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Analysis of Liquid Organic Hydrogen Carrier Systems

Properties of liquid organic hydrogen carriers, operation conditions and catalytic materials employed

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Liquid organic hydrogen carriers (LOHCs) provide attractive opportunities for hydrogen storage and transportation. In this study, a detailed examination of the most prominent LOHCs is performed, with a focus on their properties and scope for successful process implementation, as well as catalytic materials used for the hydrogenation and dehydrogenation steps. Different properties of each potential LOHC offer significant flexibility within the technology, allowing bespoke hydrogen storage and transportation solutions to be provided. Among different LOHC systems, dibenzyltoluene/ perhydro-dibenzyltoluene has been identified as one of the most promising candidates for future deployment in commercial LOHC-based hydrogen storage and transport settings, based on its physical and toxicological properties, process conditions requirements, availability and its moderate cost. Platinum group metal (pgm)-based catalysts have been proven to catalyse both the hydrogenation and dehydrogenation steps for various LOHC systems, though base metal catalysts might have a potential for the technology.

1. Introduction

The LOHC technology could be an attractive solution for storing and transporting green hydrogen, facilitating the transition to the hydrogen economy (1–16). To better assess the implementation potential of the technology, it is necessary to review the most promising LOHC candidates, catalysts and system operating conditions in further detail.

Early investigations into the LOHC technology were conducted in the 1980s and were focused around using benzene/cyclohexane or toluene/ methylcyclohexane systems (2, 17–20). Such systems were chosen for their high energy storage capacities and thus were predicted to allow the development of an efficient technology (10). Interestingly, even at the very outset of these experiments, the efficiency of the technology was evaluated in a combined scheme with water electrolysis (17). In terms of toxicity, a toluene/ methylcyclohexane system was considered preferable, but the benzene/cyclohexane system was also studied further; in 2000 it was reported that 100% conversion of cyclohexane to benzene could be achieved at 175°C if a palladium membrane reactor was used (17). In the time since, numerous LOHC molecules have been investigated and assessed in terms of their technoeconomic and environmental impacts, with several carriers being noted to have a great potential for the LOHC technology.

Once established that a benzene/cyclohexane system facilitated the storage of hydrogen, substitutes to the known carcinogen, benzene, have been sought to reduce the hazards associated with the technology and facilitate its deployment (**Table I**). In addition, alternative systems which

reduce the thermodynamic limitations associated with benzene (i.e. high temperature requirement for cyclohexane dehydrogenation) have been studied (21). This is important, given high temperatures increase the energy intensity, and thus the total costs of the LOHC technology.

A very common alternative to benzene is *N*-ethylcarbazole (NEC) and more generally, *N*-containing aromatic heterocycles (2). This class of compounds is recognised for their lower dehydrogenation enthalpy when compared against other LOHCs. For example, the dehydrogenation enthalpy of perhydro-NEC (53.2 kJ mol^{-1} hydrogen) is significantly lower than that of methylcyclohexane (68.3 kJ mol^{-1} hydrogen), and hence hydrogen release from perhydro-NEC is possible at lower temperatures (22). This reduces energy costs and increases system efficiency. However, NEC is significantly more expensive than toluene (€40.00 kg^{-1} and €0.30 kg^{-1}, respectively), which could hinder the large-scale commercial implementation of this particular LOHC (1, 2). Additionally, the solid state of the fully dehydrogenated NEC at room temperature complicates its handling and transport and can thus require dilution, which significantly reduces the efficiency of the system (1). Solidification of a carrier also diminishes the key liquid-nature advantage of using LOHCs as storage materials. As a result, several subsequent studies have since concentrated on seeking alternatives with higher boiling points and lower melting points, ensuring the carrier remains a liquid at ambient conditions throughout the cycle. A higher boiling point of the storage or transport

medium also reduces the likelihood of atmospheric pollution *via* evaporation and inhalatory exposure to potentially hazardous vapours, as well as lowering LOHC flammability (23).

The heterocycle quinaldine (with a lower melting point than NEC) has recently gained research interest. Decahydroquinaldine (H10-QLD) is reported to require a lower minimum temperature to achieve a dehydrogenation equilibrium corresponding to 99.99% hydrogen recovery when compared to alternative LOHC candidates, such as methylcyclohexane and dibenzyltoluene (DBT) (24). Although a quinaldine system has an ecotoxicity approximately equivalent to diesel oil, it is less biodegradable (23). Of a series of quinaldine compounds tested, only 2-methylquinoline was noted to be biodegradable: thus, a spillage of an alternative, non-biodegradable quinaldine (as is occasionally reported for fossil fuels) could persist for several years (23). In this regard, traditional fossil fuels could be considered superior over LOHCs: diesel oils primarily consist of chains of linear hydrocarbons of which the majority can decompose. Yet, for the diesel fraction of more complex structures this is not the case (23).

The potential of many more carriers has been assessed and reported in the literature, each focusing on a favourable property which would be beneficial for LOHC technology. For instance, amine boranes have been reported to have high gravimetric storage densities and comparable overall efficiencies to other LOHC candidates, although regeneration of such a carrier presents a

Table I Comparison of the Properties for Selected Liquid Organic Hydrogen Carrier Candidates (1, 6)					
LOHC candidate[a]	NEC H_0/H_{12}	DBT H_0/H_{18}	NAP H_0/H_{10}	TOL H_0/H_6	AB H_0/H_6
Hydrogen, wt%	5.8[b]	6.2	7.3[c]	6.2	7.1
Energy density, kWh l^{-1}	2.5	1.9	2.2[d]	1.6	2.4
Cost, € kg^{-1}	40	4	0.6	0.3	n.d.
Liquid range, °C	68–270 / 20–280	−39–390 / −45–354	80–218 / −43–185	−95–111 / −127–101	−45–87/ 63–87
Dehydrogenation temperature, °C	180–270	270–310	210–300	250–450	80
Hydrogenation temperature, °C	80–180	150–200	80–160	90–150	80
Reaction enthalpy, kJ mol$_{H_2}$$^{-1}$	−53.2	−65.4	−66.3	−68.3	−35.9
Hazard information	–	H305	H228, H302, H351, H400, H410	H225, H304, H315, H361d, H336, H373, H412	n.d.
Flash point, °C	186	212	78	4	22

[a]NEC: *N*-ethylcarbazole, DBT: dibenzyltoluene, NAP: naphthalene, TOL: toluene, AB: 1,2-dihydro-1,2-azaborine, n.d.: no data available
[b]NEC is a solid at room temperature, severely restricting dehydrogenation and thus hydrogen weight percent
[c]Naphthalene is also a solid at room temperature, dilution with toluene reduces hydrogen storage to 3.8 wt%
[d]Dilution with toluene reduces energy density to 1.1 kWh l^{-1}

challenge (21). Nevertheless, amine boranes have previously been employed as a disposable hydrogen source in fuel cell-based applications (25).

