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Pd catalyzed, acid accelerated, rechargeable, liquid organic hydrogen carrier system based on methylpyridines/methylpiperidines

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ABSTRACT

Efficient, solvent-free, liquid to liquid hydrogen storage systems based on reversible dehydrogenation and hydrogenation using a single heterogeneous supported Pd catalyst are reported, including (a) 2-picoline/2-methylpiperidine, and (b) 2,6-lutidine/2,6-dimethylpiperidine, having 6.1 wt% and 5.3 wt% theoretical hydrogen storage capacity, respectively. By simply blending Pd(OAc)$_2$, activated carbon and methylpiperidines, a very active supported Pd/C$_w$ (Pd/C$_w$ = Pd on activated carbon for Hydrogen Storage) and catalytic acetic acid were generated in situ, which catalyzed the dehydrogenation of 2-methylpiperidine or 2,6-dimethylpiperidine to 2-picoline or 2,6-lutidine in excellent yields (91% and 100% yields respectively), and releasing H$_2$ at a fast rate under mild conditions. Our studies revealed that mild acids or acidic groups on the support surface significantly accelerate the dehydrogenation. The reverse hydrogenation of both 2-picoline (2-7 bar) and 2,6-lutidine (1.6-5 bar) was achieved under exceptionally low H$_2$ pressure.
Furthermore, the Pd/C\textsubscript{ac} catalyst can be easily recovered and reused without decrease in catalytic activity.


**INTRODUCTION**

Hydrogen is one of the cleanest energy carriers.\textsuperscript{1-3} However, due to its volumetric low energy density and broad explosion limits, the storage of hydrogen is considered as a bottleneck for establishing a hydrogen-based energy system.\textsuperscript{3} In recent years, storing hydrogen in chemical bonds has gained much attention, and is regarded as a promising pathway for a future “hydrogen economy”.\textsuperscript{4} Several kinds of metal hydrides, metal complexes and organic compounds have been investigated in this regard.\textsuperscript{5-24} Particularly interesting are liquid organic compounds as hydrogen carriers, which can have high hydrogen capacities, close to the U.S. Department of Energy (DOE of US, 5.5 wt% and 40 g/L hydrogen storage capacity) and European Union (EU, 5 wt% and 23 g/L hydrogen storage capacity) target for 2020. Moreover, liquid organic hydrogen carriers (LOHC) can have good stability, can be stored for a long time and readily transported, and may have potential applicability for on-board usage in vehicles.\textsuperscript{5-11}

A LOHC system is based on catalytic dehydrogenation of a hydrogen rich organic liquid, forming a H\textsubscript{2}-lean compound, which upon catalytic hydrogenation can regenerate the H\textsubscript{2}-rich compound. In early studies, aromatic hydrocarbons and their hydrogenated products were investigated as couples of H\textsubscript{2}-lean and H\textsubscript{2}-rich compounds.\textsuperscript{12,13} These LOHC systems can have a wide liquid range, excellent thermal stabilities, at low price. However, the dehydrogenation of hydrocarbons for producing H\textsubscript{2} and the corresponding H\textsubscript{2}-low aromatic hydrocarbons is
thermodynamically unfavorable and requires high temperatures (above 250 °C), resulting in decomposition processes.\textsuperscript{12-14}

The presence of a nitrogen atom in LOHC systems based on \(N\)-heterocycles can reduce the enthalpy of dehydrogenation and hydrogenation, hence several \(N\)-heterocyclic LOHC systems have been investigated.\textsuperscript{15-22} One of the most attractive examples is the \(N\)-ethylcarbazole (NEC)/dodecahydro-\(N\)-ethylcarbazole (H\(_2\)-NEC) system, which has 5.80 wt\% theoretical hydrogen storage capacity (HSC), developed by Pez\textsuperscript{15} and his co-workers (Scheme 1a). However, the NEC/H\(_2\)-NEC system has significant drawbacks, hampering commercialization, including: \(N\)-ethylcarbazole is a solid at room temperature; the \(N\)-ethyl group is thermally labile, leading to undesired side products; and the reverse hydrogenation requires high \(H_2\) pressure (68 bar).

