

# Toward a Hydrogen Economy: Development of Heterogeneous Catalysts for Chemical Hydrogen Storage and Release Reactions

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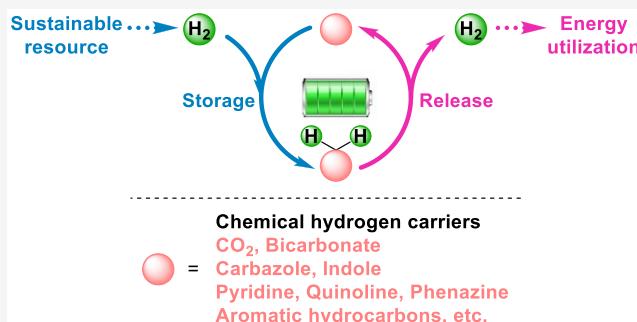
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**ABSTRACT:** Chemical hydrogen storage and release processes are essential steps for the implementation of new energy vectors. In general, the individual reactions involved in such technologies need catalysts to allow discharging and recharging hydrogen in a stable and efficient manner. In recent years, the development of hydrogen storage materials and their use in renewable energy systems have experienced rapid growth. While many academic works in this area make use of homogeneous catalysts, there is the practical need for heterogeneous catalytic systems, which often can be more easily applied on a larger industrial scale. In this Review we highlight the present status of using heterogeneous materials as catalysts for both chemical hydrogen storage and release systems, providing detailed reaction parameters for practical demonstration. The pros and cons of the currently known systems and their differences relative to homogeneous catalysts are also explained and critically discussed.

**H**ydrogen ( $\text{H}_2$ ) is considered a clean and more sustainable energy carrier compared to fossil fuels, and it offers many opportunities to solve environmental concerns originating from the vast consumption of coal, gas, and oil in the past decades.<sup>1–3</sup> In general, significant amounts of electric energy can be provided on demand via the application of hydrogen in fuel cells, on the basis of the combustion reaction equation:  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ , 284 kJ mol<sup>-1</sup>. In contrast to the combustion of fossil fuels, only water is produced as a byproduct in such hydrogen-based energy conversion processes.<sup>4–7</sup> However, still today most of the hydrogen produced is based on natural gas, nowadays so-called “grey hydrogen”. In contrast, “green hydrogen” production is driven by sustainable energy, e.g., solar, wind, and waste stream sources.<sup>4–11</sup> It is predicted that these technologies will be implemented on a large industrial scale in the coming decades.<sup>12,13</sup> On the other hand, one of the well-known fuel cell technologies, proton exchange membrane fuel cells (PEMFCs), was significantly improved, and some of them have been already adopted in fuel-cell-powered vehicles.<sup>14,15</sup> Apart from the direct usage of hydrogen, various approaches for hydrogen storage after its green production and subsequent delivery for energy conversion processes are currently being intensively studied due to the extremely low volumetric storage



density of gaseous hydrogen (2.5 Wh L<sup>-1</sup>).<sup>16</sup> In this respect, the development of chemical  $\text{H}_2$  storage–release technologies, so-called “chemical hydrogen batteries”, will help to bridge green hydrogen production and its utilization in energy vectors.

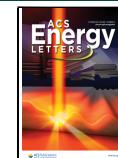
## ■ CHEMICAL HYDROGEN STORAGE

In comparison with the physical  $\text{H}_2$  storage approaches, e.g., compressed gaseous hydrogen with pressure up to 700 bar (40 g  $\text{H}_2$  L<sup>-1</sup>) or the liquid hydrogen with temperature as low as -253 °C (70 g  $\text{H}_2$  L<sup>-1</sup>),<sup>2,17,18</sup> chemical hydrogen storage is based on the reversible hydrogenation/dehydrogenation of specific organic and inorganic molecules. Following this concept, typically functionalized substrates, e.g., esters, acids, ketones, imines, nitriles, or (hetero)arenes, are hydrogenated to the corresponding alcohol, amine, and aliphatics which can

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**Table 1.** Comparative Physicochemical Data for Various Well-Recognized Hydrogen Carriers

category	storage medium	storage conditions	density (g cm <sup>-3</sup> )	hydrogen content		ref
				(wt%)	(g L <sup>-1</sup> )	
hydrogen	H <sub>2</sub> (gas)	700 bar	—	—	42	<sup>18</sup>
	H <sub>2</sub> (gas)	200 bar	—	—	14	<sup>26</sup>
	H <sub>2</sub> (liquid)	−253 °C	—	—	70	<sup>18</sup>
C1 compounds	methanol	ambient	0.791	12.6	100	<sup>27</sup>
	formic acid	ambient	1.22	4.35	53	<sup>27</sup>
	sodium formate/H <sub>2</sub> O	ambient	—	2.32	—	<sup>28</sup>
	potassium formate/H <sub>2</sub> O	ambient	—	1.97	—	<sup>28</sup>
	ammonium formate/H <sub>2</sub> O	ambient	—	2.49	—	
Cycloalkanes	cyclohexane	ambient	0.779	7.19	56	<sup>29</sup>
	methylcyclohexane	ambient	0.77	6.18	47	<sup>29</sup>
	decalin	ambient	0.869	7.23	65	<sup>29</sup>
	bicyclohexyl	ambient	0.883	7.22	64	<sup>30</sup>
	perhydroterphenyl	ambient	—	7.25	—	<sup>31</sup>
	perhydridobenzyltoluene (H <sub>18</sub> -DBT)	ambient	—	6.20	—	<sup>29</sup>
N-substituted heterocycles	dodecahydrocarbazole	ambient	1.298	6.69	87	<sup>30</sup>
	dodecahydro-N-ethylcarbazole (H <sub>12</sub> -NEC)	ambient	0.931	5.79	54	<sup>29,32</sup>
	dodecahydro-N-propylcarbazole (H <sub>12</sub> -NPC)	ambient	—	5.43	—	<sup>29</sup>
	octahydro-indole	ambient	0.938	6.39	60	<sup>29</sup>
	N-methylindoline	ambient	1.051	5.76	—	<sup>29</sup>
	N-ethylindoline	ambient	—	5.23	—	<sup>29</sup>
	octahydro-7-ethylindole	ambient	0.997	5.23	52	<sup>33</sup>
	1,2-dimethylindoline	ambient	—	5.23	—	<sup>34</sup>
	2,3-dimethylindoline	ambient	—	5.23	—	<sup>35</sup>
	1,2,3,4-tetrahydroquinoline	ambient	1.061	3.00	32	<sup>36</sup>
	1,2,3,4-tetrahydroquinaldine	ambient	0.966	2.71	26	<sup>37</sup>
	4-aminopiperidine	ambient	0.945	5.99	57	<sup>29</sup>
	piperidine-4-carboxamide	ambient	—	4.68	—	<sup>29</sup>

be recovered back to the original substrate under appropriate conditions (temperature, pressure, etc.) and thereby deliver hydrogen on demand. In general, chemical H<sub>2</sub> carriers have the following advantages: tunable hydrogen density at comparably low cost; flexible usage for mobile applications; storage possible under mild conditions, even in ambient environment (temperature and pressure); comparably easy transportation with simpler operation/handling protocol; low requirements for equipment/devices; and less environmental burden (Table 1).<sup>19–21</sup> The volumetric energy density of chemical hydrogen storage systems is generally high (ca. 2 kWh L<sup>-1</sup>) compared to H<sub>2</sub> pressure storage (0.53 kWh L<sup>-1</sup> at 200 bar). As representatives, toluene and dibenzyltoluene (DBT) proved themselves to be promising carrier systems in worldwide research activities. To substitute the toxic benzene/cyclohexane system, toluene/methylcyclohexane (MCH) provides the simplest applied hydrogen carrier system, containing 6.18 wt% hydrogen, although toluene is harmful to health and has a comparatively high vapor pressure. Similarly, the dibenzyltoluene/perhydridobenzyltoluene (DBT/H<sub>18</sub>-DBT) pair has a hydrogen content of 6.20 wt%, which corresponds to an energy density of 2.5 kWh kg<sup>-1</sup>.

Although numerous research groups have put forth extensive efforts, in the past decades, to improve the reaction rate in both H<sub>2</sub> storage and release processes, the concept of circular chemical hydrogen batteries is still in its early stage of commercialization due to the difficulties in performing the single steps under similar conditions in one device, *vide infra*.

For such integrated systems, it is not enough to develop catalysts that are practically stable and robust, but more importantly they must realize an efficient overall cyclic performance in both hydrogen storage and release reactions, ideally with the same catalyst and reaction system. In addition, the transformation/storage of hydrogen gas in stable, non-toxic solid or liquid compounds and the reverse process<sup>3,22–25</sup> should be possible for at least several thousand cycles to allow for implementation and a real shift toward alternative clean energy technologies.

**It is not enough to develop catalysts that are practically stable and robust, but more importantly they must realize an efficient overall cyclic performance in both hydrogen storage and release reactions.**

In the area of chemical hydrogen storage and release, many outstanding reviews, perspectives, and accounts on heterogeneous and homogeneous catalytic systems have sprung up,<sup>17,26,38–44</sup> most of which focus on one of the chemical H<sub>2</sub> carriers [formic acid (including formate salts),<sup>45–52</sup> N-heterocycles,<sup>18,30,53–56</sup> (aromatic) hydrocarbons,<sup>23,57–60</sup> ammonia,<sup>18,61</sup> ammonia–borane,<sup>62</sup> or dimethyl ether<sup>63</sup>] or on the individual hydrogen production/release reactions.<sup>64–71</sup> Nota-

bly, in a large proportion of the previous reports, only one individual reaction, either H<sub>2</sub> storage or H<sub>2</sub> release, is involved or discussed rather than combining those individual reactions to demonstrate the overall concept of chemical H<sub>2</sub> batteries; even the research works are very often entitled to contain the topic of "H<sub>2</sub> storage and release". Those examples are not considered in this Review. In contrast, the present Review provides a comprehensive viewpoint on a broader range of chemical hydrogen carriers. Special emphasis is put on reaction systems which allow for combined H<sub>2</sub> storage and release cycles beyond individual hydrogenation or dehydrogenation reactions. To be clear, we distinguish three development stages on the way to a hydrogen battery (Figure 1): (A) the

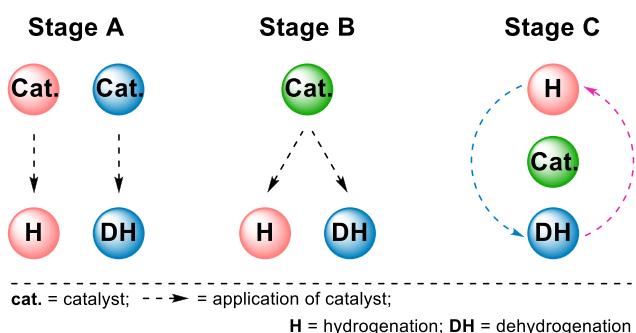


Figure 1. Catalyst development stages on the way to a chemical hydrogen battery.

development and optimization of the individual hydrogenation and dehydrogenation reactions of substrates/products known as hydrogen carrier molecules, (B) the successful application of the same catalyst system in both directions, and (C) finally the integration of the reversible (de)hydrogenation processes in one reactor/device which mimics the classic rechargeable electric battery.

## ■ THE IMPORTANCE OF CATALYSTS: PROS AND CONS OF HETEROGENEOUS AND HOMOGENEOUS CATALYSTS

To be clear, a general hydrogen storage system as described above is much more than the combination of the individual catalytic hydrogenation and dehydrogenation reactions. Nevertheless, the use of an appropriate catalyst or catalysts for these individual steps is crucial for the design and the performance of the overall system. Even though high catalytic activities (TON: turnover number, TOF: turnover frequency) in the respective hydrogen storage and release processes are achieved by using homogeneous catalysts, compared to heterogeneous ones, intrinsic drawbacks such as air sensitivity, requirement of expensive coordinating ligands, use of organic solvents and additives, difficulty in handling, and separation of the respective organometallic complex from the reaction mixture all limit their practical implementation. In this respect, at least some of the above-mentioned drawbacks could be resolved by applying suitably active catalysts based on heterogeneous materials. Since the thermal stability of heterogeneous catalysts is generally superior after annealing at high temperature, the separation, recycling, and regeneration of heterogeneous catalysts is straightforward and low-cost, providing an important consideration for industrial-scale manufacturing processes. However, limitations of heterogeneous catalysis

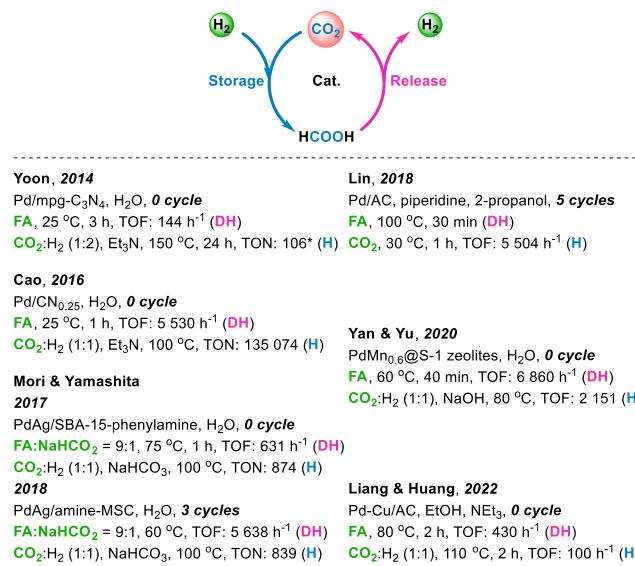
are the insufficient surface area of the catalysts and mass transfer resistance, due to which the adsorption step in a heterogeneous process is often the rate-limiting step for practical applications. Comparing the different benefits and disadvantages of homogeneous and heterogeneous catalysts, we believe at present it is more realistic that the latter ones will be used for first implementations.

## ■ CARBON DIOXIDE AND FORMIC ACID COUPLE

Apart from the nitrogen/ammonia couple, reversible hydrogen storage based on CO<sub>2</sub> is highly attractive, since CO<sub>2</sub> is one of the significant greenhouse gases and occurs as a waste in many industrial processes. In general, C1 products of, i.e., formic acid (FA) derivatives, formaldehyde, methanol, and methane can be generated by CO<sub>2</sub> hydrogenation. However, to the best of our knowledge, the above-mentioned development stages B and C (see Figure 1) have been demonstrated for the interconversion of CO<sub>2</sub> and FA so far. Advantageously, FA and its formate salts are readily available from biomass or catalytic CO<sub>2</sub> hydrogenation under relatively mild conditions.<sup>72</sup> Notably, thermal (or catalytic) decomposition of FA or formates easily generates CO as an unwanted byproduct, which hampers not only the catalytic activity of FA dehydrogenation but also subsequent fuel cell applications, as CO rapidly poisons electrocatalysts in PEMFC applications.<sup>73</sup>

Hydrogen storage in the form of FA has various advantages. First, the hydrogenation of gaseous CO<sub>2</sub> has a positive free energy change (CO<sub>2</sub>(g) + H<sub>2</sub>(g) → HCOOH(l), ΔG<sub>298K</sub> = +32.9 kJ mol<sup>-1</sup>),<sup>69,74</sup> while performing the same reaction in aqueous solution leads to low free energy (ΔG = -4 kJ mol<sup>-1</sup>).<sup>74,75</sup> On the other hand, FA decomposition via a selective dehydrogenation pathway (HCOOH(l) → CO<sub>2</sub>(g) + H<sub>2</sub>(g), ΔG<sub>298K</sub> = -32.9 kJ mol<sup>-1</sup>)<sup>69</sup> is thermodynamically favored, indicating FA is readily dehydrogenated, compared to its competing dehydration reaction (HCOOH(l) → CO(g) + H<sub>2</sub>O(l), ΔG<sub>298K</sub> = -12.4 kJ mol<sup>-1</sup>),<sup>69</sup> which is beneficial since the produced CO is not only a highly toxic gas but also capable of poisoning the electrocatalysts in the fuel cell demonstrations.<sup>73</sup> Although significant development of homogeneous organometallic complexes has taken place in the past two decades, progress with heterogeneous materials has unfortunately not reached the same level as CO<sub>2</sub> hydrogenation to FA, formates, and methanol<sup>76–83</sup> and corresponding hydrogen productions.<sup>65–68,71,84–87</sup>

As early as the 1970s, Williams et al. proposed an ideal cycle of hydrogen storage and release involving reversible FA and CO<sub>2</sub> transformations<sup>88</sup> (Figure 2, circular reaction scheme), where H<sub>2</sub> is stored together with CO<sub>2</sub> in the form of FA with 100% atom efficiency, and later FA could be dehydrogenated selectively into H<sub>2</sub> as required. On the other hand, in the presence of bases, the equivalent hydrogen storage cycle employing chemical carriers is shifted to the formate and bicarbonate salts, which are also viable approaches, as suggested by Zaidman et al. (see below, Figure 4, circular reaction scheme).<sup>89</sup> Following such concepts, chemical hydrogen batteries based on CO<sub>2</sub> or bicarbonates have been developed. As representatives, the hydrogen storage and release based on interconversion of CO<sub>2</sub> (or bicarbonate) and FA (or formate) has been established utilizing homogeneous catalysts,<sup>16,27,90–94</sup> especially applying noble metals Rh,<sup>95,96</sup> Ru,<sup>96–105</sup> and Ir<sup>106–110</sup> and base metals Ni,<sup>111</sup> Fe,<sup>105,112</sup> and Mn.<sup>113</sup> Corresponding applications based on CO<sub>2</sub>/FA and bicarbonate/formate salts promoted by hetero-



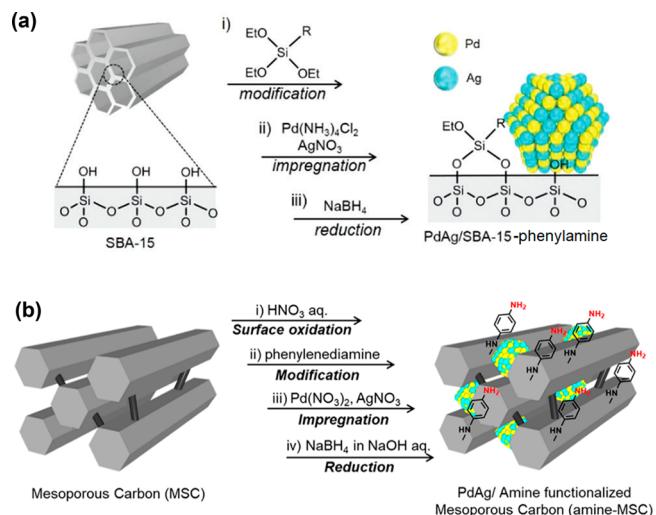
**Figure 2.** Heterogeneous catalyst-promoted hydrogen storage and release cycles based on the interconversion of  $\text{CO}_2$  and formic acid. Abbreviations: DH, dehydrogenation; H, hydrogenation; FA, formic acid; mpg- $\text{C}_3\text{N}_4$ , mesoporous graphitic carbon nitride; MSC, mesoporous carbon; AC, active carbon. \*Calculated values based on the data provided in the original publication.

geneous catalysts are summarized in Figure 2 and Figure 4, respectively.