Nevertheless, it is evident that some LOHC systems are emerging as favourites (1, 2, 26). One of the most well-studied LOHC candidates is the DBT/perhydro-DBT system. A well-known and commercially available heat transfer oil, DBT has a much lower melting point than NEC and can thus be considered like a more traditional liquid fuel (such as gasoline) with the advantage of low flammability. Yet, important differences between gasoline and DBT are the higher viscosity and lower volatility of DBT. The cost of DBT (€4 kg⁻¹) is also significantly lower than NEC (€40 kg⁻¹) (1). Moreover, DBT is commonly regarded to have a good thermal stability, low toxicity and reasonable hydrogen storage capacity (6.2 wt%), highlighting the potential of this compound for the LOHC technology (27, 28). However, possible factors impeding commercial implementation of the LOHC technology with DBT as a carrier could comprise the relatively high dehydrogenation temperature and high cost (for example, compared to toluene) (23).

The evaluation of each LOHC medium also requires the implicit assessment of hydrogenation and dehydrogenation catalysts. The studies of the hydrogenation and dehydrogenation steps of a LOHC cycle are typically performed independently, employing different catalysts. Where the dehydrogenation and hydrogenation plants are found at different locations, this allows for optimisation of the separate reactions and catalysts. However, if the LOHC technology were to be focused more around the onsite hydrogen storage function, rather than transportation ability, a catalyst which is suitable for both reactions would be most favourable, with the interchanging of hydrogenation and dehydrogenation reactions driven by a change in pressure and a moderate change in temperature in the same reactor (29–31). Clearly, the requirement for only one catalyst and one reactor for both hydrogenation and dehydrogenation reduces the costs associated with this application (10).

As the dehydrogenation process is an endothermic reaction, this part of the LOHC cycle presents greater challenges than that of hydrogenation. Thus, a great proportion of studies has focused their efforts towards evaluating effective catalysts for the dehydrogenation process. Several literature sources state that the dehydrogenation process contributes significantly to the overall cost of the LOHC technology (32, 33). In particular, it has been suggested that improvements to catalytic performance could lower the cost of the dehydrogenation reaction by almost 40% (32).

Catalysts based on pgm are commonly used for hydrogenation and dehydrogenation processes of the LOHC technology (10, 34). Nevertheless, nickel-based catalysts have shown promise for the use within the LOHC technology, but further catalyst development is required to address the selectivity issues. Monometallic nickel catalysts are so active in hydrogenation reactions that unwanted reactions, such as C–C cleavage, can occur (35). Additionally, it has been reported that nickel-based catalysts could be problematic if employed for feedstocks comprising oxygen or nitrogen functionalities. This is because nickel catalysts are also very active in hydrogenolysis side-reactions (35). For example, it has been reported that aryl ethers can be converted into arenes and alcohols without any ring hydrogenation (36). This would be an extremely unfavourable reaction for the LOHC technology, as no hydrogen storage is facilitated. Such issues might be overcome by the development of bimetallic nickel-based catalytic systems. In addition to their high activity, the addition of a second metal to a nickel-based catalyst, such as nickel-copper on activated carbon cloth, has been suggested to suppress unfavourable side reactions (for example, hydrogenolysis) by electronic modification of nickel. This improves selectivity and overall efficiency of the LOHC technology (37). Another example of improved selectivity for the ring hydrogenation when using nickel-based catalysts, is an addition of zinc which blocks sites for C–C dissociation (38, 39). The comparatively high reducibility of several bimetallic catalysts (including nickel-copper and nickel-cobalt), further highlights their potential for implementation within the LOHC technology (40).

Although the development of novel catalysts (pgm-free or with reduced pgm content) might lower the costs associated with the LOHC technology, as well as risks associated with reliance on highly fluctuating costs of pgms, the key to this technology is catalyst performance (space-time yield, selectivity, lifetime). This is essential to reduce energy intensity during loading and particularly unloading of the LOHCs (32, 33). Catalyst stability is a particular issue in the dehydrogenation step of the LOHC cycle, where reaction temperatures are typically higher than those required for the hydrogenation step (41). It is expected that over time, catalyst degradation from carbonisation will occur, although the exact identity of such residues remains largely unknown (42). Catalyst reactivation could be achieved by implementing a regular

cleaning procedure, which for noble metal catalysts often involves thermal treatment with oxidative substances (for example, air, oxygen) (42). However, this process is highly dependent on the catalyst and reactor used. For 0.5 wt% platinum on alumina core shell pellets exposed to dynamic DBT experiments for three months (dehydrogenation temperatures between 280°C and 320°C), major regeneration was achieved between 200°C and 300°C, although complete regeneration could not be attained. Oxygenates and carbon dioxide were also produced during catalyst regeneration, which were suggested to contribute to catalyst restructuring (42). The study of Oh *et al.* highlighted that a palladium catalyst supported on carbon-coated alumina was more stable than palladium on alumina or palladium on carbon catalysts as the carbon-coated alumina support prevented the sintering of palladium nanoparticles into larger particles (43). Here, perhydro-2-(*n*-methylbenzyl) pyridine was deployed as the LOHC (43). However, most literature studies discuss the stability of the catalyst over only a limited number of hydrogenation/dehydrogenation cycles. Thus, further work is required to assess catalyst stability over longer time periods.