A liquid to liquid LOHC system based on 1-methylindole/octahydro-1-methylindole was reported independently by the groups of Jessop\textsuperscript{16} and Ke\textsuperscript{17} (Scheme 1b). Jessop reported that using a Pd catalyst (5 wt\% Pd/Al\(_2\)O\(_3\), 10 wt\% Pd/C, or 5 wt\% Pd/SiO\(_2\)), at 165 °C, octahydro-1-methylindole was converted to a mixture of 1-methylindole, 1-methy-4,5,6,7-tetragdrolindole and unknown compounds in high conversions. Ke reported that using 5 wt\% Pd/Al\(_2\)O\(_3\), at 160-200 °C, octahydro-1-methylindole was converted to 1-methylindole in 100% conversion and good selectivity. However, the reverse hydrogenation of 1-methylindole to octahydro-1-methylindole requires 60 bar of \(H_2\), using 5 wt\% Ru/Al\(_2\)O\(_3\) as a catalyst. Furthermore, Suh\textsuperscript{18} and his co-workers reported a liquid to liquid hydrogen storage system based on 2-[(\(n\)-methylcyclohexyl)methyl]piperidine/2-(\(N\)-methylbenzyl)pyridine, which requires high temperature for dehydrogenation (above 230 °C, Scheme 1c). Other reported \(N\)-based heteroaromatic/heteroalicyclic LOHCs all suffer from high melting points, some of them require an expensive catalyst, or have low selectivity.\textsuperscript{19-22}
Our group developed new LOHC systems based on dehydrogenative amide bond formation, which is thermodynamically favorable, but a solvent was required. Obviously, the development of a LOHC system based on inexpensive organic liquids (which have a wide liquid range, low melting point) with high hydrogen storage capacity, solvent-free, under mild conditions, ideally using a single catalyst for both hydrogenation and dehydrogenation is an important challenge.

Scheme 1. Solvent-free LOHC systems based on nitrogen-containing cyclic organic compounds.

a) \(N\)-ethylcarbazole (NEC)/dodecahydro-\(N\)-ethylcarbazole (H\(_{12}\)-NEC) system

\[
\begin{align*}
\text{Cat. Pd/LiAlO}_2 \\
197^\circ\text{C}, \text{H}_2 \ (1 \text{ bar}) \\
\text{Cat. Ru/LiAlO}_2 \\
160^\circ\text{C}, \text{H}_2 \ (68 \text{ bar}) \\
\end{align*}
\]

b) 1-methylindole/octahydro-1-methylindole system

\[
\begin{align*}
\text{Cat. Pd/Al}_2\text{O}_3 \\
160 - 200^\circ\text{C} \\
\text{Cat. Ru/Al}_2\text{O}_3 \\
130^\circ\text{C}, \text{H}_2 \ (60 \text{ bar}) \\
\end{align*}
\]

c) 2-(\(N\)-methylbenzyl)pyridine/2-[(\(n\)-methylcyclohexyl)methyl]piperidine system

\[
\begin{align*}
\text{Cat. Pd/C} \\
230-270^\circ\text{C} \\
\text{Cat. Ru/Al}_2\text{O}_3 \\
150^\circ\text{C}, \text{H}_2 \ (50 \text{ bar}) \\
\end{align*}
\]

d) This work

\[
\begin{align*}
\text{reflux (119 or 128^\circ\text{C}}) \\
\text{internal temperature} \\
\text{Pd/C (0.3 mol\%)} \\
\text{Acid (0.6 mol\%)} \\
\text{H}_2 \ (1.6-7 \text{ bar}), 150^\circ\text{C} \\
\end{align*}
\]

- Liquid to liquid
- Single catalyst for \(H_2\) loading/unloading
- High \(H_2\) storage capacity
- Mild reaction conditions
- Stable \(H_2\) releasing rate
- Low \(H_2\) pressure for charging
methylindole system. c) 2-(N-Methylbenzyl)pyridine/2-[(n-methylcyclohexyl)methyl]piperidine system. d) This work.