One of the first examples of a heterogeneous catalytic system for reversible  $\text{CO}_2$  hydrogenation reactions dates back to 2014, when the group of Yoon reported the preparation of Pd nanoparticles (NPs) supported on mesoporous graphitic carbon nitride (mpg- $\text{C}_3\text{N}_4$ ) and its catalytic application in FA-based hydrogen storage–release.<sup>114</sup> The Pd/mpg- $\text{C}_3\text{N}_4$  catalyst exhibits activity for the dehydrogenation of FA with a TOF of 144  $\text{h}^{-1}$  in the absence of any base/additive at room temperature (r.t., 25 °C) and a TON of 106 for  $\text{CO}_2$  hydrogenation at 150 °C with triethylamine (NEt<sub>3</sub>) as  $\text{CO}_2$  absorbent (Figure 2). Unfortunately, no combined chemical  $\text{H}_2$  storage–release cycle was achieved with such a catalyst at that time.

In 2016, Cao's group found that employing a controlled synthetic approach involving a biochitosan-based pyrolysis strategy—the incorporation of Pd NPs on flexible pyridinic-N-doped carbon hybrids (CN) as support materials—can improve the efficiency of  $\text{H}_2$  generation from aqueous FA at r.t. and base-free conditions. The Pd/CN<sub>0.25</sub> catalyst exhibited high activity in both FA dehydrogenation (TOF = 5 530  $\text{h}^{-1}$  at 25 °C) and the reversible process of  $\text{CO}_2$  hydrogenation into FA (TOF = 135 074  $\text{h}^{-1}$  at 100 °C).<sup>115</sup> Even though the authors described that the system can be used conceptually in a carbon-neutral hydrogen storage–release cycle by recycling the  $\text{CO}_2$  back to the reaction mixture, the corresponding cyclic performance of hydrogen storage and release was never shown.

In 2017, Yamashita, Mori, and co-workers reported Pd-Ag-based bimetallic NPs supported on a basic phenylamine-functionalized mesoporous silica (SBA-15, Figure 3a) as heterogeneous catalyst for the  $\text{H}_2$  storage and release reactions mediated by FA and  $\text{CO}_2$ .<sup>116</sup> Compared to the monometallic Pd analogue, the PdAg/SBA-15-phenylamine material is superior in the same reaction at least by 3-fold. On the other hand, the pure Ag catalyst is found completely inactive,



**Figure 3.** Schematic illustration of the preparation of Pd-Ag-based bimetallic nanoparticles. (a) Supported on SBA-15-phenylamine (R = *para*-phenylamine). Reprinted with permission from ref 116. Copyright 2017 Royal Society of Chemistry. (b) Supported on amine-MSC. Reprinted with permission from ref 117. Copyright 2018 American Chemical Society.

indicating the synergic alloying effect of the Pd and Ag metals. Owing to the high efficiency of such a catalyst in FA dehydrogenation (TOF = 631  $\text{h}^{-1}$ ) and  $\text{CO}_2$  hydrogenation (TON = 874) processes, experiments to recycle the catalyst were performed on the respective (de)hydrogenation reactions. However, again no combined  $\text{H}_2$  storage–release cycle was achieved (Figure 2).

One year later, the same group developed highly dispersed Pd-Ag NPs supported on phenylamine-functionalized mesoporous carbon (MSC) for the catalytic interconversion of  $\text{CO}_2$  and FA (Figure 3b).<sup>117</sup> The reversible transformation of  $\text{CO}_2$  and FA was promoted by the PdAg/amine-MSC heterogeneous catalyst, which exhibited good reusability in at least three cycles of combined  $\text{H}_2$  storage and release without significant loss of activity. Specifically, the catalyst was recovered and collected by centrifugation and redispersed to the reaction mixtures for the subsequent runs. Both experimental and theoretical studies revealed that the cooperative performance of the amine groups in the vicinity of active Pd-Ag NPs significantly affected the O–H dissociation of FA as well as the  $\text{CO}_2$  adsorption capacity of the catalyst, which greatly boosted the catalytic activity in the individual reactions. Additionally, to show the potential application for further commercialization, flow chemistry experiments on the dehydrogenation of FA were demonstrated using a fixed-bed reactor with the same catalyst.

An alternative approach in reversible hydrogen storage was developed by Lin's group in the same year via the hydrogenation of piperidine-captured  $\text{CO}_2$  in isopropanol solutions (70 wt%) and dehydrogenation of piperidine–FA adducts.<sup>118</sup> Specifically, the reactions were promoted by a palladium nanocatalyst supported on active carbon (AC) for the CO- and NH<sub>3</sub>-free hydrogen production. Based on such high efficiency in the respective reactions, combined hydrogenation–dehydrogenation cycles were achieved, which showed only slight losses of catalyst activity after 5 cyclic runs (Figure 2).

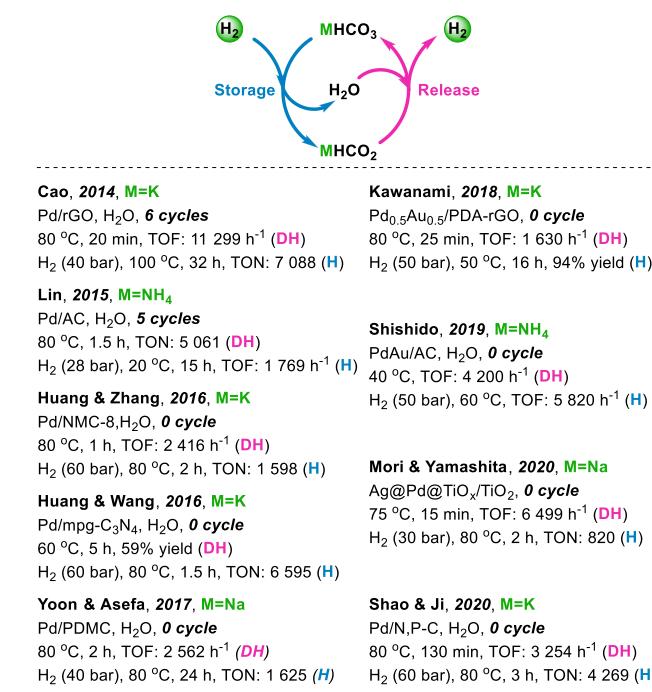
In 2020, silicalite-1 zeolites (S-1) encaging a Pd-Mn cluster ( $\text{PdMn}_{0.6}@\text{S-1}$ ) were prepared by Yan and Yu<sup>119</sup> by using direct hydrothermal methods. The optimal catalyst exhibited good catalytic activity and stability in both  $\text{CO}_2$  hydrogenations and FA dehydrogenations (Figure 2). The observed activity was attributed to the formation of ultrafine and well-dispersed metal clusters and the synergic effect between the bimetallic Pd-Mn NPs. Early this year (2022), bimetallic Pd-Au/AC catalysts were developed by using a biomass-reduction method for  $\text{CO}_2$  hydrogenation ( $\text{TOF} = 100 \text{ h}^{-1}$ ) and FA dehydrogenation ( $\text{TOF} = 403 \text{ h}^{-1}$ ), as disclosed by Liang and Huang.<sup>120</sup> Notably, the presence of a base ( $\text{NEt}_3$ ) is necessary in both  $\text{H}_2$  storage and  $\text{H}_2$  release reactions. Despite the high efficiency of such catalysts in reversible  $\text{CO}_2$  hydrogenation processes in the above-mentioned two examples,<sup>119,120</sup> the  $\text{CO}_2$ -mediated combined  $\text{H}_2$  storage–release cycle was eventually not realized.

## BICARBONATE AND FORMATE PAIRS

Like FA, various formate salts or derivatives could also be used as chemical hydrogen carriers. While only a few catalyst systems are persistent in concentrated FA due to the strong acidic conditions, formate salts are non-acidic, non-volatile, often non-toxic, and non-corrosive and thereby provide a convenient reaction medium. Although the Gibbs free energy of hydrogen production starting from formate salts (e.g.,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\Delta G = 1 \text{ kJ mol}^{-1}$ ) is not as favorable as that from FA ( $\Delta G = -32.9 \text{ kJ mol}^{-1}$ ), decomposition of formate salts is neither endergonic nor exergonic, making the formate/bicarbonate pair more thermodynamically suitable for reversible  $\text{H}_2$  storage–release cycles at ambient conditions.<sup>75</sup> On the other hand, one of the concerns in the application of the formate/bicarbonate couple is the solubility of the corresponding salts. For example, the molar solubilities (mol salt in 100 mL  $\text{H}_2\text{O}$ , 20 °C) of formate salts based on different cations are ranked in the following sequence:  $\text{Rb}^+$  (4.25) >  $\text{K}^+$  (4.01) >  $\text{NH}_4^+$  (2.26) >  $\text{Cs}^+$  (2.14) >  $\text{Na}^+$  (1.19) >  $\text{Li}^+$  (0.76).<sup>90,121</sup> This solubility likely affects the amount of  $\text{H}_2$  uptake and thereby is an important factor for the hydrogen density achievable for the overall reaction system.

One of the first heterogeneous catalytic systems for the reversible transformation of aqueous potassium bicarbonate to formate was developed by Cao and co-workers in 2014.<sup>28</sup> The generation of highly strained Pd NPs was achieved on a support based on reduced graphene oxide (rGO) nanosheets. This catalyst enabled 6 cyclic interconversions of formate and bicarbonate salts under comparably mild reaction conditions (80/100 °C), and the reversible hydrogen storage and release was regulated by modifying the reaction temperature and hydrogen pressure (Figure 4). In 2015, Lin and co-workers reported an aqueous ammonium bicarbonate–formate equilibrium as a hydrogen storage system with an advantageous higher  $\text{H}_2$  content (2.49 wt%).<sup>122</sup> Fast reaction rates of both hydrogenation and dehydrogenation were observed at 20 and 80 °C, respectively, with the same Pd/AC catalyst. By regulating reaction parameters, e.g., temperature and  $\text{H}_2$  pressure, the switch between hydrogen storage and release steps could be well controlled.

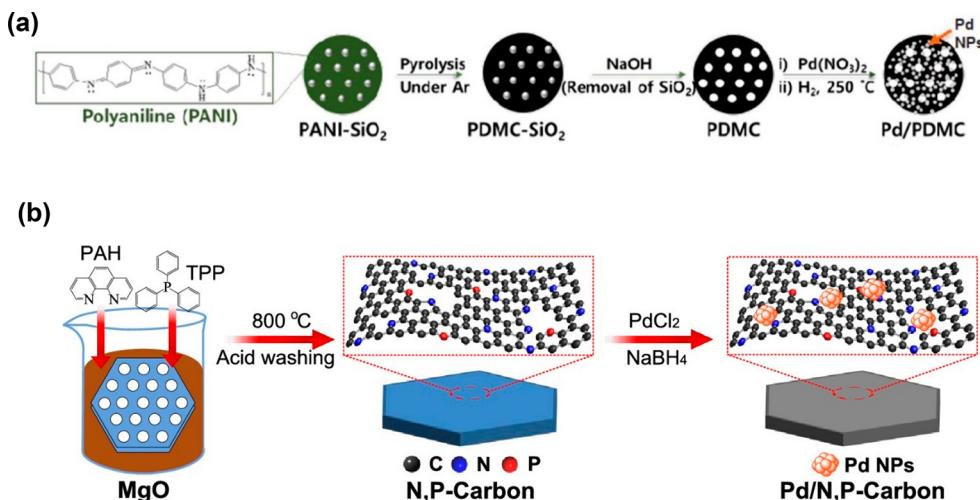
Soon after, in 2016, a catalytic system based on nitrogen-doped mesoporous carbon (NMC)-supported Pd NPs was disclosed by the groups of Huang and Zhang. Here, the support was prepared by a so-called hard template method using the mesoporous material Zr-SBA-15<sup>123</sup> and nitridated



**Figure 4.** Hydrogen storage–release cycles based on the interconversion of bicarbonate and formate salts promoted by heterogeneous Pd catalysts. Abbreviations: rGO, reduced graphene oxide; AC, activated carbon; NMC, nitrogen-doped mesoporous carbon; mpg-C<sub>3</sub>N<sub>4</sub>, mesoporous graphitic carbon nitride; PDMC, polyaniline-derived mesoporous carbon; PDA-rGO, phenylenediamine-alkalized reduced graphene oxide.

under ammonia flow.<sup>124</sup> A detailed study of the preparation procedure revealed that nitrogen doping played a crucial role in promoting the bicarbonate/formate interconversion with synergistic interaction of restraining the aggregation and increasing the electron density of Pd. In the same year, a related catalyst system, Pd NPs supported on mesoporous graphitic carbon nitride (mpg-C<sub>3</sub>N<sub>4</sub>), was reported for potassium formate-based reversible hydrogen storage at 60/80 °C by Huang and Wang.<sup>125</sup> The reusability of the Pd catalyst was demonstrated up to 6 times in hydrogenation and 3 times in dehydrogenation without obvious catalyst deactivation observed. It was proposed that the large number of nitrogen atoms in the mpg-C<sub>3</sub>N<sub>4</sub> support is likely the origin of the catalytic activity.

One year later, Asefa and Yoon reported the synthesis of polyaniline-derived N-doped mesoporous carbon (PDMC)-supported Pd NPs (Pd/PDMC, Figure 5a), which showed excellent catalytic activity in sodium formate dehydrogenation ( $\text{TOF} = 2562 \text{ h}^{-1}$ ) and sodium bicarbonate hydrogenation ( $\text{TON} = 1625$ , Figure 4).<sup>126</sup> Fundamental mechanistic studies based on density functional theory (DFT) calculations of the reversible reaction pathways for (de)hydrogenation on Pd-based heterogeneous catalyst were reported by Lim and Yoon as a basis for further reactivity improvement.<sup>128</sup> The rate-determining steps for the reversible reaction were found to be the desorption of hydrogen in dehydrogenation (1.24 eV) and hydrogenation (1.49 eV). Further, the appropriate level of N-doping is necessary to improve the efficiency of the reversible reactions, based on the optimal electronic and geometrical properties of the catalyst material.



**Figure 5.** (a) Schematic illustration of the preparation of polyaniline-derived N-doped mesoporous carbon-supported Pd nanoparticles (Pd/PDMC) materials. Reprinted with permission from ref 126. Copyright 2017 Elsevier. (b) Schematic illustration of the preparation of N,P-C support and Pd/N,P-C catalyst. Reprinted with permission from ref 127. Copyright 2020 American Chemical Society.

The appropriate level of N-doping is necessary to improve the efficiency of the reversible reactions.

More recently, a Pd-Au bimetallic catalyst supported on phenylenediamine-alkalized reduced graphene oxide (PDA-rGO) was developed by Kawanami and co-workers to promote the CO<sub>2</sub>-bicarbonate hydrogenation and FA-formate dehydrogenation.<sup>129</sup> In this work, the Pd<sub>0.5</sub>Au<sub>0.5</sub>/PDA-rGO catalyst provided 94% and 90% yields in the hydrogenation of KHCO<sub>3</sub> at 50 and 30 °C, respectively, within 16 h. Initial TOFs up to 1630 h<sup>-1</sup> and 6980 h<sup>-1</sup> were achieved at 80 °C in the dehydrogenation of KHCO<sub>2</sub> and FA, respectively (Figure 4).

Similarly, activated carbon supported Pd-Au alloy catalysts (Pd<sub>x</sub>Au<sub>x</sub>/AC) were prepared by Shishido's group in 2019 for the ammonium bicarbonate-formate-based reversible hydrogen storage and release processes.<sup>130</sup> Without further additive present, Pd-Au bimetallic catalysts exhibited superior activities compared to the monometallic Pd or Au analogues in hydrogenative (5820 h<sup>-1</sup>) and dehydrogenative (4200 h<sup>-1</sup>) reaction steps under ambient conditions. TOFs of the hydrogenation reactions were found to increase with the Au/Pd ratio, while a catalyst with Pd:Au = 1:1 showed optimal TOF in the dehydrogenation reaction.

Compared to the previously reported examples of binary alloys, Mori and Yamashita<sup>131</sup> presented in 2020 a study in which bimetallic Pd-Ag alloy NPs supported on rutile (TiO<sub>2</sub>) exhibited higher productivity in sodium bicarbonate hydrogenation (TON = 820) and higher activity in sodium formate dehydrogenation (TOF = 6499 h<sup>-1</sup>). Kinetic studies for both reaction directions revealed that it is the presence of the Ag sites and the TiO<sub>x</sub> shell in the periphery of the Pd which promoted the rate-limiting C-H bond dissociation process during dehydrogenation and facilitated bicarbonate adsorption and activation during the hydrogenation step. In the same year, Shao and Ji reported another Pd NPs catalyst supported on N and P co-doped porous carbon by direct thermal annealing of a mixture of 1,10-phenanthroline and triphenylphosphine for reversible formate-bicarbonate transformations (Figure

5b).<sup>127</sup> The synergistic effects of N and P co-dopants in regulating the electronic properties of carbon support were verified by DFT studies. Moreover, the Pd/N,P-C catalyst possessed an excellent stability with no observed deactivation after 5 times of dehydrogenation and 3 times of hydrogenation, respectively (Figure 4).

## ■ N-HETEROCYCLES: CARBAZOLE AND INDOLE DERIVATIVES

In addition to the FA/CO<sub>2</sub> couple, especially (hetero)arenes have been demonstrated to be reversible hydrogen storage media. Typically, the substrates represent stable, non-flammable, high-boiling compounds with higher molecular weights that are able to take up and release more hydrogen molecules.<sup>132</sup> Hydrogen storage and release systems based on the interconversion of N-heterocyclic aromatic compounds and their hydrogenated/saturated counterparts have been evaluated with a variety of homogeneous organometallic catalysts,<sup>133</sup> e.g., Ir,<sup>134–141</sup> Fe,<sup>142,143</sup> Co,<sup>144</sup> Mn<sup>145</sup> (quinolines), and Ir<sup>146</sup> (pyrazine), and photoredox Ru complexes with Co or Ir co-catalysts (quinolines).<sup>147</sup> It should be noted that the oxidative dehydrogenation of N-heterocycles, for example under aerobic conditions,<sup>148–151</sup> is not considered as a hydrogen production process, since no hydrogen molecule could be delivered.

