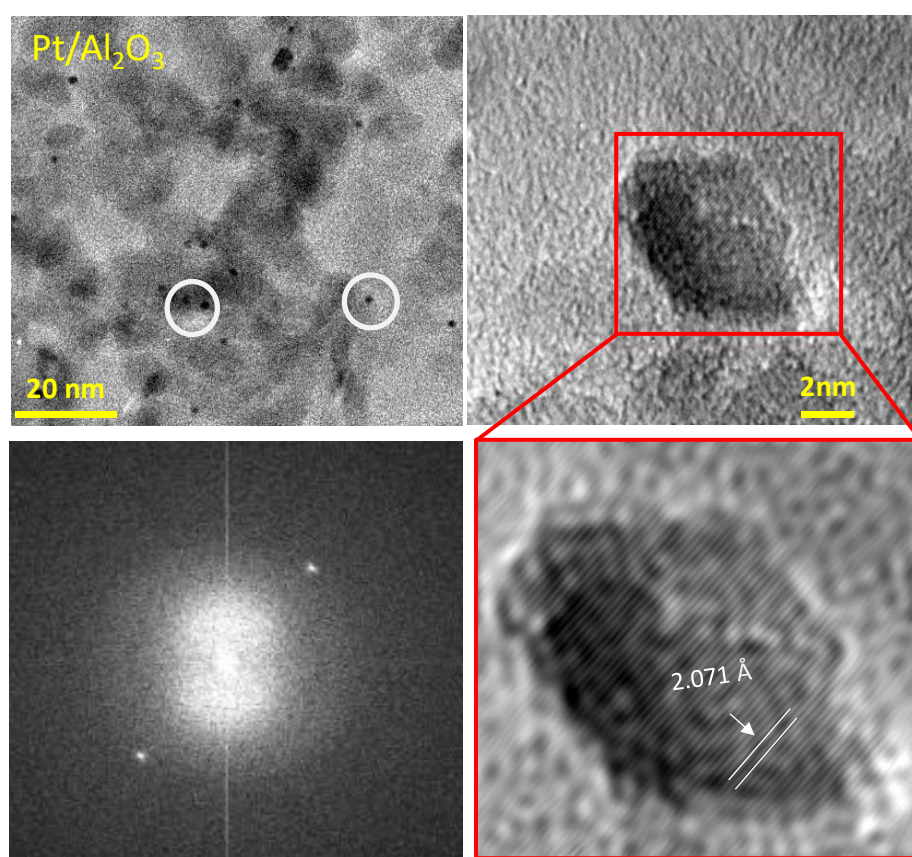


Figure 4-17a. TEM images, nanoparticles size distribution histograms and FFT images of the Pt/Al₂O₃ catalyst.

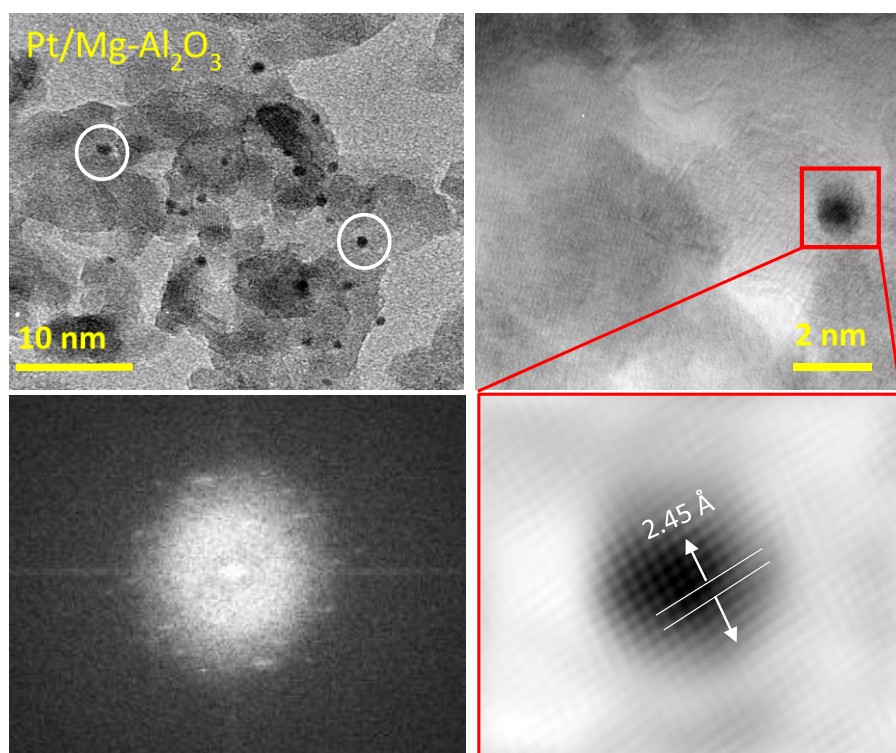


Figure 4-17b. TEM images, nanoparticles size distribution histograms and FFT images of the Pt/Mg-Al₂O₃ catalyst.

