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A potential liquid organic hydrogen carrier: 2-(*n*-methylbenzyl) pyridine with fast H$_2$ release and stable activity in consecutive hydrogenation-dehydrogenation cycles

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Abstract: For H$_2$ storage based on reversible hydrogenation and dehydrogenation of a liquid organic hydrogen carrier (LOHC), we herein demonstrate a potential of 2-(*n*-methylbenzyl)pyridine (MBP) with the H$_2$ storage density of 6.15 wt%. This material and the corresponding perhydro product (H12-MBP) exist in liquid state at room temperature. Remarkably, H$_2$ release is much faster from H12-MBP over Pd/C than from the benchmark perhydro benzyltoluene over Pt/C at lower temperatures than 270 °C due to the addition of N atom into the benzene ring. Since this positive effect is unfavorable to the hydrogenation reaction, more Ru/Al$_2$O$_3$ catalyst or prolonged reaction time would be applied for complete H$_2$ storage. Experiments for repeated hydrogenation/dehydrogenation cycles reveal that reversible H$_2$ storage and release are possible without degradation of the pair MBP/H12-MBP. The prepared MBP satisfies the requirements in chemical stability, handling properties, and cytotoxicity test.

The hydrogen economy is based on three elements such as production, storage, and utilization of hydrogen as an energy carrier.[1] H$_2$ is currently produced by steam reforming of fossil fuels, and future H$_2$ production is likely based on the electrolysis of water using electricity generated from renewable energy resources. The produced hydrogen can be utilized, for example, in fuel cells or in internal combustion engines while fuel cells available at a lower cost are being developed. However, there are a number of issues to be addressed for efficient hydrogen storage. Among three types of conversion to overcome storage limitations associated with elemental hydrogen, reversible H$_2$ storage by means of chemical bonds (i.e., hydrogenation and dehydrogenation) is proposed to be a promising solution.[2] In this concept a H$_2$-lean molecule is hydrogenated at a site supplying abundant, cheap hydrogen into the corresponding H$_2$-rich molecule that can be stored for extended periods and transported using present energy transport infrastructures. H$_2$ is finally released at energy demand sites via catalytic dehydrogenation and then H$_2$-lean molecule can go back to

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every H$_2$ supply sites for energy storage. In such "chemical storage" a favorable chemical state is liquid phase rather than gas phase, thus named liquid organic hydrogen carrier (LOHC) materials. LOHCs are high-boiling organic molecules that can be easily and reversibly hydrogenated and dehydrogenated in catalytic processes.

N-ethylcarbazole (NEC) is a promising LOHC that was suggested by the company Air Products and Chemicals.[3] H$_2$-lean NEC is converted to the corresponding perhydro product (H12-NEC) by the hydrogenation reaction, where the added H$_2$ per mol NEC are 6 mol yielding H$_2$ storage capacity of 5.8 wt%.[4] However, the pair NEC/H12-NEC has two main drawbacks to complicate implementation for practical applications; a) the fully dehydrogenated, pure NEC is a solid at room temperature due to the melting point of 68 °C and NEC even at the hydrogenation degrees above 10% can be solid under ambient conditions;[5] b) the thermal stability of NEC is limited by the dealkylation to carbazole possibly happening above 270 °C in the presence of dehydrogenation catalysts, although the typical temperature for H12-NEC dehydrogenation is around 230 °C. To overcome these limitations, Wasserscheid and coworkers suggested alternative LOHC systems using isomeric benzyltoluenes (BT) and dibenzyltoluenes (DBT) that have been widely used as industrial heat-transfer fluids.[6] Despite their practical attractiveness, the dehydrogenation of H$_2$-rich BT (H12-BT) and DBT (H18-DBT) requires elevated temperatures compared to H12-NEC; for instance, full dehydrogenation is achieved at temperatures higher than 270 °C and needs prolonged exposure to catalyst particles.