Among the various studied heterocycles, N-ethylcarbazole (NEC) is considered as the most prominent example. Compared to the aromatic compounds (e.g., toluene), the reaction enthalpy of NEC/H<sub>12</sub>-NEC is reduced by ca. 30% owing to the heteroaromatic character, thus providing a higher efficiency of dehydrogenation. However, the poor availability of NEC and its melting point of 69 °C prove to be disadvantageous. For this substrate also heterogeneous catalysts were applied for hydrogenation and dehydrogenation under relatively mild reaction conditions.<sup>152,153</sup> NEC has a hydrogen capacity of 5.79 wt% (Table 1) and low toxicity, whereas the hydrogenated product, dodecahydro-N-ethylcarbazole (H<sub>12</sub>-NEC), is a liquid under ambient conditions with a boiling point above 220 °C.<sup>154,155</sup> Those physical properties make it convenient for transportation and handing. The respective hydrogenation and dehydrogenation reactions

(stage A, Figure 1) were well-developed with heterogeneous catalysts, e.g., hydrogenation of carbazole derivatives with Ru,<sup>156–162</sup> Ru-Ni,<sup>163,164</sup> Ni/Al<sub>2</sub>O<sub>3</sub>-YH<sub>3</sub><sup>165</sup> based catalysts and dehydrogenation<sup>166</sup> of H<sub>12</sub>-NEC with Pt,<sup>167,168</sup> Pd,<sup>32,169–176</sup> Au/Pd<sup>177</sup> based catalysts and octahydroindole.<sup>178–181</sup>

NEC hydrogenation and H<sub>12</sub>-NEC dehydrogenation are exothermic and endothermic reactions, respectively (76 kJ mol<sup>−1</sup>). As an example, the activation energy barrier of NEC hydrogenation is 99 kJ mol<sup>−1</sup> on a specific supported Ru catalyst, where Ru/Al<sub>2</sub>O<sub>3</sub> generally offers the optimal reactivity.<sup>30</sup> The sequences of the catalytic activity of several metals in the hydrogenation and the dehydrogenation steps are Ru > Pd > Pt > Ni<sup>182,183</sup> and Pd > Pt > Ru > Rh,<sup>184</sup> respectively. Based on this general trend, bimetallic Pd-Ru composite catalysts were proposed as suitable catalyst systems,<sup>29,185</sup> while the single Pd or Ru metal catalysts are unqualified to promote both hydrogenation and dehydrogenation reactions. However, due to the more complex structures of those multicarbon H<sub>2</sub> carriers, side reactions with selectivity issues are often reported, too. Therefore, the main goal for the catalyst development of such substrates is to decrease the dehydrogenation temperature, control the chemoselectivity, and increase the stability.

As early as 2005, in the patents of Pez et al.,<sup>186–191</sup> several (hetero)arenes were applied as liquid organic hydrogen carriers (LOHCs) in a single reactor for the catalytic hydrogenation and dehydrogenation reactions. For example, (de)-hydrogenation of NEC/H<sub>12</sub>-NEC proceeded in the presence of commercial Rh/C as catalyst at 125 °C. The catalyst could be reused for consecutive (de)hydrogenations (stage C, Figure 1) after removing the substrates and/or products by extraction with acetone. The incorporation of heteroatoms such as N, S, and O into the aromatic ring of the substrates favored especially the thermodynamics and kinetics of the dehydrogenation processes, which can be performed at comparably low temperature (<200 °C). The reversible transformation between NEC and H<sub>12</sub>-NEC was also investigated by Smith and co-workers in 2009<sup>32</sup> and 2010.<sup>192</sup> The hydrogenation of NEC follows a first-order kinetics and was faster than that of the unsubstituted carbazole over a Ru/Al<sub>2</sub>O<sub>3</sub> catalyst at 130–150 °C, with >95% selectivity. The reverse dehydrogenation process of H<sub>12</sub>-NEC proceeded at 150–170 °C to quantitative conversion in the presence of Pd/SiO<sub>2</sub> within 1 h (Figure 6). However, only 28% of the stored H<sub>2</sub> in dodecahydrocarbazole was recovered due to a strong carbazole adsorption on the catalyst surface, which makes the NEC/H<sub>12</sub>-NEC pair more suitable for the H<sub>2</sub> storage and release. The latter system was improved by Cheng in 2012 utilizing Ru/Al<sub>2</sub>O<sub>3</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> catalysts respectively for the reversible transformation of NEC and H<sub>12</sub>-NEC.<sup>193</sup> Notably, the individual dehydrogenation steps of H<sub>12</sub>-NEC dehydrogenation take place at different temperatures (128, 145, and 178 °C), with formation of the corresponding pyrrole as the first step. From an academic point of view, the H<sub>12</sub>-NEC/NEC system shows an excellent cyclic performance with very little deactivation after 10 cycles of reversible hydrogenation and dehydrogenation, providing high-purity H<sub>2</sub> (>99.99%, Figure 6).

In 2016, Kempe's group developed a particularly interesting catalyst that was able to promote the reversible (de)-hydrogenation of NEC in quantitative yields at 110/180 °C, respectively. The silicon carbonitride (SiCN)-supported bimetallic Pd-Ru catalyst (Pd<sub>2</sub>Ru@SiCN, Figure 7) showed improved performance in H<sub>2</sub> storage and release reactions

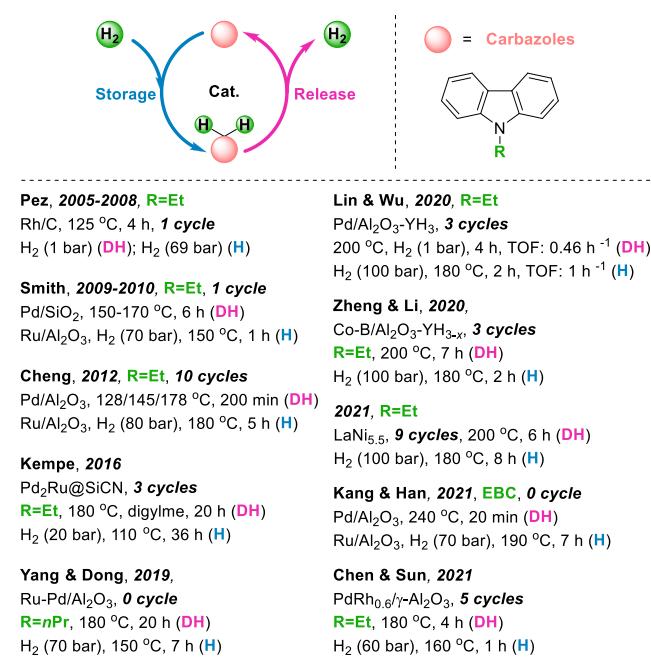
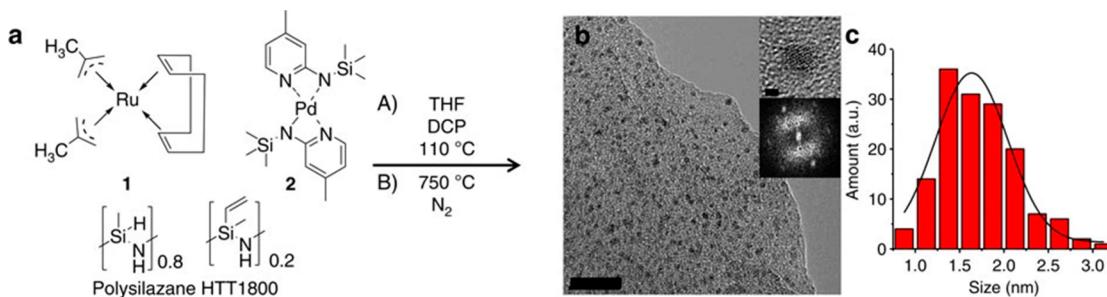


Figure 6. Heterogeneous catalyst-promoted hydrogen storage and release cycles applying carbazole derivatives. SiCN, silicon carbonitride.

(>98% yields) compared to a variety of commercial Pd and Ru catalysts. In principle, the reusability of the Pd<sub>2</sub>Ru@SiCN catalyst was proven by 3 consecutive hydrogen storage–release cycles.<sup>185</sup>

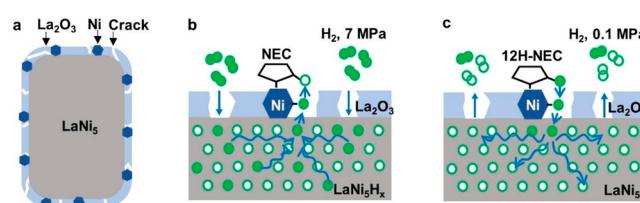
Another bimetallic Ru-Pd catalyst supported on Al<sub>2</sub>O<sub>3</sub> was prepared by Yang and Dong in 2019 via a facile impregnation–hydrogen reduction method. This catalyst was active and gave full conversion for both hydrogenation of *N*-propylcarbazole (NPC) and dehydrogenation of dodecahydro-*N*-propylcarbazole (H<sub>12</sub>-NPC). The performance was better than that of commercial Pd/Al<sub>2</sub>O<sub>3</sub> and Ru/Al<sub>2</sub>O<sub>3</sub> catalysts.<sup>29</sup> No significant activity decrease was observed after applying the same catalyst 3 times in NPC hydrogenation and H<sub>12</sub>-NEC dehydrogenation, respectively (Figure 6). One year later, a rare earth hydride (YH<sub>3</sub>)-promoted palladium catalyst (Pd/Al<sub>2</sub>O<sub>3</sub>-YH<sub>3</sub>) was developed by Lin and Wu.<sup>194</sup> This catalyst system showed high selectivity, and no activity decay was observed during 3 combined hydrogen storage and release cycles. The good performance derived from the presence of both Pd/Al<sub>2</sub>O<sub>3</sub> and YH<sub>3</sub>.

Although most of the catalysts developed in this area are based on noble metals, Zheng and Li reported in 2020 a Co-based catalyst with non-stoichiometric amounts of yttrium hydride incorporated (Co-B/Al<sub>2</sub>O<sub>3</sub>-YH<sub>3-x</sub>).<sup>195</sup> In the presence of this material, interconversion of NEC/H<sub>12</sub>-NEC was possible in >94% yields, and no significant loss of catalyst activity was observed after 3 rounds of combined hydrogen storage and release cycles. As indicated by XRD (X-ray crystallography) and HRTEM (high-resolution transmission electron microscopy) studies, the recycled catalyst showed no obvious change in structure and morphology. In general, the presented Co-B/Al<sub>2</sub>O<sub>3</sub>-YH<sub>3-x</sub> catalyst exhibited efficiency in (de)hydrogenation reactions comparable with that of Ru/Al<sub>2</sub>O<sub>3</sub> and Pd/Al<sub>2</sub>O<sub>3</sub>. Interestingly, this hydrogen storage system was applied to power a small-scale fuel cell (8 W) application.



**Figure 7.** Synthesis and characterization of the catalyst. (a) Synthesis procedure of Pd<sub>2</sub>Ru@SiCN. (b) High-resolution TEM image of the catalyst (scale bar, 20 nm) with magnification of one Pd nanoparticle and fast Fourier transform (FFT, scale bar, 1 nm). (c) Pd particle size distribution. Reprinted with permission from ref 185. Copyright 2016 Springer Nature.

Recently, also the classic hydrogen storage alloy LaNi<sub>5</sub><sup>197</sup> was reported by the same group to catalyze the reversible hydrogen storage in NEC.<sup>196</sup> No significant decrease of the total hydrogen storage capacity was observed after 9 consecutive cycles of hydrogenation and dehydrogenation, although the reaction kinetics became slower. The catalytic performance and the reversibility originated from the well-engineered Ni/LaNi<sub>5</sub> interface and the LaNi<sub>5</sub>-H solid solution (Figure 8).

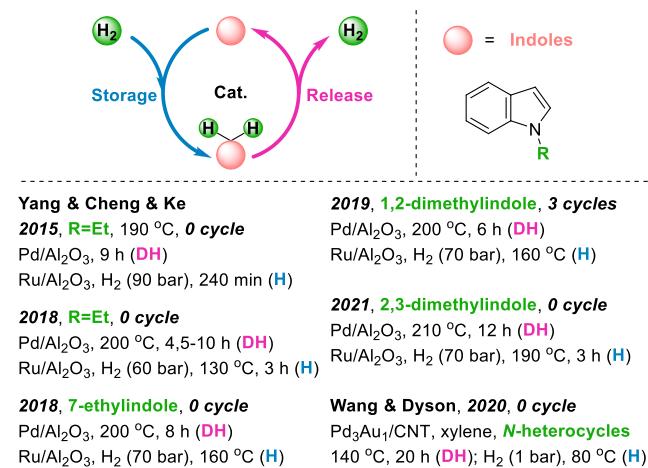


**Figure 8.** (a) Structure illustration of LaNi<sub>5</sub> nanoparticles. H<sub>2</sub> transfer processes in (b) NEC hydrogenation and (c) H<sub>12</sub>-NEC dehydrogenation. Reprinted with permission from ref 196. Copyright 2021 Elsevier.

Several novel H<sub>2</sub> storage materials with a carbazole backbone were prepared and fully characterized by Kang and Han in the same year. As a representative example, 9,9'-(2-ethylpropane-1,3-diy)bis(9H-carbazole) (EBC) was identified as the best candidate due to its fast reaction kinetics and gravimetric H<sub>2</sub> density (5.67 wt%). All these heteroarenes showed quantitative hydrogenation yields with Ru/Al<sub>2</sub>O<sub>3</sub> at 190 °C in 24 h. The reverse dehydrogenation reactions were performed with Pd/Al<sub>2</sub>O<sub>3</sub> at 280 °C in short time (10 min).<sup>198</sup> In the same year, Chen and Sun reported reusable bimetallic Pd-Rh NPs for both NEC hydrogenation and H<sub>12</sub>-NEC dehydrogenation. The optimal supported catalyst allowed for 5 consecutive cycles of reversible hydrogen uptake and release in 89–94% yields without significant loss of activity and hydrogen storage capacity.<sup>199</sup>

N-Substituted indole derivatives were also evaluated as another class of potential hydrogen carrier molecules. From 2015 to 2021, especially the group of Yang, Cheng, and Ke reported the catalytic hydrogenation of indole derivatives, e.g., N-ethylindole,<sup>33</sup> N-methylindole,<sup>200</sup> 7-ethylindole,<sup>201</sup> 1,2-dimethylindole,<sup>34</sup> and 2,3-dimethylindole,<sup>35</sup> and the reverse reactions. In the temperature range of 120–200 °C, two different heterogeneous catalysts, Pd/Al<sub>2</sub>O<sub>3</sub> (5 wt%) and Ru/Al<sub>2</sub>O<sub>3</sub> (5 wt%), were used in the corresponding (de)-hydrogenation reactions, respectively. The reaction kinetics of the hydrogenation of various indoles and reverse

dehydrogenations were mainly influenced by the steric hindrance of the substituted side chains (Figure 9). Although



**Figure 9.** Heterogeneous catalyst-promoted hydrogen storage and release cycles applying indole derivatives. CNT, carbon nanotubes.

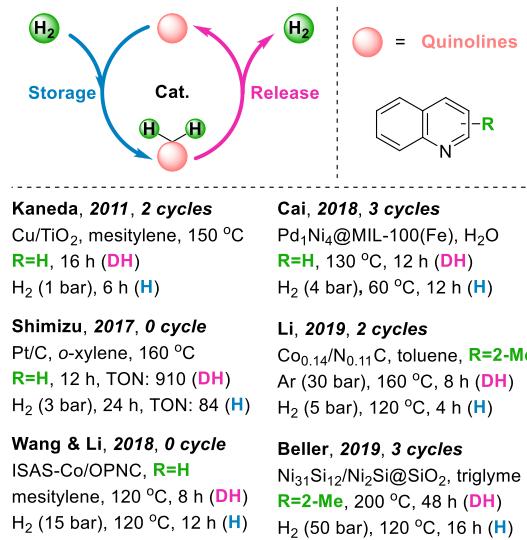
in their previous works<sup>33,200,201</sup> no catalyst reusability was investigated, Yang and co-workers successfully recycled their catalysts 3 times for individual hydrogenation and dehydrogenation reactions (stage B, Figure 1).<sup>35</sup> Furthermore, 3 combined cycles of hydrogen storage and release (stage C, Figure 1) were realized with >95% yields.<sup>34</sup> However, when the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst was reused in the dehydrogenation reaction after a longer reaction time (12 h), obvious catalyst degradation was observed due to carbon formation on the Pd surface and metal agglomeration.<sup>35</sup>

As reported by Wang and Dyson in 2020, bimetallic Pd-Au NPs supported on multi-wall carbon nanotubes (CNTs) exhibited generally high yields (>90%) in the reversible dehydrogenation and hydrogenation of heterocyclic compounds, amines/imines, and alcohols/ketones.<sup>202</sup> DFT calculations showed that the Pd<sub>3</sub>Au<sub>1</sub>(111) facet leads to lower-energy barriers than those observed on the Pd(111) surface for the elementary steps in both dehydrogenation and hydrogenation reactions of indole derivatives.

## ■ N-HETEROCYCLES: PYRIDINE, QUINOLINE, AND PHENAZINE DERIVATIVES

Cu NPs supported on TiO<sub>2</sub> (Cu/TiO<sub>2</sub>), reported by Kaneda in 2011, were used for reversible hydrogenation of quinoline derivatives. Notably, the hydrogenation process took place

under an atmospheric pressure of H<sub>2</sub> (1 bar).<sup>203</sup> The reversibility of the present tetrahydroquinoline/quinoline system was investigated with two consecutive hydrogenation and dehydrogenation experiments. However, besides the high metal loading of their catalyst (20 mol% Cu), the individual reaction steps required additional pre-activation of the catalyst under a H<sub>2</sub> atmosphere (1 bar) at 180 °C (Figure 10).



**Figure 10.** Heterogeneous catalyst-promoted hydrogen storage and release cycles applying quinoline derivatives. Abbreviations: ISAS, isolated single-atom sites; OPNC, ordered porous nitrogen-doped carbon.

