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Aromatic liquid organic hydrogen carriers for hydrogen storage and release

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Abstract

Hydrogen production from renewable energy sources has the potential to significantly reduce the carbon footprint of critical economic sectors that rely heavily on fossil fuels. Liquid organic hydrogen carrier (LOHC) technology has the capability to overcome the limitations associated with conventional hydrogen storage technologies. To date, dibenzyltoluene and benzyltoluene are the benchmark LOHC molecules due to the unique hydrogen storage properties. However, the reaction temperature for dehydrogenation reaction is high and catalysts need to be further developed so that efficient release of hydrogen can be realized. Exploration of various catalyst preparation methods such as supercritical carbon-dioxide deposition, the selection on support material with relevant textural and chemical properties and optimization of catalyst modifiers are rewarding approaches of improving the catalyst performance. In addition to this, the lowering of the dehydrogenation temperature by employing electrochemical methods and reactive distillation approaches are strategies that will make the LOHC technology competitive.

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Introduction

Renewable energy sources such as wind and solar are increasingly adopted by households and industries to reduce greenhouse gas emissions. However, wind and solar are intermittent power suppliers that require efficient energy storage methods to supply power when natural sources are unavailable. Hydrogen is a well-known clean energy carrier, which produces water and heat when used as a fuel in hydrogen fuel cells for mobile and stationary power applications. Interestingly, clean hydrogen can be produced from the electrolysis of water using renewable energy resources (wind turbines and photovoltaics panels). Hydrogen is also used as a feedstock in petrochemicals and chemicals (e.g., hydroprocessing in the petrochemical industry, methanol synthesis, ammonia production, etc.) as well as in the production of glass, cement and steel [1—4]. Therefore, clean hydrogen is a promising candidate for decarbonising various sectors of the economy. As a result of the storage challenges associated with the low density of hydrogen, many researchers have explored techniques for the storage of hydrogen in large volumes [5—7]. Conventional hydrogen storage techniques are reported to be costly, inefficient and, furthermore, they also have some limitations to certain applications [8—10].

Liquid organic hydrogen carriers (LOHCs) have recently emerged—they offer many advantages compared to conventional hydrogen storage technologies [8]. The key components of the so-called “LOHC technology” include the hydrogen carrier molecule, the catalyst and the reactor vessel. In LOHC technology, hydrogen is stored through the hydrogenation of a hydrocarbon molecule in the presence of a catalytic material. The reversibility of the carrier molecule then allows the hydrogen to be released by a catalytic dehydrogenation process.

Currently, the heat transfer fluid commonly known as Marlotherm SH (Eastman Chemicals Company, Germany) is the benchmark LOHC molecule [8,11,12]. The hydrogen-lean Marlotherm SH is commercially available as a mixture of dibenzyltoluene (H0-DBT) isomers and the hydrogen-rich form is perhydrodibenzyltoluene (H18-DBT). It offers unique properties, such as high hydrogen storage capacity (6.2 wt %; 1 m^3 LOHC = 57 kg H_2), low vapour pressure due to a high boiling point (380 °C), available in abundance (it is produced on a multi-tonne scale), affordability, and compatibility with the existing infrastructure for fuel [8,12]. However, one of the main challenges faced when using Marlotherm SH is the high temperature (>300 °C) required for the dehydrogenation reaction [8]. The H18-DBT reaction enthalpy of 65.4 kJ/mol-H_2 was calculated at 298.15 K and 0.1 MPa by

Müller et al. [9] and this value is expected to be higher at temperatures required for the dehydrogenation reaction. This is because the specific heat capacity of H18-DBT is not constant at various temperatures [9]. Other challenges include the deactivation of the catalyst used, loss of stability and low performance in the dehydrogenation process. These issues have a direct negative impact on the storage capacity of the LOHC molecule because of the inability to maintain the total recovery of stored hydrogen [13]. Therefore, optimization of the catalyst material is aimed at improving the hydrogen recovery.