In this respect, the substitution with nitrogen in aromatic rings is worth being considered, as demonstrated in the NEC/H12-NEC pair. Crabtree described that nitrogen atoms have a positive effect on thermodynamic properties concerning their use as hydrogen carriers.[7] Müller et al. also confirmed the potential of nitrogen-containing aromatic compounds to experience enthalpy changes during hydrogenation and thereby favor the dehydrogenation reaction.[2c] Thus, we examined the enthalpy of dehydrogenation reaction ($\Delta H_{dehydro}$) by density functional theory (DFT) calculations (details in Supporting Information), when the perhydro product of diphenylmethane is modified by N substitution and CH$_3$ addition. Figure 1 clearly shows that the substitution of N atom into the aromatic ring makes the release of hydrogen thermodynamically favorable by reducing the overall dehydrogenation enthalpy while it decreases H$_2$ storage capacity in relatively small extents (marked by blue arrows). The addition of methyl group is also effective in the reduction of the dehydrogenation enthalpy but lowers H$_2$ storage capacity by at least 0.41 wt% per methyl group. Since the enthalpy of dehydrogenation for the heterocyclic ring is lower than that for the homocyclic ring, the materials containing at least one N-containing heterocycle like **2**, **4**, **5**, **6**, and **7** have lower overall dehydrogenation values compared to benchmark H12-BT (**3**). However, some problems were found for the materials **2**, **4**, and **6**; 1) the opening of the N-containing ring was observed in the dehydrogenation of the material **2** over Pd/C at 270 °C; 2) it was hard to technically prepare the dehydrogenation product of the materials **4** and **6** as liquid state due to strong intermolecular interaction of N atoms. Since the theoretical H$_2$ storage capacity of the material **7** is below 6 wt%, the material **5** (marked by a red star) was selected for this communication and demonstrated for the first time as a potential LOHC material.

Figure 1. Effect of N substitution and CH$_3$ addition to dicyclohexylmethane on the calculated dehydrogenation enthalpy value and theoretical hydrogen storage capacity. The value in parentheses indicates the difference of $\Delta H_{dehydro}$ between the molecules in each arrow.

Scheme 1. Synthesis protocol for MBP starting from 2-methylpyridine.

The molecular weights of the as-prepared MBP and its perhydro product, 2-[(n-methylcyclohexyl)-methyl]piperidine isomers (H12-MBP), were measured to be 183.1124 (calcd. 183.1126 for $C_{13}H_{13}N$) and 195.2064 (calcd. 195.2065 for $C_{13}H_{25}N$) by high-resolution mass spectra, respectively (Figure S2). This represents the theoretical H$_2$ storage capacity of 6.15 wt% similar to the pairs toluene/methylcyclohexane (6.12 wt%) and BT/H12-BT (6.22 wt%). The melting points of MBP and H12-MBP were measured to be in the range −50.1 to −46.2 °C and −19.3 to −18.0 °C, respectively (Figure S3), indicating that they both exist in liquid state at room temperature. Their boiling points were estimated to be ca. 291–293 °C. These thermal properties are comparable to those of the pair BT/H12-BT and clearly fulfill thermal requirement for reversible LOHC materials. Therefore, the process conditions for H$_2$ storage and release will be nearly similar with both pairs.

Next, we examined catalytic H$_2$ release from H12-MBP with supported Pt and Pd catalysts (metal/reactant (M/R) = 0.1 mol%) at 270 °C typical for the dehydrogenation of H12-BT (Table 1). In the dehydrogenation of H12-MBP, supported Pd catalysts on carbon and alumina were more active than Pt analogues on the same supports, where Pd/C showed nearly 100% efficiency in H$_2$ release. This is contrary to the results in the dehydrogenation of H12-BT; consistent with Wasserscheid et al.,[6] our activity results identified the superior performance of supported Pt to Pd. Further tests at 230 and 250 °C confirmed the higher dehydrogenation activities of Pd/C in the conversion of H12-MBP. In order to validate experimental results, we are making DFT calculations as examined for catalytic behaviors of Pt and Pd in the dehydrogenation of decalin to naphthalene,[9] which will be reported later.

The important finding is much faster H$_2$ release from H12-MBP over Pd/C compared to the benchmark H12-BT over Pt/C at 230, 250, and 270 °C (Figure 2a). The addition of N atom into the benzene ring is beneficial to the dehydrogenation reaction, similar to the dehydrogenation performance of Pd catalysts for H12-NEC.[10] However, catalyst deactivation cannot be ruled out because the catalytic dehydrogenation of H12-MBP became saturated at 230 and 250 °C by preferential adsorption of the pyridine ring. As the piperidine ring is dehydrogenated much