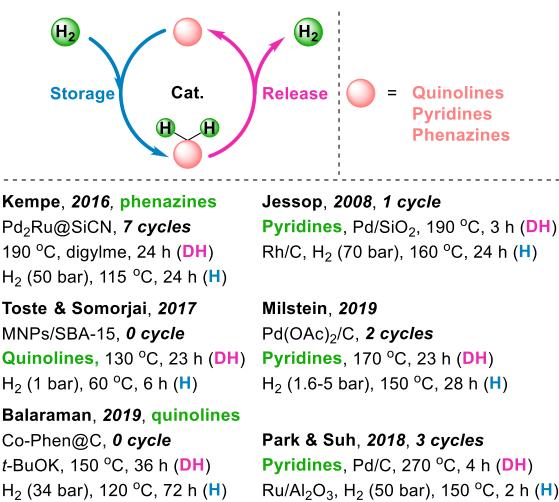
In 2017, Shimizu's group found that Pt NPs supported on carbon (Pt/C) constitute an effective and reusable heterogeneous catalyst for dehydrogenation of different *N*-heterocycles.<sup>36</sup> Additionally, the catalyst was active for the reverse reaction, i.e., hydrogenation of quinoline with 3 bar H<sub>2</sub>, leading to 84% 1,2,3,4-tetrahydroquinoline and 6% decahydroquinoline. One year later, cobalt-based single-atom catalysts (SACs) were applied in the reversible catalytic hydrogenation of *N*-heterocycles by Wang and Li.<sup>204</sup> The isolated single-atom sites (ISAS) of cobalt were stabilized on an ordered porous nitrogen-doped carbon matrix (OPNC, see Figure 12a, below). Such catalyst (ISAS-Co/OPNC) exhibited high efficiency (>99% conversion) in dehydrogenation of *N*-heterocycles to release H<sub>2</sub> and (transfer) hydrogenation of *N*-heterocycles in the presence of FA or H<sub>2</sub>. The catalyst reusability was tested in dehydrogenation and transfer hydrogenation up to 6 runs, respectively.

Another catalyst development was reported by Cai's group in 2018, where bimetallic NPs based on Pd and Ni supported in metal–organic frameworks (MOFs) MIL-100(Fe) were prepared and utilized for the reversible hydrogenation of quinoline derivatives in water (Figure 10).<sup>205</sup> Good performance of the Pd-Ni@MIL-100(Fe) catalyst in both reaction directions was demonstrated in >80% yields owing to the alloying Pd with Ni. The Lewis acidity and ordered mesoporous structure of the MIL-100(Fe) support were both beneficial to the host–guest functional synergy, due to the bimetallic NPs stabilization, reduction of the Pd electron density, and strong absorability of substrates and H<sub>2</sub>. Three reversible dehydrogenation and hydrogenation cycles were

done, with no decrease in activity and no obvious agglomeration of the recycled catalyst evidenced from the TEM images.

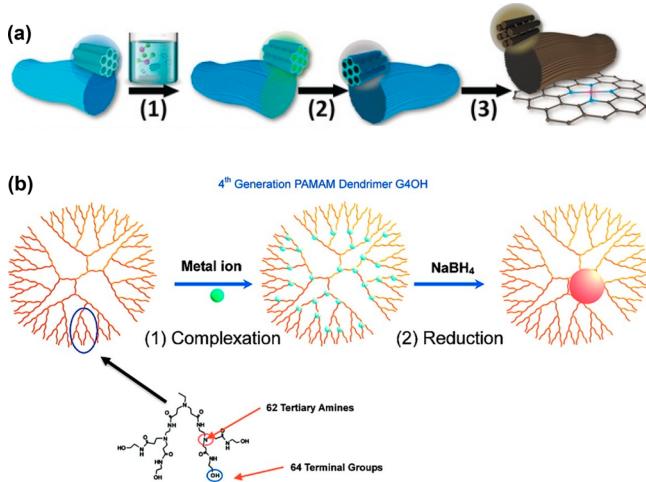
Switching to non-noble metals-based heterogeneous catalysts, Li and co-workers developed in 2019 a Co catalyst (Co/NC) with a nitrogen-thermal approach (via the reaction between transition metals and N dopants). The optimized hydrogenation and dehydrogenation yields (99%) were attributed to the well-controlled exposed interfaces of Co metal and carbon shells and the modified rectifying interfaces.<sup>206</sup> Using Co<sub>0.14</sub>/N<sub>0.11</sub>C (3.65 wt%) as catalyst and toluene as solvent, the H<sub>2</sub> storage and release reactions were performed under H<sub>2</sub> (5 bar), 120 °C, 4 h and Ar (30 bar), 160 °C, 8 h, respectively. Two reversible hydrogenation–dehydrogenation cycles were demonstrated successfully (Figure 10). In the same year, our group reported one of the first nickel-based nanocatalysts (Ni<sub>31</sub>Si<sub>12</sub>/Ni<sub>2</sub>Si@SiO<sub>2</sub>) for reversible hydrogenation of *N*-heterocycles (e.g., quinaldine). The individual hydrogenation and dehydrogenation reactions were performed by using the same solvent (triglyme) and catalyst. This system was used for 3 combined hydrogenation and dehydrogenation cycles with 20 mol% Ni loading under optimized conditions without significant loss of activity of the catalyst.<sup>37</sup>

Starting from the largely available biomass lignin, a particular *N*-heterocycle, octahydrophenazine, can be synthesized in one step and utilized as a reversible hydrogen storage medium, as reported by Kempe and co-workers in 2016.<sup>185</sup> The H<sub>2</sub> storage and release reactions were promoted by using their Pd<sub>2</sub>Ru@SiCN catalyst, which is active for reversible (de)hydrogenation of the NEC system (Figure 11). The combined H<sub>2</sub> storage–release cycles were performed 7 times in >80% yields of H<sub>2</sub> by reusing the same catalyst.



**Figure 11.** Heterogeneous catalyst-promoted hydrogen storage and release cycles applying *N*-heterocycle. SiCN, silicon carbonitride.

The synthesis of heterogeneous metallic NPs stabilized by polyamido amine (PAMAM) dendrimers supported on SBA-15 (MNPs/SBA-15, M = Pd, Pt, Rh) was reported by Toste and Somorjai in 2017 (Figure 12b).<sup>207</sup> These catalysts were used in the reverse (de)hydrogenation of quinoline derivatives in toluene. No significant loss in activity was observed for the PdNPs/SBA-15 catalyst after 3 times of reuse, and the dehydrogenation of 1,2,3,4-tetrahydroquinaldine to quinaldine



**Figure 12.** (a) Schematic illustration of the synthesis of ISAS-Co/OPNC. Conditions: (1) 80 °C, H<sub>2</sub>O/ethanol, (2) 800 °C, Ar, (3) NaOH. Reprinted with permission from ref 204. Copyright 2018 Wiley. (b) Schematic illustration of the synthesis of MNPs stabilized by PAMAM-G4OH dendrimer. Reprinted with permission from ref 207. Copyright 2017 American Chemical Society.

proceeded still with 95% conversion in the third run. However, a reversible hydrogen storage/release could not be realized with this system. Balaraman and co-workers reported in 2019 a reusable cobalt-based catalyst (Co-Phen@C) for reversible hydrogenation and dehydrogenation of N-heterocycles (quinoline and indole derivatives) under standard conditions (120/150 °C).<sup>208</sup> The catalyst could be easily separated from the reaction mixture and reused 5 times in the dehydrogenation step without a notable loss of activity.

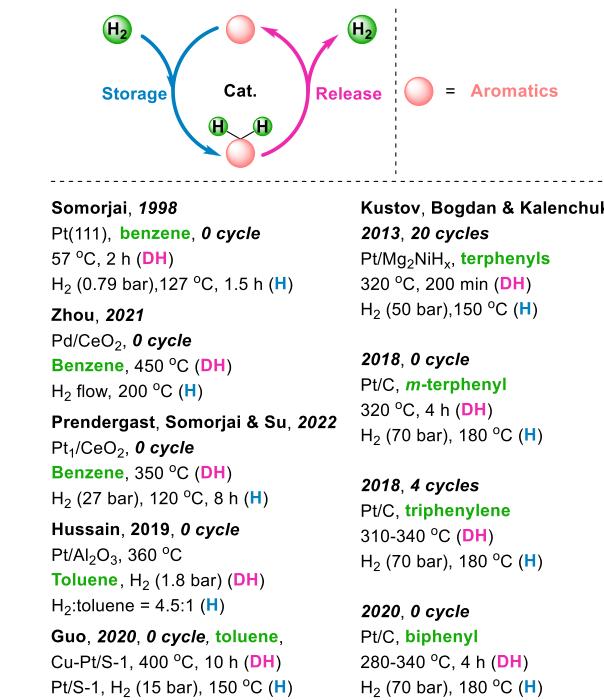
Substituted piperidines, i.e., 4-aminopiperidine and 4-piperidinocarboxamide, were identified by Jessop and co-workers in 2008 as promising reversible H<sub>2</sub> storage media among other analogues, using Rh/C and Pd/SiO<sub>2</sub> as catalysts for hydrogenation and dehydrogenation, respectively.<sup>209</sup> Quantitative conversions were obtained with 4-piperidinocarboxamide in the dehydrogenation–hydrogenation pathway. Based on 2-picoline (6.1 wt% H<sub>2</sub>) and 2,6-lutidine (5.3 wt% H<sub>2</sub>) compounds, Milstein's group reported in 2019 catalytic (de)hydrogenation with quantitative yields by using a Pd(OAc)<sub>2</sub>/C catalyst under neat conditions.<sup>210</sup> Notably, the hydrogenation proceeded at comparably low pressure (1.6–5 bar of H<sub>2</sub>). The combined H<sub>2</sub> storage–release experiments demonstrated the stability of such a system in 2 cycles (Figure 11). Mechanistic studies revealed the promoting role of acidic groups on the surface of the activated carbon support.

Another new liquid organic hydrogen carrier (LOHC), 2-(methylbenzyl)pyridine isomers (MBP, 6.15 wt% H<sub>2</sub>), was proposed by Park and Suh in 2018.<sup>211</sup> A higher H<sub>2</sub> yield was observed from H<sub>12</sub>-MBP (98%) with Pd/C as catalyst compared to the benchmark perhydro-benzyltoluene (56%) at 270 °C, owing to the incorporation of a N atom into the aromatic ring. Investigation on 3 combined reversible hydrogenation–dehydrogenation cycles led to quantitative H<sub>2</sub> yields with no obvious decomposition of the MBP/H<sub>12</sub>-MBP couple (Figure 11).

## ■ AROMATIC HYDROCARBONS

Already in 1998, Somorjai and co-workers initiated cyclohexene dehydrogenation and benzene hydrogenation on

Pt(111) crystal surfaces under vacuum and high-pressure conditions, respectively.<sup>212</sup> Based on the kinetic data and chemical nature of the surface species, both 1,3- and 1,4-cyclohexadiene were proposed as intermediates to the benzene formation (Figure 13). Recently, the group of Zhou reported a



**Figure 13.** Heterogeneous catalyst-promoted hydrogen storage and release cycles applying aromatic hydrocarbons.

Pd/CeO<sub>2</sub>-catalyzed vapor-phase benzene–cyclohexane interconversion for hydrogen storage. The benzene and cyclohexane conversions reached 99% and 65% over Pd/CeO<sub>2</sub> catalysts at 200 and 450 °C, respectively. To achieve activity, the catalyst precursor (PdO/CeO<sub>2</sub>) must be pretreated at reducing conditions (H<sub>2</sub>, 200 °C, 1 h).<sup>213</sup> Recently, Prendergast, Somorjai, and Su reported a SAC based on Pt<sub>1</sub>/CeO<sub>2</sub> which greatly enhanced the reaction rate of cyclohexane dehydrogenation.<sup>214</sup> More specifically, the activity of this catalyst system was 300-fold higher than that of conventional NPs catalysts (Pd/CeO<sub>2</sub> and Pt/Al<sub>2</sub>O<sub>3</sub>). Moreover, this SAC was applicable in the MCH/toluene system.

As an alternative for the hazardous benzene/cyclohexane system, Hussain and co-workers investigated the interconversion of MCH and toluene in 2019.<sup>215</sup> The used Pt/Al<sub>2</sub>O<sub>3</sub> catalyst (1 wt%) allowed for MCH dehydrogenation at 360 °C (under 1.8 bar of H<sub>2</sub>). The same catalyst has been found to be effective for toluene hydrogenation (Figure 13). More recently, other Pt-based catalysts were carefully designed for a reversible MCH/toluene cycle by Guo and co-workers.<sup>216</sup> In addition, toluene hydrogenation was investigated with the durability test of Pt/S-1, which retained quantitative toluene conversion and more than 99.9% selectivity in 4 runs. One of the drawbacks here is that the catalyst samples must be reduced in a H<sub>2</sub> flow at 350 °C for 2 h prior to the catalytic reactions.

The groups of Kustov, Bogdan, and Kalenchuk described the application of a series of aromatic hydrocarbons as LOHCs, including terphenyls/perhydroterphenyls (2013),<sup>31</sup> *m*-terphenyl/perhydro-*m*-terphenyl (2018),<sup>217</sup> triphenylene/perhydro-

*o*-terphenyl (2018),<sup>218</sup> and biphenyl/bicyclohexyl (2020).<sup>219</sup> Compared to many of the previously discussed systems, they performed a remarkable number of hydrogen storage cycles (up to 20) with Pt/Mg<sub>2</sub>NiH<sub>x</sub> as catalyst and terphenyls as substrates.<sup>31</sup> In these reactions, the presence of small amounts of light hydrocarbons (0.15–0.4%) due to cracking was confirmed by GC analysis. Such problems likely exist for many other LOHCs based on (hetero)arenes but are normally not investigated in detail. The applied Pt/C catalyst was activated in a hydrogen flow prior to *m*-terphenyl hydrogenation and perhydro-*m*-terphenyl dehydrogenation processes.<sup>217</sup> Interestingly, an isomerization of perhydro-*o*-terphenyl into perhydro-triphenylene was also observed in dehydrogenation reactions in a flow reactor.<sup>218</sup>

Compared to many of the previously discussed systems, the aromatic hydrocarbons performed a remarkable number of hydrogen storage cycles—up to 20.

Another potential LOHC is the dibenzyltoluene (DBT) and octadecahydro (or “perhydro-”)dibenzyltoluene (H<sub>18</sub>-DBT) pair, which provides reasonable hydrogen storage capacity (6.2 wt%) and is reported to be less toxic.<sup>60</sup> In 2014, Wasserscheid and co-workers reported a hydrogen storage–release method based on benzyltoluene or DBT mixtures using two different catalysts: (a) Ru/Al<sub>2</sub>O<sub>3</sub> (5 wt%) for the hydrogenation step and (b) Pt/C (1 wt%) for the dehydrogenation reaction.<sup>220</sup> In 2017, the same group introduced another catalyst for hydrogenation of DBT and dehydrogenation of H<sub>18</sub>-DBT. The reactions were carried out with Pt/Al<sub>2</sub>O<sub>3</sub> (0.3 wt%) in a temperature range from 290 to 310 °C (Figure 14).<sup>221</sup> An interesting heat recovery study was performed, as the heat resulting from the hydrogenation step could be provided at a

temperature level suitable for an effective dehydrogenation reaction. Thus, the “waste heat” from an energy storage device or a high-pressure steam system could be used for dehydrogenation. In addition, the equilibrium of DBT/H<sub>18</sub>-DBT was studied by the group of Wasserscheid to describe the temperature and pressure dependency of the equilibrium under experimental conditions.<sup>222</sup>

Using Pt/Al<sub>2</sub>O<sub>3</sub> (3 wt%) as catalyst, Qi’s group developed the integration of hydrogenation and dehydrogenation of the DBT/H<sub>18</sub>-DBT pair in 2019.<sup>223</sup> The hydrogen storage efficiency was >85% after 5 cyclic tests, showing reasonable thermal stability and its potential as a reversible H<sub>2</sub> storage system. In their later work, Qi and co-workers modified the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst with surface hydroxyl groups and surface oxygen vacancies (SOVs) by a H<sub>2</sub> and O<sub>2</sub> plasma treatment method.<sup>224</sup> Both the surface hydroxyl groups and SOV improved the Pt metal dispersion. The authors reported that the presence of hydroxyl groups is beneficial for the catalytic activity in (de)hydrogenation by promoting the hydrogen spillover and the proportion of Pt(0). The catalyst was reused 4 times in combined hydrogenation and dehydrogenation cycles.

Most recently, Pt catalysts supported on Mo<sub>x</sub>C-doped γ-Al<sub>2</sub>O<sub>3</sub> with different morphologies and pore structures were prepared by the same group for reversible hydrogenation of DBT.<sup>225</sup> The Mo<sub>x</sub>C doping was reported to help the formation of smaller Pt NPs size and their dispersion. The Pt/0.1%Mo–Al<sub>2</sub>O<sub>3</sub> catalyst (with 0.1 wt% Mo<sub>x</sub>C) showed a stable structure and the best activity with the least byproduct in H<sub>18</sub>-DBT dehydrogenation. The hydrogenation of DBT with H<sub>2</sub> (8 bar, 170 °C) was also investigated using Raney-Ni by Lee’s group in 2020. The corresponding dehydrogenation reaction of H<sub>18</sub>-DBT was investigated with another catalyst, Pt/C (3 wt%), at 290 °C, with >97% of the stored hydrogen released in 2 h (Figure 14).<sup>226</sup>

A mixture of biphenyl and diphenylmethane as a potential LOHC system was studied by Yoon and co-workers in 2019.<sup>227</sup> The respective mixture was hydrogenated using a Ru/Al<sub>2</sub>O<sub>3</sub> catalyst under 50 bar of H<sub>2</sub> at 120 °C with full conversion. Furthermore, the mixture of the hydrogenated products (bicyclohexyl and dicyclohexylmethane) was dehydrogenated using a Pd/C pellet catalyst in a continuous reactor, producing H<sub>2</sub> in high purity (>99.9%). The reversibility of this system was confirmed in 9 consecutive hydrogenation–dehydrogenation cycles with only a small decrease of the hydrogen storage capacity. Interestingly, a PEMFC was continuously fed by the dehydrogenation system, generating around 0.5 kWh of energy.

## PERSPECTIVE

In principle, there is enough renewable energy available to meet the (growing) energy hunger of the world’s population in the years to come. Since electricity generated from wind or sun is difficult to store on a large scale, energy storage technologies are a central component of a future sustainable energy system. Indeed, energy storage is the linchpin for a shift from fossil fuels to renewable resources such as wind, solar, and hydro power. Without efficient energy storage, it will not be possible to meet peak energy demand in densely populated regions and avoid high electricity cost spikes. In this respect, specifically chemical hydrogen storage and release is of growing interest for many scientists and ultimately for the human society.