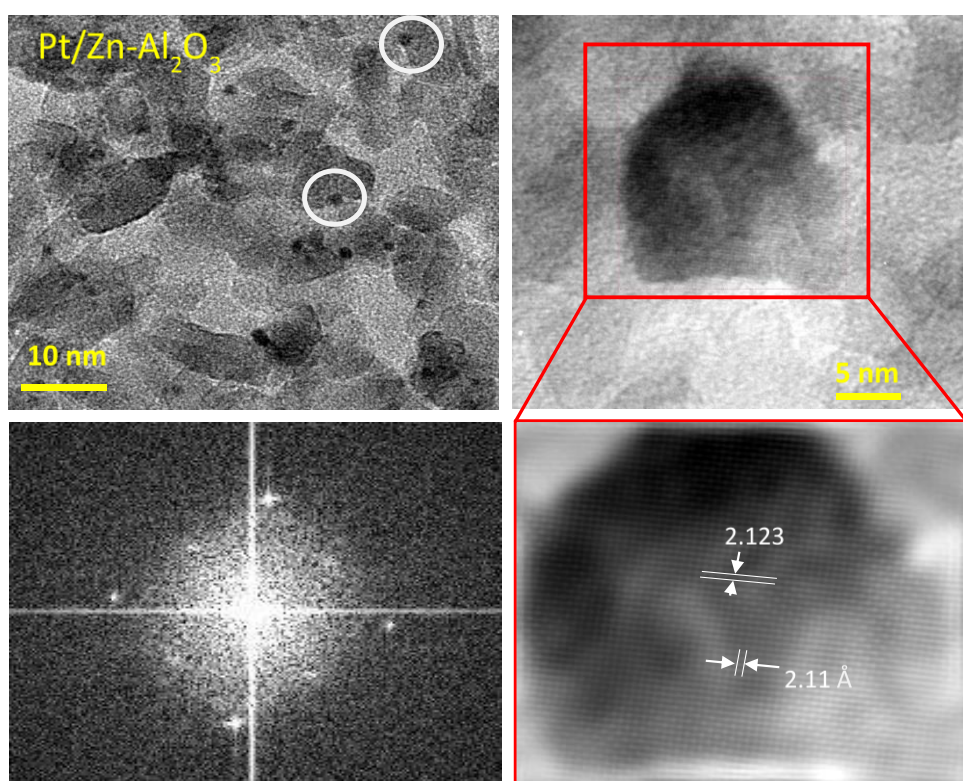


Figure 4-17c. TEM images, nanoparticles size distribution histograms and FFT images of the Pt/Zn-Al₂O₃ catalyst.

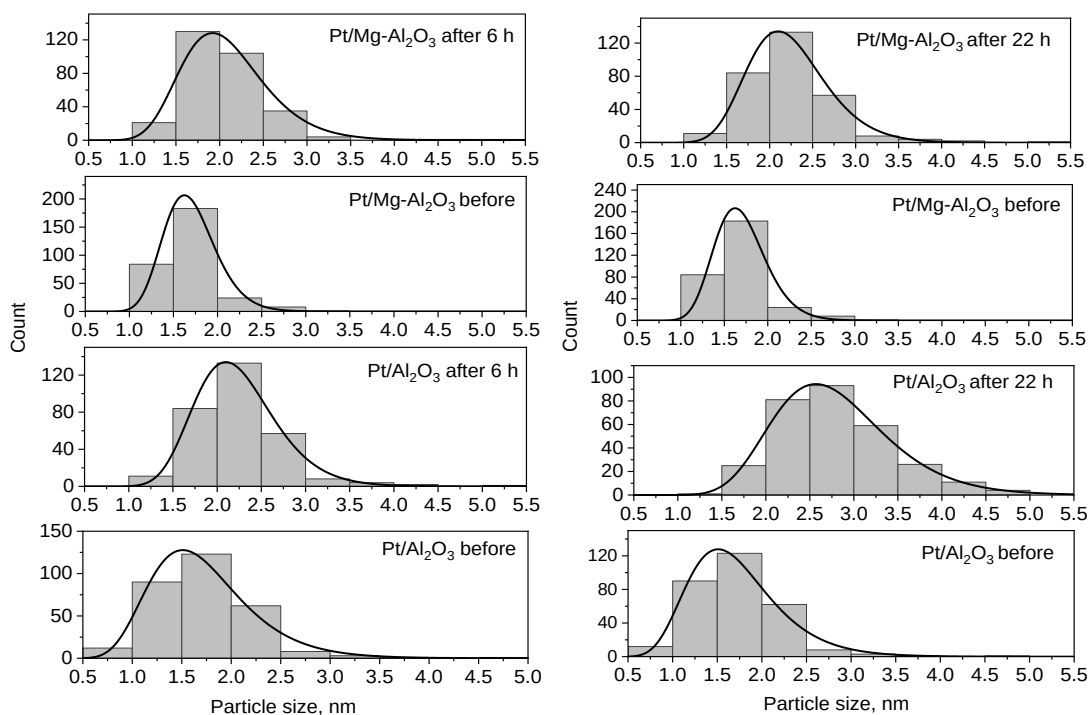


Figure 4-18. Pt nanoparticles size distribution before and after dehydrogenation, experiments carried out at 300 °C for 6 and 22 h.

4.5.8 Brunauer-Emmett-Teller (BET)

The N₂ adsorption and desorption isotherms with their corresponding pore size distribution curves for the supports and Pt loaded catalysts are shown in Figure 4-19. All catalysts exhibited a type IV isotherm with a H1 hysteresis loop between 0.7 and 0.9 P/P₀. This confirms the existence of a mesoporous structure with a narrow size distribution of uniform pores. (Dabbagh *et al.*, 2011:274).