2. Analysis of Liquid Organic Hydrogen Carrier Systems

2.1 Benzene/Cyclohexane

Although benzene, which is the hydrogen-lean form of the benzene/cyclohexane LOHC system (**Figure 1**), is a known carcinogen (the most significant drawback of this specific system), several studies have been conducted into the properties of
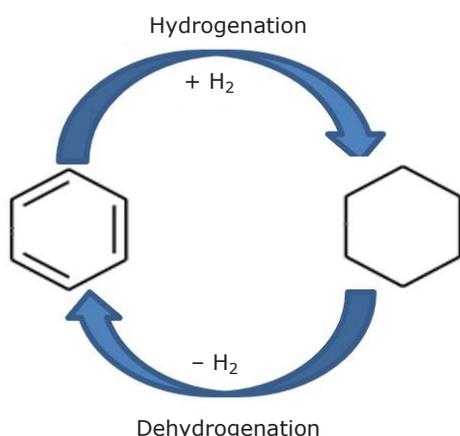

Fig. 1. Benzene/cyclohexane LOHC system

effective hydrogenation/dehydrogenation catalysts for this model feedstock.

Hydrogenation is generally accepted to occur *via* associative adsorption of benzene onto the catalytic surface. During the hydrogenation step, it is believed the carrier molecules are arranged as π-complexes and are hydrogenated in a stepwise fashion, through a series of cycloolefins (**Figure 2**) (44). This is supported with the detection of cyclohexene (44).

Early research concluded that monometallic iron-catalysts with body-centred structures were essentially inactive for the hydrogenation of benzene, while the activity of a mixed iron-cobalt catalyst decreased with increasing iron content (45). Since cobalt and nickel, both with face-centred cubic structures, were found to be active for the reaction, it was assumed the body-centred structure of iron was responsible for its inactivity (45). However, a monometallic, face-centred copper catalyst was deemed to be completely inactive unless in the presence of a suitable promoter, such as nickel (45). The inactivity of the copper catalyst has since been attributed to difficulties in obtaining a suitably high dispersion on the catalyst support, while the mechanism of the promotional effect observed with the addition of nickel remains a topic for debate (35). Several hypotheses for this have arisen, including a changing in copper crystal structure, or an alteration in surface concentration as a consequence of nickel collection (45). Interestingly, even in the very early studies, it was clear that palladium has a high activity for the reaction, but only on the condition that the surface area was sufficiently high, while the conversion is also reported to be catalysed by rhodium(I) complexes (45, 46).

Nickel-based catalysts are frequently considered for ring-hydrogenation reactions, with several detailed studies revealing key information for future catalyst development. For example, the hydrogenation of benzene using nickel catalysts has been suggested to be a structure insensitive reaction, while an unexpectedly low activity at low nickel loadings (less than 5 wt%) is the result of a nickel aluminate spinel formation, when an alumina support is used (47). More commonly however, this spinel structure is formed at high reaction temperatures. Although expected, these findings are important, signifying not only the choice of metal, but also the properties of the support (such as acidity, interaction with the metal) and reaction conditions play a role in determining catalytic performance. The move from pgm-based

Fig. 2. The stepwise hydrogenation of benzene (44)
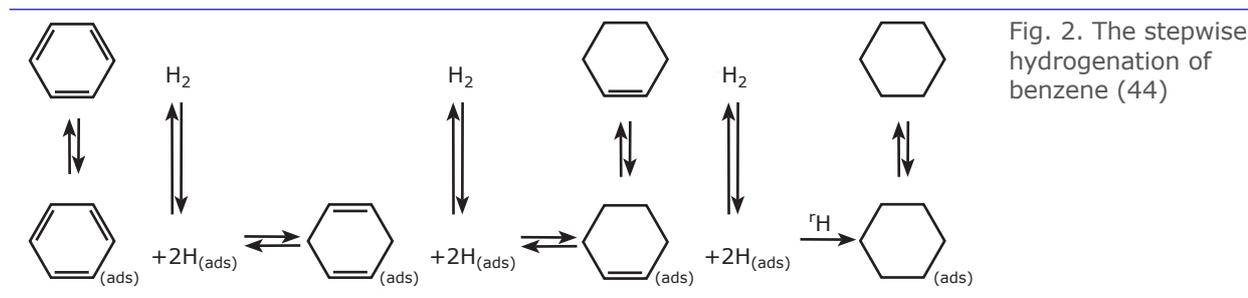
catalysts to base metal catalysts could also lower the cost associated with the LOHC technology as well as reliance on highly fluctuating costs of pgms (48, 49). This is provided that comparable or even improved catalytic performance can be achieved.

Nickel is also widely referenced for its activity in catalysing the dehydrogenation reaction of cyclohexane. Given the low boiling point of cyclohexane (81°C), this reaction is often performed in the gaseous phase. The studies have shown that when using a cyclohexane feedstock, a bimetallic nickel/platinum combination (20 wt% nickel and 0.5 wt% platinum) can improve catalytic dehydrogenation activity 60-fold when compared to using a monometallic platinum catalyst (0.5 wt% platinum on activated carbon cloth), or 1.5-fold when compared to a monometallic nickel catalyst (20 wt% nickel on activated carbon cloth) (34). In addition, selectivity in the dehydrogenation reaction was improved using various monometallic nickel catalysts with the addition of platinum (50). For these cyclohexane dehydrogenation studies, a spray-pulsed reactor was used at a temperature of 300°C (34).

The concept of improved catalytic performance through the use of bimetallic combinations has also been reported for silver-based catalysts, employed for the benzene hydrogenation reaction (34). Here, the same spray-pulse reactor and reaction temperature (300°C) as discussed for the platinum catalyst above was used. For the most significant catalytic enhancement, it was concluded that the secondary promoter must be classified as a pgm (34). As an example, the hydrogen production rate was doubled when using a platinum-promoted silver catalyst on activated carbon cloth (1 wt% platinum + 10 wt% silver) compared to the non-promoted 10 wt% silver equivalent (34). This was suggested to be the result of a synergistic effect between the two metals for breaking C–H bonds, high hydrogen reverse-spillover, or hydrogen recombination abilities of the catalyst (51). The improvement in catalytic activity of the silver catalysts promoted with 1 wt% of a pgm were

found to follow the trend: platinum > rhodium > palladium, although catalyst stability improved in the order platinum > palladium > rhodium (51). The study did not comment on expected lifetime of the catalysts, highlighting the need for further research regarding key performance indicators (activity, selectivity, lifetime).