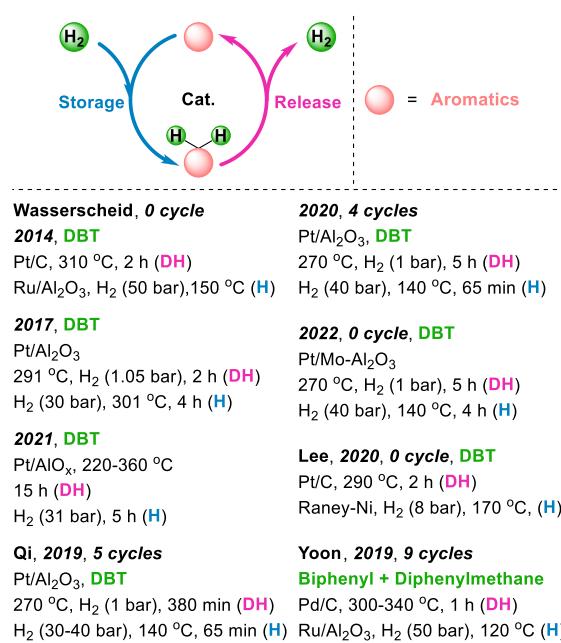


Figure 14. Heterogeneous catalyst-promoted hydrogen storage and release cycles applying polyaromatic hydrocarbons.

Specifically chemical hydrogen storage and release is of growing interest for many scientists and ultimately for the human society.

In the present Review, we have summarized current progress in the reversible chemical hydrogen storage and release applying various carbon-based hydrogen carriers, including CO<sub>2</sub>, bicarbonate, carbazole, indole, pyridine, quinoline, phenazine, and aromatic hydrocarbon compounds. Clearly, most of the developments covered in this Review are still at a stage of basic research. Crucial factors for their future application are a high hydrogen content of the carrier molecule, the availability and low cost of the feedstocks, the long-term stability of the storage system, easy transportation and convenient handling, e.g., non-flammability, and ideally no or a low toxicity. Significant efforts in the past decade focused on the optimization of various reaction parameters and the screening of heterogeneous material-based catalysts capable of promoting both the hydrogenation and dehydrogenation reactions for certain hydrogen storage media. Here, commercially available materials as well as novel supported and sometimes well-designed metal NPs as well as SACs on functionalized supports were tested and compared.

Despite all these developments, more active catalysts, specifically for the dehydrogenation step, are desirable. Thus, optimization of the active metal sites and the specific surface area of the materials is interesting. Regarding the nature of metals, available and less expensive non-noble metal catalysts based on low-cost, earth-abundant metals such as Ni, Fe, Mn, etc. are clearly preferred for reversible hydrogen storage and release processes. Another class of potentially interesting materials includes bi- and multimetallic composite catalysts. For example, the Pd-Au and Pd-Ru alloys have advantages over the respective mono-metal NPs regarding catalytic reactivity and could help to reduce the total loading of precious metals. Functionalization of the support, doping with heteroatoms (B, N, P, S), creating vacancy defect points, and modification of pore channel properties can contribute to minimize the active metal aggregation and potential leaching.

More important than this catalyst engineering is the long-term stability (reaction time scale) of the overall hydrogen storage system. In general, the stability of the reported systems has been shown for a few cycles, and this is by no means enough. In a real system, combined H<sub>2</sub> storage–release cycles must be done for several ten thousands of times. Thus, the stability of the feedstocks and catalysts under the conditions of the dehydrogenation process (which is, in general, the step needing a higher reaction temperature) should be carefully evaluated, and stability has to be demonstrated for weeks and months, rather than a few minutes and hours as found in most of the reported examples, *vide supra*. To do so, accelerated aging catalyst and substrate studies must be routinely performed. We suggest defining a standardized set of conditions for such aging processes. It should be clear that even the decomposition of 1% of a specific hydrogen carrier within 1 week typically will avoid application on a practical scale.

Finally, although difficult, the search for new and better chemical hydrogen carriers is another important aspect of future research. Obviously, those molecules not only should

inherently possess high hydrogen content, low-cost, non-flammability, low toxicity, long-term stability, and easy transportation/handling but also should have feasible compatibility with present energy infrastructures.

Despite the generally high reactivities in specific hydrogenation and dehydrogenation reactions, their combinations were often overlooked in most of the presented examples. Therefore, more effort is deserved in the follow-up research to examine the combination of hydrogenation and dehydrogenation reactions into a hydrogen battery. We believe such a review is needed at this time and will influence the future direction of this highly emerging research field associated with various promising chemical hydrogen storage–release materials.

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### Notes

The authors declare no competing financial interest.

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**Matthias Beller** is director of the Leibniz Institute for Catalysis, vice-president of the Leibniz Association, and a member of the German National Academia “Leopoldina”. The research of his group focuses on catalysis for the sustainable synthesis of fine/bulk chemicals and energy technologies and has been published in >1050 articles. <https://www.catalysis.de/en/people/beller-matthias>

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## REFERENCES

- (1) Kumar, A.; Daw, P.; Milstein, D. Homogeneous Catalysis for Sustainable Energy: Hydrogen and Methanol Economies, Fuels from Biomass, and Related Topics. *Chem. Rev.* **2022**, *122*, 385–441.
- (2) Schlapbach, L.; Züttel, A. Hydrogen-storage materials for mobile applications. *Nature* **2001**, *414*, 353–358.
- (3) Alberico, E.; Nielsen, M. Towards a methanol economy based on homogeneous catalysis: methanol to H<sub>2</sub> and CO<sub>2</sub> to methanol. *Chem. Commun.* **2015**, *51*, 6714–6725.
- (4) Roger, I.; Shipman, M. A.; Symes, M. D. Earth-abundant catalysts for electrochemical and photoelectrochemical water splitting. *Nat. Rev. Chem.* **2017**, *1*, 0003.
- (5) Tee, S. Y.; Win, K. Y.; Teo, W. S.; Koh, L.-D.; Liu, S.; Teng, C. P.; Han, M.-Y. Recent Progress in Energy-Driven Water Splitting. *Adv. Sci.* **2017**, *4*, 1600337.
- (6) Qi, J.; Zhang, W.; Cao, R. Solar-to-Hydrogen Energy Conversion Based on Water Splitting. *Adv. Energy Mater.* **2018**, *8*, 1701620.
- (7) Schneidewind, J.; Argüello Cordero, M. A.; Junge, H.; Lochbrunner, S.; Beller, M. Two-photon, visible light water splitting at a molecular ruthenium complex. *Energy Environ. Sci.* **2021**, *14*, 4427–4436.
- (8) Zou, X.; Zhang, Y. Noble metal-free hydrogen evolution catalysts for water splitting. *Chem. Soc. Rev.* **2015**, *44*, 5148–5180.
- (9) Ahmad, H.; Kamarudin, S. K.; Minggu, L. J.; Kassim, M. Hydrogen from photo-catalytic water splitting process: A review. *Renew. Sust. Energy Rev.* **2015**, *43*, 599–610.
- (10) Wang, Q.; Domen, K. Particulate Photocatalysts for Light-Driven Water Splitting: Mechanisms, Challenges, and Design Strategies. *Chem. Rev.* **2020**, *120*, 919–985.
- (11) Wang, Z.; Li, C.; Domen, K. Recent developments in heterogeneous photocatalysts for solar-driven overall water splitting. *Chem. Soc. Rev.* **2019**, *48*, 2109–2125.
- (12) Nishiyama, H.; Yamada, T.; Nakabayashi, M.; Maehara, Y.; Yamaguchi, M.; Kuromiya, Y.; Nagatsuma, Y.; Tokudome, H.; Akiyama, S.; Watanabe, T.; Narushima, R.; Okunaka, S.; Shibata, N.; Takata, T.; Hisatomi, T.; Domen, K. Photocatalytic solar hydrogen production from water on a 100-m<sup>2</sup> scale. *Nature* **2021**, *598*, 304–307.
- (13) Schneidewind, J. How Much Technological Progress is Needed to Make Solar Hydrogen Cost-Competitive? *Adv. Energy Mater.* **2022**, *12*, 2200342.
- (14) Cano, Z. P.; Banham, D.; Ye, S.; Hintennach, A.; Lu, J.; Fowler, M.; Chen, Z. Batteries and fuel cells for emerging electric vehicle markets. *Nat. Energy* **2018**, *3*, 279–289.
- (15) Ma, S.; Lin, M.; Lin, T.-E.; Lan, T.; Liao, X.; Maréchal, F.; Vanherle, J.; Yang, Y.; Dong, C.; Wang, L. Fuel cell-battery hybrid systems for mobility and off-grid applications: A review. *Renew. Sust. Energy Rev.* **2021**, *135*, 110119.
- (16) Mellmann, D.; Sponholz, P.; Junge, H.; Beller, M. Formic acid as a hydrogen storage material – development of homogeneous catalysts for selective hydrogen release. *Chem. Soc. Rev.* **2016**, *45*, 3954–3988.
- (17) Dong, Z.; Mukhtar, A.; Lin, H. Heterogeneous Catalysis on Liquid Organic Hydrogen Carriers. *Top. Catal.* **2021**, *64*, 481–508.
- (18) Makepeace, J. W.; He, T.; Weidenthaler, C.; Jensen, T. R.; Chang, F.; Vegge, T.; Ngene, P.; Kojima, Y.; de Jongh, P. E.; Chen, P.; David, W. I. F. Reversible ammonia-based and liquid organic hydrogen carriers for high-density hydrogen storage: Recent progress. *Int. J. Hydrot. Energy* **2019**, *44*, 7746–7767.
- (19) Markiewicz, M.; Zhang, Y.-Q.; Empl, M. T.; Lykaki, M.; Thöming, J.; Steinberg, P.; Stolte, S. Hazard assessment of quinaldine-, alkylcarbazole-, benzene- and toluene-based liquid organic hydrogen carrier (LOHCs) systems. *Energy Environ. Sci.* **2019**, *12*, 366–383.
- (20) Markiewicz, M.; Zhang, Y. Q.; Bösmann, A.; Brückner, N.; Thöming, J.; Wasserscheid, P.; Stolte, S. Environmental and health impact assessment of Liquid Organic Hydrogen Carrier (LOHC) systems – challenges and preliminary results. *Energy Environ. Sci.* **2015**, *8*, 1035–1045.
- (21) Teichmann, D.; Stark, K.; Müller, K.; Zöttl, G.; Wasserscheid, P.; Arlt, W. Energy storage in residential and commercial buildings via Liquid Organic Hydrogen Carriers (LOHC). *Energy Environ. Sci.* **2012**, *5*, 9044–9054.
- (22) Yadav, M.; Xu, Q. Liquid-phase chemical hydrogen storage materials. *Energy Environ. Sci.* **2012**, *5*, 9698–9725.
- (23) Preuster, P.; Papp, C.; Wasserscheid, P. Liquid Organic Hydrogen Carriers (LOHCs): Toward a Hydrogen-free Hydrogen Economy. *Acc. Chem. Res.* **2017**, *50*, 74–85.
- (24) Niermann, M.; Drünert, S.; Kaltschmitt, M.; Bonhoff, K. Liquid organic hydrogen carriers (LOHCs) – techno-economic analysis of LOHCs in a defined process chain. *Energy Environ. Sci.* **2019**, *12*, 290–307.
- (25) Shao, Z.; Li, Y.; Liu, C.; Ai, W.; Luo, S.-P.; Liu, Q. Reversible interconversion between methanol-diamine and diamide for hydrogen storage based on manganese catalyzed (de)hydrogenation. *Nat. Commun.* **2020**, *11*, 591.
- (26) Zheng, J.; Zhou, H.; Wang, C.-G.; Ye, E.; Xu, J. W.; Loh, X. J.; Li, Z. Current research progress and perspectives on liquid hydrogen rich molecules in sustainable hydrogen storage. *Energy Stor. Mater.* **2021**, *35*, 695–722.
- (27) Sordakis, K.; Tang, C.; Vogt, L. K.; Junge, H.; Dyson, P. J.; Beller, M.; Laurenczy, G. Homogeneous Catalysis for Sustainable Hydrogen Storage in Formic Acid and Alcohols. *Chem. Rev.* **2018**, *118*, 372–433.
- (28) Bi, Q. Y.; Lin, J. D.; Liu, Y. M.; Du, X. L.; Wang, J. Q.; He, H. Y.; Cao, Y. An aqueous rechargeable formate-based hydrogen battery driven by heterogeneous Pd catalysis. *Angew. Chem., Int. Ed.* **2014**, *53*, 13583–13587.
- (29) Zhu, T.; Yang, M.; Chen, X.; Dong, Y.; Zhang, Z.; Cheng, H. A highly active bifunctional Ru–Pd catalyst for hydrogenation and dehydrogenation of liquid organic hydrogen carriers. *J. Catal.* **2019**, *378*, 382–391.
- (30) Zhou, L.; Sun, L.; Xu, L.; Wan, C.; An, Y.; Ye, M. Recent Developments of Effective Catalysts for Hydrogen Storage Technology Using N-Ethylcarbazole. *Catalysts* **2020**, *10*, 648.
- (31) Kustov, L. M.; Tarasov, A. L.; Tarasov, B. P. Intermetallic catalysts for hydrogen storage on the basis of reversible aromatics hydrogenation/dehydrogenation reactions. *Int. J. Hydrot. Energy* **2013**, *38*, 5713–5716.
- (32) Sotoodeh, F.; Zhao, L.; Smith, K. J. Kinetics of H<sub>2</sub> recovery from dodecahydro-N-ethylcarbazole over a supported Pd catalyst. *Appl. Catal., A* **2009**, *362*, 155–162.