Since the material **5** is not commercially available, the synthesis protocol for acquiring in bulk quantity was investigated at first. In preliminary tests, the Friedel-Crafts alkylation of toluene with 2-chloromethyl pyridine over aluminum chloride showed a higher product yield (>90%) than coupling reactions using Grignard reagent, organozinc halide or metal catalyst with special ligands. However, since the production cost largely depends on the price of 2-chloromethyl pyridine, we developed the synthesis protocol starting from 2-methylpyridine (Scheme 1), which was described in Supporting Information. The final product identified by ^{13}C NMR spectrum (Figure S1) was 2-(n-methylbenzyl)pyridine isomers (hereafter referred to as MBP). Since the proposed synthesis needs relatively simple work-up and cheap raw materials, MBP could be prepared cheaply; for instance, the material cost approximately amounts to US $8 to $9 per kilogram when calculated from bulk quote of raw materials. Note that the retail price of technically available BT (e.g., Marlotherm® LH as a registered trademark of Sasol Germany GmbH) ranges in US $7 to $8 per kilogram. We are now pursuing to secure a cheaper synthesis protocol at several tons scale based on the direct chlorination of 2-methylpyridine.[8]

Table 1. Activity results in the dehydrogenation of H12-MBP and H12-BT for 4 h.

Catalyst	Temperature [°C]	M/R [mol%, wt%][a]	Conversion [mol%][b]	Selectivity to MBP or BT [mol%][b]	H$_2$ yield [mol%][b]	H$_2$ volume [cm^3][c,d]
H12-MBP conversion						
Pt/C (1 wt%)	270	0.1, 0.100	62.8	78.3	55.9	643.1 (56.7)
Pt/Al$_2$O$_3$ (1 wt%)	270	0.1, 0.100	58.9	79.8	53.0	605.6 (53.4)
Pd/C (1 wt%)	270	0.1, 0.054	98.7	99.9	98.7	1132.4 (99.9)
Pd/Al$_2$O$_3$ (1 wt%)	270	0.1, 0.054	92.2	99.2	91.8	1045.7 (92.2)
Pd/C (1 wt%)	250	0.1, 0.054	60.4	90.9	57.7	662.3 (58.4)
Pd/C (1 wt%)	230	0.1, 0.054	37.3	54.7	28.8	342.5 (30.2)
Pd/C (1 wt%)	250	0.2, 0.109	94.4	98.4	93.6	1082.0 (95.4)
Pd/C (1 wt%)	230	0.4, 0.217	73.6	92.7	70.9	824.5 (72.7)
Pd/C (1 wt%)	230	0.6, 0.326	86.7	97.6	85.7	968.6 (85.4)
H12-BT conversion						
Pt/C (1 wt%)	270	0.1, 0.100	99.9	98.6	99.2	1132.4 (99.9)
Pt/Al$_2$O$_3$ (1 wt%)	270	0.1, 0.100	95.0	97.2	93.7	1079.7 (95.2)
Pd/C (1 wt%)	270	0.1, 0.054	60.8	85.1	56.2	646.5 (57.0)
Pd/Al$_2$O$_3$ (1 wt%)	270	0.1, 0.054	49.1	86.3	45.7	543.3 (47.9)
Pt/C (1 wt%)	250	0.1, 0.100	61.1	80.0	55.0	641.9 (56.6)
Pt/C (1 wt%)	230	0.1, 0.100	26.9	93.7	26.1	299.4 (26.4)
Pt/C (1 wt%)	250	0.2, 0.200	98.1	92.2	94.2	1102.4 (97.2)
Pt/C (1 wt%)	230	0.4, 0.400	47.5	88.3	44.7	514.9 (45.4)
Pt/C (1 wt%)	230	0.6, 0.600	79.2	86.3	73.8	822.3 (72.5)

[a] M/R = Metal-to-reactant ratio. [b] Calculated by GC results. [c] Measured by gas burette at the end of the experiment. [d] The values in parenthesis indicate calculated H$_2$ yields (unit: %) on the basis of H$_2$ volume (1134.2 cm^3) expected upon complete dehydrogenation of the reactant.

