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A Reversible Liquid Organic Hydrogen Carrier System Based on Methanol-Ethylenediamine and Ethylene Urea

Yinjun Xie,[a] Peng Hu,[b][c] Yehoshua Ben-David,[a] and David Milstein[da]

Abstract: A novel liquid organic hydrogen carrier (LOHC) system, with a high theoretical hydrogen capacity, based on the unprecedented hydrogenation of ethylene urea to ethylenediamine and methanol, and its reverse dehydrogenative coupling, was established. For the dehydrogenation only a small amount of solvent is required. This system is rechargeable, as the H₂-rich compounds could be regenerated by hydrogenation of the resulting dehydrogenation mixture. Both directions for hydrogen loading and unloading were achieved using the same catalyst, under relatively mild conditions. Mechanistic studies reveal the likely pathway for H₂-lean compounds formation.

Hydrogen is regarded as one of the most important future renewable energy carriers, since it has the highest energy density by weight, can be readily transformed to electricity by fuel cells, and produces only water after combustion (in fuel cell or combustion chamber).[1] However, using hydrogen as an energy carrier has significant disadvantages, including low energy density by volume, safety issues, cost of compression in high-pressure tanks or cryogenically, and weight of the containers, making it problematic for wide use.[3,6,7] Thus, finding a suitable hydrogen storage method is an important challenge toward the “hydrogen economy”.[4] For decades, a variety of hydrogen storage methods were established and investigated, such as metal-hydrides, carbon nanotubes, metal-organic frameworks, and many other materials. Unfortunately, all of these methods have significant limitations.[7]

Scheme 1. Organic compounds for hydrogen storage.

One promising approach is to store hydrogen in covalent bonds of liquid organic compounds, namely liquid organic hydrogen carriers (LOHCs), which have high weight% (wt%) hydrogen storage capacity, and can be easily handled and transported.[9-16] As shown in Scheme 1, H₂ can be released by dehydrogenation of a H₂-rich organic compound, and can be stored by hydrogenation of the H₂-lean organic compound.[11-16]

a) Aromatics or N-heteroaromatics as H₂-lean compounds:

b) Amides or imides as H₂-lean compounds:

c) This work:

6.52 wt% theoretical H₂ capacity

d) Ru-pincer complexes used in this work

Scheme 2. LOHCs based on catalytic dehydrogenation and hydrogenation

Research toward storing hydrogen in LOHC systems started in the 1980s.[11a] Early LOHCs studies were focused on aromatic hydrocarbons and their hydrogenated products, such as toluene / methylcyclohexane (TOL / MCH), benzyltoluene / perhydrobenzyltoluene (BT / H₂BT), dibenzyltoluene / perhydrodibenzyltoluene (DBT / H₂DBT) and so on, showing high wt% hydrogen capacities (6.12 wt%, 6.19 wt%, and 6.20 wt%, respectively).[11] Nevertheless, because of their high heat of hydrogenation, the reverse dehydrogenation for producing H₂ and the corresponding aromatic hydrocarbons requires harsh reaction conditions (usually more than 250 °C).[3a,3c] To reduce the enthalpy of hydrogenation / dehydrogenation, a few LOHCs based on N-heteroaromatic / H₂N-heterocycle were developed (Scheme 2a).[12,13] For example, the N-ethylcarbazole (NEC) / dodecachydro-N-ethylcarbazole (H₁₂-NEC) system, which has 5.80 wt% hydrogen capacity, developed by researchers of Air Products and Chemicals. However, high temperature was still required for both hydrogenation and dehydrogenation, catalyzed by two different catalyst systems.[12] Besides, the low thermal stabilities of N-ethylcarbazole and dodecachydro-N-ethylcarbazole led to N-ethyl cleavage products.[10]

