

# Highly Efficient Hydrogen Storage System Based on Ammonium Bicarbonate/Formate Redox Equilibrium over Palladium Nanocatalysts

Ji Su, Lisha Yang, Mi Lu, and Hongfei Lin\*<sup>[a]</sup>

A highly efficient, reversible hydrogen storage–evolution process has been developed based on the ammonium bicarbonate/formate redox equilibrium over the same carbon-supported palladium nanocatalyst. This heterogeneously catalyzed hydrogen storage system is comparable to the counterpart homogeneous systems and has shown fast reaction kinetics of both the hydrogenation of ammonium bicarbonate and the dehydrogenation of ammonium formate under mild operating conditions. By adjusting temperature and pressure, the extent of hydrogen storage and evolution can be well controlled in the same catalytic system. Moreover, the hydrogen storage system based on aqueous-phase ammonium formate is advantageous owing to its high volumetric energy density.

The demand for highly efficient energy storage systems is imminent due to the rapid growth of production of renewable energies as these are usually intermittent due to the dependence on unpredictable factors such as the availability of solar light, wind speed, among others. As the cleanest chemical energy carrier, H<sub>2</sub> has received high interest during the past decades. However, the advancement of sustainable H<sub>2</sub> economy is hindered by the lack of the successful integration of H<sub>2</sub> generation from renewable materials, its storage, and its conversion into electrical energy.<sup>[1]</sup> Although research on H<sub>2</sub> production and conversion, such as photocatalytic splitting water<sup>[2]</sup> or proton exchange membrane (PEM) fuel cells,<sup>[3]</sup> has entered a sophisticated stage, the hydrogen storage technology is still waiting for its breakthrough. Significant challenges of H<sub>2</sub> storage stems from its inherent low volumetric energy density at ambient conditions. In this regard, high pressure and low temperature are required to obtain a balanced gravimetric and volumetric energy density of H<sub>2</sub> for storage. Recently, alternative approaches for the storage of H<sub>2</sub> are the development of adsorptive materials or the transformation of H<sub>2</sub> into other chemical carriers that can reversibly absorb and release H<sub>2</sub>.<sup>[1b]</sup> In particular, formic acid (FA), if obtained from CO<sub>2</sub> hydrogenation, is a promising source for carbon-neutral hydrogen storage.<sup>[4]</sup>

Efficient hydrogenation of CO<sub>2</sub> to produce FA and reversible dehydrogenation of FA to release H<sub>2</sub> can be achieved using suitable catalytic systems. If the same catalyst can be used for both CO<sub>2</sub> hydrogenation and FA dehydrogenation at mild reaction conditions, then a “hydrogen battery” can be constructed for mobile device applications. Beller and co-workers recently designed a reversible hydrogen storage cycle by controlling the temperature using a Ru-based homogeneous catalyst.<sup>[5]</sup> In their work, the hydrogenation of NaHCO<sub>3</sub> to HCO<sub>2</sub>Na was performed in a 96% yield at 70 °C in the water/THF solution, while dehydrogenation of HCO<sub>2</sub>Na was achieved at a high conversion (> 90%) at 30 °C. Using similar catalyst as Beller et al., Joó et al. first constructed a rechargeable hydrogen storage device without using organic solvents that showed excellent stability upon prolonged use.<sup>[6]</sup> Fujita's group reported a reversible hydrogen storage system with a proton-switchable homogeneous Ir catalyst.<sup>[7]</sup> Recently, Plietker's group designed a prototype of the reversible H<sub>2</sub> battery by reversibly converting a formic acid amine adduct under different H<sub>2</sub> pressures using a Ru-complex catalyst in an organic solvent.<sup>[8]</sup> To the best of our knowledge, up to date the current FA-based hydrogen storage media are homogeneous systems, in which an important aspect is missing, that is, the significant challenge related to separation, reuse, deactivation, and regeneration of the catalysts. Practically, a heterogeneous system is much easier to handle than a homogeneous one and thus could be a better option. However, compared to the homogeneous systems, the development of heterogeneous catalysts for FA-based hydrogen storage is limited. Sasson et al. first proposed the idea of using sodium formate salts as the chemical carrier for hydrogen storage using Pd supported on carbon as catalyst.<sup>[9]</sup> However, the efficiency of the hydrogenation of sodium bicarbonate was rather low.<sup>[10]</sup>