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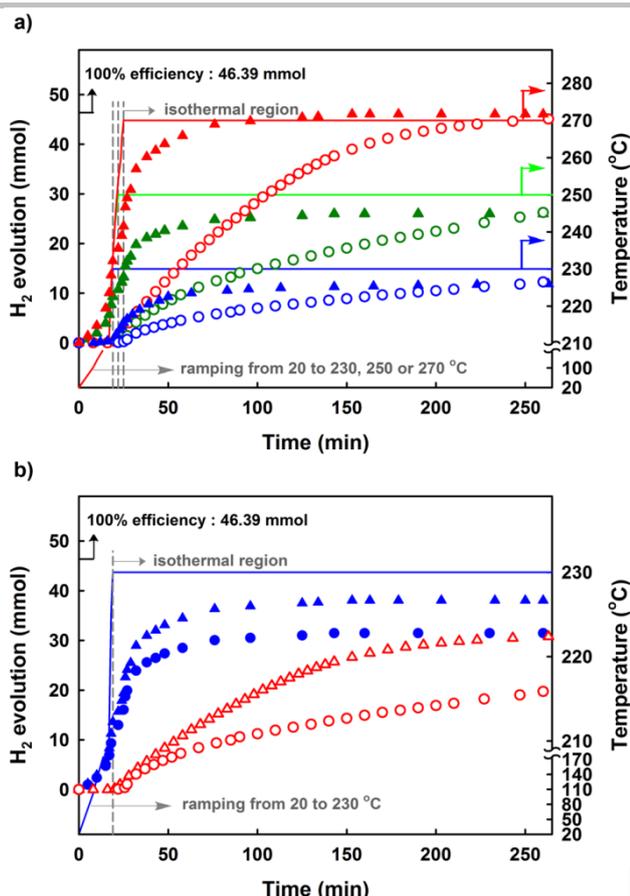
Figure 2. a) Time-dependent H₂ release curves for H12-MBP over Pd/C (filled symbols) and for H12-BT over Pt/C (open symbols) at 230, 250, and 270 °C, where the M/R value was 0.1 mol%. b) H₂ release curves at 230 °C for H12-MBP over Pd/C (blue symbols) and for H12-BT over Pt/C (red symbols), where the M/R value was 0.4 mol% (circles) or 0.6 mol% (triangles). The horizontal lines represent the isothermal region in the experiments.

faster than the cyclohexane ring, 2-[(*n*-methylcyclohexyl)-methyl]pyridine isomers were only detected as the reaction intermediate (identified by ¹H NMR spectra and GC chromatograms in Figure S4). In order to prevent this trouble, more active metals relative to the amount of H12-MBP are required; for instance, 95.4% of theoretical H₂ volume was attained at 250 °C with Pd/C with the M/R value of 0.2 mol% (Table 1). It is more remarkable that at 230 °C the dehydrogenation of H12-MBP over Pd/C is faster and, at the same time, more efficient than that of H12-BT over Pt/C, where the M/R value is sufficiently high at 0.4 and 0.6 mol% (Figure 2b). Since H₂ release is more facile from H12-MBP than from H12-BT, we can use milder conditions for the dehydrogenation of the former material.

Next, the hydrogenation of MBP into the corresponding

perhydro isomers was studied at 150 °C and 50 bar of H₂ over supported Ru catalysts, where the reaction condition is similar to that in Wasserscheid et al.[6] When the M/R value of 0.08 mol% and the reaction time of 2 h were used, H₂ loading was less efficient for MBP than for BT over a commercial 5 wt% Ru/Al₂O₃ (Table 2). Note that the pyridine ring is hydrogenated earlier than the benzene ring (identified by ¹H NMR spectra and GC chromatograms in Figure S5), as found in the synthesis of 2- and 4-substituted benzylpiperidines.[11] Even with 0.23 mol% M/R value and more active Ru catalysts demonstrated in the hydrogenation of benzylpyridine,[12] 100% selectivity to H12-MBP was not obtained at 2 h though the conversion of MBP reached 100%. This is due to an adverse effect of introducing N atom into the aromatic ring on the Gibbs free energy of hydrogenation reaction. Nevertheless, such limitation could be circumvented by applying a prolonged reaction time (e.g., 4 h) or by adding more catalyst amount relative to the MBP amount (e.g., M/R of 0.30 mol%). When considering a much lower price of Ru (US $65 per troy oz. in September 2017) than other noble metals (Pt and Pd: US $979 and $943 per troy oz., respectively), the latter option (i.e., more catalyst) would be recommended for practical application.

