

Efficient Reversible Hydrogen Carrier System Based on Amine Reforming of Methanol

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S Supporting Information

ABSTRACT: A novel hydrogen storage system based on the hydrogen release from catalytic dehydrogenative coupling of methanol and 1,2-diamine is demonstrated. The products of this reaction, *N*-formamide and *N,N'*-diformamide, are hydrogenated back to the free amine and methanol by a simple hydrogen pressure swing. Thus, an efficient one-pot hydrogen carrier system has been developed. The H₂ generating step can be termed as “amine reforming of methanol” in analogy to the traditional steam reforming. It acts as a clean source of hydrogen without concurrent production of CO₂ (unlike steam reforming) or CO (by complete methanol dehydrogenation). Therefore, a carbon neutral cycle is essentially achieved where no carbon capture is necessary as the carbon is trapped in the form of formamide (or urea in the case of primary amine). In theory, a hydrogen storage capacity as high as 6.6 wt % is achievable. Dehydrogenative coupling and the subsequent amide hydrogenation proceed with good yields (90% and >95% respectively, with methanol and *N,N'*-dimethylethylenediamine as dehydrogenative coupling partners).

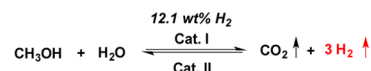
The growing use of fossil fuels since the industrial revolution has resulted in a significant increase in CO₂ concentration in the atmosphere, from 270 ppm in 1750 to over 400 ppm presently.^{1,2} CO₂, being a greenhouse gas, has contributed to an increase in Earth's average surface temperature of 0.8 °C over the last 100 years.³ According to scientific observations and predictions, the ongoing global warming will be associated with severe environmental and social changes in the near future.^{4,5} Renewable energy sources, including solar, wind, geothermal and biomass, are increasingly being implemented to complement fossil fuels. However, the intermittent and fluctuating nature of some of these sources, namely solar and wind, remains a problem for large-scale deployment. Storage of the generated energy in the form of chemical bonds, such as in hydrogen or methanol, is one of the promising pathways and has led to the proposed “hydrogen economy” and “methanol economy”.^{6,7}

As a hydrogen carrier, liquid organic hydrogen carriers (LOHC) have gained significant attention recently as they are safe to store and transport, have high wt % H₂ storage capacities and can offer fully reversible H₂ loading and unloading. They can also enable a relatively easy transition by allowing the

utilization of existing fuel infrastructures.⁸ Formic acid (HCO₂H), over the years, has been explored thoroughly as a potential LOHC, and highly efficient catalysts for both H₂ loading and unloading have been designed by us and others.⁹ However, a maximum H₂ storage of only 4.4 wt % is feasible in HCO₂H with the emission of stoichiometric amount of CO₂ for each H₂.

Methanol (CH₃OH) is a good alternative because of its 12.6 wt % H₂ content, ease of handling and convenient production.¹⁰ Steam reforming of CH₃OH is generally the preferred method to obtain H₂ and is performed at high temperatures (240–260 °C) and high pressures over heterogeneous catalysts.¹¹ Recently, it was discovered that the use of homogeneous catalysts,¹² mainly Ru¹³ and Fe¹⁴ pincer complexes, could also enable aqueous CH₃OH dehydrogenation at much lower temperatures (<100 °C). Strongly basic conditions are nevertheless required in most cases to achieve high TON. In addition, CO₂ reduction to CH₃OH has also been reported using similar pincer catalysts.^{7d,10b–e} However, to the best of our knowledge, aqueous reforming of CH₃OH and the reverse reaction (CO₂ hydrogenation to CH₃OH) in the presence of same homogeneous catalytic system has not yet been demonstrated (Scheme 1).