Most previous studies also ignored an important factor that determines the potential of liquid-phase hydrogen storage systems: the volumetric hydrogen density. For the bicarbonate/formate hydrogen storage system, the volumetric hydrogen density depends on the solubility of formate salts.<sup>[6,11]</sup> The solubility of ammonium formate is > 84 molL<sup>-1</sup> in water at 80 °C. In contrast, the solubility of sodium formate is only ~19 molL<sup>-1</sup> at the same temperature. Even at room temperature, the solubility of ammonium formate (~22 molL<sup>-1</sup>) is nearly double that of sodium formate (~12 molL<sup>-1</sup>). The solubility difference, as seen in Figure S2 in the Supporting Information, motivated us to construct a reversible hydrogen storage–evolution system based on the ammonium bicarbonate/formate equilibrium.

[a] Dr. J. Su, L. Yang, M. Lu, Prof. H. Lin  
Department of Chemical and Material Engineering  
University of Nevada, Reno,  
1664 N. Virginia St. M/S388, Reno, NV 89557 (USA)  
Fax: (+1) 7753275059  
E-mail: hongfeil@unr.edu

Supporting Information for this article is available on the WWW under <http://dx.doi.org/10.1002/cssc.201403251>.

**Table 1.** Catalytic hydrogenation of bicarbonates and carbonates.<sup>[a]</sup>

| Entry | Reagent   | Catalyst <sup>[b]</sup>           | Reaction conditions    |         | Yield [%] | TON <sup>[c]</sup> |
|-------|---|-----------------------------------|------------------------|---------|-----------|--------------------|
|       |   |                                   | $p_{\text{H}_2}$ [MPa] | $t$ [h] |           |                    |
| 1     | NaHCO <sub>3</sub>                              | Pd/AC                             | 2.75                   | 1       | 28.6      | 527                |
| 2     | Na <sub>2</sub> CO <sub>3</sub>                 | Pd/AC                             | 2.75                   | 1       | 0.05      | <1                 |
| 3     | KHCO <sub>3</sub>                               | Pd/AC                             | 2.75                   | 1       | 30.8      | 567                |
| 4     | K <sub>2</sub> CO <sub>3</sub>                  | Pd/AC                             | 2.75                   | 1       | 0.07      | <1                 |
| 5     | NH <sub>4</sub> HCO <sub>3</sub>                | Pd/AC                             | 2.75                   | 1       | 42.4      | 782                |
| 6     | (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> | Pd/AC                             | 2.75                   | 1       | 15.1      | 278                |
| 7     | NH <sub>4</sub> HCO <sub>3</sub>                | Pd/AC                             | 2.75                   | 6       | 84.9      | 1571               |
| 8     | NH <sub>4</sub> HCO <sub>3</sub>                | Pd/AC                             | 2.75                   | 15      | 95.6      | 1769               |
| 9     | NH <sub>4</sub> HCO <sub>3</sub>                | Pd/AC                             | 0.69                   | 1       | 16.9      | 312                |
| 10    | NH <sub>4</sub> HCO <sub>3</sub>                | Pd/AC                             | 1.38                   | 1       | 31.3      | 579                |
| 11    | NH <sub>4</sub> HCO <sub>3</sub>                | Pd/AC                             | 4.14                   | 1       | 53.1      | 982                |
| 12    | NH <sub>4</sub> HCO <sub>3</sub>                | Pd/AC                             | 5.52                   | 1       | 59.6      | 1103               |
| 13    | NH <sub>4</sub> HCO <sub>3</sub>                | Pd/AC                             | 5.52                   | 2       | 90.4      | 1672               |
| 14    | NH <sub>4</sub> HCO <sub>3</sub>                | Ru/AC                             | 2.75                   | 1       | 0.2       | 3                  |
| 15    | NH <sub>4</sub> HCO <sub>3</sub>                | Rh/AC                             | 2.75                   | 1       | 0.2       | 3                  |
| 16    | NH <sub>4</sub> HCO <sub>3</sub>                | Pt/AC                             | 2.75                   | 1       | 0         | 0                  |
| 17    | NH <sub>4</sub> HCO <sub>3</sub>                | Ni/AC                             | 2.75                   | 1       | 0         | 0                  |
| 18    | NH <sub>4</sub> HCO <sub>3</sub>                | Pd/Al <sub>2</sub> O <sub>3</sub> | 2.75                   | 1       | 8.9       | 278                |
| 19    | NH <sub>4</sub> HCO <sub>3</sub>                | Pd/CaCO <sub>3</sub>              | 2.75                   | 1       | 0.6       | 20                 |
| 20    | NH <sub>4</sub> HCO <sub>3</sub>                | Pd/BaSO <sub>4</sub>              | 2.75                   | 1       | 2.9       | 212                |

