



Review

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ARTICLE INFO

Article history:

Received 16 July 2015

Revised 18 August 2015

Accepted 18 August 2015

Available online 3 September 2015

Keywords:

Liquid organic hydrogen carrier

Cycloalkanes

Heterocycle

Formic acid

Catalysis

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 H₂ 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 H₂ transportation [12–14]. As a matter of fact, Japanese government has a strategic plan of importing H₂ 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

[☆] This work was supported by the Project of the National Natural Science Funds for Distinguished Young Scholar (51225206), and Projects of the National Natural Science Foundation of China (grant nos. U1232120, 51301161, 21473181 and 51472237).

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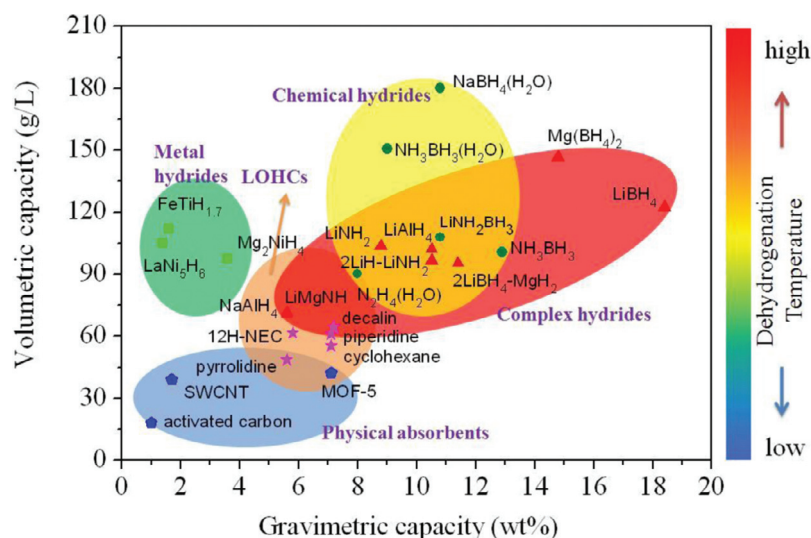


Fig. 1. Schematic view of hydrogen storage properties of different kinds of materials. The hydrogen contents of hydrolysis of NaBH_4 or NH_3BH_3 and the decomposition of N_2H_4 in water are estimated by the stoichiometric ratio of substrate and water.

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 ($^{\circ}\text{C}$)	Hydrogen evolution rate (mmol/g $_{\text{cat}}$ /min)	Ref.
Cyclohexane	Benzene	7.2	68.6	0.5% Pt–0.5% Ca/ Al_2O_3	300	3	[20]
				2% Pt/ Al_2O_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_2O_3	320	744 (mmol/L $_{\text{cat}}$ /min)	[16]
				1 wt% Pt/ Al_2O_3	350	45.8	[23]
Decalin	Naphthalene	7.3	63.9	Pt/ $\text{Al}_{0.7}\text{Y}_{0.3}\text{NiO}_3$	320	460	[22]
				10 wt% Pt/AC	320	1	[22]
				0.8 wt% Pt/ Al_2O_3	340		[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_2O_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-

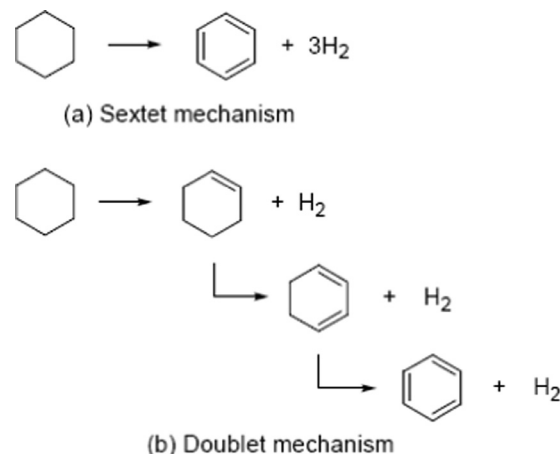


Fig. 2. Reaction mechanisms proposed for the dehydrogenation of cyclohexane [35].

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-

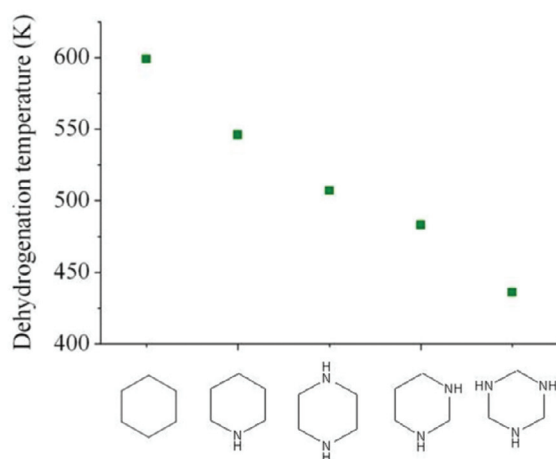


Fig. 3. The dependence of the dehydrogenation temperatures of the cyclohexane on N content [18].

zene and toluene have been used as the model reactions for the investigation of catalysts' properties [36,37]. In fact, both hydrogenation and dehydrogenation of LOHCs need highly active catalysts. Chen and coworkers put forward a novel slurry system made of metal alloy and unsaturated LOHCs, in which the metal alloys (including LaNi_5 , MnNi_5 (La-rich misch metal nickel-5), Mg_2Ni , and Raney-Ni) catalyze hydrogenation of liquid organic hydrocarbons and also absorb hydrogen by themselves under a mild reaction condition, leading to the storage of hydrogen in both solid metal alloys and liquid organic hydride [38–42]. Raney-Ni possesses much higher activity than other alloys. Although an obviously improved hydrogenation performance was observed for the slurry system, the dehydrogenation performance was not modified sufficiently. Yuan showed that the degree of dehydrogenation of cyclohexane was less than 3% in the $\text{MnNi}_5\text{-C}_6\text{H}_{12}$ slurry system [43].

Although much attention has been given to the development of cycloalkanes for hydrogen storage in the past decades, the major drawback of this type of hydrocarbon for practical application, i.e., unfavorable thermodynamic properties requiring the operational temperature over 300 °C, is still pending. Furthermore, the lack of stable dehydrogenation catalyst that could be against coking is another challenge, which may be solved by addition of alkali or alkaline earth metal promoter. Nevertheless, these cycloalkanes are suitable for the large scale and long-distance hydrogen delivery because of their low prices, high purity of hydrogen generated and abundances (for example, the world annual outputs of benzene and toluene are around 5×10^7 ton/year and 1×10^7 ton/year [44,45], respectively).