- (33) Dong, Y.; Yang, M.; Yang, Z.; Ke, H.; Cheng, H. Catalytic hydrogenation and dehydrogenation of *N*-ethylindole as a new heteroaromatic liquid organic hydrogen carrier. *Int. J. Hydrg. Energy* **2015**, *40*, 10918–10922.
- (34) Dong, Y.; Yang, M.; Li, L.; Zhu, T.; Chen, X.; Cheng, H. Study on reversible hydrogen uptake and release of 1,2-dimethylindole as a new liquid organic hydrogen carrier. *Int. J. Hydrg. Energy* **2019**, *44*, 4919–4929.
- (35) Dong, Y.; Zhao, H.; Zhao, Y.; Yang, M.; Zhang, H.; Cheng, H. Study of catalytic hydrogenation and dehydrogenation of 2,3-dimethylindole for hydrogen storage application. *RSC Adv.* **2021**, *11*, 15729–15737.
- (36) Moromi, S. K.; Siddiki, S. M. A. H.; Kon, K.; Toyao, T.; Shimizu, K.-i. Acceptorless dehydrogenation of *N*-heterocycles by supported Pt catalysts. *Catal. Today* **2017**, *281*, 507–511.
- (37) Ryabchuk, P.; Agapova, A.; Kreyenschulte, C.; Lund, H.; Junge, H.; Junge, K.; Beller, M. Heterogeneous nickel-catalysed reversible, acceptorless dehydrogenation of *N*-heterocycles for hydrogen storage. *Chem. Commun.* **2019**, *55*, 4969–4972.
- (38) Andersson, J. Application of Liquid Hydrogen Carriers in Hydrogen Steelmaking. *Energies* **2021**, *14*, 1392.
- (39) Cho, J.-Y.; Kim, H.; Oh, J.-E.; Park, B. Y. Recent Advances in Homogeneous/Heterogeneous Catalytic Hydrogenation and Dehydrogenation for Potential Liquid Organic Hydrogen Carrier (LOHC) Systems. *Catalysts* **2021**, *11*, 1497.
- (40) Shimbayashi, T.; Fujita, K.-i. Metal-catalyzed hydrogenation and dehydrogenation reactions for efficient hydrogen storage. *Tetrahedron* **2020**, *76*, 130946.
- (41) Chamoun, R.; Demirci, U. B.; Miele, P. Cyclic Dehydrogenation–(Re)Hydrogenation with Hydrogen-Storage Materials: An Overview. *Energy Technol.* **2015**, *3*, 100–117.
- (42) Zhu, Q.-L.; Xu, Q. Liquid organic and inorganic chemical hydrides for high-capacity hydrogen storage. *Energy Environ. Sci.* **2015**, *8*, 478–512.
- (43) Aakko-Saksa, P. T.; Cook, C.; Kiviah, J.; Repo, T. Liquid organic hydrogen carriers for transportation and storing of renewable energy – Review and discussion. *J. Power Sources* **2018**, *396*, 803–823.
- (44) Zell, T.; Langer, R. Iron-catalyzed hydrogenation and dehydrogenation reactions with relevance to reversible hydrogen storage applications. *Recycl. Catal.* **2015**, *2*, 87–109.
- (45) Bahuguna, A.; Sasson, Y. Formate-Bicarbonate Cycle as a Vehicle for Hydrogen and Energy Storage. *ChemSusChem* **2021**, *14*, 1258–1283.
- (46) Onishi, N.; Iguchi, M.; Yang, X.; Kanega, R.; Kawanami, H.; Xu, Q.; Himeda, Y. Development of Effective Catalysts for Hydrogen Storage Technology Using Formic Acid. *Adv. Energy Mater.* **2019**, *9*, 1801275.
- (47) Singh, A. K.; Singh, S.; Kumar, A. Hydrogen energy future with formic acid: a renewable chemical hydrogen storage system. *Catal. Sci. Technol.* **2016**, *6*, 12–40.
- (48) Asefa, T.; Koh, K.; Yoon, C. W. CO<sub>2</sub>-Mediated H<sub>2</sub> storage–release with Nanostructured Catalysts: Recent Progresses, Challenges, and Perspectives. *Adv. Energy Mater.* **2019**, *9*, 1901158.
- (49) Enthaler, S.; von Langermann, J.; Schmidt, T. Carbon dioxide and formic acid—the couple for environmental-friendly hydrogen storage? *Energy Environ. Sci.* **2010**, *3*, 1207–1217.
- (50) Al-Nayili, A.; Majdi, H. S.; Albayati, T. M.; Saady, N. M. C. Formic Acid Dehydrogenation Using Noble-Metal Nanoheterogeneous Catalysts: Towards Sustainable Hydrogen-Based Energy. *Catalysts* **2022**, *12*, 324.
- (51) Zhong, H.; Iguchi, M.; Chatterjee, M.; Himeda, Y.; Xu, Q.; Kawanami, H. Formic Acid-Based Liquid Organic Hydrogen Carrier System with Heterogeneous Catalysts. *Adv. Sustainable Syst.* **2018**, *2*, 1700161.
- (52) Liu, M.; Xu, Y.; Meng, Y.; Wang, L.; Wang, H.; Huang, Y.; Onishi, N.; Wang, L.; Fan, Z.; Himeda, Y. Heterogeneous Catalysis for Carbon Dioxide Mediated Hydrogen Storage Technology Based on Formic Acid. *Adv. Energy Mater.* **2022**, *12*, 2200817.
- (53) Tan, K. C.; He, T.; Chua, Y. S.; Chen, P. Recent Advances of Catalysis in the Hydrogenation and Dehydrogenation of *N*-Heterocycles for Hydrogen Storage. *J. Phys. Chem. C* **2021**, *125*, 18553–18566.
- (54) He, T.; Pei, Q.; Chen, P. Liquid organic hydrogen carriers. *J. Energy Chem.* **2015**, *24*, 587–594.
- (55) Makaryan, I. A.; Sedov, I. V. Hydrogenation/Dehydrogenation Catalysts for Hydrogen Storage Systems Based on Liquid Organic Carriers (A Review). *Pet. Chem.* **2021**, *61*, 977–988.
- (56) Wei, Z.; Shao, F.; Wang, J. Recent advances in heterogeneous catalytic hydrogenation and dehydrogenation of *N*-heterocycles. *Chin. J. Catal.* **2019**, *40*, 980–1002.
- (57) Makaryan, I. A.; Sedov, I. V.; Maksimov, A. L. Hydrogen Storage Using Liquid Organic Carriers. *Russ. J. Appl. Chem.* **2020**, *93*, 1815–1830.
- (58) Rao, P. C.; Yoon, M. Potential Liquid-Organic Hydrogen Carrier (LOHC) Systems: A Review on Recent Progress. *Energies* **2020**, *13*, 6040.
- (59) Jorschick, H.; Preuster, P.; Bösmann, A.; Wasserscheid, P. Hydrogenation of aromatic and heteroaromatic compounds – a key process for future logistics of green hydrogen using liquid organic hydrogen carrier systems. *Sustain. Energy Fuels* **2021**, *5*, 1311–1346.
- (60) Sisáková, K.; Podrojčová, N.; Orináková, R.; Oriňák, A. Novel Catalysts for Dibenzyltoluene as a Potential Liquid Organic Hydrogen Carrier Use—A Mini-review. *Energy Fuels* **2021**, *35*, 7608–7623.
- (61) Chatterjee, S.; Parsapur, R. K.; Huang, K.-W. Limitations of Ammonia as a Hydrogen Energy Carrier for the Transportation Sector. *ACS Energy Lett.* **2021**, *6*, 4390–4394.
- (62) Bhattacharjee, I.; Sultana, M.; Bhunya, S.; Paul, A. The curious saga of dehydrogenation/hydrogenation for chemical hydrogen storage: a mechanistic perspective. *Chem. Commun.* **2022**, *58*, 1672–1684.
- (63) Catizzone, E.; Freda, C.; Braccio, G.; Frusteri, F.; Bonura, G. Dimethyl ether as circular hydrogen carrier: Catalytic aspects of hydrogenation/dehydrogenation steps. *J. Energy Chem.* **2021**, *58*, 55–77.
- (64) Navlani-García, M.; Mori, K.; Kuwahara, Y.; Yamashita, H. Recent strategies targeting efficient hydrogen production from chemical hydrogen storage materials over carbon-supported catalysts. *NPG Asia Mater.* **2018**, *10*, 277–292.
- (65) Jiang, H.-L.; Singh, S. K.; Yan, J.-M.; Zhang, X.-B.; Xu, Q. Liquid-Phase Chemical Hydrogen Storage: Catalytic Hydrogen Generation under Ambient Conditions. *ChemSusChem* **2010**, *3*, 541–549.
- (66) Younas, M.; Rezakazemi, M.; Arbab, M. S.; Shah, J.; Rehman, W. U. Green hydrogen storage and delivery: Utilizing highly active homogeneous and heterogeneous catalysts for formic acid dehydrogenation. *Int. J. Hydrg. Energy* **2022**, *47*, 11694–11724.
- (67) Li, J.; Zhu, Q.-L.; Xu, Q. Dehydrogenation of Formic Acid by Heterogeneous Catalysts. *CHIMIA* **2015**, *69*, 348.
- (68) Li, Z.; Xu, Q. Metal-Nanoparticle-Catalyzed Hydrogen Generation from Formic Acid. *Acc. Chem. Res.* **2017**, *50*, 1449–1458.
- (69) Loges, B.; Boddien, A.; Gärtner, F.; Junge, H.; Beller, M. Catalytic Generation of Hydrogen from Formic acid and its Derivatives: Useful Hydrogen Storage Materials. *Top. Catal.* **2010**, *53*, 902–914.
- (70) Rossin, A.; Tuci, G.; Luconi, L.; Giambastiani, G. Metal–Organic Frameworks as Heterogeneous Catalysts in Hydrogen Production from Lightweight Inorganic Hydrides. *ACS Catal.* **2017**, *7*, 5035–5045.
- (71) Navlani-García, M.; Mori, K.; Salinas-Torres, D.; Kuwahara, Y.; Yamashita, H. New Approaches Toward the Hydrogen Production From Formic Acid Dehydrogenation Over Pd-Based Heterogeneous Catalysts. *Front. Mater.* **2019**, *6*, No. 44.
- (72) Chen, X.; Liu, Y.; Wu, J. Sustainable production of formic acid from biomass and carbon dioxide. *Mol. Catal.* **2020**, *483*, 110716.
- (73) Valdés-López, V. F.; Mason, T.; Shearing, P. R.; Brett, D. J. L. Carbon monoxide poisoning and mitigation strategies for polymer

- electrolyte membrane fuel cells – A review. *Prog. Energy Combust. Sci.* **2020**, *79*, 100842.
- (74) Moret, S.; Dyson, P. J.; Laurenczy, G. Direct synthesis of formic acid from carbon dioxide by hydrogenation in acidic media. *Nat. Commun.* **2014**, *5*, 4017.
- (75) Grubel, K.; Jeong, H.; Yoon, C. W.; Autrey, T. Challenges and opportunities for using formate to store, transport, and use hydrogen. *J. Energy Chem.* **2020**, *41*, 216–224.
- (76) Chatterjee, S.; Dutta, I.; Lum, Y.; Lai, Z.; Huang, K.-W. Enabling storage and utilization of low-carbon electricity: power to formic acid. *Energy Environ. Sci.* **2021**, *14*, 1194–1246.
- (77) Sun, R.; Liao, Y.; Bai, S.-T.; Zheng, M.; Zhou, C.; Zhang, T.; Sels, B. F. Heterogeneous catalysts for CO<sub>2</sub> hydrogenation to formic acid/formate: from nanoscale to single atom. *Energy Environ. Sci.* **2021**, *14*, 1247–1285.
- (78) Bulushev, D. A.; Ross, J. R. H. Heterogeneous catalysts for hydrogenation of CO<sub>2</sub> and bicarbonates to formic acid and formates. *Catal. Rev.* **2018**, *60*, 566–593.
- (79) Alvarez, A.; Bansode, A.; Urakawa, A.; Bavykina, A. V.; Wezendonk, T. A.; Makkee, M.; Gascon, J.; Kapteijn, F. Challenges in the Greener Production of Formates/Formic Acid, Methanol, and DME by Heterogeneously Catalyzed CO<sub>2</sub> Hydrogenation Processes. *Chem. Rev.* **2017**, *117*, 9804–9838.
- (80) Gunasekar, G. H.; Park, K.; Jung, K.-D.; Yoon, S. Recent developments in the catalytic hydrogenation of CO<sub>2</sub> to formic acid/formate using heterogeneous catalysts. *Inorg. Chem. Front.* **2016**, *3*, 882–895.
- (81) Li, L.; Chen, X.; Chen, Z.; Gao, R.; Yu, H.; Yuan, T.; Liu, Z.; Maeder, M. Heterogeneous catalysts for the hydrogenation of amine/alkali hydroxide solvent captured CO<sub>2</sub> to formate: A review. *Greenhouse Gas Sci. Technol.* **2021**, *11*, 807–823.
- (82) Verma, P.; Zhang, S.; Song, S.; Mori, K.; Kuwahara, Y.; Wen, M.; Yamashita, H.; An, T. Recent strategies for enhancing the catalytic activity of CO<sub>2</sub> hydrogenation to formate/formic acid over Pd-based catalyst. *J. CO<sub>2</sub> Util.* **2021**, *54*, 101765.
- (83) Xie, S.; Zhang, W.; Lan, X.; Lin, H. CO<sub>2</sub> Reduction to Methanol in the Liquid Phase: A Review. *ChemSusChem* **2020**, *13*, 6141–6159.
- (84) Grasemann, M.; Laurenczy, G. Formic acid as a hydrogen source – recent developments and future trends. *Energy Environ. Sci.* **2012**, *5*, 8171–8181.
- (85) Boddien, A.; Junge, H. Acidic ideas for hydrogen storage. *Nat. Nanotechnol.* **2011**, *6*, 265–266.
- (86) Preuster, P.; Albert, J. Biogenic Formic Acid as a Green Hydrogen Carrier. *Energy Technol.* **2018**, *6*, 501–509.
- (87) Wang, X.; Meng, Q.; Gao, L.; Jin, Z.; Ge, J.; Liu, C.; Xing, W. Recent progress in hydrogen production from formic acid decomposition. *Int. J. Hydrol. Energy* **2018**, *43*, 7055–7071.
- (88) Williams, R.; Crandall, R. S.; Bloom, A. Use of carbon dioxide in energy storage. *Appl. Phys. Lett.* **1978**, *33*, 381–383.
- (89) Zaidman, B.; Wiener, H.; Sasson, Y. Formate salts as chemical carriers in hydrogen storage and transportation. *Int. J. Hydrol. Energy* **1986**, *11*, 341–347.
- (90) Wei, D.; Sang, R.; Moazezbarabadi, A.; Junge, H.; Beller, M. Homogeneous Carbon Capture and Catalytic Hydrogenation: Toward a Chemical Hydrogen Battery System. *JACS Au* **2022**, *2*, 1020–1031.
- (91) Wang, Y.; Wang, M.; Li, Y.; Liu, Q. Homogeneous manganese-catalyzed hydrogenation and dehydrogenation reactions. *Chem.* **2021**, *7*, 1180–1223.
- (92) Bernskoetter, W. H.; Hazari, N. Reversible Hydrogenation of Carbon Dioxide to Formic Acid and Methanol: Lewis Acid Enhancement of Base Metal Catalysts. *Acc. Chem. Res.* **2017**, *50*, 1049–1058.
- (93) Eppinger, J.; Huang, K.-W. Formic Acid as a Hydrogen Energy Carrier. *ACS Energy Lett.* **2017**, *2*, 188–195.
- (94) Schaub, T. CO<sub>2</sub>-based hydrogen storage: CO<sub>2</sub> hydrogenation to formic acid, formaldehyde and methanol. *Phys. Sci. Rev.* **2018**, *3*, 20170015.
- (95) Leitner, W.; Dinjus, E.; Gaßner, F. Activation of carbon dioxide: IV. Rhodium-catalysed hydrogenation of carbon dioxide to formic acid. *J. Organomet. Chem.* **1994**, *475*, 257–266.
- (96) Himeda, Y.; Miyazawa, S.; Hirose, T. Interconversion between Formic Acid and H<sub>2</sub>/CO<sub>2</sub> using Rhodium and Ruthenium Catalysts for CO<sub>2</sub> Fixation and H<sub>2</sub> Storage. *ChemSusChem* **2011**, *4*, 487–493.
- (97) Boddien, A.; Gärtner, F.; Federsel, C.; Sponholz, P.; Mellmann, D.; Jackstell, R.; Junge, H.; Beller, M. CO<sub>2</sub>“Neutral” Hydrogen Storage Based on Bicarbonates and Formates. *Angew. Chem., Int. Ed.* **2011**, *50*, 6411–6414.
- (98) Papp, G.; Csorba, J.; Laurenczy, G.; Joó, F. A Charge/Discharge Device for Chemical Hydrogen Storage and Generation. *Angew. Chem., Int. Ed.* **2011**, *50*, 10433–10435.
- (99) Sordakis, K.; Dalebrook, A. F.; Laurenczy, G. A Viable Hydrogen Storage and Release System Based on Cesium Formate and Bicarbonate Salts: Mechanistic Insights into the Hydrogen Release Step. *ChemCatChem* **2015**, *7*, 2332–2339.
- (100) Boddien, A.; Federsel, C.; Sponholz, P.; Mellmann, D.; Jackstell, R.; Junge, H.; Laurenczy, G.; Beller, M. Towards the development of a hydrogen battery. *Energy Environ. Sci.* **2012**, *5*, 8907–8911.
- (101) Filonenko, G. A.; van Putten, R.; Schulpen, E. N.; Hensen, E. J. M.; Pidko, E. A. Highly Efficient Reversible Hydrogenation of Carbon Dioxide to Formates Using a Ruthenium PNP-Pincer Catalyst. *ChemCatChem* **2014**, *6*, 1526–1530.
- (102) Hsu, S.-F.; Rommel, S.; Eversfield, P.; Muller, K.; Klemm, E.; Thiel, W. R.; Plietker, B. A Rechargeable Hydrogen Battery Based on Ru Catalysis. *Angew. Chem., Int. Ed.* **2014**, *53*, 7074–7078.
- (103) Kothandaraman, J.; Czaun, M.; Goeppert, A.; Haiges, R.; Jones, J.-P.; May, R. B.; Prakash, G. K. S.; Olah, G. A. Amine-Free Reversible Hydrogen Storage in Formate Salts Catalyzed by Ruthenium Pincer Complex without pH Control or Solvent Change. *ChemSusChem* **2015**, *8*, 1442–1451.
- (104) Xin, Z.; Zhang, J.; Sordakis, K.; Beller, M.; Du, C.-X.; Laurenczy, G.; Li, Y. Towards Hydrogen Storage through an Efficient Ruthenium-Catalyzed Dehydrogenation of Formic Acid. *ChemSusChem* **2018**, *11*, 2077–2082.
- (105) Boddien, A.; Gärtner, F.; Mellmann, D.; Sponholz, P.; Junge, H.; Laurenczy, G.; Beller, M. Hydrogen Storage in Formic Acid – Amine Adducts. *Chimia* **2011**, *65*, 214.
- (106) Tanaka, R.; Yamashita, M.; Chung, L. W.; Morokuma, K.; Nozaki, K. Mechanistic Studies on the Reversible Hydrogenation of Carbon Dioxide Catalyzed by an Ir-PNP Complex. *Organometallics* **2011**, *30*, 6742–6750.
- (107) Hull, J. F.; Himeda, Y.; Wang, W.-H.; Hashiguchi, B.; Periana, R.; Szalda, D. J.; Muckerman, J. T.; Fujita, E. Reversible hydrogen storage using CO<sub>2</sub> and a proton-switchable iridium catalyst in aqueous media under mild temperatures and pressures. *Nat. Chem.* **2012**, *4*, 383–388.
- (108) Horváth, H.; Papp, G.; Kovács, H.; Kathó, Á.; Joó, F. Iridium(I)NHC-phosphine complex-catalyzed hydrogen generation and storage in aqueous formate/bicarbonate solutions using a flow reactor - Effective response to changes in hydrogen demand. *Int. J. Hydrol. Energy* **2019**, *44*, 28527–28532.
- (109) Horváth, H.; Papp, G.; Szabolcsi, R.; Kathó, Á.; Joó, F. Water-Soluble Iridium-NHC-Phosphine Complexes as Catalysts for Chemical Hydrogen Batteries Based on Formate. *ChemSusChem* **2015**, *8*, 3036–3038.
- (110) Wang, L.; Onishi, N.; Murata, K.; Hirose, T.; Muckerman, J. T.; Fujita, E.; Himeda, Y. Efficient Hydrogen Storage and Production Using a Catalyst with an Imidazoline-Based, Proton-Responsive Ligand. *ChemSusChem* **2017**, *10*, 1071–1075.
- (111) Enthalier, S.; Brück, A.; Kammer, A.; Junge, H.; Irran, E.; Gulkak, S. Exploring the Reactivity of Nickel Pincer Complexes in the Decomposition of Formic Acid to CO<sub>2</sub>/H<sub>2</sub> and the Hydrogenation of NaHCO<sub>3</sub> to HCOONa. *ChemCatChem* **2015**, *7*, 65–69.
- (112) Curley, J. B.; Smith, N. E.; Bernskoetter, W. H.; Hazari, N.; Mercado, B. Q. Catalytic Formic Acid Dehydrogenation and CO<sub>2</sub>