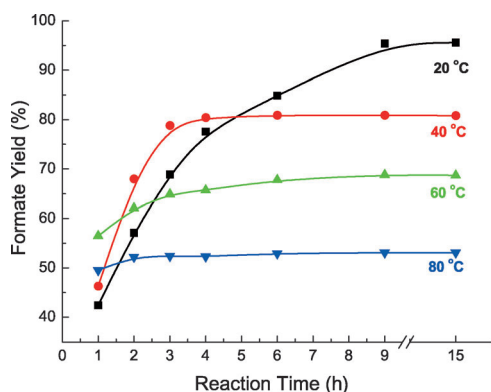
[a] Reaction conditions: 20 mL distilled H<sub>2</sub>O, 20 mmol reagent salt, 0.1 g catalyst, 20 °C. [b] All catalyst loadings were 5% metal, Ni/AC sample was prepared by impregnation method (nickel nitrate as the precursor). [c] TON is turnover number and it was calculated by the formula: total moles of formate formed/(total moles of Pd adatoms × D%), where D% is the dispersion of metal atoms on the support surface. The D% values are calculated from the CO chemisorption (Table S1).

We first compared various bicarbonate and carbonate salts with different cations, Na<sup>+</sup>, K<sup>+</sup>, and NH<sub>4</sub><sup>+</sup>, for hydrogenation. As shown in Table 1, over Pd nanocatalyst formates could be easily produced from the hydrogenation of bicarbonates with all three different cations but not from carbonates [except for (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>] at room temperature. It was much more difficult to hydrogenate carbonate salts than bicarbonate ones as the protonation of carbonate ions was considered to be the rate-limiting step in aqueous solutions, especially at low temperatures.<sup>[12]</sup> The equilibrium between bicarbonate and carbonate ions highly depends on the pH value of the solution. On increasing the pH value, the equilibrium shifted from bicarbonate to carbonate and thus the formate yield decreased (Figure S3). In a typical hydrogenation reaction system, 1 M NH<sub>4</sub>HCO<sub>3</sub> aqueous solution (20 mmol NH<sub>4</sub>HCO<sub>3</sub> in 20 mL H<sub>2</sub>O and the pH value was 7.7) using the Pd/AC nanocatalyst (AC stands for activated carbon support, 5 wt% Pd), a high yield of ammonium formate, ~59.6%, with a turnover number (TON) of 1103 was achieved after reacting for 1 h when the initial H<sub>2</sub> pressure was 5.5 MPa. By extending the reaction time to 2 h, a 90.4% formate yield with a TON of 1672 was obtained. Furthermore, higher concentrations of NH<sub>4</sub>HCO<sub>3</sub> also increased the formate yields, for example, a high turnover frequency (TOF) of 1221 h<sup>-1</sup> was achieved using a 2.5 M NH<sub>4</sub>HCO<sub>3</sub> solution and 2.75 MPa initial H<sub>2</sub> pressure, as seen in Figure S4. In comparison, Beller and co-workers reported that, under similar reaction conditions (5 MPa initial H<sub>2</sub> pressure and a 2 h reaction