3. N-Heterocycles

3.1. Effect of nitrogen

As shown in Section 2, the reduction of operating temperature for alkane–arene pairs can be kinetically alleviated by employing suitable catalysts. However, the thermodynamic improvement can only be done via compositional alteration, for example, introducing heteroatoms into cycloalkanes to form heterocycles [13], which was first proposed by Pez et al. in a series of key patents [17,46]. In those patents, it was demonstrated that better reversible de/hydrogenation properties can be obtained by using highly conjugated and/or heteroatoms (such as N, O, P or B etc.) substituted hydrocarbons. In particular, the incorporation of N into LOHCs is in favor of their enthalpy changes during de/hydrogenation [18,47]. The dependence of the dehydrogenation temperature in cyclohexane on N content in cyclohexane is shown in Fig. 3.

Crabtree and his co-workers calculated the thermodynamic data of a series of N-heterocycles and found that the hydrogen release temperature can be efficiently reduced by incorporation of N atoms into the rings (particularly in 1, 3 positions) or ring substituents. The dehydrogenation enthalpy changes of N-substituted five membered rings drop more significantly than those of six membered rings [18]. Additionally, replacing C with other heteroatoms, such as O, B and P, could also modified the properties of LOHCs by changing the dehydrogenation enthalpy [46,47].

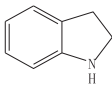
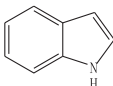
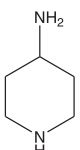
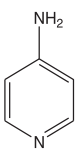
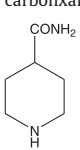
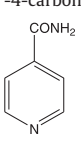
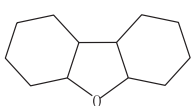
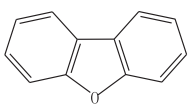
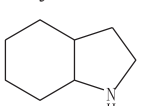
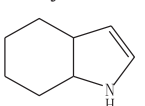
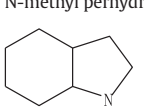
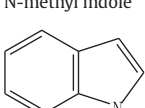
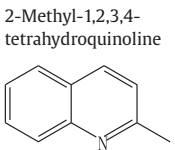
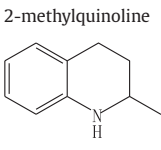
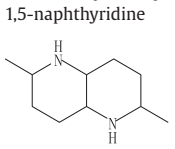
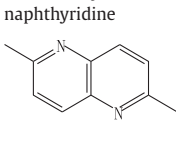
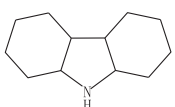
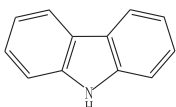
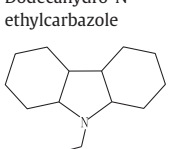
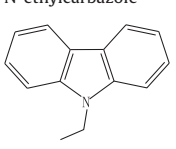
3.2. Hydrogen storage properties of N-heterocycles

Table 2 summarizes some representative N-heterocycles and the related catalysts for dehydrogenation. Crabtree and coworkers investigated the catalytic dehydrogenation of N-heterocycles and cycloalkanes and found that heteroatom substitution, particularly by nitrogen, favored low temperature hydrogen release, e.g., indoline can be fully dehydrogenated by Pd/C and Ru/C at 110 °C, while Rh/ Al_2O_3 can only reach 43% conversion [47]. Jessop and coworkers found that the attachment of electron donating or conjugated substituents to piperidine ring could increase greatly the rate of catalytic dehydrogenation, among which the highest rates were observed in 4-aminopiperidine and piperidine-4-carboxamide [48]. However, some side reactions, such as C–N cleavage, disproportionation and alkyl transfer etc., also occur during the dehydrogenation and hydrogenation. In the following research, they investigated the effect of sterics on the dehydrogenation rate of N-heterocycle and found that steric hindrance around the nitrogen atom in piperidine benefits its catalytic dehydrogenation [54]. A similar result was also observed in the dehydrogenation of dodecahydro-N-ethylcarbazole (12H-NEC) [55]. The authors attributed this phenomenon to the block of N from interacting with the catalyst surface by the steric hindrance group. The homogeneous Ir–PCP pincer complex was found by Jensen and coworkers to be highly active in the dehydrogenation of several LOHCs, including perhydro-dibenzofuran, perhydro-indole, N-methyl perhydro-indole, 4,4'-bipiperidine, 4-amino-methylpiperidine, and aminomethylcyclohexane [49]. Yamaguchi and Fujita also found that the pentamethylcyclopentadienyl (Cp^*) iridium homogeneous catalyst bearing a 2-pyridonate ligand exhibited an excellent activity in the reversible dehydrogenation/hydrogenation of 2-methyl-1,2,3,4-tetrahydroquinoline [50]. However, only the N-heterocyclic part participated in the dehydrogenation/hydrogenation cycle, resulting in a relatively low hydrogen capacity (2.7 wt%). Therefore, the authors further employed 2,6-dimethyldecahydro-1,5-naphthyridine with one N in each ring and achieved 6.0 wt% reversible hydrogen capacity using Cp^*Ir bearing bipyridonate ligand catalyst [51].

Support is an important factor to the activity and stability of a heterogeneous catalyst. Recently, Sánchez-Delgado and his coworkers reported that noble metals on basic supports (PVPy [56] or MgO [57,58]) catalyzed the hydrogenation of N-heterocycles much faster than on acidic supports (SiO_2 or Al_2O_3). In quinoline hydrogenation, the same authors demonstrated that the reaction rate increased monotonically with the basicity of the support, i.e., $\text{MgO} < \text{CaO} < \text{SrO}$ [59]. Due to the polarity of C=N bond in N-heterocycles, a catalytic mechanism involving heterolytic hydrogen splitting and ionic hydrogenation on the metal/basic support interface was proposed [58,59]. Our recent results showed that covalent triazine framework (CTF) supported Pd nanoparticles exhibited a markedly improved activity in hydrogenation of N-heterocycles as compared to the active carbon supported catalyst (see Fig. 4), confirming the promoting effect of basic support [60].

Among the N-heterocycles, the saturated-unsaturated pair of dodecahydro-N-ethylcarbazole (12H-NEC) and N-ethylcarbazole (NEC) (shown in Scheme 1) has been extensively investigated as a promising candidate for hydrogen storage [61,62]. Although the ΔH

Table 2. *N*-heterocycles and catalysts for dehydrogenation (selected cases).