In 2015, our group developed a new concept of LOHCs, which is based on amide bond formation and hydrogenation; thus dehydrogenation of 2-aminoethanol to form the cyclic peptide diketopiperazine, and hydrogenation of the latter, form the basis...
for an LOHC system with a theoretical 6.56 wt% hydrogen capacity.\textsuperscript{[14]} Because of the favorable thermodynamics, both dehydrogenation and hydrogenation processes proceeded smoothly under mild conditions. However, for the dehydrogenation, 1 mmol of 2-aminoethanol required 4 mL of solvent, which lowers the actually hydrogen content. After that, two other LOHCs based on this concept were reported, independently by our group and the Prakash group.\textsuperscript{[15]} These two LOHC systems have 5.26 wt% H₂ capacity; our system used ethylenediamine (EDA) and ethanol as the H₂-rich compounds and N,N-(ethane-1,2-diyl)diacetamide as the H₂-lea compound\textsuperscript{[15a]} while Prakash’s system used N,N-dimethylethylenediamine (DMEDA) and methanol as the H₂-rich compounds, and N,N-(ethane-1,2-diyl)bis(N-methylformamide) as the H₂-lea compound\textsuperscript{[15b]}. Obviously, the H₂ capacity of a system based on ethylenediamine-methanol / N,N-(ethane-1,2-diyl)diformamide (DFA) would be higher (6.45 wt% H₂ capacity), since methanol has one fewer carbon. Replacing ethanol by methanol can also provide an opportunity of ethylene urea (EU) formation, which has a still higher H₂ capacity (6.52 wt%) than amide (DFA) formation. However, the energy barrier of methanol activation is much higher than that of ethanol,\textsuperscript{[17]} and the hydrogenation of ethylene urea to regenerate ethylenediamine and methanol is also a great challenge, since urea derivatives are among the most challenging compounds to be hydrogenated\textsuperscript{[15b, 18]} only two examples being reported\textsuperscript{[15b, 18a]} that do not include the more challenging cyclic ureas. Therefore, neither dehydrogenative coupling of ethylenediamine and methanol to ethylene urea, nor the hydrogenation of ethylene urea, or any other cyclic urea, have been reported. Herein we present a hydrogen storage system based on the dehydrogenative coupling of methanol / ethylenediamine to form ethylene urea (EU) by releasing H₂, and the reverse hydrogenation of ethylene urea to regenerate ethylenediamine and methanol.

Our initial experiments were aimed at the unknown hydrogenation of EU. Treating a solution containing 1 mol% of the complex RuHCl(η²-PNNH)(CO)\textsuperscript{[19a]} ([Ru] \textsuperscript{1}, Scheme 2), 2.2 mol% of t-BuOK and 1 mmol EU in 2 mL dioxane under 50 bar of hydrogen at 150 °C for 2 days resulted in 29% conversion of EU and 26% yield of EDA as determined by ¹H NMR spectroscopy (Table 2, entry 1). Increasing the H₂ pressure to 60 bar and extending the reaction time (6 d) gave better results, and 48% of EU was converted to ethylenediamine and methanol (Table 1, entry 2) in good selectivity. Raising the bath temperature (170 °C) also helped to improve the conversion of EU (79%) and the yield of EDA (75%). Increasing the amount of base to 4 mol% of t-BuOK, all of the EU was converted to EDA and methanol in 100% selectivity (Table 1, entry 4). Reducing the reaction time to 5 d or 2 d, only 80% or 58%, of EU, respectively, was consumed (entries 5 and 6). Other Ru-pincer complexes RuHCl(η²-PNNH)(CO)\textsuperscript{[19a]} ([Ru]-2, and RuHCl(Bpy-PNNH)(CO)\textsuperscript{[19b]} ([Ru]-3) (Table 1, entries 7 and 8) were also examined, resulting in both cases in 100% yields and 100% conversions after 7 d. Moreover, with [Ru]-2 or [Ru]-3 as catalysts, the reaction time could be shortened to 5 d and 1.5 d, respectively (Table 1, entries 9 and 11). Using [Ru]-3 as a catalyst, under 60 bar of H₂ at 170 °C for 1 day, 81% of EU could be hydrogenated, yielding 81% of EDA and 77% of methanol (entry 12). Thus, a method for producing methanol and ethylenediamine from ethylene urea was established.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cat.</th>
<th>t (d)</th>
<th>Conv. (%)</th>
<th>EDA (%)</th>
<th>Methanol (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Ru]-1</td>
<td>2</td>
<td>29</td>
<td>26</td>
<td>Nd</td>
</tr>
<tr>
<td>2\textsuperscript{b}</td>
<td>[Ru]-1</td>
<td>1</td>
<td>6</td>
<td>48</td>
<td>41</td>
</tr>
<tr>
<td>3\textsuperscript{c,d}</td>
<td>[Ru]-1</td>
<td>6</td>
<td>79</td>
<td>75</td>
<td>54</td>
</tr>
<tr>
<td>4\textsuperscript{c,d}</td>
<td>[Ru]-1</td>
<td>7</td>
<td>100</td>
<td>100</td>
<td>79</td>
</tr>
<tr>
<td>5\textsuperscript{c,d}</td>
<td>[Ru]-1</td>
<td>5</td>
<td>80</td>
<td>80</td>
<td>67</td>
</tr>
<tr>
<td>6\textsuperscript{c,d}</td>
<td>[Ru]-1</td>
<td>2</td>
<td>58</td>
<td>58</td>
<td>48</td>
</tr>
<tr>
<td>7\textsuperscript{d}</td>
<td>[Ru]-2</td>
<td>7</td>
<td>100</td>
<td>100</td>
<td>81</td>
</tr>
<tr>
<td>8\textsuperscript{d}</td>
<td>[Ru]-2</td>
<td>5</td>
<td>100</td>
<td>100</td>
<td>70</td>
</tr>
<tr>
<td>10\textsuperscript{d}</td>
<td>[Ru]-3</td>
<td>4</td>
<td>100</td>
<td>99</td>
<td>87</td>
</tr>
<tr>
<td>11\textsuperscript{d}</td>
<td>[Ru]-3</td>
<td>1.5</td>
<td>100</td>
<td>100</td>
<td>80</td>
</tr>
<tr>
<td>12\textsuperscript{d}</td>
<td>[Ru]-3</td>
<td>1</td>
<td>81</td>
<td>81</td>
<td>77</td>
</tr>
</tbody>
</table>