time) and using the [RuCl<sub>2</sub>(benzene)]<sub>2</sub> homogeneous catalyst, a 35% formate yield with a TON of 807 was achieved from hydrogenating 24 mmol NaHCO<sub>3</sub> in a solution of 25 mL H<sub>2</sub>O and 5 mL THF (reagent concentration <1 mol L<sup>-1</sup>).<sup>[5a]</sup> Our results suggest that the hydrogen storage process based on the reduction of ammonium bicarbonate over the Pd/AC heterogeneous catalyst is more efficient than the homogeneous counterpart that Beller et al. reported.

The hydrogenation of ammonium bicarbonate with different supported metal catalysts was also investigated. Transition metals supported carbon such as Pd/AC, Ru/AC, Rh/AC, Pt/AC, and Ni/AC have been proven to be active towards hydrogenation or hydrogenolysis reactions. But due to the different properties of the metals themselves, they often show different activities in response to a specific reaction.<sup>[13]</sup> In the hydrogenation of NH<sub>4</sub>HCO<sub>3</sub>, we found that only Pd catalysts showed a clear catalytic activity, whereas other transition metals such as Ru, Rh, Pt, and Ni were inactive under the test conditions (Table 1, entries 8 and 14–17). The activated carbon support was superior to other supports including Al<sub>2</sub>O<sub>3</sub>, CaCO<sub>3</sub>, and BaSO<sub>4</sub> (Table 1, entries 18–20). Because the hydrogenation of aqueous NH<sub>4</sub>HCO<sub>3</sub> is a multiphase reaction (gas/liquid/solid), the diffusion of the reactant, H<sub>2</sub>, could be rate limiting due to its low solubility in water. Activated carbon is commonly a hydrophobic support and can store H<sub>2</sub>.<sup>[14]</sup> H<sub>2</sub> could be locally enriched in the carbon channels or on the surface of the carbon support from H<sub>2</sub> spillover from the Pd metal. Localized higher H<sub>2</sub> concentrations on the surface of the Pd/AC catalyst may thus be attributed to the higher formate yields. On the other hand, the dispersion of Pd nanoparticles (NPs) on AC was higher than that on other supports such as Al<sub>2</sub>O<sub>3</sub>, CaCO<sub>3</sub>, and BaSO<sub>4</sub> (Table S1) or other supported metal catalysts (Figure S5), and a higher dispersion implies more active Pd sites that favor hydrogenation.

In addition to the catalyst materials (metals and supports), process conditions such as initial H<sub>2</sub> pressure and reaction temperature are also the key influencing factors on the hydrogenation of ammonium bicarbonate. Stalder et al. found that a 1:1 hydrogenation reaction equilibrium ratio of formate/bicarbonate was obtained when purging the NaHCO<sub>3</sub> solution with 0.1 MPa H<sub>2</sub> gas for a long time (40–90 h).<sup>[15]</sup> In our reaction at a higher H<sub>2</sub> gas pressure of 2.75 MPa, the equilibrium ratio of HCO<sub>2</sub>NH<sub>4</sub> to NH<sub>4</sub>HCO<sub>3</sub> was shifted significantly to approximately 95:5 in 15 h (Table 1, entry 8). On the other hand, on increasing the reaction temperature from 20 to 80 °C, the hydrogenation rate was increased but the equilibrium yield of formates was decreased from ~95% to ~50%, as shown in Figure 1. Higher reaction temperatures favor the dehydrogenation reaction and shift the equilibrium to hydrogen evolution, which is in agreement with previous studies.<sup>[4d,9,10]</sup> Our results show that the equilibrium position of the hydrogen storage and evolution process depends on both the reaction temperature and the hydrogen pressure in the heterogeneously catalytic system. Note that the highest formate yield was achieved at room temperature, implying that our hydrogenation reaction system does not need additional external energy for heating.<sup>[7]</sup> However, in practice, a higher H<sub>2</sub> pressure might be needed to