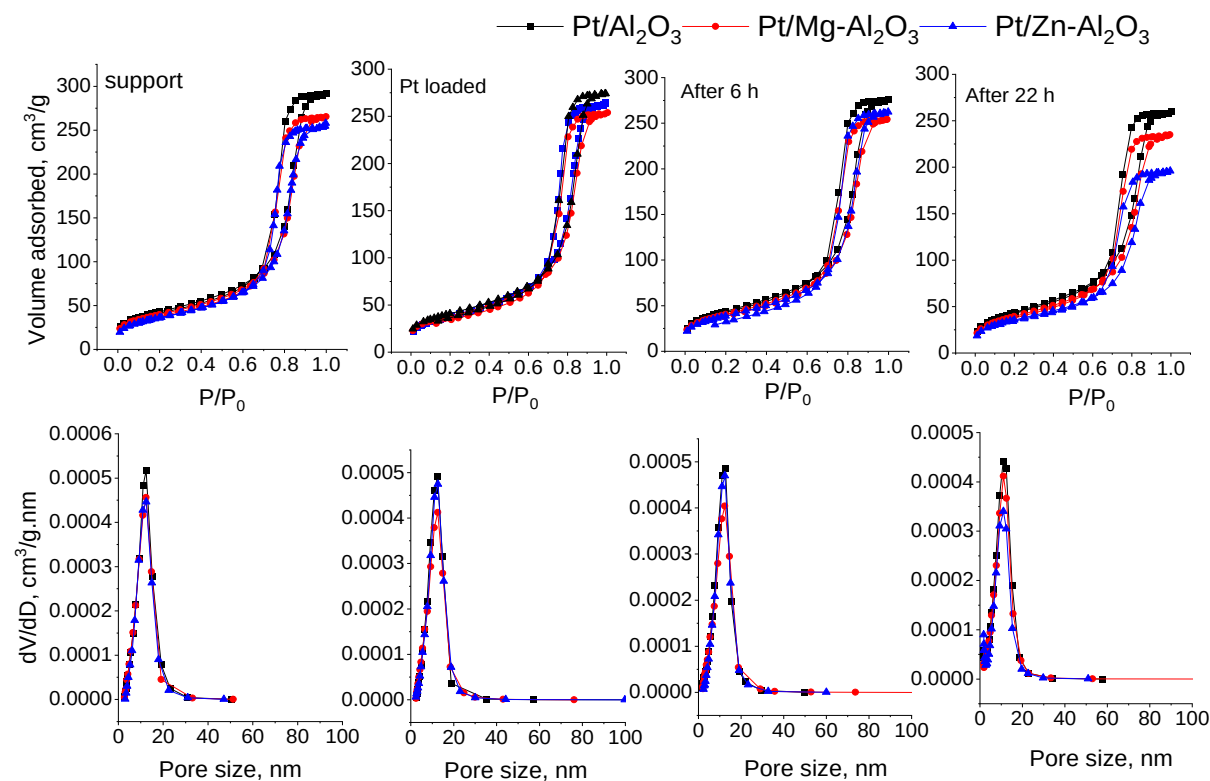


Figure 4-19. N₂ adsorption and desorption isotherms with their corresponding pore size distribution for supports, supported catalysts and the catalysts after 6 and 22 h of dehydrogenation.

The BET surface area, pore volume and pore size of Al₂O₃ were 158 m²/g, 0.43 cm³/g and 11 nm, respectively. These results are in agreement with values reported in literature (Auer, 2020:125). Findings of an investigation into the textural properties of the catalysts is summarised in Table 4-11. The addition of dopants and Pt did not change the pore diameter and surface area of the catalysts. This indicates that the dopants and Pt were well dispersed in the γ-Al₂O₃, thus the surface area and pore size remained unchanged. A post-mortem analysis after 6 and 22 h exposed a decrease in surface area, pore volume and pore size. The slight decrease in textural properties could be due to the LOHC that was not totally removed in the pores of our catalysts after cleaning. Other authors have associated this decrease with the formation of residues such as coke. The pore size of Pt/Mg-Al₂O₃ catalysts decreased

from 11 to 9.7 nm after 22 h (a 12% decrease), while that of the un-doped Pt/Al₂O₃ decreased from 11 to 9.2 nm (a 17% decrease). The effects of pore size on H18-DBT dehydrogenation have been investigated; an optimal pore diameter (24 nm) facilitates diffusion and leads to an enhanced activity (Seidel, 2019:95; Auer, 2020:125). Since the catalysts studied here had the same textural properties, the ability of the Mg catalyst to slightly suppress pore size reduction may have contributed to an improved performance. Optimal Mg loading could further contribute to the retention of the pore size, and subsequently result in better performance.

Table 4-11. BET specific surface area, pore volume and pore size of the support and catalyst before and after 6 h and 22 h of dehydrogenation

Catalyst	BET surface area, m ² /g	Pore volume, cm ³ /g	Pore size, nm
Al ₂ O ₃	158	0,451	11,1
Mg-Al ₂ O ₃	141	0,411	11,1
Zn-Al ₂ O ₃	145	0,406	10,9
Pt/Al ₂ O ₃	157	0,427	10,7
Pt/Mg-Al ₂ O ₃	142	0,393	11
Pt/Zn-Al ₂ O ₃	140	0,427	10.8
After 6 h dehydrogenation			
Pt/Al ₂ O ₃	157	0,427	10,3
Pt/Mg-Al ₂ O ₃	142	0,392	10,7
Pt/Zn-Al ₂ O ₃	138	0,392	10,5
After 22 h dehydrogenation			
Pt/Al ₂ O ₃	136	0,299	9,2
Pt/Mg-Al ₂ O ₃	137	0,367	9,7
Pt/Zn-Al ₂ O ₃	129	0,403	9,5

4.6 Characterisation of the liquid carrier molecules

Liquid analyses of the LOHC after dehydrogenation, for determination of the conversion, selectivity and presence of by-products, are now described. Since the LOHCs have several isomers, wide retention times, with more than one peak, were observed for the intermediates (see Table 4-12 and Figure 4-20).

Table 4-12. Retention times obtained during the dehydrogenation of H18-DBT using GC-MS-SQ

Substance	Retention time (min)
H18-DBT	24–27.6
H12-DBT	29.7–32.6
H6-DBT	32.3–35
H0-DBT	35.3–39.2

Figure 4-20 shows the peaks (GC-MS-SQ chromatogram) of each intermediate. The area under these peaks is intergrated and used to calculate conversion, selectivity and by-products with equations (3.14)–(3.16).