2.2 Toluene/Methylcyclohexane

To catalyse the hydrogenation of toluene to methylcyclohexane, palladium-based catalysts have been reported to be effective. For example, in 1 h a 10 wt% palladium/carbon catalyst can achieve a 90% toluene conversion at 80°C and 15 bar hydrogen pressure, when the hydrogenation reaction is performed in a batch reactor (52). Interestingly, when this palladium on carbon catalyst was coated with a liquid coordination complex (LCC), the conversion of toluene increased to 99.9%, under otherwise identical reaction conditions (52). LCCs are described as 'ionic liquid-like' Lewis acid species, with their equilibrium composition containing cations, anions and neutral components (52). In this experiment, the LCC was synthesised from aluminium chloride and urea (52). It was concluded that only a thin film of the liquid (ionic liquid coating at 13 wt%) was required to improve the catalytic performance; when larger quantities were applied to the catalyst a decrease in activity was observed as a result of pore blocking and mass diffusion limitations (52).

As for benzene hydrogenation, platinum-based catalysts have also been found to be successful in catalysing the hydrogenation of toluene to methylcyclohexane. For example, a 0.3 wt% platinum catalyst supported on zeolite CBV-780 (silicon:aluminium ratio of 40) is capable of achieving full hydrogenation at just 120°C, with a hydrogen pressure of 30 bar (53). The activity of the catalyst notably decreased when alloyed with palladium. A trimetallic combination of nickel, cobalt and molybdenum on a zeolite support was also found to effectively catalyse

this hydrogenation reaction (54). In a batch reactor, with a reaction temperature of 200°C and a hydrogen pressure of 20 bar, it was found that a HY support (silicon:aluminium ratio of 5.1) allowed for superior catalytic activity after 30 min on-stream, when compared to using mordenite, HY (silicon:aluminium ratio of 80) or ZSM-5 alternatives. In explanation, the authors propose the larger pore volume and pore diameter of the HY support (silicon:aluminium ratio of 5.1) reduces pore diffusion limitations (54).

Moreover, monometallic nickel-based catalysts are effective for toluene hydrogenation (55). For example, one study highlighted the increase in catalytic activity observed for a 20 wt% nickel catalyst, compared to a 5 wt% nickel catalyst, both supported on gamma-alumina (55). Since it is generally accepted that an increase in the number of metallic active sites increases catalytic activity, this result is unsurprising (55). However, it was also found that employing supports of different alumina phases (γ-Al$_2$O$_3$ or κ-Al$_2$O$_3$) has different effects on catalytic activity when different nickel loadings are used. For instance, a significantly higher catalytic activity was reported for a 5 wt% Ni/κ-Al$_2$O$_3$ catalyst than for a 5 wt% Ni/γ-Al$_2$O$_3$ (toluene conversions of 98% and 28%, respectively), under the same reaction conditions (55). Yet at higher nickel loadings an opposite trend was observed: a 20 wt% Ni/κ-Al$_2$O$_3$ catalyst resulted in a lower toluene conversion than that of a 20 wt% Ni/γ-Al$_2$O$_3$ catalyst, although the difference in activities between the catalysts is smaller at this higher nickel loading (55). In explanation, it was concluded that changes in reducibility of the surface nickel sites has a larger effect on the observed activity than simply the number of active sites present (55). These reactions were performed in a plug-flow reactor, using 0.1 g of catalyst (55).

Nickel on kaolinite catalysts have also been considered for the hydrogenation of toluene (56). Using a flow-type system at ambient pressures, it was found that modification of the catalyst with a small amount (2 wt%) of either potassium or zinc (using KNO$_3$ or Zn(NO$_3$)$_2$) increased catalytic activity, which was attributed to a decrease in interaction strength between the nickel and kaolinite. Yet, a larger modification (3–7 wt%) resulted in a significant decrease in activity (56). This was proposed to be a result of potassium covering the nickel active sites, or an unfavourable zinc-nickel interaction (56).

The dehydrogenation reaction (methylcyclohexane to toluene, **Figure 3**) typically employs a platinum or nickel-based catalyst, supported on alumina (1). Reaction temperatures for such catalysts often vary between 350°C and 450°C (with a general increase in temperature increasing the conversion of methylcyclohexane to toluene before equilibrium is reached) (57, 58). Another study highlighted the influence of process conditions on increasing conversion of methylcyclohexane and lowering operating temperatures by using efficient palladium or palladium-alloy membranes in catalytic membrane reactors. Such reactors combine the catalytic dehydrogenation reaction with the extraction of hydrogen in a single unit (58).

Interestingly, a potassium-platinum on alumina catalyst was reported to achieve a hydrogen yield of 95%, when employed at 320°C in a fixed-bed reactor, which is slightly above the typical yield range given above (1). Moreover, an excellent selectivity (>99.9%) was reported for this reaction (1). A Raney-nickel catalyst has also been reported to achieve a 65% yield after 30 min on-stream, under multiphase reaction conditions (59). Although this reaction was performed at the lower reaction temperature of 250°C, the Raney-nickel catalyst is not a suitable candidate to catalyse the reactions of the LOHC technology (1). This is in view of the accompanying isomerisation and disproportionation reactions which would ultimately necessitate the need for more frequent LOHC replacement (1). It should be noted that from a thermodynamic viewpoint, the dehydrogenation of methylcyclohexane, like all LOHC candidates,
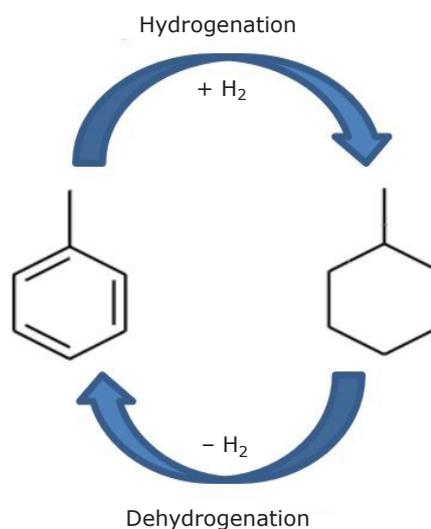

Fig. 3. Toluene/methylcyclohexane LOHC system

should be performed at the lowest possible pressure as this facilitates the use of the lowest possible temperature for full conversion to toluene (34). However, in practice, it has been found that such conditions may not be compatible with the catalyst, potentially resulting in side reactions and catalyst deactivation (34).