Piperidines are considered as potentially ideal candidates as LOHCs, because they are abundant and inexpensive, have low melting points, wide liquid ranges, high hydrogen storage capacities (details see SI, Figure S1). To our knowledge, the solvent-free, acceptorless dehydrogenation of piperidines requires harsh conditions (above 300 °C), using a supported Pd or Pt catalyst and needs to be performed under H₂ or H₂/N₂ flow (details see SI, Table S1). Noteworthy, acceptorless dehydrogenation of 2-methylpiperidine to 2-picoline has not been reported. Therefore, developing a suitable catalytic system for mild, reversible dehydrogenation/hydrogenation of piperidines/pyridines is not only theoretically significant, but also of practical interest. Herein, we present solvent-free LOHC systems based on piperidines, using a single heterogeneous Pd catalyst for both dehydrogenation and hydrogenation under mild conditions, which have a theoretical 5.3-6.1 wt% hydrogen storage capacities.

RESULTS AND DISCUSSION

Initially, we chose 2-methylpiperidine as the model H₂-rich compound, since it has a high, 6.1 wt% theoretical HSC, and the electron-donating methyl group at the 2-position could be beneficial regarding both electronic and steric effects. At the beginning, several heterogeneous catalysts were screened in p-xylene as solvent (for details see SI). Palladium on activated carbon (Pd/C, 4 wt%) was found to be the most efficient catalyst for the acceptorless dehydrogenation of 2-methylpiperidine to 2-picoline. Then, Pd/C was studied as a catalyst for solvent-free dehydrogenation of 2-methylpiperidine. Applying commercial Pd/C (5 wt%) resulted in 42-48% yield of 2-picoline and 9-10% side products, depending on the supplier (Table 1, entries 1 and 2).
Importantly, addition of a catalytic amount of acetic acid (entry 3) improved both the yield (60%) and the selectivity (only ~3% of byproducts were formed). Then, an *in situ* supported catalyst generation strategy was planned for the dehydrogenation process. We chose Pd(OAc)$_2$ as the palladium precursor and dried activated carbon$^{31,32}$ as the support, conditions under which we envisioned that Pd/C and 2 equivalents of acetic acid (from the complex) could potentially be generated. Interestingly, this *in situ* generated palladium catalyst is more active than the pre-prepared commercial ones, resulting in 72% yield of 2-picoline (entry 4). Other palladium sources including PdCl$_2$, Pd(TFA)$_2$ and Pd$_2$(dba)$_3$ had much lower catalytic activities than Pd(OAc)$_2$ (entries 5-7). Next, Pd(OAc)$_2$ was chosen as the best palladium precursor for studying the effect of supports (Table 1, entries 7-11). Replacing activated carbon by SiO$_2$, BN, γ-Al$_2$O$_3$ or CeO$_2$ resulted in very low yields of 2-picoline. In the absence of support, only 3% of 2-picoline was detected, and a palladium mirror was observed at the bottom of Schlenk tube, showing that a Pd$^0$ species was generated in the reaction system (entry 12). Thus, the combination of Pd(OAc)$_2$ and activated carbon is the most efficient catalyst for 2-methylpiperidine dehydrogenation.