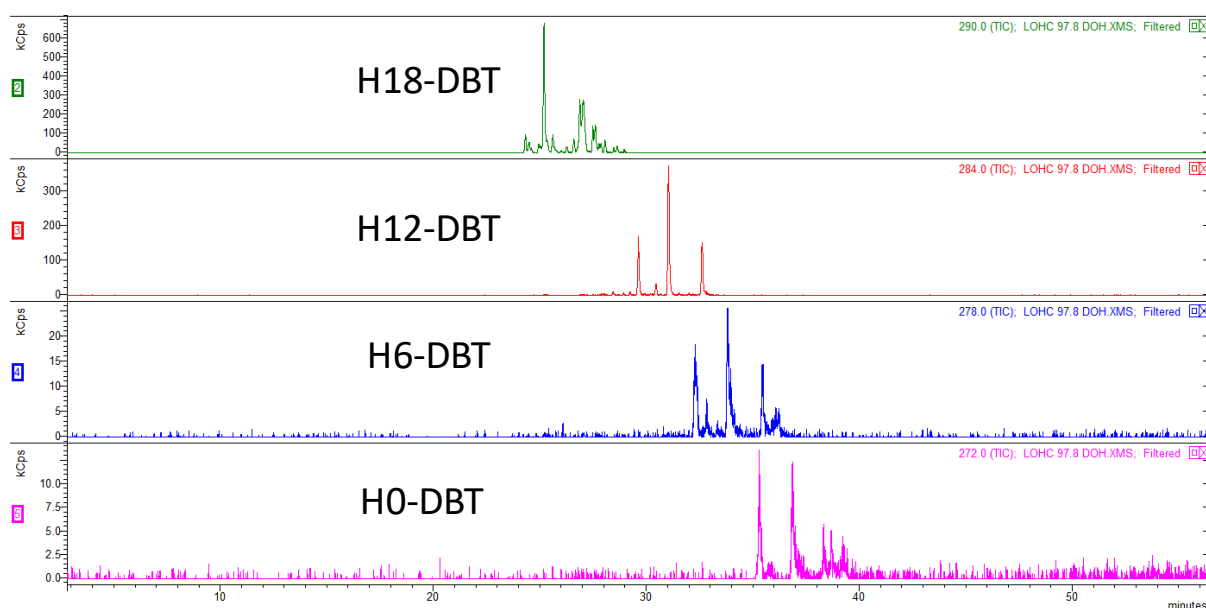


Figure 4-20. GC-MS-SQ chromatograms showing the retention time and peaks of the stable intermediates and their isomers when H18-DBT is converted to H0-DBT during dehydrogenation.

Investigations were also carried out to determine whether the by-products formed as a result of thermal cracking, or whether they were due to the nature of the support material or Pt catalyst. First, H18-DBT was heated without any catalyst or support material for 1.5 h at 300 °C. Second, in separate experiments, each support material (Al_2O_3 , $\text{Mg-Al}_2\text{O}_3$ and $\text{Zn-Al}_2\text{O}_3$) was added to fresh H18-DBT and treated under the same conditions as mentioned above. $\text{Pt/Al}_2\text{O}_3$ catalyst was added at a later stage. Results did not indicate the presence of any by-products in the low- and high-boiler region of the spectrum when H18-DBT and the various supports were used (see Figure 4-21). However, by-products did appear when catalyst ($\text{Pt/Mg-Al}_2\text{O}_3$) was used. These by-products can be seen in Figure 4-21 as peaks in the retention time window of low- (5–20 min) and high-boilers (40–50 min). The aromatic molecules (H0-DBT) produced during dehydrogenation are susceptible to the acid sites of the support, which

provides the cracking function. Hence, by-products were not seen in the testing of blank supports because there was no formation of aromatic compounds.

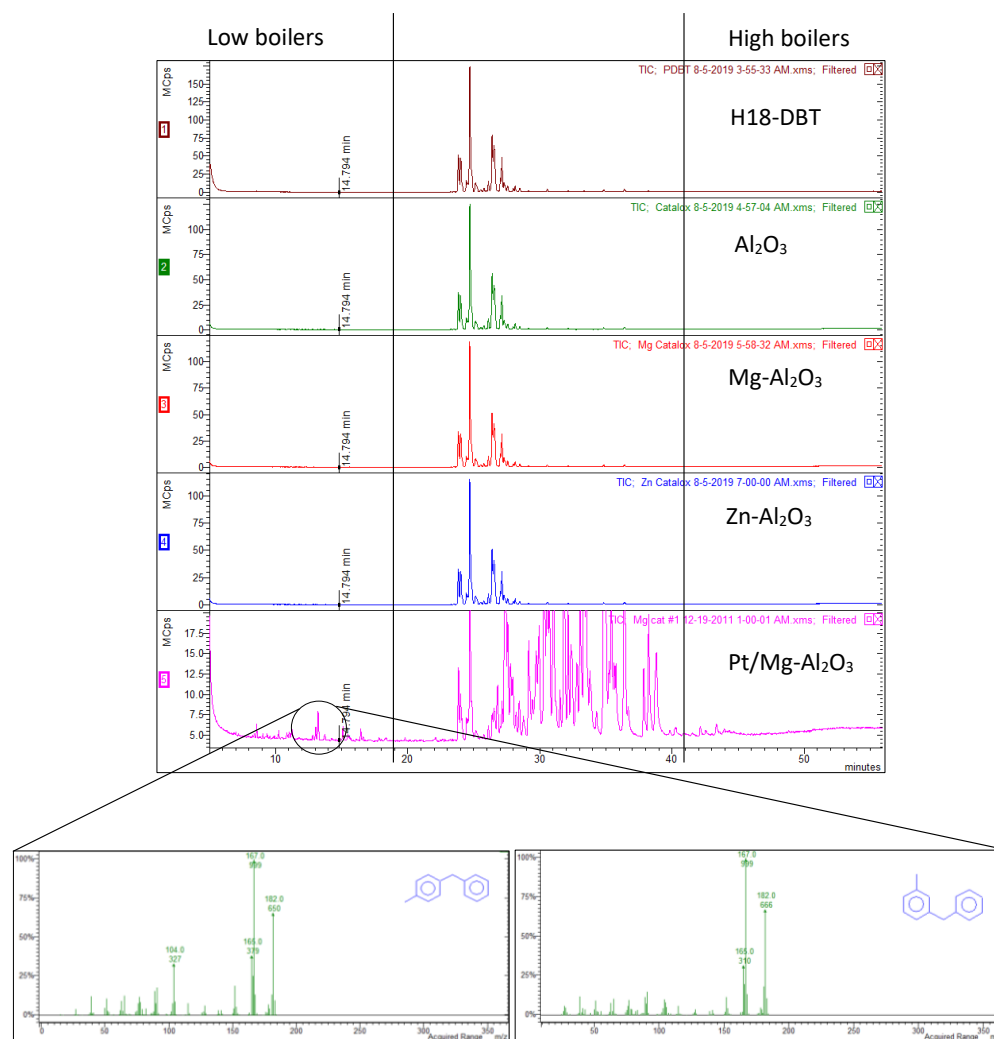


Figure 4-21. Chromatograms of H18-DBT heated at 300 °C for 90 min with and without support; and a representative chromatogram and MS spectra showing low boiling point by-products of Pt/Mg-Al₂O₃ catalyst. (NIST 17 mass spectral library was used to identify the compounds.)