Scheme 1. Aqueous Reforming of Methanol

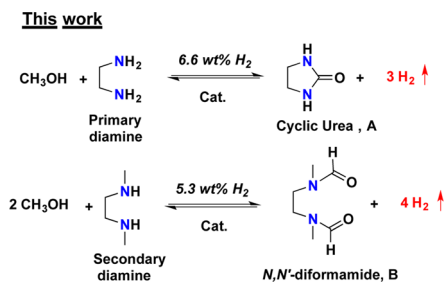


Different catalytic system for forward and reverse reaction

Herein, we present a reversible hydrogen storage system based on a CH₃OH/amine system, where H₂ is generated by what we call “amine reforming of CH₃OH”, in analogy with the steam reforming of CH₃OH. CH₃OH and amine are regenerated in the reverse hydrogenation reaction, thus closing the cycle. Both H₂ “loading” and “unloading” are performed in the presence of the same Ru-pincer catalysts by a simple H₂ pressure swing (Scheme 2). This process has three main advantages over traditional CH₃OH steam reforming in the context of sustainable H₂ storage and transportation: (1) it is reversible in the presence of the same catalytic system, (2) the dehydrogenative coupling products, formamide (or urea),

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Scheme 2. Amine Reforming of Methanol^a

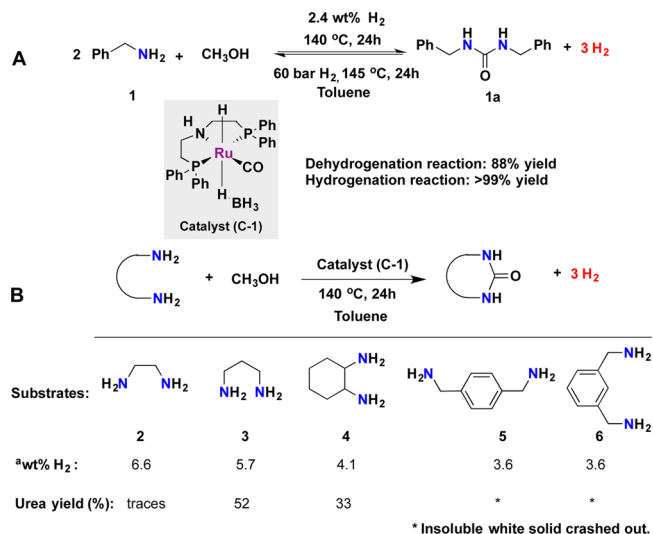
^aAdvantages: (i) carbon neutral cycle, (ii) liquid fuel at room temperature, (iii) easily reversible and (iv) pure H₂ gas produced

unlike CO₂ from steam reforming, do not need to be recaptured as they remain in solution and are readily available for the subsequent H₂ loading step, and (3) pure H₂ gas is produced, which can be potentially used in H₂/Air fuel cells without purification. In 2016, Milstein et al. reported an ethanol based reversible hydrogen storage system in the presence of ethylenediamine.¹⁵ However, because CH₃OH has one fewer carbon, a CH₃OH based hydrogen storage system could provide higher hydrogen storage density when coupled with diamines.

Activation of smaller alcohols such as CH₃OH is considered challenging because the energy barrier for their activation is much higher than for higher alcohols.¹⁶ In 2013, Beller^{13b} and Grützmacher¹⁷ showed independently the dehydrogenation of CH₃OH (aqueous CH₃OH reforming) in the presence of homogeneous ruthenium catalysts. Later, CH₃OH was used as a formyl source for the N-formylation of amines and nitriles with Ru(NHC) complexes.¹⁸ Recently, Hong et al. reported the synthesis of urea compounds from amines using CH₃OH as the C1 source in the presence of a ruthenium pincer catalyst, producing H₂ as a byproduct.¹⁹ Inspired by these independent studies, we envisioned a reversible and practical H₂ storage system based on amine and CH₃OH.

The dehydrogenative coupling of benzylamine (**1**) and CH₃OH with Ru-MACHO-BH catalyst (**C-1**) in a closed reactor formed *N,N'*-dibenzylurea (**1a**) in 88% yield (Scheme 3A). To our surprise, at a H₂ pressure of 60 bar, **1a** was completely converted back to CH₃OH and **1** (Figure S8). However, the high molecular weight of **1** makes it an inefficient H₂ storage material. An ideal amine for this application must have low carbon content for efficient H₂ storage along with low volatility for easy handling. We therefore turned our focus to diamines which satisfy both criteria. However, when reacted with CH₃OH, the yields of corresponding cyclic ureas were low in the presence of primary diamines as can be seen in Scheme 3B. With xylylenediamines, **5** and **6**, the intermolecular polymeric urea products crashed out as white solids, which could not be hydrogenated back to free amines and CH₃OH under H₂ pressure. These white solids were insoluble in water and in most organic solvents.