It is for this reason that the sherLOHCk consortium (European Union) aims to develop an innovative, cost-efficient and sustainable catalytic solution for improved LOHC technology [14]. According to the consortium, this will be achieved by, lowering the thermal energy of dehydrogenation to ≤ 6 kWh/kg H_2, improving the reaction kinetics (>3 g H_2/g catalyst/min) and keeping the loss of performance at $< 0.01\%$ per cycle. Moreover, the catalyst should have a lifetime of five years, whilst both conversion and selectivity are retained at $> 90\%$ and $>99.8\%$, respectively [14].

Despite the interesting and very useful hydrogen storage properties of LOHC compounds, the LOHC technology nonetheless still suffers from high costs and inefficiencies in thermal management. This contribution assesses the current developments in solving the challenges associated with LOHC technology.

LOHC catalyst development

Catalyst preparation methods

The catalysts used for the dehydrogenation of H0-DBT-based LOHCs are platinum-based (Pt/Al_2O_3 pellets) and the most common preparation method is wet impregnation using chloroplatinic acid. Alternative to pellet-based catalysts, Solymosi et al. investigated the application of catalytically activated stainless steel (SS) plates for the dehydrogenation of LOHCs [15]. The plates were grafted with Pt/Al_2O_3, with the aid of doctor's blade, following the wet impregnation method. It was envisaged that, hereby, better heat transfer to the active sites would be achieved than with the pellets, and for integration of the LOHC dehydrogenation units in high-temperature fuel cells. A Pt catalyst modified with sulphur and grafted on SS steel plates exhibited an activity of $>35\%$ with a 90% reduction in by-product formation [16].

Supercritical deposition (SCD), and particularly the use of supercritical CO_2 ($scCO_2$), for the synthesis of catalysts has benefits over conventional methods of catalyst synthesis. $ScCO_2$ has a moderate critical temperature and pressure ($T_c = 304.15$ K, $P_c = 7.38$ MPa), is affordable, inert, non-flammable and non-toxic [16,17]. In our previous studies we have reported, for the first time, the use of $ScCO_2$ prepared Pt/Al_2O_3 for the dehydrogenation of H18-DBT [18]. The $ScCO_2$ catalyst was compared with catalysts prepared by conventional methods; the catalyst from the original equipment manufacturer was employed as a benchmark. Improved catalytic performance was observed when the $ScCO_2$ catalyst was used for the dehydrogenation of H18-DBT. Catalyst characterisation results indicated that the $ScCO_2$ catalyst had a larger dispersion of smaller Pt particles. This is attributed to the fact that the gas-like diffusivity of $ScCO_2$ has greater mass transfer rates than a liquid-based solvent [17]. After 10 dehydrogenation runs, the $ScCO_2$ catalyst was the least deactivated; it exhibited a productivity of 1.82 gH_2/gPt/min, H18-DBT conversion of 67% and selectivity to H0-DBT of 25% [18]. Earlier work of Gunes et al. also confirms that the use of $ScCO_2$ offers an effective method for the preparation of Pt/Al_2O_3 catalysts with small average particle sizes and narrow particle size distribution [17].

Catalyst modification

The modification of surface hydroxyl groups and surface oxygen vacancies (SOVs) of the Pt/Al_2O_3 catalyst using O_2 and H_2 plasma treatment has offered improvement in the catalytic dehydrogenation of H18-DBT [19]. Increasing surface hydroxyl groups and adequately reducing SOVs on Pt/Al_2O_3 is beneficial for enhancing both the reactivity and reducing the occurrence of side reactions for the long-term cycle performance of the catalyst. Using a H_2 plasma-treated catalyst, high Pt dispersion and a degree of dehydrogenation (dod) of $>60\%$ has been recorded. Despite this, the best performing catalyst ($Pt/Al_2O_3{-}H_2$ plasma treated) showed a deactivation of 52% within four dehydrogenation cycles.