**Table 1.** Optimization of 2-methylpiperidine dehydrogenation$^\dagger$.

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Pd]</th>
<th>Support</th>
<th>2-Picoline (%)</th>
<th>Byproducts (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd/C (Fluka)</td>
<td>-</td>
<td>42</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>Pd/C (BDH)</td>
<td>-</td>
<td>48</td>
<td>10</td>
</tr>
<tr>
<td>3$^\dagger$</td>
<td>Pd/C (Fluka)</td>
<td>-</td>
<td>60</td>
<td>3</td>
</tr>
<tr>
<td>4$^\dagger$</td>
<td>Pd(OAc)$_2$</td>
<td>C</td>
<td>72</td>
<td>10</td>
</tr>
<tr>
<td>5$^\dagger$</td>
<td>PdCl$_2$</td>
<td>C</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>6$^\dagger$</td>
<td>Pd(TFA)$_2$</td>
<td>C</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>Entry</td>
<td>Catalyst</td>
<td>Support</td>
<td>Reaction Conditions</td>
<td>Yield</td>
</tr>
<tr>
<td>-------</td>
<td>----------</td>
<td>---------</td>
<td>---------------------</td>
<td>-------</td>
</tr>
<tr>
<td>7</td>
<td>Pd(dba)$_3$</td>
<td>C</td>
<td>2-methylpiperidine (10 mmol), catalyst (0.2 mol% of [Pd]), 170 °C (oil bath, internal temperature is 119 °C, measured by an inserted thermometer), open system under argon flow through the top of the condenser, with cold water circulation. Yields and conversions were determined by GC, using n-heptane as an internal standard.</td>
<td>6</td>
</tr>
<tr>
<td>8</td>
<td>Pd(OAc)$_2$</td>
<td>SiO$_2$</td>
<td>0.04 mmol HOAc was added.</td>
<td>3</td>
</tr>
<tr>
<td>9</td>
<td>Pd(OAc)$_2$</td>
<td>BN</td>
<td>Support (50 mg). Pd(dba)$_3$ = tris(dibenzylideneacetone)dipalladium(0), Pd(TFA)$_2$ = palladium(II) trifluoroacetate, C = activated carbon, BN = boron nitrile.</td>
<td>8</td>
</tr>
<tr>
<td>10</td>
<td>Pd(OAc)$_2$</td>
<td>γ-Al$_2$O$_3$</td>
<td>0.03 mmol Pd(OAc)$_2$, 170 °C (oil bath, internal temperature is 119 °C, measured by inserted thermometer), 27.1 mmol (90% yield) of H$_2$ was released after 51 h (entry 1).</td>
<td>9</td>
</tr>
<tr>
<td>11</td>
<td>Pd(OAc)$_2$</td>
<td>CeO$_2$</td>
<td>The dehydrogenation was also achieved at a lower bath temperature; at 150 °C (oil bath, internal temperature is also 119 °C, measured by inserted thermometer), after 117 h, H$_2$ in 84% yield was collected (entry 2).</td>
<td>12</td>
</tr>
<tr>
<td>12</td>
<td>Pd(OAc)$_2$</td>
<td>-</td>
<td>Moreover, with the same amount of catalyst, doubling the scale of 2-methylpiperidine, the dehydrogenation resulted in similar initial rate, and produced 54.5 mmol (91% yield) of H$_2$ after 94 h (entry 3). Gratifyingly, the reverse hydrogenation was accomplished by directly pressurizing the same reaction mixture with H$_2$. Under 2-7 bar of H$_2$, 2-picoline in the mixture was fully converted to 2-methylpiperidine in 90% yield (Figure 1b).</td>
<td>3</td>
</tr>
</tbody>
</table>

Next, the reaction vessel was connected to a gas collection system (see SI, Figure S2), and the time-dependent H$_2$ release was monitored. As shown in Figure 1a, under the catalysis of Pd(OAc)$_2$/C (Pd(OAc)$_2$ = 0.03 mmol, C = 40 mg), at 170 °C (oil bath, internal temperature is 119 °C, measured by inserted thermometer), 27.1 mmol (90% yield) of H$_2$ was released after 51 h (entry 1). The dehydrogenation was also achieved at a lower bath temperature; at 150 °C (oil bath, internal temperature is also 119 °C, measured by inserted thermometer), after 117 h, H$_2$ in 84% yield was collected (entry 2). Moreover, with the same amount of catalyst, doubling the scale of 2-methylpiperidine, the dehydrogenation resulted in similar initial rate, and produced 54.5 mmol (91% yield) of H$_2$ after 94 h (entry 3). Gratifyingly, the reverse hydrogenation was accomplished by directly pressurizing the same reaction mixture with H$_2$. Under 2-7 bar of H$_2$, 2-picoline in the mixture was fully converted to 2-methylpiperidine in 90% yield (Figure 1b). These results indicate that dehydrogenation and hydrogenation are catalyzed by the same single metal heterogeneous catalyst, and the total amount of byproducts was less than 10%. 

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Figure 1. Hydrogen storage based on 2-picoline/2-methylpiperidine. a) Pd(OAc)$_2$/C catalyzed dehydrogenation of 2-methylpiperidine. b) Reversible interconversion of 2-methylpiperidine and 2-picoline via dehydrogenation and hydrogenation.