[a] Conditions: ethylene urea (1 mmol), t-BuOK (2.2 or 4 mol%), catalyst (1 mol%) and dioxane (2 mL). In 50 mL autoclave, 50 or 60 bar of hydrogen, 150 or 170 °C (oil bath temperature), yields and conversions were determined by ¹H NMR, using pyridine as internal standard. [b] H₂ (60 bar). [c] 170 °C (oil bath temperature). [d] t-BuOK (4.0 mol%). Nd = not determined.

Next, we studied whether dehydrogenative coupling of ethylenediamine and methanol to form ethylene urea is feasible. Using [Ru]-3 (1 mol%) as pre-catalyst neither N-(2-aminomethyl)formamide FA nor EU were observed after heating in dioxane at 150 °C (bath temperature) in a closed 50 mL Young-type Schlenk tube for 24 hours (Table 2, entry 1). Using [Ru]-1 as the pre-catalyst, 30% yield of FA, 32% yield of EU, and 27% yield of N,N-(ethane-1,2-diyl)diformamide DFA were obtained, as determined by ¹H NMR (entry 2). In addition, 63 mL of H₂ (88% yield of H₂, with respect to full conversion of EDA and methanol to EU and hydrogen) was collected and was analyzed by GC to determine the purity (> 99.8%, see SI). When [Ru]-2 was chosen as the pre-catalyst, only 2% yield of FA, and 13% yield of EU were generated (entry 3). We found that the headspace of the reactor had a strong influence on the performance of the reaction, probably because the smaller free space results in an increase of the pressure and benefits the trapping of the low boiling methanol. When a 25 mL Young-type Schlenk was used, 96% yield of H₂ was collected, and the yield of EU increased to 62% (entry 4). Reducing the amount of t-BuOK to 1.1 mol%, a similar amount of H₂ (70 mL) was obtained, but the purity of H₂ decreased to 99.1%.