As has already been stated, the catalyst support materials can be modified to increase catalytic performance (34). For the toluene/methylcyclohexane system, it was concluded that the hybrid composite support alumina-titania was responsible for a huge increase in catalytic dehydrogenation activity, when compared to alumina (99% and 16.5% methylcyclohexane conversion, respectively, where nickel is the active site) (34). In addition, properties of the perovskite $La_{0.7}Y_{0.3}NiO_3$, and metal oxides including La_2O_3, CeO_2 and MnO_2 have been evaluated in terms of their suitability as catalyst supports for the dehydrogenation of methylcyclohexane (34, 60). Most notably, it was found the hydrogen production rate more than doubled when comparing the Pt/La_2O_3 and $Pt/La_{0.7}Y_{0.3}NiO_3$ catalysts (21.1 mmol g_{met}^{-1} min^{-1} and 45 mmol g_{met}^{-1} min^{-1}, respectively) (60). These reactions were conducted in a spray-pulsed reactor.

This particular LOHC system has also been studied alongside a palladium membrane reactor, which allows for purification of the hydrogen released from the LOHC (34). Contaminants of the hydrogen can include carbon monoxide, CO_2, methane and cyclic hydrocarbons and have been reported to be present in quantities between 100 ppm and 1000 ppm, depending upon the operating conditions of the LOHC system (61). The exact origins of the impurities remain unknown, but it is believed a combination of atmospheric oxygen and residual moisture in the LOHC is responsible for the formation of carbon monoxide and CO_2, while partial decomposition of the LOHC at high reaction temperatures, or contaminants from the production of the LOHC, can explain the hydrocarbon presence (61). The quality of the hydrogen released depends upon the intended application: for example, several fuel cells have specific regulations on compatible hydrogen purity (61). Despite this, only a few examples of hydrogen purification processes exist in the literature, most of which employ palladium membranes. This is not surprising, considering palladium has a high hydrogen solubility, permitting effective separation of hydrogen and contaminants at high temperatures (typically above 300°C) (61).

A palladium membrane reactor has been reported to have a dual functionality, acting both as a dehydrogenation reactor and a hydrogen purification system (34). The dehydrogenation of methylcyclohexane using such a reactor and a 1 wt% platinum on alumina catalyst, permitted the use of a 20°C decrease in temperature than would otherwise be required to achieve the same conversion (70%) without employing the membrane (225°C and 245°C, respectively) (34). In addition, the platinum catalyst demonstrated good stability and selectivity within the temperature range 150–325°C, with no significant deactivation for approximately 600 h time on-stream (62). A 5 μm palladium-silver membrane, coupled with a microstructured system, has also been reported to effectively purify the hydrogen released (61).

2.3 Naphthalene/Decalin

Boasting a high theoretical hydrogen storage capacity of up to 7.4 wt%, a naphthalene/decalin LOHC system has been considered (**Figure 4**). However, in practice, dilution with a solvent such as toluene is necessary to keep the LOHC cycle within the liquid phase (melting point of naphthalene: 80°C). This lowers the overall hydrogen capacity to 3.8 wt% (1). For this reason, the naphthalene/decalin system is less widely studied than other possible carriers, although important learnings have been gained, which can be transferred to other LOHC systems. It is worth noting that decalin exists as structural isomers, and thus an approximately equimolar mixture of the *cis*- and *trans*-isomers are produced upon hydrogenation of naphthalene, despite the thermodynamic favourability of the *trans*-isomer (1). The exact *cis*:*trans* ratio is naturally dependent on reaction conditions, in addition to the catalyst itself (1).
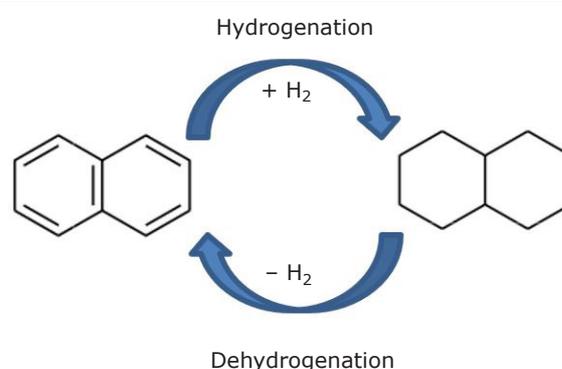
Fig. 4. Naphthalene/decalin LOHC system

Much like other LOHC systems, platinum-based catalysts have also been the focus of most studies on the hydrogenation of naphthalene (1, 63). Yet, in contrast to other systems discussed, an aluminium Mobil Composition of Matter No. 41 (Al-MCM-41) support was investigated (63). Harsher reaction conditions (temperatures of 300°C and pressures of 69 bar) than employed for alternative systems were required to achieve full hydrogenation to decalin in 150 min, in a batch reactor (1). It was found that the reaction temperature could be lowered to 200°C under the same reaction pressure, but this imposed the requirement of a drastically increased reaction time (480 min) (1). Generally, conclusions from this study are similar to those of other systems: hydrogenation activity and selectivity are both strongly dependent on support properties (63).

Although the hydrogenation process presents its relative challenges, it is the dehydrogenation step which confirms the incompatibility of this system with the LOHC technology. For instance, this step is likely to produce intermediates including tetralin (**Figure 5**). Although tetralin itself can be dehydrogenated and become part of the LOHC process, it is unlikely that no tetralin molecules will remain following the dehydrogenation reaction. As tetralin is still partially hydrogenated, the hydrogen storage capacity of the LOHC is lowered in subsequent cycles. Thus, regular replacement of the carrier material would be required to ensure a constant hydrogen storage capacity (34). This would increase the operating expenditure of the technology (more LOHC required) in the case of naphthalene. In light of these challenges, a pilot scale demonstration is yet to be achieved (1).

Research into the dehydrogenation reaction of naphthalene has, however, produced some interesting results. Typically, when employing a platinum catalyst supported on carbon at conditions slightly milder than those used for the hydrogenation reaction (280°C for 150 min at atmospheric pressure), almost full conversion of
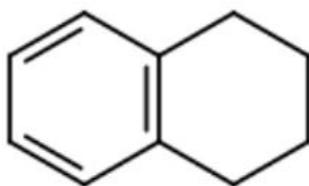
decalin to naphthalene can be achieved in a batch reactor system. Furthermore, adding rhenium to the catalyst (platinum-rhenium on carbon) can decrease the reaction time from 150 min to 120 min under otherwise identical conditions (1, 64).