4.7 Summary: catalysts and H18-DBT characterisation

Catalysts were characterised in an effort to determine the physicochemical properties that contributed to the dehydrogenation performance of H18-DBT. All catalysts were successfully modified with Mg and Zn, while Pt was loaded with a target of 0.5 wt %. ICP-OES revealed a Pt loading of 0.48 wt % for Pt/Al₂O₃ and Pt/Zn-Al₂O₃, and 0.49 wt % for Pt/Mg-Al₂O₃. EDS line scan analysis indicated an eggshell type of catalyst for Pt/Al₂O₃ and Pt/Zn-Al₂O₃ catalysts, while a uniform distribution was observed for Pt/Mg-Al₂O₃. The reduction temperatures obtained from H₂-TPR increased from 350–400 °C for Mg-doped catalysts and to 450 °C for Zn-doped catalysts, indicating the existence of strong MSI after doping, which is desirable in

suppressing Pt agglomeration. The addition of Mg slightly decreased the Pt dispersion from 38% to 34%, while Zn decreased it to 23%. This is attributed to the adsorptive properties that were altered due to strong MSI, resulting in low adsorption of CO. Unexpectedly, the Pt size decreased from 1.72 to 1.70 (Mg) and 1.54 (Zn). After dehydrogenation for 6 h and 22 h, there was no significant change in Pt particle size. Pt phases could not be detected with XRD; however, high-resolution TEM revealed the existence of Pt (111) and Pt (200) phases with acceptable accuracy. The textural properties of the catalysts were basically the same, even after doping. Mg-doped catalysts seemed to exhibit some retention of the pore size (changed from 11 to 9.7 nm) after dehydrogenation. Otherwise, it is the acidity that was the major difference.

Mg reduced the acidity of alumina by 37%—this could have led to better performance than in the cases of Zn-doped and undoped catalysts with similar acidity values. The presence of by-products was a function of catalyst activity rather than the acidity of catalysts. Moreover, no by-products were observed when the supports were heated at 300 °C, meaning that by-products formation is the result of catalyst activity. In conclusion, Mg doped catalysts performed better because of its favourable acidity feature, which suppressed deactivation and facilitated easy diffusion, thus resulting in better catalytic activity. Moreover, the Mg doped catalyst had more active Pt sites as indicated by the highest frequency factor and TOF values which resulted in high activity.

CHAPTER 5. CONCLUSIONS AND RECOMMENDATIONS

This chapter presents the conclusions drawn from the findings of this study, specifically, regarding the effect of Mg- and Zn-doped Pt/Al₂O₃ catalysts on the catalytic dehydrogenation performance and stability of the hydrogen-rich molecule perhydro-dibenzyltoluene (H18-DBT). The original objectives are given (in italic), followed by their findings/conclusions. The document concludes with recommendations for future work.

5.1 Conclusions

From this study's specific objectives, the following conclusions are deduced:

Preparation of the Mg-Al₂O₃ and Zn-Al₂O₃ by modification of Al₂O₃ support material using incipient wet impregnation method

The supports were successfully modified with Mg and Zn to produce Mg-Al₂O₃ and Zn-Al₂O₃, with a Mg and Zn loading of 3.4 and 3.9 wt %, respectively. The target loading for both dopants was 3.8 wt %. The presence of Mg and Zn was confirmed by ICP-OES and SEM-EDS.

Impregnation of the Al₂O₃, Mg-Al₂O₃ and Zn-Al₂O₃ support materials using a Pt precursor, to afford 0.5 wt.% Pt/Al₂O₃, 0.5 wt. % Pt/Mg-Al₂O₃ and 0.5 wt. % Pt/Zn-Al₂O₃

The wet impregnation method used for Pt deposition on alumina-based supports was successful and reproducible as ICP values between 0.48 and 0.49 wt % were close to the target loading of 0.5 wt %.

Evaluation of the catalysts' performance (e.g., productivity, conversion, selectivity) at various reaction temperatures (260–300 °C) for the dehydrogenation of H18-DBT using a batch reactor

The evaluation of catalytic performance in a batch reactor indicated strong dependence of activity on temperature. The highest activities were obtained at 300 °C for all catalysts. Overall, Pt/Mg-Al₂O₃ was the best performing catalysts in a batch reactor—it achieved full dehydrogenation at 290 °C and 300 °C, while Pt/Al₂O₃ and Pt/Zn-Al₂O₃ never reached full dehydrogenation. The best performing catalyst (Pt/Mg-Al₂O₃) had a yield, productivity, conversion and selectivity of 100%, 1.84 gH₂/g_{Pt}/min, 99.9% and 99%, respectively. After run 4, catalytic activity for all catalysts decreased due to catalyst deactivation. The extent of deactivation expressed as deactivation parameter highlighted that Mg lowered deactivation of Pt/Al₂O₃ by a factor of three. The superior activity of Mg-doped catalysts in both reactors was

attributed to the low acidity of the support which then afforded improved selectivity towards H0-DBT. The high selectivity could be an effect of Mg weakening the adsorption of H0-DBT on the Pt surface and promoting the H0-DBT desorption. The higher the reaction activity, the higher the amounts of by-products formed. This is because the higher the catalytic activity, the more aromatic molecules are produced, and these aromatic molecules are susceptible to the acid sites of the support, which causes C-C cracking. Furthermore, the formation of by-products could also be facilitated by the hydrogenolytic effect of Pt/Mg-Al₂O₃.

Kinetics study for dehydrogenation H18-DBT using a batch reactor i.e., determination of kinetics parameters such as, rate constant, reaction rate, activation energy and turn-over frequency (TOF)

The kinetic study indicated that addition of dopants resulted in high turnover frequencies (TOF) of 202, 586 and 269 min⁻¹ for Pt/Al₂O₃, Pt/Mg-Al₂O₃ and Pt/Zn-Al₂O₃, respectively. The highest rate constant and rate of reaction at 300 °C for Pt/Mg-Al₂O₃ were 0.0137 min⁻¹ and 0.17640 M.min⁻¹.g_{cat}⁻¹, respectively. This indicate that Pt/Mg-Al₂O₃ catalyst has the highest amount of active metal sites available for dehydrogenation reaction. This was also confirmed by a high frequency factor (2.3 × 10¹¹) min⁻¹ which suggests high rate of molecular collisions. The dehydrogenation of H18-DBT followed first order reaction kinetics and the obtained activation energy of Pt/Al₂O₃, Pt/Mg-Al₂O₃ and Pt/Zn-Al₂O₃ are 101, 151 and 131 kJ/mol, respectively. In this case, high amount of active sites corresponds to high value of frequency factor and this is connected to high activation energy. Therefore, lower activation energy for dehydrogenation of H18-DBT will not always produce high reaction rate. The high activation energy of the doped catalysts, particularly Pt/Mg-Al₂O₃ points out the facile diffusion of reactant and products which led to its better performance.