In order to understand the processes leading to side reactions, the mixture of byproducts was analyzed by gas chromatography–mass spectrometry (GCMS, Figure S12 and S13). These byproducts have similar retention times (some of them partially overlap) and similar molecular weights, likely py-py and py-pi, which are probably formed via the palladium catalyzed addition of intermediates enamine to imine (See SI, Figure S14a). Therefore, retarding the addition of enamine to imine might be an effective method to improve the selectivity. Our strategy was to increase the steric hindrance of both nucleophilic and electrophilic intermediates (See SI, Figure S14b).
Table 2. Dehydrogenation of piperidine and methylpiperidines

<table>
<thead>
<tr>
<th>Entry</th>
<th>H₂-rich compound</th>
<th>Product (%)</th>
<th>Byproducts (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>piperidine</td>
<td>pyridine (11)</td>
<td>trace</td>
</tr>
<tr>
<td>2</td>
<td>2-methylpiperidine</td>
<td>2-picoline (72)</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>3-methylpiperidine</td>
<td>3-picoline (11)</td>
<td>trace</td>
</tr>
<tr>
<td>4</td>
<td>4-methylpiperidine</td>
<td>4-picoline (46)</td>
<td>7</td>
</tr>
<tr>
<td>5</td>
<td>2,6-dimethylpiperidine</td>
<td>2,6-lutidine (&gt;99)</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>2,6-dimethylpiperidine</td>
<td>2,6-lutidine (100)</td>
<td>0</td>
</tr>
</tbody>
</table>

- Conditions: piperidines (10 mmol), Pd(OAc)₂ (0.2 mol%), C (50 mg), 170 °C (bath temperature), 48h, open system under argon flow through the top of condenser, with cold water circulation. Yields and conversions were determined by GC, using n-heptane as an internal standard. Determined by ¹H NMR, using mesitylene as an internal standard. Determined by GC, based on the peak areas. Open system, argon atmosphere, the condenser was connected to a gas collection system (see SI, Figure S2).

With the above idea, we studied the effect of the substituent group. Piperidine, 3-methylpiperidine, 4-methylpiperidine and 2,6-dimethylpiperidine were investigated (Table 2). Using piperidine or 3-methylpiperidine as the H₂-rich compounds resulted in good selectivity, but low yields of the H₂-lean products (entries 1 and 3). Using 4-methylpiperidine resulted in 46% yield of 4-picoline and about 7% of byproducts (entry 4). Gratifyingly, using 2,6-dimethylpiperidine resulted in more than 99% yield and 100% selectivity (entry 5). The electron-donating methyl groups at 2- and 6-positions prevent deactivation of the catalyst and the increasing the product dissociation constant from the catalyst. Significantly, quantitative dehydrogenation of 2,6-dimethylpiperidine was achieved also with no argon flow (entry 6), and gave 100% yield of pure H₂ gas (H₂ purity > 99.99%, confirmed by GC, no impurity was observed, Figure S17). Thus,
a LOHC system based on 2,6-lutidine/2,6-dimethylpiperidine, which has a theoretical HSC of 5.3 wt\%, using the same catalyst system for dehydrogenation/hydrogenation is promising. In addition, the physicochemical properties of 2,6-lutidine and 2,6-dimethylpiperidine meet all the requirements of an ideal LOHC.

The time-dependent H₂ release curves for 2,6-dimethylpiperidine dehydrogenation were recorded by the gas collection system. Under the catalysis by Pd (0.3 mol%), the dehydrogenation of 2,6-dimethylpiperidine proceeded very well, yielding 97% of H₂ after 13 h, and 100% of H₂ after 23 h (Figure 2a). Interestingly, the H₂ release rate was constant before reaching 95% yield of H₂ after 12 h (see blue square in Figure 2a). These results suggest a zero-order rate dependence in 2,6-dimethylpiperidine, likely as a result of saturation of the surface of the catalyst by 2,6-dimethylpiperidine. In addition, measuring the H₂ release rates using different catalyst loadings likely indicate first-order rate dependence in Pd (see SI Figure S19 and Table S7 for details).

Moreover, the regeneration of 2,6-dimethylpiperidine by reverse hydrogenation of 2,6-lutidine was achieved in 100% yield by pressurizing the reaction mixture with only 1.6-5 bar of H₂, at 150 °C for 18 h (Figure 2b, red column 1). The resulting mixture was reused for the second round of dehydrogenation (93% yield, blue column 2) and hydrogenation (100% yield, red column 2), and no decomposition of 2,6-dimethylpiperidine and 2,6-lutidine took place. Additionally, using 0.3 mol% of catalyst, under H₂ pressure of 30-50 bar, at 150 °C, the hydrogenation of 2,6-lutidine yielded 2,6-dimethylpiperidine in 87%, 95% and 98% yields, after 1.5 h, 2 h and 3 h, respectively, which enables fast H₂ loading (see SI Table S8 for details). Thus, an N-heterocycle-based solvent-free, liquid to liquid LOHC system was established, catalyzed by a single catalyst for both dehydrogenation and hydrogenation under relatively mild conditions.
Figure 2. [Pd] catalyzed interconversion of 2,6-dimethylpiperidine and 2,6-lutidine. a) Time-dependent H₂ release curves. b) Conversions of dehydrogenation and hydrogenation.