The combustion nanocatalyst synthesis method, known as the glycine nitrate process (GNP), has been used for the preparation of Pt/Al_2O_3 and Pt/CeO_2 with similar textural properties [20]. Dehydrogenation with Pt/CeO_2 was substantially more rapid than with Pt/Al_2O_3: 80.5% in 2.5 h compared to 3.5% in 2.5 h, respectively. This is attributed to mass transport issues, considering the large kinetic diameter of H0-DBT and the smaller pore sizes of the catalysts. Pt/CeO_2 catalyst prepared by the GNP had larger pore sizes and a metal dispersion of 12.6 nm and 48%, whereas values for Pt/Al_2O_3 were 9.8 nm and 22%, respectively [20]. This, in turn, has contributed to a larger metallic surface of 118.6 m^2/g for Pt/CeO_2 compared to 54.5 m^2/g for Pt/Al_2O_3 [20].

Aakko-Saksa et al. prepared $Pt/TiO_{2\,anatase}$, $Pt/TiO_{2\,rutile}$ and Pt/Al_2O_3 catalysts following the incipient wetness impregnation method and using chloroplatinic acid as a precursor [21]. The catalysts were evaluated for dehydrogenation of H18-DBT using a batch reactor at 290 °C and benchmarked against Pt/C. $Pt/TiO_{2rutile}$ was highly active; a hydrogen release rate of 65% was obtained within 45 min, which is close to the activity of the Pt/C catalyst with a release rate of 68%. Pt/Al_2O_3 gave a hydrogen release of 55% while a low hydrogen release rate of 32% was observed for $Pt/TiO_{2\ anatase}$. The high performance of $Pt/TiO_{2rutile}$ is proposed to be due to the strong metal support interaction that keeps the Pt in a reduced state. According to Aakko-Saksa et al., there was no proof that the textural properties and the size of nanoparticles contributed to the improved catalytic performance with $Pt/TiO_{2rutile}$ [21].

Mg- and Zn-modified Pt/Al_2O_3 were prepared by the wet impregnation method using hexachloroplatinic acid as a precursor. The $Pt/Mg-Al_2O_3$ exhibited improved catalytic performance for the dehydrogenation of H18-DBT at 300 °C, using a fixed bed reactor, within 22 h time-on-stream. According to Garidzirai et al., the Mg enhanced the metal support interaction and promoted the Pt oxide reduction, which increased the number of active sites [22]. This has resulted in the improved catalytic activity of $Pt/Mg-Al_2O_3$ when compared to $Pt/Zn-Al_2O_3$ and Pt/Al_2O_3. However, the higher the catalytic activity the higher the formation of by-products—deactivation was also persistent.

Auer et al. optimised sulphur doping (0.125–0.32 wt % S) on a Pt/Al_2O_3 catalyst and evaluated the effect on the catalytic dehydrogenation of H18-DBT, using a batch reactor at 310 °C [22]. Sulphur doping of 0.25 wt % gave improved catalytic performance: productivity >2 gH_2/gPt/min, dod >90%, and with reduced side reactions. It is reported that optimum sulphur modification results in selective blocking of low-coordinated Pt sites and promotes desorption of aromatic compounds [23]. Furthermore, Ouma et al. have demonstrated, using density functional theory, that Si, P and Se surface additives are capable of boosting the catalytic activity of Pt-based catalysts for the dehydrogenation of methylcyclohexane in a similar manner to sulphur additive [24].