A 3 wt% platinum on carbon catalyst was also used to investigate the effect of varying the catalyst preparation method on catalytic performance for the dehydrogenation of decalin (34). It was found that advanced methods of preparation, including ion-exchange and polyol-assisted synthesis (in which ethylene glycol was used as a solvent and reducing agent), resulted in a greater dispersion of platinum (19.6% and 14%, respectively) than the more conventional precipitation and impregnation methods (10% and 5.4% platinum dispersion, respectively) (34, 65). Increasing the platinum dispersion increases the surface area of the metal over which the reaction can occur, consequently resulting in a greater rate of hydrogen release from decalin (34, 65). Again, optimisation of the support must also be considered. Several carbon-based possibilities including nanofibers, carbon black, carbon xerogel and ordered mesoporous carbon have been evaluated, with the high surface area of ordered mesoporous carbon believed to be responsible for demonstrating the highest activity for the dehydrogenation of decalin (34). Yet, over longer operation times catalyst deactivation was observed as a result of pore blockages with the bulky LOHC feedstock (34). Thus, it can be argued that as carbon black has wider pores than the ordered mesoporous carbon, this would be the most suitable support, despite a lower activity. These experiments were performed at 260°C, in a batch reactor (34).

Catalytic activity, in addition to selectivity, has also been reported to be improved with the addition of tin to platinum on activated carbon (66). The effect is two-fold: (a) the electronic modification of platinum by tin prevents the cleavage of C–C bonds on the catalyst surface, facilitating the adsorption and desorption of reactant and product molecules; (b) the addition of tin as a catalytic promoter improves catalyst stability by preventing the sintering and agglomeration of platinum at high temperatures (34).

2.4 *N*-Ethylcarbazole/Perhydro-*N*-Ethylcarbazole

The most significant advantage of the NEC/perhydro-NEC LOHC system (**Figure 6**) is the relatively low energy required for dehydrogenation
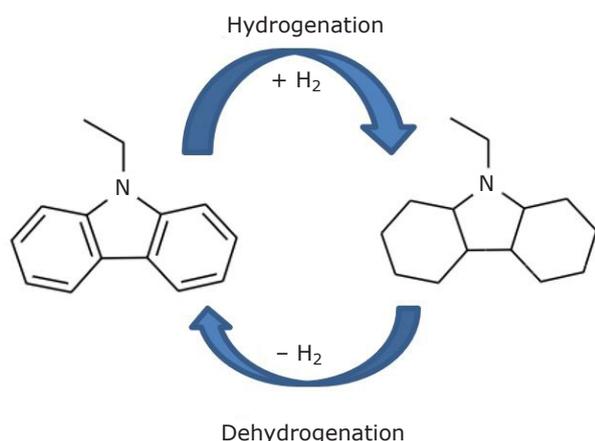

Fig. 5. Structure of tetralin, a probable naphthalene dehydrogenation intermediate

Fig. 6. NEC/perhydro-NEC LOHC system

(53.2 kJ mol^{-1} hydrogen, **Table I**) (1). This lower reaction enthalpy facilitates a lower temperature for the dehydrogenation reaction and consequently improves the overall efficiency of the system. As such, interest into the potential applications of NEC has significantly grown in recent years, culminating in its use as a feedstock for the LOHC technology. However, like other LOHC candidates discussed thus far, NEC also possesses unfavourable properties for its employment within LOHC technology. Arguably the most significant of these is the solid nature of NEC at ambient temperatures. To ensure the key liquid property of the LOHC technology is not lost, employing NEC would thus require NEC dilution (1). This reduces the efficiency of the LOHC technology (1). Moreover, NEC is significantly more expensive than alternative LOHCs, such as toluene (€40.00 kg^{-1} and €0.30 kg^{-1}, respectively) (1).

The dehydrogenation reaction is again most commonly performed with pgm-based catalysts, particularly palladium on alumina or platinum on alumina at metal loadings of around 5 wt%. These catalysts have been reported to have the highest catalytic activities, when compared to ruthenium and rhodium equivalents (67). Specifically, catalyst dehydrogenation activity follows the trend palladium > platinum > ruthenium > rhodium under atmospheric pressure and at 180°C (67). Full dehydrogenation to NEC was observed for palladium and platinum catalysts, after reaction times of 240 min and 300 min, respectively, while employment of a ruthenium catalyst over the same time frame produced a mixture of both the fully dehydrogenated NEC (71.28%) and the partially hydrogenated species, 4H-NEC (28.54%) (67). Using the catalyst with the lowest dehydrogenation

activity (rhodium on alumina), even less of the fully dehydrogenated NEC is obtained (10.64%) (67). Important to note, all reactions are carried out below 270°C. Beyond this temperature, NEC becomes susceptible to dealkylation reactions, producing the byproduct carbazole (1, 68).

Like the dehydrogenation reaction, the hydrogenation of NEC is frequently catalysed by a pgm. However, given the comparative ease of the hydrogenation reaction (in comparison to the dehydrogenation reaction), a palladium or ruthenium-based catalyst is more frequently employed than for the dehydrogenation reaction. For example, full hydrogen loading onto NEC has been achieved in 3 h at 150°C and 50 bar hydrogen pressure using a 5 wt% ruthenium on alumina catalyst in a batch reactor (68). The molar ratio of LOHC to ruthenium used in these experiments was 400:1 (68). The catalyst Pd$_2$Ru on silicon carbonitride has also been reported to successfully catalyse the hydrogenation of NEC (69). In comparison to the 5 wt% ruthenium on alumina catalyst discussed previously, a milder reaction temperature (110°C) and hydrogen pressure (20 bar) can be employed (69). However, a significantly longer reaction time (36 h) is required for full hydrogenation of NEC to perhydro-NEC, and a greater amount of active metal is also required, compared to the ruthenium on alumina catalyst described above (0.52 mol% and 0.25 mol%, respectively) (68, 69). The same Pd$_2$Ru@SiCN catalyst has also been reported to successfully catalyse the dehydrogenation of perhydro-NEC at 180°C in a reaction time of 7 h, in a batch reactor (69).

