Review

Liquid organic hydrogen carriers ☆

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ABSTRACT

The development of efficient hydrogen storage materials is one of the biggest technical challenges for the coming "hydrogen economy". The liquid organic hydrogen carriers (LOHCs) with high hydrogen contents, reversibilities and moderate dehydrogenation kinetics have been considered as an alternative option supplementing the extensively investigated inorganic hydride systems. In this review, LOHCs for long distance H_2 transport and for onboard application will be discussed with the focuses of the design and development of LOHCs and their hydrogenation & dehydrogenation catalyses.

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1. Introduction

The ever severe global energy and environmental crises impel the change of energy carriers from current fossil fuels to clean and renewable energy sources, among which hydrogen energy has long been viewed as a potential solution. However, the lack of proper onboard hydrogen storage systems meeting the US Department of Energy's (DOE) targets (5.5 wt% and 40 g/L hydrogen capacity in 2020) [1] is one of the bottlenecks for the coming "hydrogen economy" [2,3] albeit various approaches in storing hydrogen, such as high pressure and cryo-liquid hydrogen, physisorption by porous materials [4,5], metal hydrides [6], complex hydrides [7] and chemical hydrides [8], have been explored over the years. Compressed hydrogen tank is adopted to store hydrogen onboard by several car companies [9], however, there are concerns on safety and cost [10,11]. Cryo-liquid hydrogen has high gravimetric hydrogen density and is suitable for large scale hydrogen store. For onboard application, however, the energy cost in liquefaction and boil-off problem are the drawbacks. Research activities over the past two decades mainly devoted to the condensed materials that can store hydrogen chemically or physically. Fig. 1 displays the gravimetric and volumetric hydrogen densities together with the operating temperatures for a number of representative

materials systems. Chemical hydrides have relatively high hydrogen contents and moderate dehydrogenation temperatures, but they suffer from irreversibility and energy consuming regeneration. Complex and metal hydride, on the other hand, encounter the drawbacks of unsuitable thermodynamics, sluggish kinetics and/or low hydrogen content. Comparatively, the liquid organic hydrogen carriers (LOHCs) with hydrogen content of 5–8 wt%, reversibility, moderate dehydrogenation temperature, commercial availability and more importantly, the compatibility with existing gasoline infrastructure, hold the promises as hydrogen carriers for both onboard application and large scale long-distance H_2 transportation [12–14]. As a matter of fact, Japanese government has a strategic plan of importing H_2 from overseas by means of liquefied hydrogen or organic hydrides [15].

Early researches on liquid organic hydrides for hydrogen storage focused on cycloalkanes [16], i.e., cyclohexane, methylcyclohexane, and decalin etc. The dehydrogenation of cycloalkanes to corresponding aromatics, however, occurs at relatively high temperatures due to the unfavorable enthalpy changes (see Table 1). It was then demonstrated experimentally by Pez et al. [17] and theoretically by Crabtree and coworkers [18] that the incorporation of heteroatoms, such as N or B, into LOHCs reduces the energy input in dehydrogenation. Those findings triggered considerable investigations on heterocycles [13,14]. More recently, formic acid (FA) with energy density of 4.4 wt% has also been demonstrated as a promising hydrogen carrier. It is obvious that catalysis in hydrogenation and dehydrogenation is an important issue in the application of those LOHCs as hydrogen storage media. Herein below the properties of representative LOHCs, i.e., cycloalkanes, *N*-heterocycles, and FA, and the catalysts development will be reviewed and discussed, with the hope to provide the readers a brief
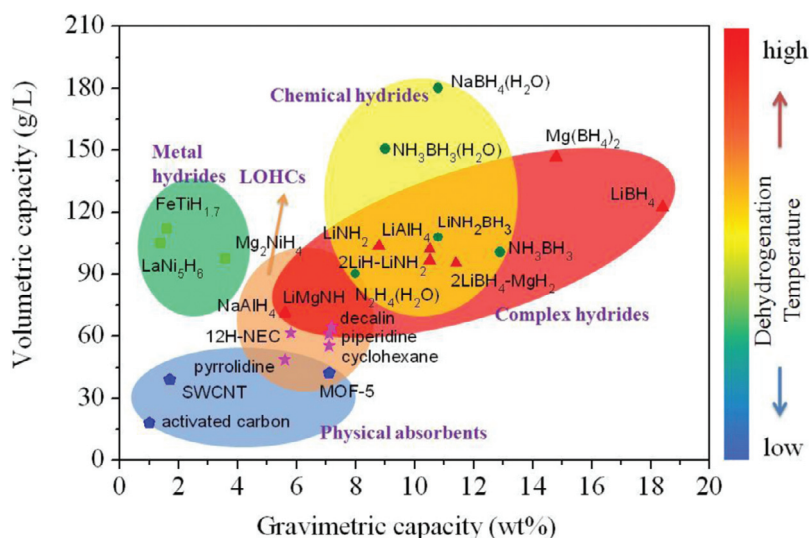
Fig. 1. Schematic view of hydrogen storage properties of different kinds of materials. The hydrogen contents of hydrolysis of $NaBH_4$ or NH_3BH_3 and the decomposition of N_2H_4 in water are estimated by the stoichiometric ratio of substrate and water.