Then, the effect of substrates ratio was studied. With methanol / EDA = 1.5, only 46% yield of H₂ was collected after 24 hours (entry 6); using methanol / EDA = 2, H₂ in 83% yield was collected after 24 hours (entry 7), which was almost as much as when methanol / EDA = 3 was used. In the case of methanol / EDA = 2, 36% yield of FA, 44% yield of EU, and 11% yield of DFA were detected. Extending the reaction time to 48 hours resulted in 99%...
yield of H₂ (entry 8), with a lower yield of the intermediate product FA (15%), increased yield of EU (76%), and 9% yield of DFA.
Reducing 1,4-dioxane to 1 mL, dehydrogenation also worked very well, yielding 97% H₂ after 12 hours (entry 9). Furthermore, reducing the catalyst loading to 0.5 mol%, 98% yield H₂ was collected after 12 hours (entry 10). Importantly, using a 5-times larger substrate scale in only 1 mL, 1,4-dioxane and 0.5 mol% catalyst loading the dehydrogenation resulted in 79% yield of H₂ (entry 11), in more than 99.9% purity. However, a reaction without solvent only produce 17% yield of H₂ (entry 12). In addition, the measured H₂ volumes agree very well with the calculated values (entries 2, 4-12, in square brackets).

Table 2. Dehydrogenative coupling of ethylenediamine and methanol[8]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cat. (mol%)</th>
<th>H₂ (mL)/yield (%)</th>
<th>FA (%)</th>
<th>EU (%)</th>
<th>DFA (%)</th>
<th>CO (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1[a]</td>
<td>[Ru]-3 (1)</td>
<td>69 (79)[± (88)]</td>
<td>30</td>
<td>32</td>
<td>27</td>
<td>0.16</td>
</tr>
<tr>
<td>2</td>
<td>[Ru]-1 (1)</td>
<td>23</td>
<td>62</td>
<td>15</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>3[b]</td>
<td>[Ru]-1 (1)</td>
<td>69 (75)[± (96)]</td>
<td>18</td>
<td>71</td>
<td>11</td>
<td>0.90</td>
</tr>
<tr>
<td>4[c]</td>
<td>[Ru]-1 (1)</td>
<td>18</td>
<td>33</td>
<td>4</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>5[d]</td>
<td>[Ru]-1 (1)</td>
<td>69 (79)[± (96)]</td>
<td>19</td>
<td>63</td>
<td>18</td>
<td>0.04</td>
</tr>
<tr>
<td>7[e]</td>
<td>[Ru]-1 (1)</td>
<td>23</td>
<td>44</td>
<td>11</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>8[f]</td>
<td>[Ru]-1 (1)</td>
<td>71 (74)[± (99)]</td>
<td>15</td>
<td>76</td>
<td>9</td>
<td>0.20</td>
</tr>
<tr>
<td>9[g]</td>
<td>[Ru]-1 (1)</td>
<td>69 (71)[± (96)]</td>
<td>19</td>
<td>63</td>
<td>18</td>
<td>0.04</td>
</tr>
<tr>
<td>10[h,i]</td>
<td>[Ru]-1 (0.5)</td>
<td>70 (71)[± (97)]</td>
<td>25</td>
<td>54</td>
<td>21</td>
<td>Nd</td>
</tr>
<tr>
<td>11[j]</td>
<td>[Ru]-1 (0.5)</td>
<td>287 (289)[± (79)]</td>
<td>76</td>
<td>7</td>
<td>17</td>
<td>0.04</td>
</tr>
<tr>
<td>12[k]</td>
<td>[Ru]-1 (0.5)</td>
<td>61 (59)[± (17)]</td>
<td>24</td>
<td>0</td>
<td>0.11</td>
<td></td>
</tr>
</tbody>
</table>

[a] Conditions: ethylenediamine (1.0 mmol), methanol (3 mmol), catalyst (0.01 mmol), t-BuOK (0.022 mmol), 1,4-dioxane (2 mL), in 50 mL Young-type Schlenk tube, 150 °C (oil bath temperature), 24 h; yields of FA, EU and DFA were determined by 1H NMR, using pyridine as the internal standard; yield of H₂ (in parenthesis) was calculated on the basis of H₂ volume (72 mL per mmol ethylenediamine, at 20 °C) with respect to 100% yield of product EU. CO was determined by GC. [b] t-BuOK (0.011 mmol). [c] In 25 mL Young-type Schlenk tube. [d] Methanol (1.5 mmol). [e] Methanol (2 mmol). [f] 48 h. [g] Calculated H₂ volume based on the yields of products, in square brackets. [h] 12 h. [i] Ethylenediamine (5.0 mmol), methanol (15 mmol), [Ru]-1 (0.025 mmol), t-BuOK (0.055 mmol), in 100 mL Young-type Schlenk tube, 30 h. [j] 1,4-Dioxane (1 mL). Nd = not determined.