Determination of the catalyst stability for dehydrogenation of H18-DBT using a fixed bed reactor

In a fixed bed reactor, Pt/Mg-Al₂O₃ was the most stable catalysts during the 22 h time on stream compared to Pt/Al₂O₃ and Pt/Zn-Al₂O₃. The improved activity of Pt/Mg-Al₂O₃ is attributed to the acidity and possible densification of Al₂O₃ grain size by Mg addition which have an effect on minimizing the pore diffusion limitation and increasing the catalytic activity. This was indicated by the ability of Mg to slightly suppress pore size, consequently deactivation was minimised.

Characterisation of the catalysts, before and after the dehydrogenation reaction, to investigate the effect of modification in the physico-chemical properties of the catalysts

The characterisation techniques revealed that the addition of Mg and Zn dopants to Pt/Al₂O₃ resulted in strong metal support interaction which resisted Pt agglomeration and improved activity. The textural properties were the same for all catalysts leading to similar activity in fresh catalysts. However, the ability of Mg to slightly suppress/retain pore size could have led to its improved performance. Moreover, Mg lowered support acidity (as proven by NH₃-TPD) and the less acidic catalyst is found to be more selective towards the product H0-DBT. Therefore, Mg weakens the adsorption of H0-DBT on Pt surface and promotes H0-DBT desorption.

5.2 Recommendations for future work

The following recommendations for further studies are proposed based on what has been established in this dissertation.

- i. Evaluation and optimisation of different types of dopants—The optimisation of the loading of dopants (e.g., Mg and Zn) is essential to ensure that not only the best activity is achieved, but also to attain the most selective and stable catalyst. This is so because too little or too much loading of the dopant could have no effect or be detrimental to catalytic performance.
- ii. Further characterisation of catalysts—The use of other characterisation techniques, such as temperature programmed oxidation and diffuse reflectance infrared Fourier transform spectroscopy could be useful to determine the cause of catalyst deactivation.
- iii. Exploring different synthesis methods for catalysts—For example, the control of nanoparticles dispersion, size and distribution in the support material can be achieved by supercritical CO₂ impregnation.
- iv. Coupling the dehydrogenation set-up with a FC—The effect of any volatile substance (benzene, toluene, xylene) or gas phase by-products (CO, CO₂, CH₄ etc.) on the performance of FC is worthwhile to investigate.

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APPENDIX A – SUPPLEMENTARY MATERIAL

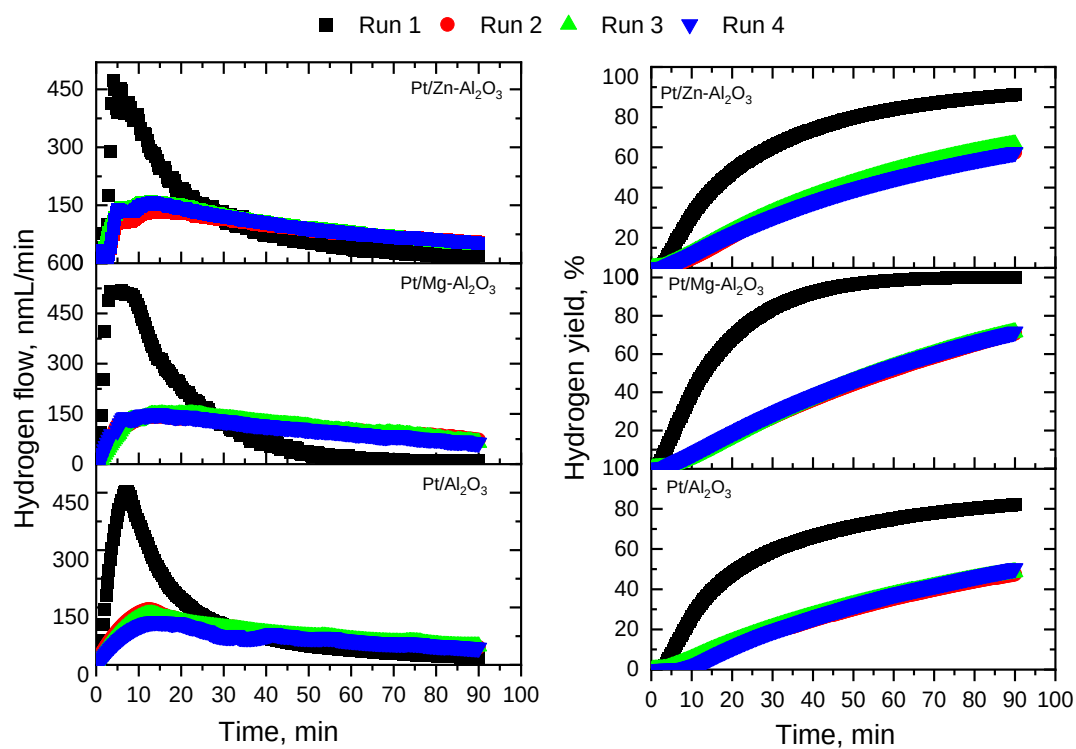


Figure A-1. The effect of Mg and Zn dopants on the hydrogen flow and yield in a batch reactor. Reaction parameters as a function of dehydrogenation temperature in a batch reactor. Reaction parameters: H18-DBT, 99% doh; 0.5 wt % Pt; n_{Pt}/n_{LOHC} , 0.2 mol %; temperature, 300 °C; time, 90 min.