- Hydrogenation Using Iron PNRP Pincer Complexes with Isonitrile Ligands. *Organometallics* **2018**, *37*, 3846–3853.
- (113) Wei, D.; Sang, R.; Sponholz, P.; Junge, H.; Beller, M. Reversible hydrogenation of carbon dioxide to formic acid using a Mn-pincer complex in the presence of lysine. *Nat. Energy* **2022**, *7*, 438–447.
- (114) Lee, J. H.; Ryu, J.; Kim, J. Y.; Nam, S.-W.; Han, J. H.; Lim, T.-H.; Gautam, S.; Chae, K. H.; Yoon, C. W. Carbon dioxide mediated, reversible chemical hydrogen storage using a Pd nanocatalyst supported on mesoporous graphitic carbon nitride. *J. Mater. Chem. A* **2014**, *2*, 9490–9495.
- (115) Bi, Q.-Y.; Lin, J.-D.; Liu, Y.-M.; He, H.-Y.; Huang, F.-Q.; Cao, Y. Dehydrogenation of Formic Acid at Room Temperature: Boosting Palladium Nanoparticle Efficiency by Coupling with Pyridinic-Nitrogen-Doped Carbon. *Angew. Chem., Int. Ed.* **2016**, *55*, 11849–11853.
- (116) Mori, K.; Masuda, S.; Tanaka, H.; Yoshizawa, K.; Che, M.; Yamashita, H. Phenylamine-functionalized mesoporous silica supported PdAg nanoparticles: a dual heterogeneous catalyst for formic acid/CO<sub>2</sub>-mediated chemical hydrogen delivery/storage. *Chem. Commun.* **2017**, *53*, 4677–4680.
- (117) Masuda, S.; Mori, K.; Futamura, Y.; Yamashita, H. PdAg Nanoparticles Supported on Functionalized Mesoporous Carbon: Promotional Effect of Surface Amine Groups in Reversible Hydrogen Delivery/Storage Mediated by Formic Acid/CO<sub>2</sub>. *ACS Catal.* **2018**, *8*, 2277–2285.
- (118) Lu, M.; Zhang, J.; Yao, Y.; Sun, J.; Wang, Y.; Lin, H. Renewable energy storage via efficient reversible hydrogenation of piperidine captured CO<sub>2</sub>. *Green Chem.* **2018**, *20*, 4292–4298.
- (119) Sun, Q.; Chen, B. W. J.; Wang, N.; He, Q.; Chang, A.; Yang, C.-M.; Asakura, H.; Tanaka, T.; Hulse, M. J.; Wang, C.-H.; Yu, J.; Yan, N. Zeolite-Encaged Pd–Mn Nanocatalysts for CO<sub>2</sub> Hydrogenation and Formic Acid Dehydrogenation. *Angew. Chem., Int. Ed.* **2020**, *59*, 20183–20191.
- (120) Zou, L.; Liu, Q.; Zhang, Q.; Zhu, Z.; Huang, Y.; Liang, Z. Synthesis of Bimetallic Pd-Based/Activated Carbon Catalyst by Biomass-Reduction Method for Highly Efficient Hydrogen Storage System Based on CO<sub>2</sub>/Formate. *Ind. Eng. Chem. Res.* **2022**, *61*, 2455–2468.
- (121) CRC Handbook of Chemistry and Physics, 102nd ed.; Rumble, J. R., Ed.; CRC Press, 2021.
- (122) Su, J.; Yang, L.; Lu, M.; Lin, H. Highly Efficient Hydrogen Storage System Based on Ammonium Bicarbonate/Formate Redox Equilibrium over Palladium Nanocatalysts. *ChemSusChem* **2015**, *8*, 813–816.
- (123) Chen, S.-Y.; Tang, C.-Y.; Chuang, W.-T.; Lee, J.-J.; Tsai, Y.-L.; Chan, J. C. C.; Lin, C.-Y.; Liu, Y.-C.; Cheng, S. A Facile Route to Synthesizing Functionalized Mesoporous SBA-15 Materials with Platelet Morphology and Short Mesochannels. *Chem. Mater.* **2008**, *20*, 3906–3916.
- (124) Wang, F.; Xu, J.; Shao, X.; Su, X.; Huang, Y.; Zhang, T. Palladium on Nitrogen-Doped Mesoporous Carbon: A Bifunctional Catalyst for Formate-Based, Carbon-Neutral Hydrogen Storage. *ChemSusChem* **2016**, *9*, 246–251.
- (125) Shao, X.; Xu, J.; Huang, Y.; Su, X.; Duan, H.; Wang, X.; Zhang, T. Pd@C<sub>3</sub>N<sub>4</sub> nanocatalyst for highly efficient hydrogen storage system based on potassium bicarbonate/formate. *AIChE J.* **2016**, *62*, 2410–2418.
- (126) Koh, K.; Jeon, M.; Chevrier, D. M.; Zhang, P.; Yoon, C. W.; Asefa, T. Novel nanoporous N-doped carbon-supported ultrasmall Pd nanoparticles: Efficient catalysts for hydrogen storage and release. *Appl. Catal., B* **2017**, *203*, 820–828.
- (127) Shao, X.; Miao, X.; Zhang, T.; Wang, W.; Wang, J.; Ji, X. Pd Nanoparticles Supported on N- and P-Co-doped Carbon as Catalysts for Reversible Formate-Based Chemical Hydrogen Storage. *ACS Appl. Nano Mater.* **2020**, *3*, 9209–9217.
- (128) Shin, D. Y.; Kim, M.-S.; Kwon, J. A.; Shin, Y.-J.; Yoon, C. W.; Lim, D.-H. Fundamental Mechanisms of Reversible Dehydrogenation of Formate on N-Doped Graphene-Supported Pd Nanoparticles. *J. Phys. Chem. C* **2019**, *123*, 1539–1549.
- (129) Zhong, H.; Iguchi, M.; Chatterjee, M.; Ishizaka, T.; Kitta, M.; Xu, Q.; Kawanami, H. Interconversion between CO<sub>2</sub> and HCOOH under Basic Conditions Catalyzed by PdAu Nanoparticles Supported by Amine-Functionalized Reduced Graphene Oxide as a Dual Catalyst. *ACS Catal.* **2018**, *8*, 5355–5362.
- (130) Nakajima, K.; Tominaga, M.; Waseda, M.; Miura, H.; Shishido, T. Highly Efficient Supported Palladium–Gold Alloy Catalysts for Hydrogen Storage Based on Ammonium Bicarbonate/Formate Redox Cycle. *ACS Sustain. Chem. Eng.* **2019**, *7*, 6522–6530.
- (131) Masuda, S.; Shimoji, Y.; Mori, K.; Kuwahara, Y.; Yamashita, H. Interconversion of Formate/Bicarbonate for Hydrogen Storage/Release: Improved Activity Following Sacrificial Surface Modification of a Ag@Pd/TiO<sub>x</sub> Catalyst with a TiO<sub>x</sub> Shell. *ACS Appl. Energy Mater.* **2020**, *3*, 5819–5829.
- (132) Safronov, S. P.; Vostrikov, S. V.; Samarov, A. A.; Verevkin, S. P. Reversible storage and release of hydrogen with LOHC: Evaluation of thermochemical data for methyl-quinolines with complementary experimental and computational methods. *Fuel* **2022**, *317*, 123501.
- (133) Giustra, Z. X.; Ishibashi, J. S. A.; Liu, S.-Y. Homogeneous metal catalysis for conversion between aromatic and saturated compounds. *Coord. Chem. Rev.* **2016**, *314*, 134–181.
- (134) Vivancos, Á.; Beller, M.; Albrecht, M. NHC-Based Iridium Catalysts for Hydrogenation and Dehydrogenation of N-Heteroarenes in Water under Mild Conditions. *ACS Catal.* **2018**, *8*, 17–21.
- (135) Yamaguchi, R.; Ikeda, C.; Takahashi, Y.; Fujita, K.-i. Homogeneous Catalytic System for Reversible Dehydrogenation–Hydrogenation Reactions of Nitrogen Heterocycles with Reversible Interconversion of Catalytic Species. *J. Am. Chem. Soc.* **2009**, *131*, 8410–8412.
- (136) Manas, M. G.; Sharnghausen, L. S.; Lin, E.; Crabtree, R. H. Iridium catalyzed reversible dehydrogenation – Hydrogenation of quinoline derivatives under mild conditions. *J. Organomet. Chem.* **2015**, *792*, 184–189.
- (137) Wang, S.; Huang, H.; Bruneau, C.; Fischmeister, C. Iridium-Catalyzed Hydrogenation and Dehydrogenation of N-Heterocycles in Water under Mild Conditions. *ChemSusChem* **2019**, *12*, 2350–2354.
- (138) Zhang, D.; Iwai, T.; Sawamura, M. Ir-Catalyzed Reversible Acceptorless Dehydrogenation/Hydrogenation of N-Substituted and Unsubstituted Heterocycles Enabled by a Polymer-Cross-Linking Bisphosphine. *Org. Lett.* **2020**, *22*, 5240–5245.
- (139) Fujita, K.-i.; Tanaka, Y.; Kobayashi, M.; Yamaguchi, R. Homogeneous Perdehydrogenation and Perhydrogenation of Fused Bicyclic N-Heterocycles Catalyzed by Iridium Complexes Bearing a Functional Bipyridonate Ligand. *J. Am. Chem. Soc.* **2014**, *136*, 4829–4832.
- (140) Li, H.; Jiang, J.; Lu, G.; Huang, F.; Wang, Z.-X. On the “Reverse Gear”Mechanism of the Reversible Dehydrogenation/Hydrogenation of a Nitrogen Heterocycle Catalyzed by a Cp\*Ir Complex: A Computational Study. *Organometallics* **2011**, *30*, 3131–3141.
- (141) Kaiwa, Y.; Oka, K.; Nishide, H.; Oyaizu, K. Facile reversible hydrogenation of a poly(6-vinyl-2,3-dimethyl-1,2,3,4-tetrahydroquinoxaline) gel-like solid. *Polym. Adv. Technol.* **2021**, *32*, 1162–1167.
- (142) Chakraborty, S.; Brennessel, W. W.; Jones, W. D. A Molecular Iron Catalyst for the Acceptorless Dehydrogenation and Hydrogenation of N-Heterocycles. *J. Am. Chem. Soc.* **2014**, *136*, 8564–8567.
- (143) Sawatlon, B.; Surawatanawong, P. Mechanisms for dehydrogenation and hydrogenation of N-heterocycles using PNP-pincer-supported iron catalysts: a density functional study. *Dalton Trans.* **2016**, *45*, 14965–14978.
- (144) Xu, R.; Chakraborty, S.; Yuan, H.; Jones, W. D. Acceptorless, Reversible Dehydrogenation and Hydrogenation of N-Heterocycles with a Cobalt Pincer Catalyst. *ACS Catal.* **2015**, *5*, 6350–6354.
- (145) Zubair, V.; Borghs, J. C.; Rueping, M. Hydrogenation or Dehydrogenation of N-Containing Heterocycles Catalyzed by a Single Manganese Complex. *Org. Lett.* **2020**, *22*, 3974–3978.

- (146) Fujita, K.-i.; Wada, T.; Shiraishi, T. Reversible Interconversion between 2,5-Dimethylpyrazine and 2,5-Dimethylpiperazine by Iridium-Catalyzed Hydrogenation/Dehydrogenation for Efficient Hydrogen Storage. *Angew. Chem., Int. Ed.* **2017**, *56*, 10886–10889.
- (147) He, K.-H.; Tan, F.-F.; Zhou, C.-Z.; Zhou, G.-J.; Yang, X.-L.; Li, Y. Acceptorless Dehydrogenation of *N*-Heterocycles by Merging Visible-Light Photoredox Catalysis and Cobalt Catalysis. *Angew. Chem., Int. Ed.* **2017**, *56*, 3080–3084.
- (148) Ge, D.; Hu, L.; Wang, J.; Li, X.; Qi, F.; Lu, J.; Cao, X.; Gu, H. Reversible Hydrogenation–Oxidative Dehydrogenation of Quinolines over a Highly Active Pt Nanowire Catalyst under Mild Conditions. *ChemCatChem.* **2013**, *5*, 2183–2186.
- (149) Li, J.; Liu, G.; Long, X.; Gao, G.; Wu, J.; Li, F. Different active sites in a bifunctional Co@N-doped graphene shells based catalyst for the oxidative dehydrogenation and hydrogenation reactions. *J. Catal.* **2017**, *355*, 53–62.
- (150) Wu, Y.; Chen, Z.; Cheong, W.-C.; Zhang, C.; Zheng, L.; Yan, W.; Yu, R.; Chen, C.; Li, Y. Nitrogen-coordinated cobalt nanocrystals for oxidative dehydrogenation and hydrogenation of *N*-heterocycles. *Chem. Sci.* **2019**, *10*, 5345–5352.
- (151) He, Z.-H.; Sun, Y.-C.; Wang, K.; Wang, Z.-Y.; Guo, P.-P.; Jiang, C.-S.; Yao, M.-Q.; Li, Z.-H.; Liu, Z.-T. Reversible aerobic oxidative dehydrogenation/hydrogenation of *N*-heterocycles over AlN supported redox cobalt catalysts. *Mol. Catal.* **2020**, *496*, 111192.
- (152) Mehranfar, A.; Izadyar, M.; Esmaeili, A. A. Hydrogen storage by N-ethylcarbazol as a new liquid organic hydrogen carrier: A DFT study on the mechanism. *Int. J. Hydrol. Energy* **2015**, *40*, 5797–5806.
- (153) Emel'yanenko, V. N.; Varfolomeev, M. A.; Verevkin, S. P.; Stark, K.; Müller, K.; Müller, M.; Bösmann, A.; Wasserscheid, P.; Arlt, W. Hydrogen Storage: Thermochemical Studies of *N*-Alkylcarbazoles and Their Derivatives as a Potential Liquid Organic Hydrogen Carriers. *J. Phys. Chem. C* **2015**, *119*, 26381–26389.
- (154) Stark, K.; Keil, P.; Schug, S.; Müller, K.; Wasserscheid, P.; Arlt, W. Melting Points of Potential Liquid Organic Hydrogen Carrier Systems Consisting of *N*-Alkylcarbazoles. *J. Chem. Eng. Data* **2016**, *61*, 1441–1448.
- (155) Stark, K.; Emel'yanenko, V. N.; Zhabina, A. A.; Varfolomeev, M. A.; Verevkin, S. P.; Müller, K.; Arlt, W. Liquid Organic Hydrogen Carriers: Thermophysical and Thermochemical Studies of Carbazole Partly and Fully Hydrogenated Derivatives. *Ind. Eng. Chem. Res.* **2015**, *54*, 7953–7966.
- (156) Wan, C.; An, Y.; Chen, F.; Cheng, D.; Wu, F.; Xu, G. Kinetics of N-ethylcarbazole hydrogenation over a supported Ru catalyst for hydrogen storage. *Int. J. Hydrol. Energy* **2013**, *38*, 7065–7069.
- (157) Wu, Y.; Yu, H.; Guo, Y.; Jiang, X.; Qi, Y.; Sun, B.; Li, H.; Zheng, J.; Li, X. A rare earth hydride supported ruthenium catalyst for the hydrogenation of *N*-heterocycles: boosting the activity via a new hydrogen transfer path and controlling the stereoselectivity. *Chem. Sci.* **2019**, *10*, 10459–10465.
- (158) Wan, C.; An, Y.; Xu, G.; Kong, W. Study of catalytic hydrogenation of N-ethylcarbazole over ruthenium catalyst. *Int. J. Hydrol. Energy* **2012**, *37*, 13092–13096.
- (159) Eblagon, K. M.; Tam, K.; Yu, K. M. K.; Tsang, S. C. E. Comparative Study of Catalytic Hydrogenation of 9-Ethylcarbazole for Hydrogen Storage over Noble Metal Surfaces. *J. Phys. Chem. C* **2012**, *116*, 7421–7429.
- (160) Eblagon, K. M.; Rentsch, D.; Friedrichs, O.; Remhof, A.; Zuettel, A.; Ramirez-Cuesta, A. J.; Tsang, S. C. Hydrogenation of 9-ethylcarbazole as a prototype of a liquid hydrogen carrier. *Int. J. Hydrol. Energy* **2010**, *35*, 11609–11621.
- (161) Li, P.; Dong, Y.; Ding, Y.; Zhang, H.; Yang, M.; Cheng, H. Effect of hydrogen spillover on the surface of tungsten oxide on hydrogenation of cyclohexene and N-propylcarbazole. *Int. J. Hydrol. Energy* **2021**, *46*, 3945–3953.
- (162) Yang, M.; Xing, X.; Zhu, T.; Chen, X.; Dong, Y.; Cheng, H. Fast hydrogenation kinetics of acridine as a candidate of liquid organic hydrogen carrier family with high capacity. *J. Energy Chem.* **2020**, *41*, 115–119.
- (163) Yu, H.; Yang, X.; Wu, Y.; Guo, Y.; Li, S.; Lin, W.; Li, X.; Zheng, J. Bimetallic Ru-Ni/TiO<sub>2</sub> catalysts for hydrogenation of N-ethylcarbazole: Role of TiO<sub>2</sub> crystal structure. *J. Energy Chem.* **2020**, *40*, 188–195.
- (164) Li, C.; Yang, M.; Liu, Z.; Zhang, Z.; Zhu, T.; Chen, X.; Dong, Y.; Cheng, H. Ru–Ni/Al<sub>2</sub>O<sub>3</sub> bimetallic catalysts with high catalytic activity for N-propylcarbazole hydrogenation. *Catal. Sci. Technol.* **2020**, *10*, 2268–2276.
- (165) Wu, Y.; Yu, H.; Guo, Y.; Zhang, Y.; Jiang, X.; Sun, B.; Fu, K.; Chen, J.; Qi, Y.; Zheng, J.; Li, X. Promoting hydrogen absorption of liquid organic hydrogen carriers by solid metal hydrides. *J. Mater. Chem. A* **2019**, *7*, 16677–16684.
- (166) Papp, C.; Wasserscheid, P.; Libuda, J.; Steinrück, H.-P. Liquid Organic Hydrogen Carriers: Surface Science Studies of Carbazole Derivatives. *Chem. Rec.* **2014**, *14*, 879–896.
- (167) Peters, W.; Eypasch, M.; Frank, T.; Schwerdtfeger, J.; Körner, C.; Bösmann, A.; Wasserscheid, P. Efficient hydrogen release from perhydro-N-ethylcarbazole using catalyst-coated metallic structures produced by selective electron beam melting. *Energy Environ. Sci.* **2015**, *8*, 641–649.
- (168) Gong, X.; Jiang, Z.; Fang, T. Enhancing selectivity and reducing cost for dehydrogenation of dodecahydro-N-ethylcarbazole by supporting platinum on titanium dioxide. *Int. J. Hydrol. Energy* **2020**, *45*, 6838–6847.
- (169) Dong, Y.; Yang, M.; Mei, P.; Li, C.; Li, L. Dehydrogenation kinetics study of perhydro-N-ethylcarbazole over a supported Pd catalyst for hydrogen storage application. *Int. J. Hydrol. Energy* **2016**, *41*, 8498–8505.
- (170) Shuang, H.; Chen, H.; Wu, F.; Li, J.; Cheng, C.; Li, H.; Fu, J. Catalytic dehydrogenation of hydrogen-rich liquid organic hydrogen carriers by palladium oxide supported on activated carbon. *Fuel* **2020**, *275*, 117896.
- (171) Wang, B.; Chang, T.-y.; Jiang, Z.; Wei, J.-j.; Zhang, Y.-h.; Yang, S.; Fang, T. Catalytic dehydrogenation study of dodecahydro-N-ethylcarbazole by noble metal supported on reduced graphene oxide. *Int. J. Hydrol. Energy* **2018**, *43*, 7317–7325.
- (172) Wang, B.; Yan, T.; Chang, T.; Wei, J.; Zhou, Q.; Yang, S.; Fang, T. Palladium supported on reduced graphene oxide as a high-performance catalyst for the dehydrogenation of dodecahydro-N-ethylcarbazole. *Carbon* **2017**, *122*, 9–18.
- (173) Yang, M.; Dong, Y.; Fei, S.; Ke, H.; Cheng, H. A comparative study of catalytic dehydrogenation of perhydro-N-ethylcarbazole over noble metal catalysts. *Int. J. Hydrol. Energy* **2014**, *39*, 18976–18983.
- (174) Dong, Y.; Yang, M.; Zhu, T.; Chen, X.; Cheng, G.; Ke, H.; Cheng, H. Fast Dehydrogenation Kinetics of Perhydro-N-propylcarbazole over a Supported Pd Catalyst. *ACS Appl. Energy Mater.* **2018**, *1*, 4285–4292.
- (175) Wang, B.; Chen, Y.-T.; Chang, T.-Y.; Jiang, Z.; Huang, Z.-Q.; Wang, S.-Y.; Chang, C.-R.; Chen, Y.-S.; Wei, J.-J.; Yang, S.; Fang, T. Facet-dependent catalytic activities of Pd/rGO: Exploring dehydrogenation mechanism of dodecahydro-N-ethylcarbazole. *Appl. Catal., B* **2020**, *266*, 118658.
- (176) Dong, C.; Gao, Z.; Li, Y.; Peng, M.; Wang, M.; Xu, Y.; Li, C.; Xu, M.; Deng, Y.; Qin, X.; Huang, F.; Wei, X.; Wang, Y.-G.; Liu, H.; Zhou, W.; Ma, D. Fully exposed palladium cluster catalysts enable hydrogen production from nitrogen heterocycles. *Nat. Catal.* **2022**, *5*, 485–493.
- (177) Wang, B.; Chang, T.-y.; Gong, X.; Jiang, Z.; Yang, S.; Chen, Y.-s.; Fang, T. One-Pot Synthesis of Au/Pd Core/Shell Nanoparticles Supported on Reduced Graphene Oxide with Enhanced Dehydrogenation Performance for Dodecahydro-N-ethylcarbazole. *ACS Sustain. Chem. Eng.* **2019**, *7*, 1760–1768.
- (178) Bachmann, P.; Schwarz, M.; Steinhauer, J.; Späth, F.; Düll, F.; Bauer, U.; Nascimento Silva, T.; Mohr, S.; Hohner, C.; Scheuermeyer, M.; Wasserscheid, P.; Libuda, J.; Steinrück, H. P.; Papp, C. Dehydrogenation of the Liquid Organic Hydrogen Carrier System Indole/Indoline/Octahydroindole on Pt(111). *J. Phys. Chem. C* **2018**, *122*, 4470–4479.