	Products of dehydrogenation	Hydrogen capacity (wt%)	Calculated ΔH (kJ/mol _{H₂})	Catalyst and activity	Ref.
Indoline 	indole 	1.7	51.9	5% Pd/C: 110 °C, conversion 100% 5% Ru/C: 110 °C, conversion 100%	[47] [47]
4-Aminopiperidine 	4-aminopyridine 	6.1	56.7	10% Pd/SiO ₂ : 170 °C, conversion 66%	[48]
Piperidine-4-carboxamide 	pyridine-4-carboxamide 	4.7		5% Pd/SiO ₂ : 170 °C, conversion 100%	[48]
Perhydrodibenzofuran 	dibenzofuran 	6.7		IrH ₂ [2,6-C ₆ H ₃ -OPPr _i ₂] ₂ : 200 °C, conversion 100% selectivity: 8%	[49]
Perhydroindole 	tetrahydroindole 	1.8		IrH ₂ [2,6-C ₆ H ₃ -OPPr _i ₂] ₂ : 200 °C, conversion 100%	[49]
N-methyl perhydroindole 	N-methyl indole 	5.8		IrH ₂ [2,6-C ₆ H ₃ -OPPr _i ₂] ₂ : 200 °C, conversion 99% selectivity: 62%	[49]
2-Methyl-1,2,3,4-tetrahydroquinoline 	2-methylquinoline 	2.7		Cp*Ir bearing a 2-pyridonate ligand: 138 °C	[50]
2,6-Dimethyldecahydro-1,5-naphthyridine 	2,6-dimethyl-1,5-naphthyridine 	6.0		Cp*Ir bearing bipyridonate ligand: 138 °C	[51]
Dodecahydrocarbazole 	carbazole 	6.7	51.1	5% Pd/C: 170 °C, conversion 100%	[19]
Dodecahydro-N-ethylcarbazole 	N-ethylcarbazole 	5.8	50.6	5% Pd/C: 170 °C, conversion 100% 4% Pd/Lithium aluminate: 197 °C 5% Pd/SiO ₂ : 170 °C IrH ₂ [2,6-C ₆ H ₃ -(OPBu ^t) ₂] ₂ : 200 °C	[19] [46] [52] [53]

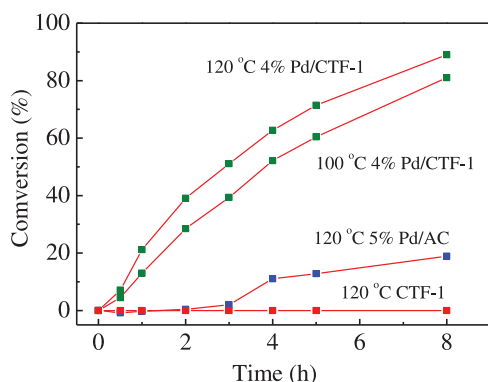
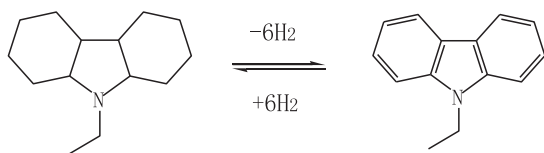


Fig. 4. Hydrogenation of *N*-methylpyrrole at 100 °C and 120 °C using neat CTF-1, 4% Pd/CTF-1 and 4% Pd/AC under 20 bar H₂, respectively.



Scheme 1. Dehydrogenation and hydrogenation of 12H-NEC and NEC pair.

for dehydrogenation of 12H-NEC is similar to that of dodecahydrocarbazole and a certain amount of hydrogen capacity will be sacrificed inevitably by attaching an ethyl group to carbazole, the melting point reduces dramatically by attaching substituents, for example, the NEC has a melting point of 68 °C which is ca. 180 °C lower than carbazole (247 °C). Another advantage of NEC over carbazole is that the nitrogen atom is blocked by the ethyl group from the interaction with catalyst surface, and thus, the deactivation of catalyst can be alleviated.

The use of NEC as a reversible hydrogen storage material under moderate conditions was firstly proposed by Pez et al. from Air Products [17,46]. 5% Ru and 4% Pd on lithium aluminate were employed as hydrogenation and dehydrogenation catalysts, respectively. NEC can reversibly store and release ca. 5.6 wt% hydrogen with slight capacity drop in five cycles. Pd/SiO₂ catalyst appears to be highly active. Smith and coworkers found nearly 100% conversion of 12-NEC at 170 °C over 5% Pd/SiO₂ [52]. Unfortunately, the dehydrogenation products contain NEC and the partially dehydrogenated intermediates, such as octa- and tetrahydro-*N*-ethylcarbazole (8H-NEC and 4H-NEC). In the following studies, the same authors found the turnover frequency (TOF) and selectivity of the dehydrogenation were strongly dependent upon the Pd size, i.e., the maxima in both activity and selectivity were obtained on Pd with an average particle size of 9 nm [55,63,64]. The mechanistic studies on the catalytic dehydrogenation demonstrate that the dehydrogenation of 12H-NEC starts from the five-membered ring by weakening the axial C–H bonds adjacent to N atom, producing 8H-NEC as the primary intermediate on Pd- and Pt-based model catalysts [65–67]. The Ir-PCP pincer homogeneous catalyst was found to dehydrogenate 12H-NEC at 200 °C [53]. However, the dehydrogenation to the final NEC is difficult to be achieved in most cases.

The catalytic hydrogenation of NEC to 12H-NEC can be carried out using Ru- and Rh-based catalysts. A commercial Ru/Al₂O₃ catalyst exhibits a selectivity of 97% to the fully hydrogenated products at 7 MPa and 130–150 °C [52,68]. Tsang and coworkers found that Ru was the most active transition metal for the hydrogenation of NEC [62,69,70,71]. However, Ru catalyst suffers from a relatively low selectivity to the desired product due to the accumulation of kinetically stable intermediate, 8H-NEC [61]. The Rh-based catalyst, on the other

hand, exhibits a higher selectivity to 12H-NEC under comparable conditions. Cheng and coworkers realized full hydrogenation and dehydrogenation of NEC and 12H-NEC pair using Ru/Al₂O₃ and Pd/Al₂O₃, respectively, with slight degradation after 10 cycles [72].

Besides *N*-heterocycles, B–N-based heterocycles, including 1,2-BN-cyclohexane and 3-methyl-1,2-BN-cyclopentane etc., with moderate dehydrogenation temperature have been developed as a new class of liquid hydrogen materials recently [73,74]. However, the two main issues, i.e., the cost of B–N-heterocycles and the economic viable way of regeneration of spend fuels, need to be solved to satisfy the large scale application in the future [75].

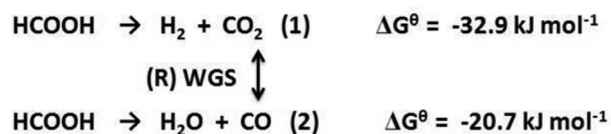
Although the unfavorable thermodynamic properties of cycloalkanes were optimized by incorporation of heteroatoms resulting in lower operational temperature, there are still pending issues, such as cost, toxicity, stability and kinetic barrier etc., worthy of further evaluation and investigations. The development of efficient catalysts could overcome the kinetic barrier. However, the metal catalyst is easy to be poisoned due to the existence of lone electron pair in N. Furthermore, some *N*-heterocycles are no longer in liquid state after hydrogenation or dehydrogenation under ambient conditions, which may not be a good news for the practical application [76]. Users need to warm up the car and liquefy the hydrogen carrier before starting the engine, which is unacceptable for consumers. Therefore, searching for organic compound that can maintain its liquid state even at the temperature as low as –40 °C is essentially necessary. As mentioned above, homogeneous catalysts in general show excellent activities in the hydrogenation or dehydrogenation. However, the thermal stability of homogeneous catalysts is still unsatisfactory. Additionally, the separation of homogeneous catalyst and reactant after deactivation will be a complicate procedure.