More recently, full hydrogenation has also been attained using ruthenium supported on a rare earth hydride catalyst, Ru/YH$_3$ (70). Reporting both the mildest conditions (100°C, 10 bar) and the highest catalytic activity for the hydrogenation of NEC to date, it is clear that such rare earth supported catalysts have potential for LOHC applications (70). This was highlighted by concluding the high stereoselectivity of the Ru/YH$_3$ catalyst for the all-*cis* product would be advantageous for any subsequent dehydrogenation reactions, since the *cis* product is more easily dehydrogenated than the *trans* equivalent. In explanation, the authors propose the *cis* product is less sterically hindered on the catalyst surface (70). However, despite an excellent catalytic performance and satisfactory stability, a high hydrogen pressure is required to achieve high selectivity (70). Manufacturing costs, handling and scale-up considerations were not

discussed and may present challenges for such a material.

The Ru/YH$_3$ catalyst has also been reported to effectively catalyse the hydrogenation of another *N*-heterocycle: 2-methylindole, which has been suggested as a suitable LOHC candidate (70, 71). However, much like NEC, 2-methylindole is a solid at ambient temperatures and possesses a slightly lower hydrogen storage capacity than NEC (5.7 wt% and 5.8 wt%, respectively) (71).

2.5 Dibenzyltoluene/Perhydro-dibenzyltoluene

To achieve an effective and efficient hydrogen storage and transportation system, the choice of LOHC is of critical importance. For commercial implementation of the LOHC technology, DBT can be seen as the most suitable candidate, considering its key advantages: relatively low-cost, low toxicity and high hydrogen storage capacity (6.2 wt%, **Table I**). In addition, DBT is already mass produced as it is used as a heat transfer agent. As a result, there is a vast exploration of DBT as a potential carrier molecule in the literature.

Several catalysts have been evaluated for the hydrogenation and dehydrogenation reactions of the DBT/perhydro-DBT system (**Figure 7**). Much like NEC, DBT hydrogenation is also typically catalysed with an alumina-supported pgm, namely platinum or ruthenium (1). As an example, in a batch reaction, a ruthenium on alumina catalyst can achieve full hydrogen loading of DBT in 4 h at 150°C with a 50 bar hydrogen pressure, which is longer than that of NEC (3 h) under the same conditions (68).

The more in-depth studies on this feedstock have also revealed that the catalytic hydrogen-loading does not have to be performed with pure hydrogen. As DBT hydrogenation is selective, and provided the catalyst is not negatively affected by the presence of other components, a mixed gas stream (for example, including methane, CO$_2$) can be used (34). From an industrial perspective this is very attractive, enabling otherwise low-value hydrogen present in waste gas streams, from processes including reforming and gasification reactions, to be stored and transported. The first example of such a process was reported in 2017 by Dürr *et al.*, in which a mixture of hydrogen and methane from the decomposition of methane (obtained from offshore drilling) was fed directly to the hydrogenation unit containing the DBT feedstock (72). Separation of the loaded (hydrogenated) LOHC and gaseous methane can then be facilitated. It has also been reported that the presence of methane does not negatively affect the hydrogenation or dehydrogenation of DBT/perhydro-DBT (30). In contrast, methane was remarkably found to slightly improve the hydrogenation rate, postulated to be a result of a lower DBT viscosity and thus improved hydrogen mass transport (34).

In a similar vein, hydrogenation of DBT has been investigated using a hydrogen/CO$_2$ stream (up to 30% CO$_2$) (73). However, with such a hydrogenating mixture, both methanation (CO$_2$ to methane) and reverse water gas shift (CO$_2$ to carbon monoxide) processes were found to occur, with the extent of such side-reactions being strongly dependent on the catalyst employed (34). Even with the most promising palladium on alumina and rhodium on alumina catalysts, the degree of hydrogenation in a batch reactor reached only 0.8 and required elevated temperatures (210°C and 270°C for the rhodium and palladium catalysts, respectively)
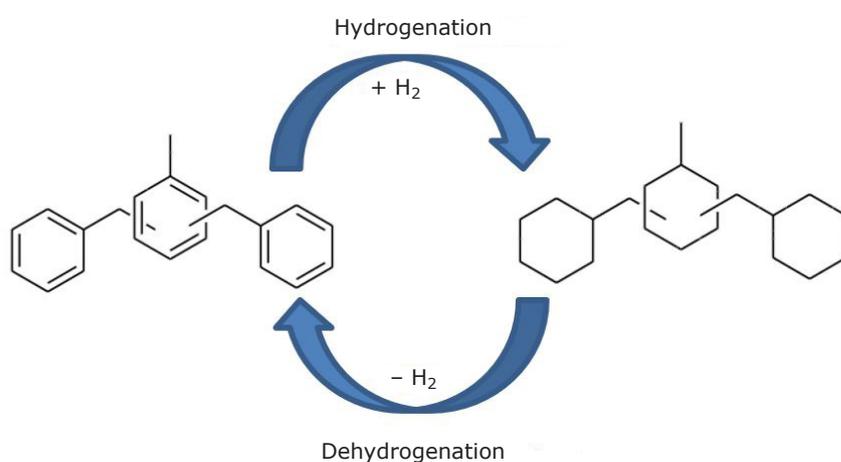

Fig. 7. DBT/Perhydro-DBT LOHC system

when compared to using a pure hydrogen stream (34). For the rhodium catalyst, moderate methane formation (methane:CO_2 ratio of less than 0.1) can be achieved at temperatures between 120°C and 150°C (rhodium on alumina), while the palladium catalyst showed a lower selectivity for methane formation, with a methane:CO_2 ratio of less than 0.1 between 120°C and 270°C (palladium on alumina) (34, 73).

Despite the frequent employment of platinum and ruthenium catalysts with pure hydrogen streams, these catalysts were found to be ineffective for the selective hydrogenation of DBT using a hydrogen and CO_2 stream (34). Their respective unsuitability was concluded to be a result of platinum catalyst poisoning from the reduction product carbon monoxide formed *via* reverse water gas shift of CO_2 and facilitation of CO_2 methanation by ruthenium.