A few control experiments were carried out to find out if the catalytic dehydrogenation involves homogeneous or heterogeneous catalysis. Heating a mixture of 2,6-dimethylpiperidine, Pd(OAc), and activated carbon at 170 °C (bath temperature) for 5 h, 46% yield of H₂ was collected, which matches very well with the yield (46.2%) of the formed 2,6-lutidine (Scheme 2, eq. 1). The mixture was filtered to give a colorless mixture of 2,6-dimethylpiperidine and 2,6-lutidine. Heating the obtained mixture at 170 °C for another 20 h, no gas was formed, and the amount of 2,6-lutidine didn’t change (eq. 2). Thus, a homogeneous catalysis process is unlikely. Analyzing the final mixture by inductively coupled plasma mass spectrometry (ICP-MS) showed only 0.172 ppm of Pd, indicating that virtually no Pd leaching to the reaction solution took place. Thirdly, a reaction without using a support gave only 5% yield of 2,6-lutidine and generated a Pd mirror (eq. 3). Furthermore, we found that by adding 2 equivalents of HOAc (with respect to Pd), the recovered catalyst (from a quantitative yield reaction) had similar catalytic activity to the in situ generated...
catalyst (See SI Figure S23). Taken together these results show that a homogeneous process can be ruled out.

**Scheme 2.** Control experiments for mechanistic studies. 1) Dehydrogenation of 2,6-dimethylpiperidine under standard conditions for 5 hrs. 2) Heating the reaction mixture after catalyst removal and the ICP-MS result. 3) Dehydrogenation of 2,6-dimethylpiperidine without support.

Next, we prepared Pd/C\textsubscript{HS} (Pd/C\textsubscript{HS} = palladium on activated carbon for Hydrogen Storage; for the procedure see SI) from Pd(OAc)\textsubscript{2} and acidic activated carbon to study the effect of acid. The prepared Pd/C\textsubscript{HS} was characterized by Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). We found that the palladium nanoparticles bound to the carboxyl groups of the activated carbon surface were distributed uniformly, the average diameter of Pd nanoparticles being 1.93 ± 0.44 nm. Then, the catalytic activity of Pd/C\textsubscript{HS} for 2,6-dimethylpiperidine dehydrogenation was tested; the time-dependent H\textsubscript{2} release curves and average turnover frequency within 90% yield (ATOF\textsubscript{90} = 85 mol
H₂ per mol Pd per hour) are shown in Figure 3. The ATOFₙ using Pd/Cₜₚ as a catalyst is close to that of the Pd(OAc)/C system (ATOFₙ = 91).

![Figure 3](image)

**Figure 3.** The effect of acid on the dehydrogenation process. Conditions: 2,6-dimethylpiperidine (10 mmol), Pd/Cₜₚ (43 mg, ~7.4 wt% Pd/C) and acid (0.6 mol%), or a combination of Pd(OAc)₂ (6.7 mg, 0.3 mol%) and activated carbon (40 mg), 170 °C (bath temperature, internal temperature is 128 °C, measured by an inserted thermometer). ATOFₙ = average turnover frequency within 90% yield (mol H₂ per mol Pd per hour). BA = benzoic acid, CPS = carboxypolystyrene, PAA = polyacrylic acid.