4. Formic acid (FA)

FA with a hydrogen content of 4.4 wt%, stable and low toxic at ambient condition, easiness in transportation, handling and storage, holds the promises as a safe and convenient liquid hydrogen carrier [77,78]. As shown in the Scheme 2 the decomposition of FA follows two competitive reactions: the R1 – the dehydrogenation, yielding H₂ and CO₂ and, the R2 – the dehydration, yielding CO and H₂O [78]. In addition, the water-gas shift (WGS) reaction may take apart in affecting the distribution of decomposition products. The dehydration pathway is undesirable and should be strictly controlled to minimize the concentration of CO. The R1 is a reversible process. By using efficient catalysts CO₂ can be hydrogenated back to FA [79]. Therefore, in this section, the decomposition and regeneration of FA will be discussed.

4.1. Decomposition of formic acid

Early studies on both homogeneous and heterogeneous catalytic decomposition of FA didn't aim to hydrogen storage [80–82], but rather refer the reaction of FA decomposition as a model reaction for the mechanistic study of catalysis. It is until 2008 that the catalytic dehydrogenation of FA gained renaissance featuring the follow-up extensive investigations for the purpose of hydrogen storage thanks to the independent researches from Beller's group [80] and Laurenczy's group [81].



Scheme 2. Possible reaction pathways for the decomposition of formic acid: dehydrogenation (1) and dehydration (2) [78].

Rh- and Ru-based homogeneous catalysts have been well studied for the catalytic decomposition of FA [83–87]. Beller and coworkers investigated the catalytic activity of Rh using a number of different precursors, including $[\text{RhCl}_2(p\text{-cymene})]_2$, $\text{RhCl}_2(\text{PPh}_3)_3$, $[\text{RhCl}_3(\text{benzene})_2]_2$ and $\text{RhBr}_3 \cdot x\text{H}_2\text{O}$, in the presence of different ligands and different amines. Both $\text{RhBr}_3 \cdot x\text{H}_2\text{O}$ and $\text{RhCl}_2(\text{PPh}_3)_3$ precursors exhibit higher activities, showing a TOF higher than 300 h^{-1} at 40°C without the detection of any CO as a by-product [83,85]. Later, the same authors reported a turnover number (TON) of 260,000 with an average TOF of 900 h^{-1} using an optimized $\text{RuCl}_2(\text{benzene})_2$ -based soluble catalyst [88]. Laurenczy and coworkers added HCOONa into the aqueous FA solution and found the accelerated catalytic activity by a factor of 50 in the presence of $\text{Ru}(\text{H}_2\text{O})_6$ or $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ combined with met-trisulfonated triphenylphosphine (mTPPTS) ligand [86,87]. Furthermore, no deactivation of catalyst and no detection of CO were observed for more than 100 cycles at 90°C in this system. Considering the high price of noble metal catalysts, Beller and coworkers developed a highly active Fe-based catalyst for the decomposition of FA (TOF: 9425 h^{-1} at 80°C). The Fe-based catalyst could be formed in situ from $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and a tetradentate phosphine ligand ($\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$) [89]. Later, a number of efficient Fe-based homogeneous catalysts for FA decomposition were developed [90–93], in which a pincer supported Fe catalyst exhibits a high TON of ca. 1×10^6 [90].

For the heterogeneous catalytic decomposition of FA, on the other hand, the monometallic noble metal catalysts, including Au, Pd, Ir, Pt, Ru and Rh etc., were investigated recently. Ojeda and Iglesia synthesized nanosized Au particles supported on Al_2O_3 and found a high FA decomposition activity without the evolution of CO [94]. The commercial Pd/C, Au/TiO₂ and Au/C were found active in gas phase by Ross and coworkers as well [95]. Solymosi, however, found that the Pd/AC exhibited a poor activity and selectivity for the FA decomposition in aqueous phase [96,97]. Alloying Au or Ag to Pd could markedly increase the activity and selectivity, which can be interpreted as a change in the electronic properties of the active Pd alloy [98]. Recently, Xu and coworkers introduced Au-Pd alloy into metal organic framework (MOF) and synthesized Au-Pd/MOFs catalyst, which is the first highly active MOF immobilized metal catalyst for FA decomposition [99]. Besides alloys, catalysts with core-shell structure also exhibit distinguished properties. Xing and coworkers synthesized PdAu@Au core shell nanoparticles supported on activated carbon and found considerably improved activity and stability as compared to the Au/C and Pd/C [100]. More recently, catalysts with multiple metal components and high activities for FA decomposition were developed in order to reduce the content of noble metals [101–103]. Furthermore, Xu et al. reported immobilization of ultrafine Pd nanoparticles on diamine-alkalized reduced graphene oxide (Pd/PDA-rGO), which exhibited the highest TOF value (3810 h^{-1} at 50°C) for aqueous FA decomposition. Several selected heterogeneous catalysts for decomposition of FA in aqueous phase are summarized in Table 3.

Table 3. Selected heterogeneous catalysts for the decomposition of aqueous FA.

Catalyst	Temperature ($^\circ\text{C}$)	TOF (h^{-1})	Ref.
Pd/C	25	64	[97]
AgPd/C	50	382	[98]
AuPd/C	50	230	[98]
AuPd/ED-MIL-101	90	106	[99]
PdAu@Au/C	80		[100]
$\text{Co}_{0.3}\text{Au}_{0.35}\text{Pd}_{0.35}/\text{C}$	RT	80	[101]
PdNi@Pd/GNs-CB	RT	150	[102]
CoAuPd/DNA-rGO	RT	85	[103]
Pd/PDA-rGO	50	3810	[104]

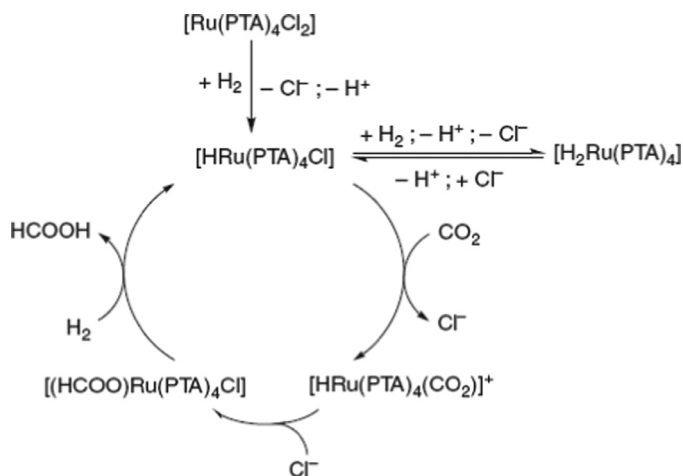


Fig. 5. Catalytic cycle of the hydrogenation of CO_2 using $[\text{RuCl}_2(\text{PTA})_2]$ in water or DMSO [114].