Table 1. Hydrogen storage properties of selected cycloalkanes and the related catalysts for dehydrogenation [19].

Cycloalkanes	Product of dehydrogenation	Hydrogen capacity (wt%)	Heat of desorption ΔH (kJ/mol$_{H_2}$)	Selected catalyst for dehydrogenation	Dehydrogenation temperature (°C)	Hydrogen evolution rate (mmol/g$_{cat}$/min)	Ref.
Cyclohexane	Benzene	7.2	68.6	0.5% Pt–0.5% Ca/Al$_2$O$_3$	300	3	[20]
				2% Pt/Al$_2$O$_3$	315	29	[21]
				10 wt% Pt/AC	330	510	[22]
Methylcyclohexane	Toluene	6.2	68.3	10 wt% Pt/AC	298	520	[22]
				0.1 wt% K–0.6 wt% Pt/Al$_2$O$_3$	320	744 (mmol/L$_{cat}$/min)	[16]
				1 wt% Pt/Al$_{0.7}$Y$_{0.3}$NiO$_3$	350	45.8	[23]
Decalin	Naphthalene	7.3	63.9	10 wt% Pt/AC	320	460	[22]
				0.8 wt% Pt/Al$_2$O$_3$	340	1	[24]

summary of the on-going activities and perspectives of the near-term direction.

2. Cycloalkanes

With the advantages of relatively higher hydrogen capacity (6–8 wt%), liquid state at room temperature, high boiling points, production of CO$_x$-free hydrogen and low toxicity, cycloalkanes have been proposed and investigated as liquid hydrogen carriers [25]. The candidate cycloalkanes reported by far include cyclohexane, methylcyclohexane, and decalin as shown in Table 1. However, because the dehydrogenation of cycloalkanes is highly endothermic (63–69 kJ/mol$_{H_2}$), high temperature for hydrogen release has to be applied [19,25]. It was reported that methylcyclohexane is more easily dehydrogenated than cyclohexane because of the presence of side methyl group [16]. Dehydrogenation of decalin is even more thermodynamically favored than methylcyclohexane. There are a large number of publications concerning the catalysts development for dehydrogenation of cycloalkanes through the decades [16,24,26]. Noble metal catalysts particularly Pt-based catalysts have been well studied [21,23,27–29] (shown in Table 1). However, the deactivation of highly active catalyst because of coking is the main issue to be overcome. The addition of second metal (such as W, Ir, Re, Rh and Pd etc. [21,22]) and/or promoter (such as Ca [20,30]) and selection of suitable support (such as CNF [28] and Al$_2$O$_3$ [16]) are effective against coking. Besides Pt, non-noble metal based catalysts, such as Ni and Mo, are alternatives for dehydrogenation because of their low costs and comparable catalytic activities [31,32]. For cyclohexane, there are two dehydrogenation mechanisms: the sextet mechanism and the dou-
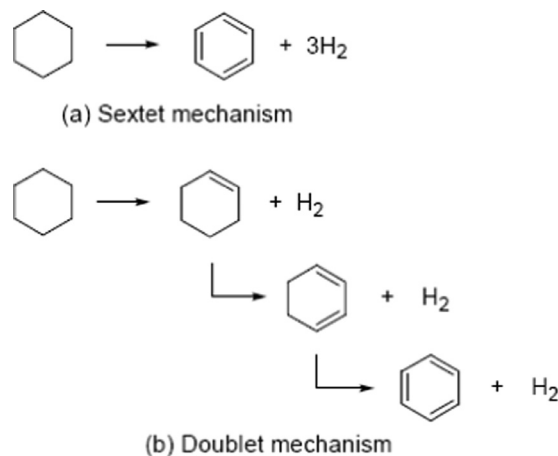

Fig. 2. Reaction mechanisms proposed for the dehydrogenation of cyclohexane [35].

blet mechanism [33,34]. As shown in Fig. 2 the difference between these two mechanisms lies in whether there are intermediate products during dehydrogenation. In the sextet mechanism, cyclohexane overlies on the catalyst surface and undergoes dehydrogenation directly to benzene (Fig. 2a). However, the hydrogen will be released step by step in the doublet mechanism because of the side adsorption through C=C double bond on catalyst surface (Fig. 2b).

Re-hydrogenation is a relatively easy process. Noble metal catalysts display excellent performances. Usually, hydrogenations of ben-