In light of somewhat unsatisfying results obtained with primary diamines, we decided to screen a secondary 1,2-diamine for the dehydrogenative coupling reaction. *N,N'*-Dimethylethylenediamine (**7**) has a relatively high boiling point (119 °C) and at the same time low molecular weight, leading to a high wt/wt H₂ storage potential (5.3 wt %) (Table 1). Diamine **7** in the presence of CH₃OH and 1 mol % **C-1** catalyst loading at 140 °C in toluene gave a H₂ yield of 29% after 24 h

Scheme 3. From Primary Amines to Urea^a

^aReaction conditions: (A) **1** (2 mmol), CH₃OH (2 mmol), toluene (3 mL), **C-1** (10 μmol); (B) substrate (1 mmol), CH₃OH (2 mmol), **C-1** (10 μmol), toluene (1.5 mL), reaction time (24 h). Yields based on ¹H NMR using 1,3,5-trimethoxybenzene (TMB) as an internal standard. ^aMaximum theoretical wt % H₂ obtainable. NMR yield calculations error = ±5%.

Table 1. Condition Screening for the Dehydrogenative Coupling of **7** and CH₃OH

Entry	CH ₃ OH (mmol)	K ₃ PO ₄ (mol %)	7a yield (%)	7b yield (%)	H ₂ yield (%) ^b	CO ^c (%)
1 ^d	2	0	16	25	29	2.8
2	2	0	15	29	30	0.2
3	2	25	23	52	49	2.8
4	4	0	40	31	56	0.4
5	4	25	70	21	82	3.3
6 ^e	4	25	52	28	66	2.6
7	4	10	67	24	79	2.7
8	4	5	75	22	86	2.8
9 ^f	4	5	56	39	76	0.2
10	3	5	40	49	65	3
11 ^g	4	5	na	na	nd	nd

^aReaction conditions: **7** (1 mmol), **C-1** (1 mol %), toluene (1.5 mL), reaction time (24 h). ^bThe theoretical H₂ yield is taken as 4 mmol and the H₂ yield was calculated indirectly from the amount of -NCHO (from **7a** + **7b**) formed, which is determined by ¹H NMR using TMB as an internal standard. ^cDetermined by GC. ^d140 °C. ^e1,4-Dioxane (1.5 mL) was used as a solvent instead of toluene. ^f100 °C. ^gEthylenediamine (**2**) was used instead of **7**. nd = not detected. NMR yield calculations error = ±5%. na = not applicable.

(entry 1, Table 1). As the ¹H NMR signals of **7a** and **7b** overlap with each other, it was difficult to differentiate them from the crude reaction mixture. However, after concentration, all ¹H NMR signals of the rotamers of **7a** (4 rotamers, 8, 7.96, 7.90 and 7.89 ppm) and **7b** (2 rotamers, 7.94 and 7.97 ppm) were clearly assigned (Figures S5–7). A total 41% of the corresponding formamide products **7a** and **7b** was obtained.

Gas evolved during dehydrogenation was collected and analyzed by GC. A small amount of CO was detected along with H₂ due to dehydrogenation of the formaldehyde intermediate to CO.²⁰

Decreasing the reaction temperature to 120 °C produced a similar H₂ yield (30%), with a significant decrease in CO formation (entry 2, Table 1). In reactions catalyzed by Ru–PNP complexes, K₃PO₄ is often used as a base additive to enhance catalytic activity via a favorable –NH assisted pathway.^{7d,21,10c} Indeed, when 25 mol % of K₃PO₄ was added to the reaction mixture, the H₂ yield increased to 49% (entry 3, Table 1). Using more CH₃OH (4 mmol) induced a better H₂ yield (82%) (entry 5, Table 1). In 1,4-dioxane, a low H₂ yield was observed (entry 6, Table 1). Lower amounts of K₃PO₄ gave similar yields, and 5 mol % was found to be an optimum for our reaction conditions with 86% H₂ yield (entry 8, Table 1). When 3 mmol of CH₃OH was used instead of 4, the H₂ yield dropped to 65% (entry 10, Table 1). Ethylenediamine, **2**, was screened under these optimized condition, but only traces of N-formyl and urea products were obtained (entry 11, Table 1).