4.2. Regeneration of formic acid

The regeneration of FA from the hydrogenation of CO_2 needs to operate in a basic environment to favor the formation of FA thermodynamically. It is not essential to remove the base after hydrogenation since base is also needed in the decomposition of FA [105]. The Rh-, Ru- and Ir-based homogeneous catalysts have been well investigated. Leitner and coworkers found that the Rh-based catalysts with different ligands are highly active for the hydrogenation of CO_2 in water or DMSO solution [106,107]. Himeda et al. reported a pH-dependent catalyst $[\text{Cp}^*\text{Ir}(\text{dhbp})\text{Cl}]^+$ for the hydrogenation of CO_2 and found this catalytic system bears the advantages of high efficiency, easy separation, catalyst recycling, waste-free and aqueous catalysis [108]. To realize the in situ reversibility of dehydrogenation and re-hydrogenation of FA by using the same catalyst, Hull et al. developed the first reversible and recyclable system by using a homogeneous Ir catalyst with a proton responsive ligand [109]. The hydrogen production and consumption can be controlled through switching pH [109,110]. Beller and coworkers developed a Ru catalyst for the selective hydrogenation of CO_2 to formates and dehydrogenation of formates back to bicarbonates [111]. However, the solubilities of CO_2 and H_2 in solvent are usually insufficient, resulting in unfavorable kinetics and low conversion. Therefore, the hydrogenation of CO_2 under supercritical condition, which promotes the mass transfer, could significantly enhance the yield of FA [112,113]. Since the addition of base to CO_2 solution would complicate the separation of FA from the solution and decrease the hydrogen capacity, the hydrogenation of CO_2 without alkaline additives is more promising. Laurenczy and coworkers described the direct hydrogenation of CO_2 into FA using $[\text{RuCl}_2(\text{PTA})_2]$ catalyst in water or DMSO without any additives [114]. They found the catalyst can be reused for multiple times without a decrease in activity. The catalytic cycle for this reaction was proposed as shown in Fig. 5.

Although the homogeneous catalysts are investigated extensively for the regeneration of FA, the separation of catalyst during recycling is one of the pending issues [77]. Therefore, the heterogeneous catalysts, which have yet to be developed [115–117], are the next step to be taken. In additional, the separation and collection of CO_2 from the gaseous products of decomposition of FA is another important problem to be considered in the real application.

5. Other potential LOHCs

The technical targets of onboard hydrogen storage system for light-duty vehicles are 5.5 wt% in capacity and -40 – 60°C for

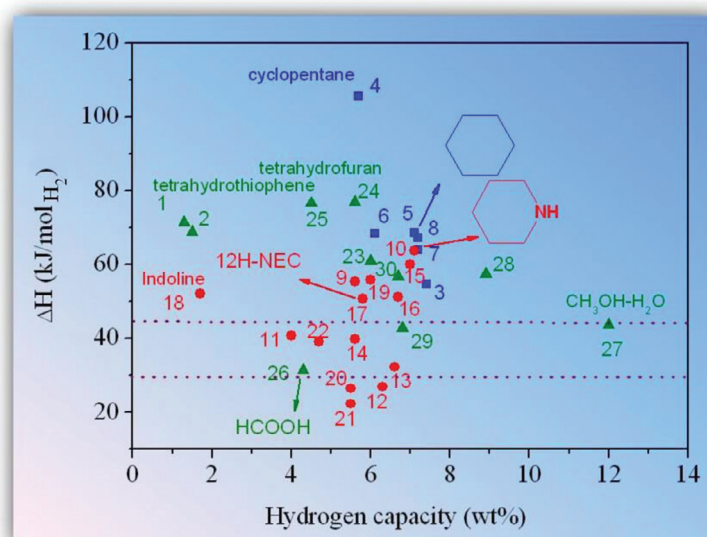


Fig. 6. Potential LOHC candidates. Blue: cycloalkanes; Red: N-heterocycles; Green: other potential organic hydrogen carriers. The names of the LOHCs can be found in the supporting information.

operational temperature, which means that, in this temperature region, at least 1 bar equilibrium hydrogen is needed. The equilibrium pressure strongly depends on the enthalpy and entropy changes in dehydrogenation Reaction [2]. The entropy change of the dehydrogenation mainly comes from the molecular hydrogen, which is about 130 J/K/mol H_2 . Therefore, to reach an equilibrium pressure of 1 bar hydrogen in the temperature range of $-40\text{ }^{\circ}\text{C}$ to $60\text{ }^{\circ}\text{C}$ [1], ΔH should be in the range of 30–44 kJ/mol H_2 , a quite narrow thermodynamic window for the materials design and development of hydrogen storage (the space within the dotted lines in Fig. 6).

Besides the abovementioned three kinds of LOHCs, there are other candidates as listed in Fig. 6 that are worth of serious considerations. Since the bonding strength of C–H is higher than that of C–C, the selectivity to H_2 from decomposition of aliphatic alkanes to corresponding alkenes or alkynes is usually low even in the presence of noble metal catalyst. More importantly, the dehydrogenation enthalpies of aliphatics are high, and more energy input is needed to obtain H_2 . Furthermore, the short-chain alkanes are in gaseous state under ambient conditions. Calculations [46] show that better reversible de/hydrogenation properties can be obtained using larger conjugated molecules as shown in Fig. 6, e.g., the dehydrogenation enthalpy of tetracosahydrocoronene (3 in Fig. 6) is further decreased as compared with mono-aromatics and di-aromatics. Therefore, searching for a polycyclic aromatic hydrocarbon with suitable molecular size and moderate dehydrogenation enthalpy may be one of the directions for LOHCs.

Fortunately, several candidates, such as imidazolidine, 1,2,3,5,6,7-hexamethyldodecahydropyrrolo[3,2-f]indole, dodecahydro-1H-pyrrolo[2,3-b:4,5-b']dipyrazine and 1-methylimidazolidine are located in the optimal region (Fig. 6). However, some of the dehydrogenation enthalpies are too low to stabilize the compounds at ambient temperature, for example, 1,2,4-triazolidine, 1,2,3-triazolidine and octahydro-1H-purine. Recently, a new hydrogen storage system based on $RCH_2NH_2/RC\equiv N$ couple was proposed [118]. Although the hydrogenation of nitrile has been intensively investigated before, the reversible catalytic dehydrogenation is challenging. Szymczak and coworkers employed the homogeneous $[HRu(bmpi)(PPh_3)_2]$ catalyst to selectively dehydrogenate primary amines into the corresponding nitriles under moderate conditions [119]. However, R groups in

primary amines are too large, sacrificing the hydrogen capacity significantly. The primary amines with smaller R group usually deammoniate rather than dehydrogenation. Very recently, we introduced alkali metal into primary amines forming metalated amines and demonstrated the direct dehydrogenation under relatively mild conditions [120,121]. However, the reversible hydrogenation is by far unsuccessful. Therefore, the key issues to be addressed in the future for the N-heteroalkanes are the development of efficient catalysts and compositional alteration for the liquid hydrides to achieve high gravimetric hydrogen density and suitable reaction enthalpy.