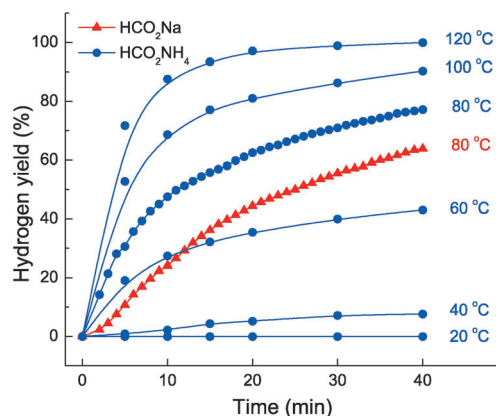


**Figure 1.** Effect of temperature on the hydrogenation of ammonium bicarbonate. Reaction conditions: 20 mL distilled H<sub>2</sub>O, 1 mol L<sup>-1</sup> NH<sub>4</sub>HCO<sub>3</sub>, 0.1 g Pd/AC catalyst, 2.75 MPa initial H<sub>2</sub> pressure.

obtain a reasonably fast hydrogenation rate at room temperature.

It is interesting to find that the hydrogenation efficiency of ammonium bicarbonate is much higher than that of sodium bicarbonate, for example, the TOFs were 782 and 527 h<sup>-1</sup> for the hydrogenation of NH<sub>4</sub>HCO<sub>3</sub> and NaHCO<sub>3</sub>, respectively, under identical reaction conditions (Table 1, entries 1 and 5). We hypothesize that the cations of bicarbonate salts may shift the equilibrium between carbonate or bicarbonate ions. To verify our hypothesis, C<sup>13</sup> NMR spectra were recorded. The peaks from 155 to 170 ppm in the C<sup>13</sup> NMR spectra were assigned to the bicarbonate/carbonate ion pair with fast proton exchange. The ratio of HCO<sub>3</sub><sup>-</sup> to CO<sub>3</sub><sup>2-</sup> has an effect on the chemical shift. As the ratio increases, the peak of the bicarbonate/carbonate ion pair shifts to lower ppm values.<sup>[16]</sup> As shown in Figure S6, the bicarbonate salts have a higher HCO<sub>3</sub><sup>-</sup> concentration than the corresponding carbonate salts since the peaks of the HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> ion pair are located at lower ppm values for bicarbonate salts. The peak positions also suggest that the concentrations of bicarbonate ions are in the order: NaHCO<sub>3</sub> (0.61 M) < KHCO<sub>3</sub> (0.89 M) < NH<sub>4</sub>HCO<sub>3</sub> (0.92 M) (Table S2). Thus, NH<sub>4</sub>HCO<sub>3</sub> has the highest concentration of HCO<sub>3</sub><sup>-</sup> in the aqueous solution, which leads to the highest formate yield of the hydrogenation reaction.

Another important aspect of our work is the dehydrogenation of ammonium formate that closes the hydrogen storage/evolution cycle. We conducted the dehydrogenation of HCO<sub>2</sub>NH<sub>4</sub> at a relatively high temperature range in the N<sub>2</sub> atmosphere with an initial pressure of 0.1 MPa. As shown in Figure 2, no decomposition reaction occurred at 20 °C. As the reaction temperature increased to 80 °C, the yield of H<sub>2</sub> reached 63% and 77% after 20 and 40 min, respectively, and increased to 92.1% with a TON of 1698 after 1.5 h reaction (Table S3). As the reaction temperature increased further, the generation of H<sub>2</sub> from HCO<sub>2</sub>NH<sub>4</sub> became much faster. For example, when the reaction temperature reached 120 °C, the yield of H<sub>2</sub> reached 97% within 20 min and ~100% after 40 min. A comparison of the H<sub>2</sub> evolution efficiencies of HCO<sub>2</sub>NH<sub>4</sub> and HCO<sub>2</sub>Na, as shown in Figure 2, revealed that the yield of H<sub>2</sub> from HCO<sub>2</sub>Na only reached 44% after 20 min at