The effect of acid was investigated by adding 2 equivalents (with respect to Pd) of acetic acid (pKₐ = 4.76), benzoic acid (pKₐ = 4.20), 4-methylbenzenesulfonic acid (p-TsOH, pKₐ = 1.99), carboxypolystyrene (monomer pKₐ = 4.35) or polyacrylic acid (pKₐ = 4.75) into the reaction mixture (Figure 3, entries 2-6). Acetic acid, benzoic acid, and carboxypolystyrene showed positive effects on the dehydrogenation process, resulting in ATOFₙ numbers of 103, 128 and 107, respectively. Using polyacrylic acid as an additive, the ATOFₙ slightly decreased to 80, and use of the strong acid p-TsOH had a negative effect, resulting in ATOFₙ of 45. However, treatment of Pd/Cₜₚ with t-BuOK before use, upon which the interaction of the carboxyl groups and Pd...
nanoparticles might be broken by the base, the catalyst became completely inactive (entry 8). These results indicate that carboxylic acids and the carboxyl group on the activated carbon surface accelerate the palladium catalyzed dehydrogenation of 2,6-dimethylpiperidine. Furthermore, Pd/C₆ and carboxypolystyrene could be easily recovered by centrifugation without loss of catalytic activity (ATOFₙ = 101, entry 9). The third and fourth times of dehydrogenation produced 100% and 83% yields of H₂ respectively (Figure S26).

Dotted lines indicate the presence of either single bonds or double bonds
Scheme 3. a) Plausible dehydrogenation mechanism. b) Pathway of 2-picoline and 2,6-lutidine formation.

On the basis of the control experiments, preliminary mechanistic studies, and the literature, a plausible dehydrogenation mechanism (Scheme 3a) and pathway (Scheme 3b) of 2-picoline and 2,6-lutidine formation is proposed. The oxidative addition of carboxylic acid (from added acid or the carboxyl group on the activated carbon surface) to Pd(0) generate an active Pd(II) species RCO₂-Pd-H. Coordination of the N-heterocycle to Pd(II) on the nanoparticles surface results in an increase of the acidity of the N-H group, which could be deprotonated by the counter carboxylate anions of Pd(II) to generate an amido-palladium species and carboxylic acid. This is followed by β-hydride elimination to generate an imine and a palladium dihydride species. Finally, with the assistance of carboxylic acid, H₂ is released and the active catalyst Pd(II) is regenerated. Another possible role of the carboxylic acid in the reaction system is acceleration of the tautomerization of imines to key intermediate enamines. The cascade steps of dehydrogenation and tautomerization produce the final H₂-lean product 2-picoline or 2,6-lutidine and H₂.

CONCLUSIONS

In summary, we have developed a LOHC system based on Pd-catalyzed dehydrogenation and hydrogenation of methylpiperidines, and discovered a significant catalytic acid effect. Two couples of H₂-lean/H₂-rich compounds are promising LOHC systems. One is the unprecedented 2-picoline/2-methylpiperidine system, which has a 6.1 wt% theoretical hydrogen storage capacity, that satisfies the US DOE on-board hydrogen storage target for 2020 very well; however, small amounts of side products (less than 10%) are formed at this stage. The other one is the 2,6-lutidine/2,6-dimethylpiperidine system, which generates no side products and has 5.3 wt%
theoretical hydrogen storage capacity, which is close to the US DOE target. All the compounds have wide liquid ranges and lower than 0 °C melting points. Both dehydrogenation and hydrogenation were achieved in excellent yields using the same catalyst under mild conditions. Particularly, for 2,6-lutidine/2,6-dimethylpiperidine system, the complete dehydrogenation of 2,6-dimethylpiperidine was performed at 170 °C bath temperature (internal temperature only 128 °C, measured by an inserted thermometer), with fast and reliable H₂ release rate. Mechanistic studies revealed the special role of acids and acidic groups on the surface of activated carbon. Noteworthy, the reverse hydrogenation only required low H₂ pressure of (2-7 bar for 2-picoline, and 1.6-5 bar for 2,6-lutidine). Catalyst recycling, and interconversion experiments demonstrated that the catalyst and 2,6-dimethylpiperidine and 2,6-lutidine have good stability. Further studies are underway aimed at enhancing the selectivity of the 2-picoline/2-methylpiperidine LOHC system.

ASSOCIATED CONTENT

Supporting Information. Experimental procedure, GC, GCMS and NMR data of products, SEM and TEM images of catalyst, IR spectra of catalyst and support, schematic drawing of hydrogen collection system. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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REFERENCES


(31) Darco@KB activated carbon, surface area: 1500 m²/g, pH<sub>PZC</sub> = 4.25: pH value at the point of zero charge.