Besides amines, alcohols, R-SH, R-BH and R-PH are potential hydrogen carriers worthy of extensive evaluations. One case from Air Products' patent shows that the dehydrogenation of dodecahydro-1H-dibenzo[b,d]borole (29 in Fig. 6) to 1H-dibenzo[b,d]borole possesses a suitable enthalpy, showing the promise as hydrogen carrier. Methanol, a liquid with large annual global production, reacts with H_2O yielding 12.1 wt% H_2 following the reaction (3) [122]. Such a process holds the promises for the on-site hydrogen production.



6. Summary

The design, synthesis and evaluation of new organic hydrides and the development of efficient, non-noble metal catalysts are the areas worthy of intensive research inputs. With the vast versatility of organic hydrides, suitable candidates for both onboard applications and large scale-long distance H_2 transport are expectable.

Supplementary Materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.jechem.2015.08.007](https://doi.org/10.1016/j.jechem.2015.08.007).

References

- [1] <http://energy.gov/eere/fuelcells/downloads/target-explanation-document-onboard-hydrogen-storage-light-duty-fuel-cell>.
- [2] L. Schlapbach, A. Züttel, *Nature* 414 (2001) 353.
- [3] C. Liu, F. Li, L.P. Ma, H.M. Cheng, *Adv. Mater.* 22 (2010) E28.
- [4] D. Zhao, D.J. Timmons, D. Yuan, H.C. Zhou, *Acc. Chem. Res.* 44 (2010) 123.