Palladium-based catalysts have low activities for the dehydrogenation reaction of perhydro-DBT, and have thus been identified as catalysts to avoid (34). Under the same reaction conditions (270°C, 3.5 h, batch reactor), a stark difference in the degree of dehydrogenation between a palladium on carbon (5 wt%) catalyst and its platinum equivalent has been observed (16% and 55%, respectively) (68). In a different study, a lower metal loading has proven to be advantageous (lowering the metal content of the platinum on carbon catalyst to 1 wt% from 5 wt% increased the degree of dehydrogenation from 55% to 71%), while the support preference for this particular dehydrogenation reaction was found to follow carbon > alumina > silica (34, 68). In these experiments, the catalysts were used in batch reactions in quantities of 0.15 mol% with respect to perhydro-DBT (68).

Interestingly, the wider research around the use of DBT as a LOHC has included a study in which the same platinum on alumina (0.3 wt%) catalyst has been used for both hydrogenation and dehydrogenation reactions (34). Under the same reaction temperature (291°C), Jorschick *et al.* reported that the two reactions could be interchanged by varying the pressure between 1.05 bar (dehydrogenation) and 30 bar (hydrogenation) in a hot pressure swing reactor (30). However, the use of a non-optimised catalyst for the dehydrogenation process resulted in a lengthy reaction time (20 h), when compared to the examples discussed previously. In addition, it must be noted that the productivity of the dehydrogenation (and thus catalyst activity) decreased significantly over the first cycle, before stabilising for the following three cycles. This was concluded to be a consequence of bulky, high boiling point byproduct formation *via* thermal cracking of DBT. Such molecules, including diphenylmethane and 2,6-dimethyldiphenylmethane, were found to increase per cycle and can be expected to block active sites of the catalyst (34, 74). It has also been suggested that some of the possible byproducts of the dehydrogenation reaction are unstable and thus undergo cracking during a subsequent hydrogenation reaction. Such an example would be the conversion of perhydromethylfluorene to perhydrobenzyltoluene (74).

DBT exists as structural isomers and consequently, more than 24 stable intermediates can be found in a partially hydrogenated solution. These can be categorised into four main groups: DBT (H0-DBT), hexahydro-DBT (H6-DBT), dodecahydro-DBT (H12-DBT) and octadecahydro-DBT (H18-DBT) (75). Laboratory studies regarding selectivity would require advanced analytical detection methods. DBT conversion can be studied using ultraviolet-visible spectroscopy (i.e. the degree of ring hydrogenation, providing information about conversion levels only), but detailed studies probing catalyst selectivity would be challenging, requiring either a complex high-performance liquid chromatography (HPLC) method or ^{1}H nuclear magnetic resonance (NMR) analysis (29, 76, 77).

As such, alternative model carriers are often sought for fundamental academic studies aimed at deepening the chemical understanding of how to improve the performance of catalytic materials for the LOHC technology. In addition to being easily characterisable, the ideal carrier would have high boiling points and low melting points of both hydrogen-rich and hydrogen-lean molecules. This enables the whole cyclic process to be carried out in the liquid phase. A high melting point would result in the formation of a solid at ambient temperatures, with a dissolving process or incomplete hydrogen-unloading significantly lowering storage efficiency. Whereas a low boiling point would require extra economic expense in gas condensation equipment. Frequently, toluene is employed as such a model compound. Given its structural similarities to the central motif of DBT, this is a logical choice. Yet, the environmental health and safety hazards associated with its usage are quite significant, being noted for serious concern regarding both human and aquatic toxicity (23). Thus, to lower the hazards associated with the feedstock, other aromatic compounds similar in structure to toluene might be chosen.

3. Summary and Perspectives

In this study, the most prominent carriers for the LOHC technology are discussed in terms of their properties, typical reaction conditions, and catalytic materials employed in the respective hydrogenation and dehydrogenation reactions. The following LOHC systems are reviewed: benzene/cyclohexane, toluene/methylcyclohexane, naphthalene/ decalin, NEC/perhydro-NEC, DBT/perhydro-DBT. Each LOHC candidate has properties which are advantageous for use within the LOHC technology, but also has disadvantages associated with its use. Among these LOHC systems, NEC/perhydro-NEC and DBT/perhydro-DBT were found to be the most attractive for commercial deployment, given their favourable physical properties and demands on process conditions. For example, employment of NEC lowers the dehydrogenation temperature, yet at ambient conditions the fully dehydrogenated NEC is a solid. DBT on the other hand, is a more cost-effective LOHC option than NEC, given its relatively moderate price, and has lower toxicity compared to toluene which results in fewer regulatory restrictions to its use. However, higher temperatures for the dehydrogenation process are required to release the hydrogen. Typically, to achieve such temperatures, a portion of the hydrogen released from the LOHC is burned, which clearly reduces the efficiency of the technology. Using the waste heat from fuel cells (for example, in a LOHC – fuel cell coupled system) to provide the heat for the dehydrogenation reaction, can diminish this effect and increase the overall efficiency of the technology. These competing advantages and disadvantages of each LOHC candidate arguably increase the complexity of the LOHC technology but provide an opportunity to develop bespoke hydrogen storage and transportation solutions.

According to the literature, pgm-based catalysts have been proven to catalyse both the hydrogenation and dehydrogenation steps for various LOHC systems, though base metal catalysts might have a potential for the LOHC technology. Given the lack of information currently available in the literature and understanding of key performance indicators, such as catalyst lifetime, selectivity and activity under truly industrial conditions (technology readiness level 6 and above), further research into the LOHC technology is still required. Specifically, developments should attempt to reduce the energy intensity associated with the hydrogenation and dehydrogenation reactions, while increasing catalyst lifetime and cycle efficiency. This might be achieved either through the catalyst or reactor technology development.

In summary, to improve economic viability and enable widespread commercial deployment of the LOHC technology, further work might be required, focusing on: development of novel cost-effective catalysts with improved space-time yield, activity, selectivity and lifetime; increased lifetime of the LOHC (i.e. number of cycles before a replacement is required); reduction of total costs for transporting the LOHC, including the cost of transporting the unloaded LOHC back to the hydrogenation plant; high purity of the hydrogen released in the dehydrogenation reaction; deployment and system integration of LOHCs with different industries. Furthermore, the selection of a suitable LOHC candidate must also be considered: it should remain a liquid throughout the LOHC cycle, have a low toxicity and low cost, and a high hydrogen loading capacity.

Acknowledgments

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