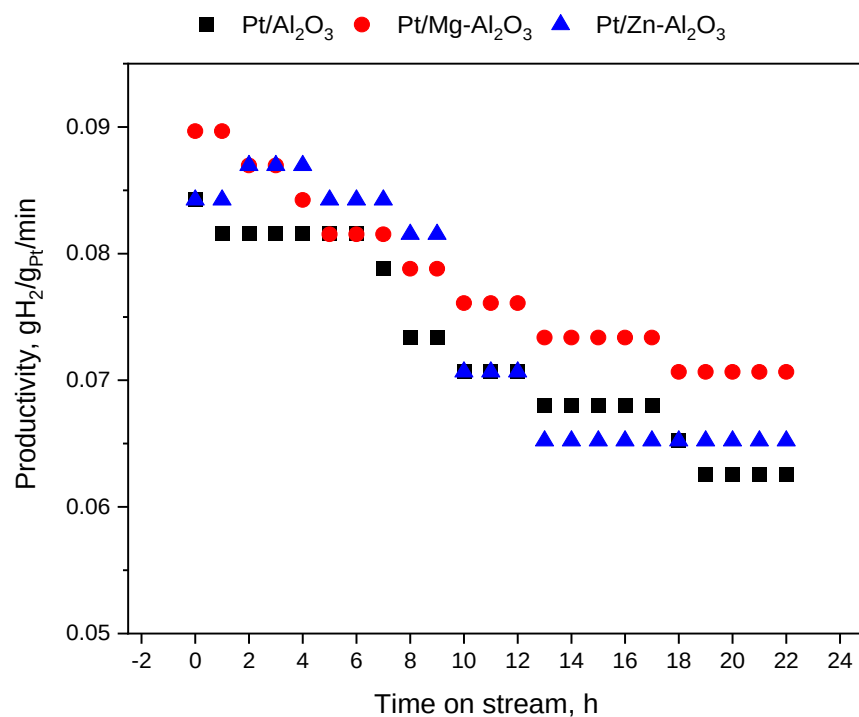


Figure A-2. Productivity of the catalysts obtained in a fixed bed reactor during the dehydrogenation of H18-DBT for 22 h time on stream. Reaction parameters: Pt loading 0.5 wt. %; H18-DBT, doh 99.6%; reaction temperature, 300 °C; feed flow, 1.3 ml/min; catalyst mass, 110 g; weight hourly space velocity, 0.61 h⁻¹.

APPENDIX B – CALIBRATION CURVES

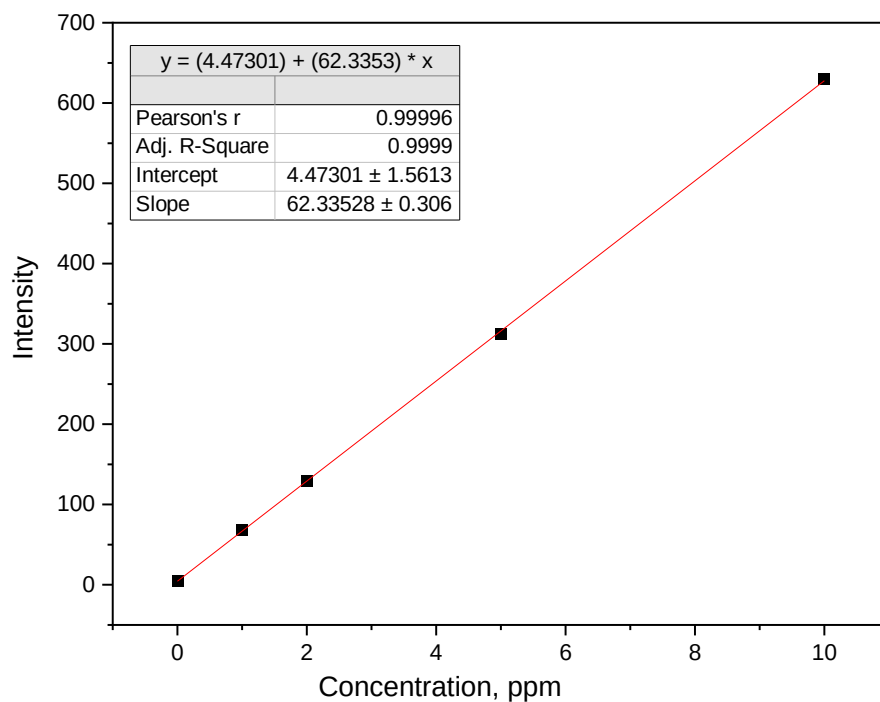


Figure B-1. Calibration curve of Pt (214.424 nm) obtained from ICP-OES.

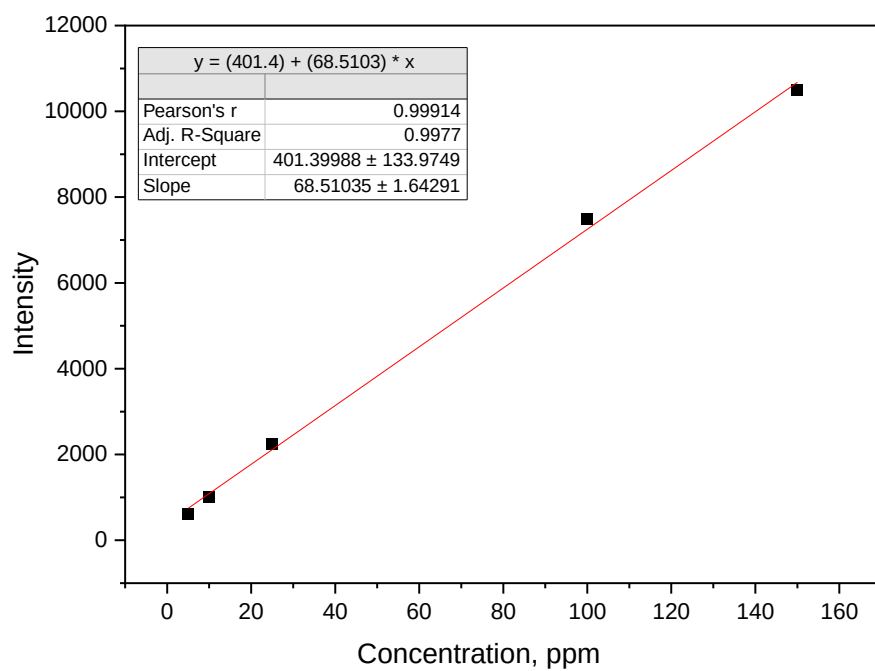


Figure B-2. Calibration curve of Mg (278.142 nm) obtained from ICP-OES.