- [5] H.W. Li, Y. Yan, S.-i. Orimo, A. Züttel, C.M. Jensen, *Energies* 4 (2011) 185.
- [6] B. Sakintuna, F. Lamari-Darkrim, M. Hirscher, *Int. J. Hydrogen Energy* 32 (2007) 1121.
- [7] S.-i. Orimo, Y. Nakamori, J.R. Eliseo, A. Züttel, C.M. Jensen, *Chem. Rev.* 107 (2007) 4111.
- [8] F.H. Stephens, V. Pons, R.T. Baker, *J. Chem. Soc. Dalton Trans.* (2007) 2613.
- [9] http://www.toyota-global.com/innovation/environmental_technology/fuelcell_vehicle/# (accessed 07.09.15).
- [10] http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/04_warner_quantum.pdf.
- [11] <http://energy.gov/eere/fuelcells/physical-hydrogen-storage>.
- [12] Q.-L. Zhu, Q. Xu, *Energy Environ. Sci.* (2015).
- [13] R.H. Crabtree, *Energy Environ. Sci.* 1 (2008) 134.
- [14] D. Teichmann, K. Stark, K. Mueller, G. Zoetli, P. Wasserscheid, W. Arlt, *Energy Environ. Sci.* 5 (2012) 9044.
- [15] http://www.meti.go.jp/english/press/2014/0624_04.html (accessed 07.09.15).
- [16] Y. Okada, E. Sasaki, E. Watanabe, S. Hyodo, H. Nishijima, *Int. J. Hydrogen Energy* 31 (2006) 1348.
- [17] G.P. Pez, A.R. Scott, A.C. Cooper, H. Cheng US patent, 7101530, 2006.
- [18] E. Clot, O. Eisenstein, R.H. Crabtree, *Chem. Commun.* (2007) 2231.
- [19] R.B. Biniwale, S. Rayalu, S. Devotta, M. Ichikawa, *Int. J. Hydrogen Energy* 33 (2008) 360.
- [20] J. Yu, Q. Ge, W. Fang, H. Xu, *Appl. Catal., A* 395 (2011) 114.
- [21] N. Kariya, A. Fukuoka, M. Ichikawa, *Appl. Catal., A* 233 (2002) 91.
- [22] N. Kariya, A. Fukuoka, T. Utagawa, M. Sakuramoto, Y. Goto, M. Ichikawa, *Appl. Catal. A* 247 (2003) 247.
- [23] A.A. Shukla, P.V. Gosavi, J.V. Pande, V.P. Kumar, K.V.R. Chary, R.B. Biniwale, *Int. J. Hydrogen Energy* 35 (2010) 4020.
- [24] B. Wang, D.W. Goodman, G.F. Froment, *J. Catal.* 253 (2008) 229.
- [25] A. Shukla, S. Karmakar, R.B. Biniwale, *Int. J. Hydrogen Energy* 37 (2012) 3719.
- [26] S. Hodoshima, H. Arai, S. Takaiwa, Y. Saito, *Int. J. Hydrogen Energy* 28 (2003) 1255.
- [27] R.W. Coughlin, K. Kawakami, A. Hasan, *J. Catal.* 88 (1984) 150.
- [28] M.P. Lázaro, E. García-Bordejé, D. Sebastián, M.J. Lázaro, R. Moliner, *Catal. Today* 138 (2008) 203.
- [29] L.M. Kustov, A.L. Tarasov, B.P. Tarasov, *Int. J. Hydrogen Energy* 38 (2013) 5713.
- [30] J. Yu, R. Wang, S. Ren, X. Sun, C. Chen, Q. Ge, W. Fang, J. Zhang, H. Xu, D.S. Su, *Chemcatcher* 4 (2012) 1376.
- [31] S. Yolcular, Ö. Olgun, *Catal. Today* 138 (2008) 198.
- [32] M. Riad, S. Mikhail, *Catal. Commun.* 9 (2008) 1398.
- [33] C.D. MacPherson, K.T. Leung, *Surf. Sci.* 356 (1996) L399.
- [34] R. Schulz, J. Huot, G. Liang, S. Boily, G. Lalande, M.C. Denis, J.P. Dodelet, *Mater. Sci. Eng.: A* 267 (1999) 240.
- [35] S. Qi, J. Huang, H. Chen, Z. Gao, B. Yang, *Acta Chimica Sinica* 70 (2012) 2467.
- [36] D. Poondi, M. Albert Vannice, *J. Catal.* 161 (1996) 742.
- [37] S.D. Lin, M.A. Vannice, *J. Catal.* 143 (1993) 554.
- [38] S.Y. Dai, G.H. Xu, Y. An, C.P. Chen, L.X. Chen, Q.D. Wang, *Chin. J. Chem. Eng.* 11 (2003) 571.
- [39] H.J. Yuan, Y. An, G.H. Xu, C.P. Chen, *J. Rare Earths* 22 (2004) 385.
- [40] G.M. Cai, C.P. Chen, Y. An, G.H. Xu, L.X. Chen, Q.D. Wang, *J. Rare Earths* 20 (2002) 28.
- [41] C.P. Chen, G.M. Cai, Y. Chen, Y. An, G.H. Xu, Q.D. Wang, *J. Alloys Compd.* 350 (2003) 275.
- [42] Z. Kou, Z. Zhi, G. Xu, Y. An, C. He, *Appl. Catal., A* 467 (2013) 196.
- [43] Yuan, H., Zhejiang University, 2004.
- [44] <http://mcgroup.co.uk/news/20140502/benzene-production-exceed-5095-mln-tonnes.html> (accessed 07.09.15).
- [45] <http://zh.wikipedia.org/wiki/甲苯>
- [46] G.P. Pez, A.R. Scott, A.C. Cooper, H. Cheng, F.C. Wilhelm, A.H. Abdourazak, US patent, 7351395 2008.
- [47] A. Moores, M. Poyatos, Y. Luo, R.H. Crabtree, *New J. Chem.* 30 (2006) 1675.
- [48] Y. Cui, S. Kwok, A. Bucholtz, B. Davis, R.A. Whitney, P.G. Jessop, *New J. Chem.* 32 (2008) 1027.
- [49] Z. Wang, J. Belli, C.M. Jensen, *Faraday Discuss* 151 (2011) 297.
- [50] R. Yamaguchi, C. Ikeda, Y. Takahashi, K.-i. Fujita, *J. Am. Chem. Soc.* 131 (2009) 8410.
- [51] K.-i. Fujita, Y. Tanaka, M. Kobayashi, R. Yamaguchi, *J. Am. Chem. Soc.* 136 (2014) 4829.
- [52] F. Sotoodeh, L. Zhao, K. Smith, *J. Appl. Catal., A* 362 (2009) 155.
- [53] Z. Wang, I. Tonks, J. Belli, C.M. Jensen, *J. Organomet. Chem.* 694 (2009) 2854.
- [54] D. Dean, B. Davis, P.G. Jessop, *New J. Chem.* 35 (2011) 417.
- [55] F. Sotoodeh, B.J.M. Huber, K. Smith, *J. Appl. Catal., A* 419 (2012) 67.
- [56] M. Fang, N. Machalaba, R.A. Sanchez-Delgado, *Dalton Trans.* 40 (2011) 10621.
- [57] M.F. Fang, R.A. Sanchez-Delgado, *J. Catal.* 311 (2014) 357.
- [58] R. Rahi, M.F. Fang, A. Ahmed, R.A. Sanchez-Delgado, *Dalton Trans.* 41 (2012) 14490.
- [59] A. Sanchez, M.F. Fang, A. Ahmed, R.A. Sanchez-Delgado, *Appl. Catal., A* 477 (2014) 117.
- [60] T. He, L. Liu, G. Wu, P.J. Chen, *Mater. Chem. A* 3 (2015) 16235.
- [61] K.M. Eblagon, K. Tam, S.C.E. Tsang, *Energy Environ. Sci.* 5 (2012) 8621.
- [62] K.M. Eblagon, K. Tam, K.M.K. Yu, S.C.E. Tsang, *J. Phys. Chem. C* 116 (2012) 7421.
- [63] F. Sotoodeh, K.J. Smith, *J. Catal.* 279 (2011) 36.
- [64] F. Sotoodeh, B.J.M. Huber, K.J. Smith, *Int. J. Hydrogen Energy* 37 (2012) 2715.
- [65] M. Amende, S. Schernich, M. Sobota, I. Nikiforidis, W. Hieringer, D. Assenbaum, C. Gleichweit, H.J. Drescher, C. Papp, H.P. Steinrück, A. Gorling, P. Wasserscheid, M. Laurin, J. Libuda, *Chem.-Eur. J.* 19 (2013) 10854.
- [66] M. Arnende, C. Gleichweit, K. Werner, S. Schernich, W. Zhao, M.P.A. Lorenz, O. Höfert, C. Papp, M. Koch, P. Wasserscheid, M. Laurin, H.P. Steinrück, J. Libuda, *ACS Catal.* 4 (2014) 657.