Under the best conditions for the hydrogenation and dehydrogenation reactions, the reversibility of only the pair MBP/H12-MBP was tested (Figure S6). In the first cycle, the H₂ storage efficiency of the as-prepared MBP was estimated to be 100% over Ru/Al₂O₃ and the measured H₂ yield released from the hydrogenation product H12-MBP was also 100 mol% over Pd/C. The same values of H₂ storage efficiency and H₂ yield were achieved in the second and third cycles. When the gas chromatograms of the product mixtures obtained in the three-cycle test were compared, no decomposition products were found in the liquid phase (Figure 3). Also, light boiling decomposition products were not detected in the gas phase (Figure S7), which will be investigated more accurately in our further work. Therefore, the pair MBP/H12-MBP can be used reversibly. Notably, the hydrogenation and dehydrogenation products obtained from the experiments were used repeatedly, for example, at least fifty times due to difficulty in the consistent supply of fresh MBP.

The stability of H₂-lean MBP was also tested under three different conditions. As listed in Table S1, MBP was very stable under air at 100 °C and under N₂ at 270 °C for 72 hours, similar to BT under identical conditions. This indicates that MBP can be stored at ambient temperature and even at high temperatures if inert atmosphere is applied. However, the test in the presence of a typical dehydrogenation catalyst Pd/C (M/R = 0.2 mol%) under N₂ at 270 °C showed the formation of decomposition products whose amount was slightly higher than from BT with Pt/C, which is similar to the NEC case.[6] Such formation could be significantly reduced at a lower temperature of 250 °C showing nearly complete dehydrogenation of H12-MBP.

Additionally, the MBP properties relevant to practical transportation and storage were investigated. First, the apparent viscosity of H₂-lean MBP was measured in the temperature

Table 2. Catalytic H₂ storage of H₂-lean BT and MBP at 150 °C and 50 bar over Ru/Al₂O₃

Reactant (20 ml)	Catalyst	M/R [mol%, wt%][a]	Time [h]	Conversion [mol%][b]	Selectivity to H12-BT or H12-MBP [mol%][b]	H₂ storage eff. [%][c]
BT	5 wt% Ru[d]	0.05, 0.03	2	100.0	77.6	88.8
BT	5 wt% Ru[d]	0.08, 0.05	2	100.0	100.0	100.0
MBP	5 wt% Ru[d]	0.08, 0.05	2	21.0	0.0	10.5
MBP	5 wt% Ru[d]	0.23, 0.13	2	100.0	44.2	72.1
MBP	5 wt% Ru[e]	0.23, 0.13	2	100.0	66.8	83.4
MBP	1 wt% Ru[e]	0.23, 0.13	2	100.0	77.7	88.8
MBP	1 wt% Ru[e]	0.23, 0.13	4	100.0	100.0	100.0
MBP	1 wt% Ru[e]	0.30, 0.17	2	100.0	100.0	100.0

[a] M/R = Metal-to-reactant ratio. [b] calculated by GC results. [c] H₂ storage efficiency = (full hydrogenation product [mol] × 6H₂ + single-ring hydrogenation product [mol] × 3H₂)/(reactant [mol] × 6H₂) × 100%. [d] 5 wt.% Ru/Al₂O₃ (Alfa Aesar) used after reduction by H₂ at 250 °C for 4 h. [e] 1 and 5 wt% Ru/γ-Al₂O₃ prepared by H₂ activation of Al₂O₃-supported Ru₃(CO)₁₂ precursor at 500 °C for 5 h.

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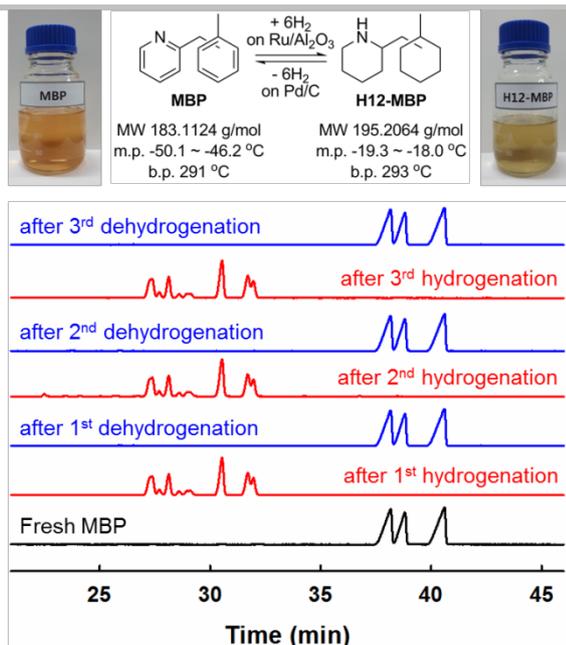
Figure 3. GC chromatograms of the product mixtures obtained thorough three cycles of MBP hydrogenation over 1 wt% Ru/Al$_2$O$_3$ (reaction condition: M/R = 0.3 mol%, 150 °C, 50 bar, 2 h) and H12-MBP dehydrogenation over 1 wt% Pd/C (reaction condition for H$_2$ release: M/R = 0.1 mol%, 270 °C, 4 h). For GC analysis, the oven program A (presented in Supporting Information) was used.