**Figure 2.** Effect of temperature on the dehydrogenation of ammonium formate and sodium formate (Reaction conditions: 20 mL distilled H<sub>2</sub>O, 1 M formate, 0.1 g Pd/AC catalyst, and 0.1 MPa initial N<sub>2</sub> pressure.)

80 °C, which means that the H<sub>2</sub> evolution efficiency of HCO<sub>2</sub>Na was only ~70% of that of HCO<sub>2</sub>NH<sub>4</sub> in the initial stage of reaction (0–20 min). The NH<sub>4</sub><sup>+</sup> ion effect on the dehydrogenation reaction may be attributed to the H<sub>2</sub> evolution efficiency being higher for HCO<sub>2</sub>NH<sub>4</sub> than for HCO<sub>2</sub>Na. For the dehydrogenation of HCO<sub>2</sub>NH<sub>4</sub>, the conjugate acid ion, NH<sub>4</sub><sup>+</sup>, can easily supply H<sup>+</sup> to complete the reaction, whereas H<sup>+</sup> has to be derived from H<sub>2</sub>O for the dehydrogenation of HCO<sub>2</sub>Na, which is more difficult.<sup>[17]</sup>

An advantage of ammonium formate as H<sub>2</sub> storage material is its high solubility in water. As shown in Figure S7, on increasing the initial concentration of HCO<sub>2</sub>NH<sub>4</sub> from 1 to 15 M, the TOF of dehydrogenation of HCO<sub>2</sub>NH<sub>4</sub> at 80 °C increased from 2135 to 5061 h<sup>-1</sup>, which is comparable to that of FA dehydrogenation in the presence of nano-Pd on nanoporous carbon MSC-30 catalyst<sup>[13f]</sup> at low temperatures. In contrast, the saturated solubility of HCO<sub>2</sub>Na is only 11.6 M at 20 °C as seen in Figure S2. Therefore, a H<sub>2</sub> battery with a high volumetric energy density could be realized by using the highly concentrated HCO<sub>2</sub>NH<sub>4</sub> aqueous solutions with appropriate loading of the commercial Pd/AC catalyst; the performance of such a H<sub>2</sub> battery system may be further enhanced by developing new Pd-on-carbon catalysts.

At elevated temperatures, HCO<sub>2</sub>NH<sub>4</sub> can be decomposed to NH<sub>3</sub>, H<sub>2</sub>O, and CO<sub>2</sub> and then rehydrated to form NH<sub>4</sub>HCO<sub>3</sub>. In general, formic acid or its derived formate salts can be decomposed through either a dehydrogenation or a dehydration pathway. For the subsequent conversion of H<sub>2</sub> into electrical energy, the latter pathway should be avoided as it produces CO as impurity, which is toxic to fuel cell catalysts.<sup>[18]</sup> Figure S8 indicates that H<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub> were the gaseous products and that the volume percentage of H<sub>2</sub> was 93.6%. No CO was detected, implying that the Pd/AC catalyst selectively catalyzed the dehydrogenation reaction. The very small amount of CO<sub>2</sub> and trace amount of NH<sub>3</sub> are the by-products of the decomposition of HCO<sub>2</sub>NH<sub>4</sub> or NH<sub>4</sub>HCO<sub>3</sub> at elevated reaction temperatures. Note that even a trace amount of NH<sub>3</sub> in the H<sub>2</sub> fuel could severely decrease the performance of a proton exchange membrane (PEM) fuel cell.<sup>[19]</sup> Therefore, NH<sub>3</sub> must be removed

before use in a fuel cell. Unlike CO, NH<sub>3</sub> is a basic gas and can be removed easily by passing the gas stream through a scrubber containing acidic solutions.<sup>[20]</sup>