- [67] C. Gleichweit, M. Amende, S. Schernich, W. Zhao, M.P.A. Lorenz, O. Höfert, N. Brückner, P. Wasserscheid, J. Libuda, H.-P. Steinrück, C. Papp, *ChemSusChem* 6 (2013) 974.
- [68] F. Sotoodeh, K.J. Smith, *Ind. Eng. Chem. Res.* 49 (2010) 1018.
- [69] K.M. Eblagon, D. Rentsch, O. Friedrichs, A. Remhof, A. Züttel, A.J. Ramirez-Cuesta, S.C. Tsang, *Int. J. Hydrogen Energy* 35 (2010) 11609.
- [70] K. Morawa Eblagon, K. Tam, K.M.K. Yu, S.-L. Zhao, X.-Q. Gong, H. He, L. Ye, L.-C. Wang, A.J. Ramirez-Cuesta, S.C. Tsang, *J. Phys. Chem. C* 114 (2010) 9720.
- [71] K.M. Eblagon, S.C.E. Tsang, *Appl. Catal., B* 160–161 (2014) 22.
- [72] M. Yang, C. Han, G. Ni, J. Wu, H. Cheng, *Int. J. Hydrogen Energy* 37 (2012) 12839.
- [73] W. Luo, L.N. Zakharov, S.-Y. Liu, *J. Am. Chem. Soc.* 133 (2011) 13006.
- [74] W. Luo, P.G. Campbell, L.N. Zakharov, S.-Y. Liu, *J. Am. Chem. Soc.* 133 (2011) 19326.
- [75] P.G. Campbell, L.N. Zakharov, D.J. Grant, D.A. Dixon, S.-Y. Liu, *J. Am. Chem. Soc.* 132 (2010) 3289.
- [76] N. Brückner, K. Obesser, A. Bösmann, D. Teichmann, W. Arlt, J. Dungs, P. Wasserscheid, *ChemSusChem* 7 (2014) 229.
- [77] S. Enthaler, J. von Langermann, T. Schmidt, *Energy Environ. Sci.* 3 (2010) 1207.
- [78] M. Grasemann, G. Laurenczy, *Energy Environ. Sci.* 5 (2012) 8171.
- [79] A. Boddien, F. Gärtner, C. Federsel, P. Sponholz, D. Mellmann, R. Jackstell, H. Junge, M. Beller, *Angew. Chem.-Int. Edit.* 50 (2011) 6411.
- [80] R.S. Coffey, *Chem. Commun.* (1967) 923b.
- [81] T. Yoshida, Y. Ueda, S. Otsuka, *J. Am. Chem. Soc.* 100 (1978) 3941.
- [82] R.S. Paonessa, W.C. Troglor, *J. Am. Chem. Soc.* 104 (1982) 3529.
- [83] A. Boddien, B. Loges, H. Junge, M. Beller, *ChemSusChem* 1 (2008) 751.
- [84] H. Junge, A. Boddien, F. Capitta, B. Loges, J.R. Noyes, S. Gladiali, M. Beller, *Tetrahedron Lett.* 50 (2009) 1603.
- [85] B. Loges, A. Boddien, H. Junge, M. Beller, *Angew. Chem.-Int. Edit.* 47 (2008) 3962.
- [86] C. Fellay, P.J. Dyson, G. Laurenczy, *Angew. Chem.-Int. Edit.* 47 (2008) 3966.
- [87] C. Fellay, N. Yan, P.J. Dyson, G. Laurenczy, *Chem.-Eur. J.* 15 (2009) 3752.
- [88] A. Boddien, B. Loges, H. Junge, F. Gärtner, J.R. Noyes, M. Beller, *Adv. Synth. Catal.* 351 (2009) 2517.
- [89] A. Boddien, D. Mellmann, F. Gärtner, R. Jackstell, H. Junge, P.J. Dyson, G. Laurenczy, R. Ludwig, M. Beller, *Science* 333 (2011) 1733.
- [90] E.A. Bielinski, P.O. Lagaditis, Y. Zhang, B.Q. Mercado, C. Würtele, W.H. Bernskoetter, N. Hazari, S. Schneider, *J. Am. Chem. Soc.* 136 (2014) 10234.
- [91] A. Boddien, B. Loges, F. Gärtner, C. Torborg, K. Fumino, H. Junge, R. Ludwig, M. Beller, *J. Am. Chem. Soc.* 132 (2010) 8924.
- [92] C. Federsel, A. Boddien, R. Jackstell, R. Jennerjahn, P.J. Dyson, R. Scopelliti, G. Laurenczy, M. Beller, *Angew. Chem. Int. Ed.* 49 (2010) 9777.
- [93] A. Boddien, F. Gärtner, R. Jackstell, H. Junge, A. Spannenberg, W. Baumann, R. Ludwig, M. Beller, *Angew. Chem. Int. Ed.* 49 (2010) 8993.
- [94] M. Ojeda, E. Iglesia, *Angew. Chem. Int. Ed.* 48 (2009) 4800.
- [95] D.A. Bulushev, S. Beloshapkin, J.R.H. Ross, *Catal. Today* 154 (2010) 7.
- [96] F. Solymosi, Á. Köös, N. Liliom, I. Ugrai, *J. Catal.* 279 (2011) 213.
- [97] Z.-L. Wang, J.-M. Yan, H.-L. Wang, Y. Ping, Q. Jiang, *Sci Rep* 2 (2012) 598.
- [98] X. Zhou, Y. Huang, W. Xing, C. Liu, J. Liao, T. Lu, *Chem. Commun.* (2008) 3540.
- [99] X. Gu, Z.-H. Lu, H.-L. Jiang, T. Akita, Q. Xu, *J. Am. Chem. Soc.* 133 (2011) 11822.
- [100] Y. Huang, X. Zhou, M. Yin, C. Liu, W. Xing, *Chem. Mater.* 22 (2010) 5122.
- [101] Z.-L. Wang, J.-M. Yan, Y. Ping, H.-L. Wang, W.-T. Zheng, Q. Jiang, *Angew. Chem. Int. Ed.* 52 (2013) 4406.
- [102] Y.-L. Qin, J. Wang, F.-Z. Meng, L.-M. Wang, X.-B. Zhang, *Chem. Commun.* 49 (2013) 10028.
- [103] Z.-L. Wang, H.-L. Wang, J.-M. Yan, Y. Ping, S.-I. O, S.-J. Li, Q. Jiang, *Chem. Commun.* 50 (2014) 2732.
- [104] F.-Z. Song, Q.-L. Zhu, N. Tsumori, Q. Xu, *ACS Catal.* (2015) 5141.
- [105] T. Schaub, R.A. Paciello, *Angew. Chem. Int. Ed.* 50 (2011) 7278.
- [106] R. Fornika, H. Gölz, B. Seemann, W. Leitner, *Chem. Commun.* (1995) 1479.
- [107] F. Gassner, W. Leitner, *Chem. Commun.* (1993) 1465.
- [108] Y. Himeda, N. Onozawa-Komatsuzaki, H. Sugihara, K. Kasuga, *Organometallics* 26 (2007) 702.
- [109] J.F. Hull, Y. Himeda, W.-H. Wang, B. Hashiguchi, R. Periana, D.J. Szalda, J.T. Muckerman, E. Fujita, *Nat Chem* 4 (2012) 383.
- [110] Y. Maenaka, T. Suenobu, S. Fukuzumi, *Energy Environ. Sci.* 5 (2012) 7360.
- [111] A. Boddien, F. Gärtner, C. Federsel, P. Sponholz, D. Mellmann, R. Jackstell, H. Junge, M. Beller, *Angew. Chem. Int. Ed.* 50 (2011) 6411.
- [112] P.G. Jessop, T. Ikariya, R. Noyori, *Nature* 368 (1994) 231.
- [113] P. Munshi, A.D. Main, J.C. Linehan, C.-C. Tai, P.G. Jessop, *J. Am. Chem. Soc.* 124 (2002) 7963.
- [114] S. Moret, P.J. Dyson, G. Laurenczy, *Nat Commun* (2014) 5.
- [115] M.W. Farlow, H. Adkins, *J. Am. Chem. Soc.* 57 (1935) 2222.
- [116] H. Wiener, J. Blum, H. Feilchenfeld, Y. Sasson, N. Zalmanov, *J. Catal.* 110 (1988) 184.
- [117] D. Preti, C. Resta, S. Squarcialupi, G. Fachinetti, *Angew. Chem. Int. Ed.* 50 (2011) 12551.
- [118] M. Grellier, S. Sabo-Etienne, *Dalton Trans.* 43 (2014) 6283.
- [119] K.N.T. Tseng, A.M. Rizzi, N.K. Szymczak, *J. Am. Chem. Soc.* 135 (2013) 16352.
- [120] J. Chen, G. Wu, Z. Xiong, H. Wu, Y.S. Chua, W. Zhou, B. Liu, X. Ju, P. Chen, *Chem.-Eur. J.* 20 (2014) 13636.
- [121] J. Chen, H. Wu, G. Wu, Z. Xiong, R. Wang, H. Fan, W. Zhou, B. Liu, Y. Chua, X. Ju, P. Chen, *Chem.-Eur. J.* 20 (2014) 6632.
- [122] M. Nielsen, E. Alberico, W. Baumann, H.-J. Drexler, H. Junge, S. Gladiali, M. Beller, *Nature* 495 (2013) 85.