- (179) Dean, D.; Davis, B.; Jessop, P. G. The effect of temperature, catalyst and sterics on the rate of *N*-heterocycle dehydrogenation for hydrogen storage. *New J. Chem.* **2011**, *35*, 417–422.
- (180) Ouma, C. N. M.; Modisha, P. M.; Bessarabov, D. Catalytic dehydrogenation of the liquid organic hydrogen carrier octahydroindole on Pt(111) surface: *Ab initio* insights from density functional theory calculations. *Appl. Surf. Sci.* **2019**, *471*, 1034–1040.
- (181) Oh, J.; Bathula, H. B.; Park, J. H.; Suh, Y.-W. A sustainable mesoporous palladium-alumina catalyst for efficient hydrogen release from *N*-heterocyclic liquid organic hydrogen carriers. *Commun. Chem.* **2019**, *2*, 68.
- (182) Amende, M.; Schernich, S.; Sobota, M.; Nikiforidis, I.; Hieringer, W.; Assenbaum, D.; Gleichweit, C.; Drescher, H.-J.; Papp, C.; Steinrück, H.-P.; Görling, A.; Wasserscheid, P.; Laurin, M.; Libuda, J. Dehydrogenation Mechanism of Liquid Organic Hydrogen Carriers: Dodecahydro-*N*-ethylcarbazole on Pd(111). *Chem. - Eur. J.* **2013**, *19*, 10854–10865.
- (183) Fei, S.; Han, B.; Li, L.; Mei, P.; Zhu, T.; Yang, M.; Cheng, H. A study on the catalytic hydrogenation of *N*-ethylcarbazole on the mesoporous Pd/MoO<sub>3</sub> catalyst. *Int. J. Hydrg. Energy* **2017**, *42*, 25942–25950.
- (184) Sobota, M.; Nikiforidis, I.; Amende, M.; Zanón, B. S.; Staudt, T.; Höfert, O.; Lykhach, Y.; Papp, C.; Hieringer, W.; Laurin, M.; Assenbaum, D.; Wasserscheid, P.; Steinrück, H.-P.; Görling, A.; Libuda, J. Dehydrogenation of Dodecahydro-*N*-ethylcarbazole on Pd/Al<sub>2</sub>O<sub>3</sub> Model Catalysts. *Chem. - Eur. J.* **2011**, *17*, 11542–11552.
- (185) Forberg, D.; Schwob, T.; Zaheer, M.; Friedrich, M.; Miyajima, N.; Kempe, R. Single-catalyst high-weight% hydrogen storage in an *N*-heterocycle synthesized from lignin hydrogenolysis products and ammonia. *Nat. Commun.* **2016**, *7*, 13201.
- (186) Pez, G. P.; Scott, A. R.; Cooper, A. C.; Cheng, H. Hydrogen storage by reversible hydrogenated of pi-conjugated substrates. US7101530B2, 2006.
- (187) Pez, G. P.; Scott, A. R.; Cooper, A. C.; Cheng, H. Hydrogen storage by reversible hydrogenated of pi-conjugated substrates. US20050002857A1, 2005.
- (188) Pez, G. P.; Scott, A. R.; Cooper, A. C.; Cheng, H.; Bagzis, L. D.; Appleby, J. B. Hydrogen storage reversible hydrogenated of pi-conjugated substrates. WO2005000457A3, 2005.
- (189) Pez, G. P.; Scott, A. R.; Cooper, A. C.; Cheng, H.; Wilhelm, F. C.; Abdourazak, A. H. Hydrogen storage reversible hydrogenated of pi-conjugated substrates. US7351395B1, 2008.
- (190) Pez, G. P.; Cooper, A. C.; Scott, A. R. Autothermal hydrogen storage and delivery systems. US8003073B2, 2008.
- (191) Pez, G. P.; Scott, A. R.; Cooper, A. C.; Cheng, H.; Bagzis, L. D.; Appleby, J. B. Hydrogen storage reversible hydrogenated of pi-conjugated substrates. EP1660404A4, 2006.
- (192) Sotoodeh, F.; Smith, K. J. Kinetics of Hydrogen Uptake and Release from Heteroaromatic Compounds for Hydrogen Storage. *Ind. Eng. Chem. Res.* **2010**, *49*, 1018–1026.
- (193) Yang, M.; Han, C.; Ni, G.; Wu, J.; Cheng, H. Temperature controlled three-stage catalytic dehydrogenation and cycle performance of perhydro-9-ethylcarbazole. *Int. J. Hydrg. Energy* **2012**, *37*, 12839–12845.
- (194) Yang, X.; Wu, Y.; Yu, H.; Sun, M.; Zheng, J.; Li, X.; Lin, W.; Wu, Y. A YH<sub>3</sub> promoted palladium catalyst for reversible hydrogen storage of *N*-ethylcarbazole. *Int. J. Hydrg. Energy* **2020**, *45*, 33657–33662.
- (195) Wu, Y.; Guo, Y.; Yu, H.; Jiang, X.; Zhang, Y.; Qi, Y.; Fu, K.; Xie, L.; Li, G.; Zheng, J.; Li, X. Nonstoichiometric Yttrium Hydride-Promoted Reversible Hydrogen Storage in a Liquid Organic Hydrogen Carrier. *CCS Chem.* **2021**, *3*, 974–984.
- (196) Yu, H.; Yang, X.; Jiang, X.; Wu, Y.; Chen, S.; Lin, W.; Wu, Y.; Xie, L.; Li, X.; Zheng, J. LaNi<sub>5.5</sub> particles for reversible hydrogen storage in *N*-ethylcarbazole. *Nano Energy* **2021**, *80*, 105476.
- (197) Nowak, M.; Jurczyk, M., LaNi<sub>5</sub>-Based Hydrogen Storage Alloys. In *Handbook of Nanomaterials for Hydrogen Storage*, 1st ed.; Jurczyk, M., Ed.; Jenny Stanford Publishing, 2017; pp 199–225.
- (198) Jung, J.; Shin, B. S.; Kang, J. W.; Han, W.-S. Catalytic Hydrogenation and Dehydrogenation Reactions of *N*-alkyl-bis-(carbazole)-Based Hydrogen Storage Materials. *Catalysts* **2021**, *11*, 123.
- (199) Xue, W.; Liu, H.; Mao, B.; Liu, H.; Qiu, M.; Yang, C.; Chen, X.; Sun, Y. Reversible hydrogenation and dehydrogenation of *N*-ethylcarbazole over bimetallic Pd-Rh catalyst for hydrogen storage. *Chem. Eng. J.* **2021**, *421*, 127781.
- (200) Yang, M.; Cheng, G.; Xie, D.; Zhu, T.; Dong, Y.; Ke, H.; Cheng, H. Study of hydrogenation and dehydrogenation of 1-methylindole for reversible onboard hydrogen storage application. *Int. J. Hydrg. Energy* **2018**, *43*, 8868–8876.
- (201) Chen, Z.; Yang, M.; Zhu, T.; Zhang, Z.; Chen, X.; Liu, Z.; Dong, Y.; Cheng, G.; Cheng, H. 7-ethylindole: A new efficient liquid organic hydrogen carrier with fast kinetics. *Int. J. Hydrg. Energy* **2018**, *43*, 12688–12696.
- (202) Cui, X.; Huang, Z.; van Muyden, A. P.; Fei, Z.; Wang, T.; Dyson, P. J. Acceptorless dehydrogenation and hydrogenation of N- and O-containing compounds on Pd<sub>3</sub>Au<sub>1</sub>(111) facets. *Sci. Adv.* **2020**, *6*, eabb3831.
- (203) Mikami, Y.; Ebata, K.; Mitsudome, T.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. Reversible dehydrogenation-hydrogenation of tetrahydroquinoline-quinoline using a supported copper nanoparticle catalyst. *Heterocycles* **2011**, *82*, 1371–1377.
- (204) Han, Y.; Wang, Z.; Xu, R.; Zhang, W.; Chen, W.; Zheng, L.; Zhang, J.; Luo, J.; Wu, K.; Zhu, Y.; Chen, C.; Peng, Q.; Liu, Q.; Hu, P.; Wang, D.; Li, Y. Ordered Porous Nitrogen-Doped Carbon Matrix with Atomically Dispersed Cobalt Sites as an Efficient Catalyst for Dehydrogenation and Transfer Hydrogenation of N-Heterocycles. *Angew. Chem., Int. Ed.* **2018**, *57*, 11262–11266.
- (205) Zhang, J.-W.; Li, D.-D.; Lu, G.-P.; Deng, T.; Cai, C. Reversible Dehydrogenation and Hydrogenation of N-Heterocycles Catalyzed by Bimetallic Nanoparticles Encapsulated in MIL-100(Fe). *ChemCatChem.* **2018**, *10*, 4966–4972.
- (206) Su, H.; Sun, L.-H.; Xue, Z.-H.; Gao, P.; Zhang, S.-N.; Zhai, G.-Y.; Zhang, Y.-M.; Lin, Y.-X.; Li, X.-H.; Chen, J.-S. Nitrogen-thermal modification of the bifunctional interfaces of transition metal/carbon dyads for the reversible hydrogenation and dehydrogenation of heteroarenes. *Chem. Commun.* **2019**, *55*, 11394–11397.
- (207) Deraedt, C.; Ye, R.; Ralston, W. T.; Toste, F. D.; Somorjai, G. A. Dendrimer-Stabilized Metal Nanoparticles as Efficient Catalysts for Reversible Dehydrogenation/Hydrogenation of N-Heterocycles. *J. Am. Chem. Soc.* **2017**, *139*, 18084–18092.
- (208) Jaiswal, G.; Subaramanian, M.; Sahoo, M. K.; Balaraman, E. A Reusable Cobalt Catalyst for Reversible Acceptorless Dehydrogenation and Hydrogenation of N-Heterocycles. *ChemCatChem.* **2019**, *11*, 2449–2457.
- (209) Cui, Y.; Kwok, S.; Bucholtz, A.; Davis, B.; Whitney, R. A.; Jessop, P. G. The effect of substitution on the utility of piperidines and octahydroindoles for reversible hydrogen storage. *New J. Chem.* **2008**, *32*, 1027–1037.
- (210) Xie, Y.; Milstein, D. Pd Catalyzed, Acid Accelerated, Rechargeable, Liquid Organic Hydrogen Carrier System Based on Methylpyridines/Methylpiperidines. *ACS Appl. Energy Mater.* **2019**, *2*, 4302–4308.
- (211) Oh, J.; Jeong, K.; Kim, T. W.; Kwon, H.; Han, J. W.; Park, J. H.; Suh, Y.-W. 2-(*N*-Methylbenzyl)pyridine: A Potential Liquid Organic Hydrogen Carrier with Fast H<sub>2</sub> Release and Stable Activity in Consecutive Cycles. *ChemSusChem* **2018**, *11*, 661–665.
- (212) Su, X.; Kung, K.; Lahtinen, J.; Shen, R. Y.; Somorjai, G. A. Cyclohexene dehydrogenation and hydrogenation on Pt(111) monitored by SFG surface vibrational spectroscopy: different reaction mechanisms at high pressures and in vacuum. *Catal. Lett.* **1998**, *54*, 9–15.
- (213) Zhou, G.; Li, T.; Chen, J.; Deng, L.; Xie, H. Nano-Pd/CeO<sub>2</sub> catalysts for hydrogen storage by reversible benzene hydrogenation/dehydrogenation reactions. *Int. J. Hydrg. Energy* **2021**, *46*, 14540–14555.

- (214) Chen, L.; Verma, P.; Hou, K.; Qi, Z.; Zhang, S.; Liu, Y.-S.; Guo, J.; Stavila, V.; Allendorf, M. D.; Zheng, L.; Salmeron, M.; Prendergast, D.; Somorjai, G. A.; Su, J. Reversible dehydrogenation and rehydrogenation of cyclohexane and methylcyclohexane by single-site platinum catalyst. *Nat. Commun.* **2022**, *13*, 1092.
- (215) Hamayun, M. H.; Hussain, M.; Maafa, I. M.; Aslam, R. Integration of hydrogenation and dehydrogenation system for hydrogen storage and electricity generation – simulation study. *Int. J. Hydrol. Energy* **2019**, *44*, 20213–20222.
- (216) Zhang, X.; He, N.; Lin, L.; Zhu, Q.; Wang, G.; Guo, H. Study of the carbon cycle of a hydrogen supply system over a supported Pt catalyst: methylcyclohexane–toluene–hydrogen cycle. *Catal. Sci. Technol.* **2020**, *10*, 1171–1181.
- (217) Kalenchuk, A. N.; Davshan, N. A.; Bogdan, V. I.; Dunaev, S. F.; Kustov, L. M. Reversible hydrogenation–dehydrogenation reactions of meta-terphenyl on catalysts with various supports. *Russ. Chem. Bull.* **2018**, *67*, 28–32.
- (218) Kalenchuk, A. N.; Bogdan, V. I.; Dunaev, S.; Kustov, L. M. Effect of Isomerization on the Reversible Reaction of Hydrogenation–Dehydrogenation of ortho-Terphenyl on a Pt/C Catalyst. *Chem. Eng. Technol.* **2018**, *41*, 1842–1846.
- (219) Kalenchuk, A.; Bogdan, V.; Dunaev, S.; Kustov, L. Influence of steric factors on reversible reactions of hydrogenation-dehydrogenation of polycyclic aromatic hydrocarbons on a Pt/C catalyst in hydrogen storage systems. *Fuel* **2020**, *280*, 118625.
- (220) Brückner, N.; Obesser, K.; Bösmann, A.; Teichmann, D.; Arlt, W.; Dungs, J.; Wasserscheid, P. Evaluation of Industrially Applied Heat-Transfer Fluids as Liquid Organic Hydrogen Carrier Systems. *ChemSusChem* **2014**, *7*, 229–235.
- (221) Jorschick, H.; Preuster, P.; Dürr, S.; Seidel, A.; Müller, K.; Bösmann, A.; Wasserscheid, P. Hydrogen storage using a hot pressure swing reactor. *Energy Environ. Sci.* **2017**, *10*, 1652–1659.
- (222) Dürr, S.; Zilm, S.; Geißelbrecht, M.; Müller, K.; Preuster, P.; Bösmann, A.; Wasserscheid, P. Experimental determination of the hydrogenation/dehydrogenation - Equilibrium of the LOHC system H<sub>0</sub>/H<sub>18</sub>-dibenzyltoluene. *Int. J. Hydrol. Energy* **2021**, *46*, 32583–32594.
- (223) Shi, L.; Qi, S.; Qu, J.; Che, T.; Yi, C.; Yang, B. Integration of hydrogenation and dehydrogenation based on dibenzyltoluene as liquid organic hydrogen energy carrier. *Int. J. Hydrol. Energy* **2019**, *44*, 5345–5354.
- (224) Shi, L.; Zhou, Y.; Qi, S.; Smith, K. J.; Tan, X.; Yan, J.; Yi, C. Pt Catalysts Supported on H<sub>2</sub> and O<sub>2</sub> Plasma-Treated Al<sub>2</sub>O<sub>3</sub> for Hydrogenation and Dehydrogenation of the Liquid Organic Hydrogen Carrier Pair Dibenzyltoluene and Perhydridobenzyltoluene. *ACS Catal.* **2020**, *10*, 10661–10671.
- (225) Shi, L.; Zhou, Y.; Tan, X.; Qi, S.; Smith, K. J.; Yi, C.; Yang, B. The effects of alumina morphology and Pt electron property on reversible hydrogenation and dehydrogenation of dibenzyltoluene as a liquid organic hydrogen carrier. *Int. J. Hydrol. Energy* **2022**, *47*, 4704–4715.
- (226) Ali, A.; G, U. K.; Lee, H. J. Parametric study of the hydrogenation of dibenzyltoluene and its dehydrogenation performance as a liquid organic hydrogen carrier. *J. Mech. Sci. Technol.* **2020**, *34*, 3069–3077.
- (227) Jang, M.; Jo, Y. S.; Lee, W. J.; Shin, B. S.; Sohn, H.; Jeong, H.; Jang, S. C.; Kwak, S. K.; Kang, J. W.; Yoon, C. W. A High-Capacity, Reversible Liquid Organic Hydrogen Carrier: H<sub>2</sub>-Release Properties and an Application to a Fuel Cell. *ACS Sustain. Chem. Eng.* **2019**, *7*, 1185–1194.

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