Catalysts C-2–C-8 were also screened under the optimized conditions from entry 8, Table 1 (Figure 1). Ru-MACHO C-2 gave a lower H₂ yield (75%) compared to Ru-MACHO-BH C-

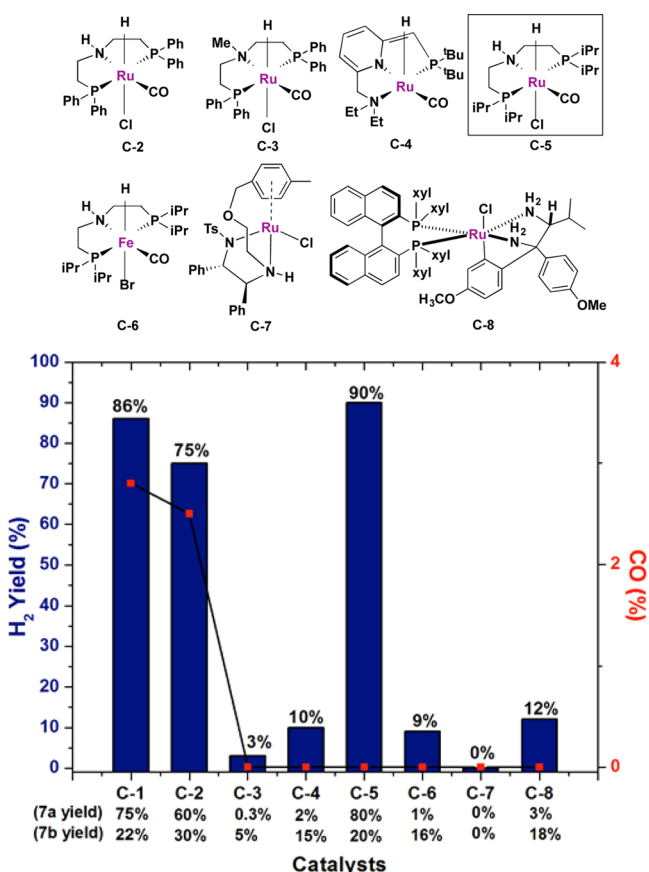


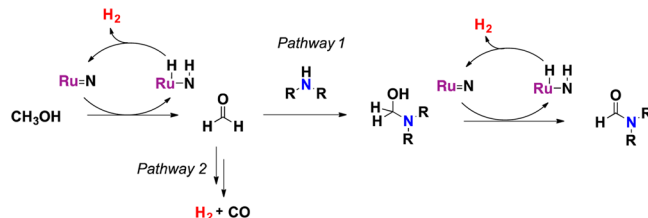
Figure 1. Catalysts screening for the dehydrogenative coupling of **7** and CH₃OH. Reaction conditions: **7** (1 mmol), CH₃OH (4 mmol), catalysts (1 mol %), K₃PO₄ (5 mol %), toluene (1.5 mL), time (24 h), and *T* = 120 °C. H₂ yields are based on the amount of –NCHO (from **7a** + **7b**) formed, which is determined by ¹H NMR using TMB as an internal standard. CO content determined by GC. In the case of C-3, C-4, C-6 and C-7, an insufficient amount of gas was produced to collect and analyze by GC. NMR yield calculations error = ±5%.

1 (86%). Interestingly, *N*-methylated pincer catalyst C-3 showed low catalytic activity, further demonstrating the involvement of a N–H assisted mechanistic pathway (outer-sphere bifunctional mechanism).^{22,7d} Milstein's catalyst C-4 gave 10% of H₂ yield. Ru–PNP^{IPr} C-5 gave good H₂ yield (90%), and to our delight no CO was observed in the gas mixture (GC: CO detection limit = 0.099 v/v%) (Figure S4). When the evolved gas mixture was collected in a gas buret, a H₂ yield of 88% (85 mL) was obtained, which is in close accordance with the NMR yield (90%).