A few control experiments were carried out for mechanistic insight. As shown in Figure 1, equation (a), FA could be converted to EU, DFA, and EDA, indicating that FA is a likely intermediate in EU formation, and the self-aminoysis of FA generates EDA and DFA. Heating a mixture of EDA and DFA in dioxane under the standard dehydrogenation conditions, FA, EU and H₂ were detected (equation b). These results indicate that the aminolysis of EDA and DFA can also take place in the mixture. In the presence of EDA, DFA can be converted to FA. A reaction of methanol in absence of ethylenediamine (equation c) yielded only 2 mL of gas, together with 2% yield of methyl formate, revealing that the dehydrogenative ester formation is unfavorable and insignificant, and that amide formation does not proceed via aminolysis of methyl formate and EDA.

Figure 1. Control experiments for mechanistic studies

Based on our previous research[19] and these results (see SI), a reaction pathway is proposed in Scheme 3. Dehydrogenative coupling of ethylenediamine and methanol catalyzed by [Ru]-1 via metal–ligand cooperation could produce formamide (FA) and diformamide (DFA) with release of H₂. Further dehydrogenation of FA generates EU and H₂. Diformamide (DFA) could be converted to FA in the presence of EDA, then generate EU via dehydrogenation.

Scheme 3. Proposed reaction pathway

After establishing systems for hydrogenation of EU and dehydrogenation of methanol and EDA, hydrogenation of DFA was studied. As shown in Figure 2, equation (a), in the presence of [Ru]-1, DFA was hydrogenated to methanol (88% yield) and ethylenediamine (100% yield) in 100% conversion. Furthermore, we examined the reversible interconversion of H₂-rich compounds and H₂-lean compounds by dehydrogenation and hydrogenation. Firstly, by adding new catalyst, the mixture of the products can be hydrogenated to EDA and methanol in full conversion (equation b). Interestingly, without adding new catalyst, only adding t-BuOK (4 mol%), the mixture of H₂-lean compounds were also converted to ethylenediamine in high yield and methanol, after reacting under 60 bar of H₂, at 170 °C for 5 days (equation c). Because of the likely catalyst decomposition, the dehydrogenation of regenerated ethylenediamine and methanol (without adding new catalyst) produced only 1 mL of H₂. In addition, mercury-drop tests indicated that heterogeneous Ru nanoparticle-catalyzed...
processes are unlikely in both the dehydrogenation and hydrogenation processes (see SI). Thus, a reversible hydrogen storage system on basis of hydrogenation of ethylene urea and dehydrogenation of methanol and ethylenediamine was established.

\[
\begin{align*}
\text{DFA} + \text{H}_2 & \rightarrow [\text{Ru}(\text{DFA})\text{BuOK}][\text{H}_2] + \text{EDA} + \text{CH}_3\text{OH} \\
\text{H}_2 (1 \text{ atm}) & \rightarrow \text{CH}_3\text{OH} (1 \text{ atm}) + 2 \text{H}\text{upd}.
\end{align*}
\]

Figure 2. a) Hydrogenation of DFA. b) Hydrogenation of the dehydrogenated products. c) Intercalation between H\text{r}ich compounds and H\text{l}ean compounds by dehydrogenation and hydrogenation.

In conclusion, we have developed a new, rechargeable hydrogen storage system, which is based on the unprecedented hydrogenation of the ethylene urea, and its formation by dehydrogenative coupling of the inexpensive and abundant ethylenediamine and methanol, catalyzed by the same Ru-pincer complex. The dehydrogenation could be achieved using a very small amount of solvent. This LOHC system has a theoretically high hydrogen capacity of 6.52 wt% and enjoys excellent yields for both loading and unloading hydrogen. Mechanistic studies demonstrated that N\text{-}(2-aminoethyl)formamide is one of the key intermediate products, which could be converted to ethylene urea or N,N\text{-}(ethane-1,2-diyldiformamide in the presence of [Ru\text{I}].

Acknowledgements

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Keywords: hydrogen storage • urea hydrogenation • ruthenium pincer complex • methanol • ethylenediamine

The first example of ethylene urea hydrogenation to ethylenediamine and methanol was developed. Based on it, we established a rechargeable hydrogen storage system.