Low-temperature dehydrogenation

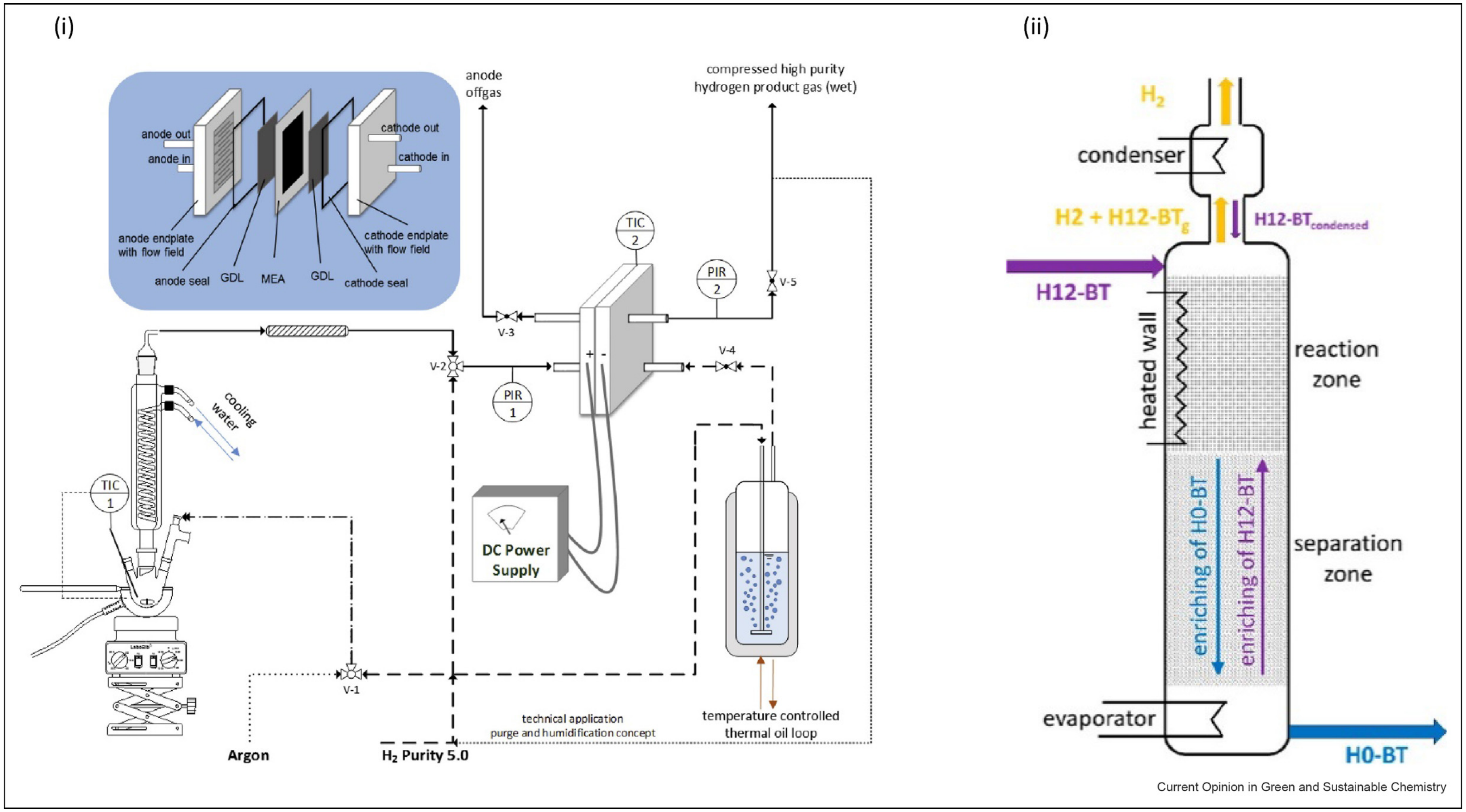
In an attempt to reduce the dehydrogenation temperature, Rüde et al. compared the performance of a benzyltoluene (BT) and H0-DBT system by executing hydrogenation and dehydrogenation cycles, using a Pt-based catalyst [25]. At a pressure of 2 bar and equilibrium temperature of 314 °C, 90% of hydrogen is released when H18-DBT is used, whilst the same is achieved for perhydrobenzyltoluene (H12-BT) when the equilibrium temperature was 292 °C [25]. Therefore, H12-BT is favourable because the same dod can be achieved but at lower reaction temperatures. The H12-BT dehydrogenation cycles demonstrated extremely stable productivities for up to a total operation period of 216 h at a constant temperature of 290 °C, making it 30% more productive than the H18-DBT dehydrogenation. The latter showed some decline with the number of cycles, however. Four distinct methylfluorene regioisomers were identified as by-products during H12-BT dehydrogenation, whereas H18-DBT generates both low and high boiling point by-products [25]. This could be the reason for the faster performance degradation of H18-DBT compared to H12-BT. According to the findings of Rüde et al., BT is more technically feasible than H0-DBT [25].