Fe–PNP^{IPr} C-6 produced no CO, but the H₂ yield was poor (9%). Addition of K₂CO₃ additive (2 mol %) along with K₃PO₄ (5 mol %) further increased the H₂ yield to 26%. No trace of **7a/7b** appeared in ¹H NMR with a transfer hydrogenation catalyst, (*R,R*)-Ts-DENEB (C-7).²³ On the other hand, the hydrogenation catalyst (*R*)-RUCY-xylBINAP (C-8) gave small amounts (12%) of H₂.²⁴ As shown in Figure 1, C-5 was the best catalyst for the dehydrogenative coupling of **7** and CH₃OH, both in terms of selectivity and yield of H₂.

CO detected by GC in the dehydrogenation reactions is associated with a competing mechanistic pathway, where the formaldehyde formed after initial dehydrogenation of CH₃OH is rapidly dehydrogenated further before the nucleophilic addition of amine to form the α -amino alcohol can take place (Scheme 4).

Scheme 4. Proposed Mechanism Based on Metal–Ligand Cooperation



Formamides are reported to be generally amenable to reduction under moderate H₂ pressures with metal-pincer complexes.²⁵ To optimize the reverse reaction, the reactor was charged with H₂ upon completion of the dehydrogenation reaction, and heated to 120 °C (in the presence of same catalyst (C-5)) (Table 2). When a H₂ pressure of 40 bar was applied, 92% of **7** formed, 4% of **7b** remained unreacted and no trace of **7a** was observed (entry 1, Table 2). At 60 bar pressure, 95% of

Table 2. Hydrogenation of in Situ Formed **7a**^a

Entry	Catalyst	H ₂ (bar)	time (h)	Unreacted 7a/7b (%) ^b	7 (%) ^b
1	C-5	40	24	0/4	92
2	C-5	60	24	0/0	95

^aReaction conditions: After the dehydrogenation, the reaction mixture from C-5, Figure 1 contained no trace of **7** and 1.9 mmol CH₃OH and this mixture was used to check the reversibility under high H₂ pressure. CH₃OH yield for both entry 1 and 2 = ~75%. ^bdetermined by ¹H NMR using TMB as an internal standard. NMR yield calculations error = ± 5%.

7 formed after 24 h and no traces of 7a/7b were observed by ^1H NMR (entry 2, Table 2). In these reactions (entry 1–2, Table 2), lower CH_3OH yields ($\sim 75\%$) are due to the loss of CH_3OH during the hydrogen release.²⁶ The recyclability of the catalyst (C-5) was studied on 1 mmol scale (Figure S12) and the catalyst was recycled three times. More than 80% of its initial activity was retained after three cycles with a total production of 230 mL of H_2 .

To extend further the scope of this hydrogen storage system (7/ CH_3OH), a neat reaction was performed without solvent by scaling up the reaction 5-fold (5 mmol). Excitingly, both dehydrogenation and hydrogenation gave good to moderate yield (76% and 60%, respectively) even in the absence of any solvent.²⁷

In conclusion, a novel reversible hydrogen carrier system based on the dehydrogenative coupling of 1,2-diamine and CH_3OH is demonstrated, where an overall carbon neutral cycle is achieved by trapping the carbon in the form of N-formamides (or urea). One of the major challenges was the CO contamination of the gas mixture, which was overcome by using a well-defined homogeneous $\text{RuHCl}(\text{CO})\text{HN}(\text{CH}_2\text{CH}_2\text{PiPr}_2)_2$ catalyst. Even in the absence of any solvent, this system exhibited good catalytic activity. Our future efforts in the context of CH_3OH /amine hydrogen storage systems will be directed toward broadening the substrate scope to high boiling polyamines.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b11637.

Experimental details (PDF)

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Notes

The authors declare no competing financial interest.

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- (26) When the remaining H_2 from the autoclave was released through a liq. N_2 cooled trap, condensation of methanol, toluene and traces of 7 was observed.
- (27) Reaction conditions are given in the Supporting Information.