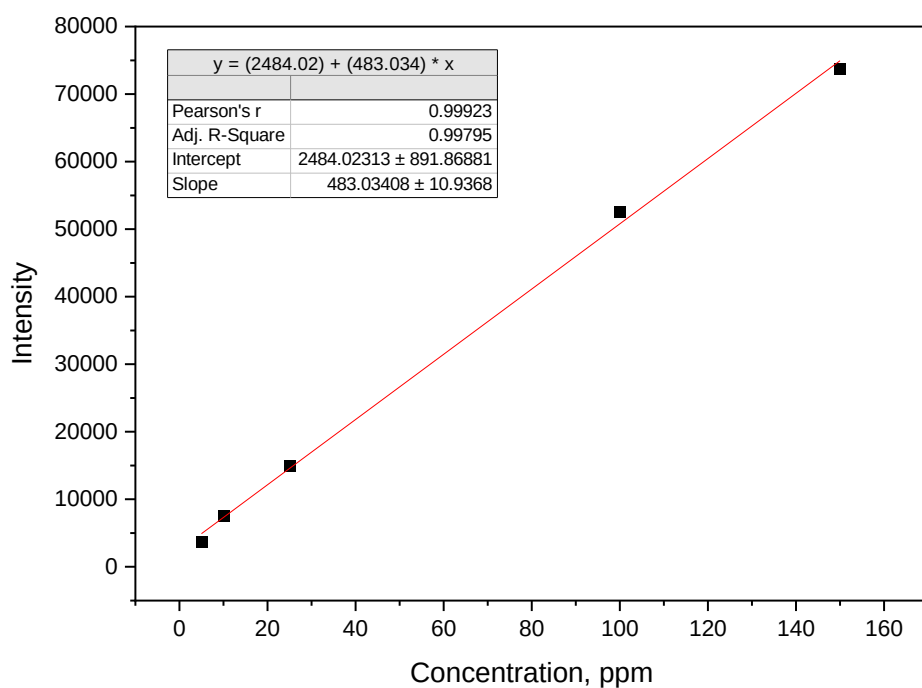


Figure B-3. Calibration curve of Zn (334.502 nm) obtained from ICP-OES.

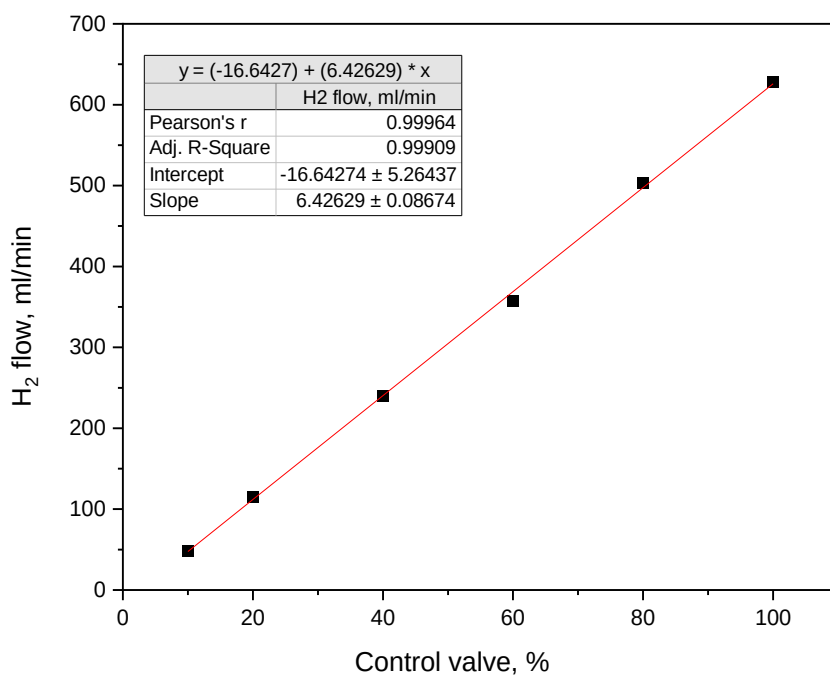


Figure B-4. Calibration curve of H₂ flow meter using a bubble flow meter.

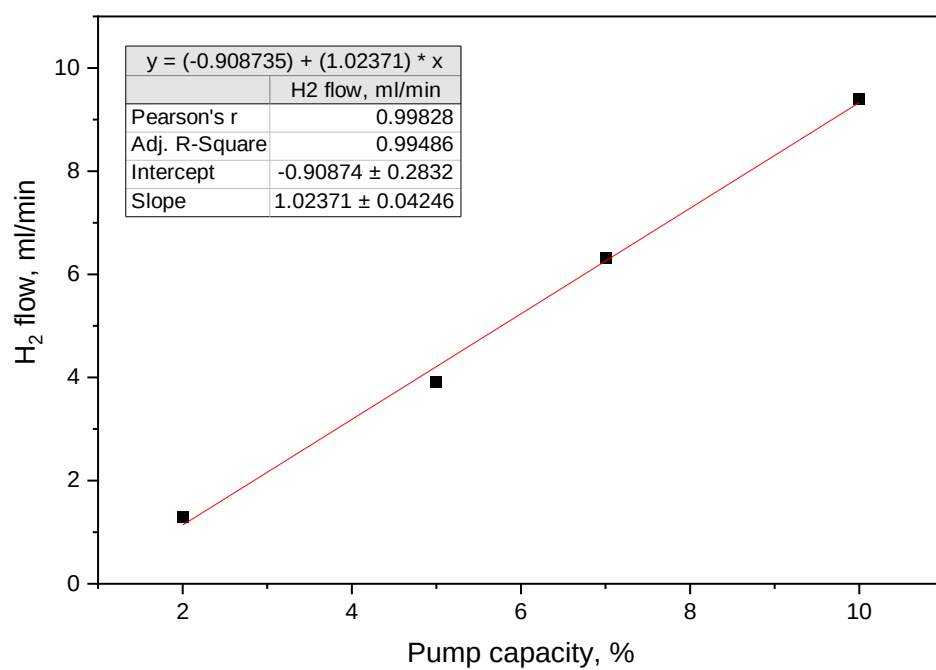


Figure B-5. Calibration curve of H18-DBT flow using a horizontal fixed bed reactor.