Studies carried out by our research group confirmed the formation of low and high boiling point by-products during the dehydrogenation of H18-DBT [26]. The possible reaction mechanisms of the by-product formation are reported based on the analysis of the product samples using the gas chromatography–mass spectrometry technique [26,27]. The by-products obtained include methane in the gas phase and in the liquid phase, benzene, C21, xylene, C13–C15, toluene and BT [26]. This indicates that H0-DBT produces different types of by-products compared to BT. Furthermore, BT contributed 60% of the total by-products produced and which could modify the properties of the H0-DBT by lowering its viscosity. The number of hydrogenation and dehydrogenation cycles of the H18-DBT molecule could be improved if the catalyst and reaction conditions are optimized such that small quantities of by-products are produced [26].

Müller et al. have reported the application of the reactive distillation dehydrogenation method to effectively remove product in efforts to reach full conversion, thermodynamically [28]. A BT and H0-DBT system was successfully used for reactive distillation. This method promotes shifting of the dehydrogenation reaction equilibrium to the product side. It is further reported that the dehydrogenation equilibrium can be shifted by the effective removal of hydrogen. The partial pressure of hydrogen can be reduced by reducing the total pressure in the reactor (using a vacuum pump, electrochemical hydrogen compression (EHC), hydrogen fuel cell, etc.) or diluting the hydrogen using inert gas [28,29]. Kiermaier et al. demonstrated the feasibility of reducing the system pressure for low-temperature dehydrogenation [29]. Electrochemical systems mentioned utilise hydrogen and, as a result, this generates vacuum pressure on the dehydrogenation system. Figure 1 shows examples of methods applied in attempts to reduce the dehydrogenation temperature and increase the process efficiency.

The energy demand reported for the dehydrogenation of H12-BT at 200 °C using 100 mbar vacuum pressure, 100 mbar EHC, reactive distillation and dilution with hexane to the partial pressure of 100 mbar is 152.1, 112.2, 94.2 and 328.2 kJ/mol-H_2, respectively [29].

Figure 1



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Schematic showing examples of methods applied to reduce the dehydrogenation pressure: (i) electrochemical methods and (ii) reactive distillation using benzyltoluene. Adapted with permission from Müller et al., Mrusek et al. [28,31].

Hexane can be removed from the system by condensation, for which the energy required is negligible because its boiling point is low [29]. The concept of reactive distillation offers the advantage of low energy demand and the conversion at the reaction zone was improved by introducing 200 mbar vacuum pressure to the system [30,31]. Reactive distillation may not be feasible, however, compared to conventional fixed bed reactors, especially for on-board hydrogen production in mobile applications.

In this context, the electrochemical methods are currently the most feasible options because, in any case, EHC will be needed to compress hydrogen for applications such as refuelling stations for vehicles. Similarly, a hydrogen fuel cell connected to the LOHC system also lowers the H_2 partial pressure. For this reason, there will be no additional energy required to keep the LOHC system at low pressure.

Summary and outlook

SCD, that includes the use of $ScCO_2$, is a promising method for catalyst preparation to achieve the properties required for the dehydrogenation of H0-DBT-based LOHCs. This method has been widely used for extraction purposes on large scale, which should make it easier for the scalability of catalyst preparation. Implementation of the method could be used for (i) modification of the support material (e.g., Al_2O_3) using Mg as an example, (ii) deposition of Pt metal and (iii) catalyst modification with sulphur. The combined effect of the catalyst preparation method and modification could be the most rewarding strategy in the development of a new catalytic material more suitable for the dehydrogenation of LOHCs. In addition, coating the above catalyst on a heat conductive material, such as SS pellets, would also improve the heat transfer and, in turn, the efficiency of the system. The most critical issues encountered with the low-enthalpy LOHC compounds are the high cost per kilogram, low hydrogen storage capacity and unavailability of LOHC molecules. Hence, these will favour the H0-DBT-based LOHC compounds because of the abundant availability (H0-DBT is produced on an industrial scale), high H_2 capacity and affordability. Some of the drawbacks of H0-DBT could be solved by using BT, which has almost similar properties. The application of electrochemical methods to reduce the hydrogen partial pressure in the dehydrogenation of BT-based LOHC improves the reaction efficiency. The strategies for lowering dehydrogenation temperature and for the development of efficient catalysts should surely make the LOHC technology more competitive.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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