Similar to the hydrogenation of ammonium bicarbonate, the Pd/AC catalyst also possesses the best performance among the tested catalysts towards the dehydrogenation of ammonium formate (Table S3), which makes it feasible to build a reversible hydrogen storage–evolution system based on the same catalytic system if the catalyst stability issue is addressed. The TEM images and XRD patterns both indicated that the Pd/AC catalysts were stable. As shown in Figure S9, after one cycle (hydrogenation of NH<sub>4</sub>HCO<sub>3</sub> and then dehydrogenation of HCO<sub>2</sub>NH<sub>4</sub> without regenerating the spent catalyst), no clear sintering or aggregation of the Pd NPs was observed. The XRD patterns of the Pd/AC catalyst (shown in Figure S10) reveal that the peaks, which are assigned to the lattice planes [111], [220], [311], and [200] of Pd, are almost unchanged before and after reactions. Even after five cycles, the activity of the spent catalyst was still as high as that of the fresh catalyst, as shown in Table S4. The XPS spectra of the fresh and spent Pd/AC samples (Figure S11) show that Pd<sup>2+</sup> in the fresh catalyst was completely reduced to Pd<sup>0</sup> after one cycle.

In conclusion, we have demonstrated that the ammonium bicarbonate/formate redox equilibrium system is feasible for reversible hydrogen storage and evolution. High yields of formates and hydrogen were obtained from the hydrogenation of ammonium bicarbonate and the dehydrogenation of ammonium formate, respectively, using the same Pd/AC nanocatalyst. Reaction temperature and H<sub>2</sub> pressure are key factors in controlling the hydrogen storage–evolution equilibrium in this system. Up to 96% yield of ammonium formate was achieved when the hydrogenation reaction was carried out at room temperature at an initial hydrogen pressure of 2.75 MPa, whereas nearly 100% hydrogen yield was obtained from the dehydrogenation of ammonium formate at 80 °C at an initial nitrogen pressure of 0.1 MPa. Compared to the homogeneous catalytic system, this heterogeneous system has the following advantages: no organic solvents or inorganic additives are needed; high volumetric energy density of hydrogen (stored in concentrated ammonium formate aqueous solutions) is achieved; the solid salts or their aqueous solutions can be easily transported and distributed; and the Pd/AC catalyst is stable, being more easily recycled and handled than homogeneous catalysts. We are working on the design and test of the first hydrogen battery device based on this heterogeneous catalytic system.

## Experimental Section

Experimental details can be found in the Supporting Information.

**Keywords:** carbamate · CO<sub>2</sub> conversion · efficiency · hydrogenation · palladium

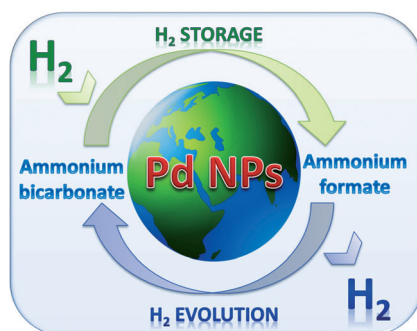
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Received: November 9, 2014

Published online on ■■■■■, 0000

## COMMUNICATIONS

**Revolution of H<sub>2</sub> evolution?** A highly efficient hydrogen storage–evolution process has been developed based on the ammonium bicarbonate/formate redox equilibrium over a carbon-supported palladium nanocatalyst. Ammonium ion improves the efficiencies of both the hydrogenation of bicarbonate and the dehydrogenation of formate. By adjusting the reaction temperature and pressure, the extent of chemical reaction of hydrogen storage and evolution can be well controlled within the same catalytic system.



*J. Su, L. Yang, M. Lu, H. Lin\**

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**Highly Efficient Hydrogen Storage System Based on Ammonium Bicarbonate/Formate Redox Equilibrium over Palladium Nanocatalysts**