range −5 to 50 °C (details in Supporting Information). The values are higher than those of BT at all temperatures (Figure S8), but the difference at 25 °C is only 2.1 cP (3.8 cP for BT vs. 5.9 cP for MBP). When compared with DBT (ca. 37.8 cP) and ethylene glycol (16.1 cP) at 25 °C, MBP is much less viscous. Next, the corrosion rate of MBP and H12-MBP was evaluated by the copper strip corrosion test (ASTM D130-12) to visually compare with the Copper Strip Corrosion Standards a color of Cu strips obtained after immersion in a solution at 100 °C specific for diesel fuels for 3 h, (Figure S9).[13] In the tests with fresh H12-MBP and MBP solutions at 100 °C, the corrosion rate was estimated to be 1a or 1b ("slight tarnish"), as shown in Figure S10. The similar corrosion rate was examined with the MBP solution obtained after the third dehydrogenation in the three-cycle test at 100 °C and even at the elevated temperature of 270 °C, which was also observed in the tests with BT at 100 and 270 °C. Therefore, MBP can be transported through existing pipelines without difficulty.

In summary, we examined the potential of the pair MBP/H12-MBP as a possible LOHC material, where the melting points of both molecules are lower than 0 °C and their boiling points are ca. 291–293 °C. Overall, this pair showing H$_2$ storage density of 6.15 wt% fairly satisfies the requirements in chemical reversibility without decomposition, chemical and thermal stability, and handling property. Particularly, the full dehydrogenation of H12-MBP could be performed at lower temperatures with faster rates than that of the benchmark BT used as a heat transfer fluid, which is the favorable effect of N atom present in the pyridine ring. Although this effect influenced the hydrogenation reaction adversely, it could be overcome simply by more addition of supported Ru catalyst because Ru is much cheaper than other noble metals. Consequently, the pair MBP/H12-MBP is evaluated to contain LOHC properties comparable to or even better than the pair BT/H12-BT. Nevertheless, additional works would be done to address the possibility of our LOHC material in practical use, including the matters related with the hydrogenation and dehydrogenation reactions (typically, the preparation of more active hydrogenation and dehydrogenation catalysts (now under study) and the development of efficient reactors for H$_2$ storage and release). Particularly, toxicological aspects of MBP and H12-

MBP should be evaluated; although the cytotoxicity test showed that MBP-treated cells are more viable than BT-treated ones (Figure S11), the ecotoxicity against aquatic environments would be studied in near future.

Conflict of interest

The authors declare no conflict of interest.

Keywords: sustainable chemistry • hydrogen storage • dehydrogenation • N-containing heterocycles

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Boost up H$_2$ economy: A new liquid organic hydrogen carrier is designed by adding N atom into the benzene ring of a benchmark heat transfer fluid. The crossover between H$_2$-lean and H$_2$-rich forms of the title material is successfully reversible in repeated runs. Notably, H$_2$ release is very fast owing to a reduced dehydrogenation enthalpy by the presence of N atom. Our approach can contribute to an efficient H$_2$ storage system.
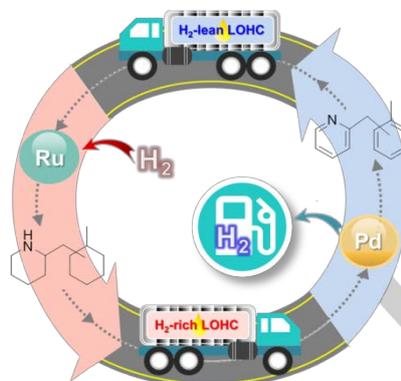
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A potential liquid organic hydrogen carrier: 2-(*n*-methylbenzyl)pyridine with fast H$_2$ release and stable activity in consecutive hydrogenation-dehydrogenation cycles