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Nanosized Co- and Ni-Catalyzed Ammonia Borane for Hydrogen Storage

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A “co-precipitation” method was applied to introduce nanosized Co- and Ni-based catalysts to ammonia borane. It was observed that approximately 1 equiv. of hydrogen was evolved from the doped ammonia borane samples at a temperature as low as 59 °C. Moreover, the catalytic dehydrogenation did not present any induction period, undesirable byproduct borazine, or sample forming. Electron paramagnetic resonance (EPR) characterization revealed that Co in a partially reduced state is the active species in the catalytic dehydrogenation of ammonia borane.

1. Introduction

Storage of hydrogen efficiently onboard is one of the most challenging technical issues for the implementation of hydrogen energy.[1] It has been demonstrated that the safest and most effective method to store hydrogen is by using solid media, such as sorbent materials[2] and hydrides.[3,4] NH_3BH_3 (AB in short) has been a subject of intensive study since 2000,[5] because of its abnormally high hydrogen content, i.e., 19.6 wt %. But its stepwise dehydrogenation encounters relatively high kinetic barriers, which render temperatures higher than 100 °C.[5,6] Other drawbacks of AB for hydrogen storage include the emission of poisoning side product (borazine) and severe material foaming and expansion in the dehydrogenation. Autrey and co-workers[7] investigated the thermolysis of AB spread in a mesoporous silica (SBA-15) and achieved an improved kinetics and thermodynamics in H_2 release. Upon dissolving AB in an ionic liquid, Sneddon et al.[8] observed an enhanced rate of dehydrogenation and intermediates formed in the process. Heinekey,[9] Baker,[10] and Burrell[11] et al. reported that AB dissolved in organic solvents can be effectively catalyzed by Ir, Ni, Pt-based, or acid catalysts. Chen[12] and Xu[13] et al. used in situ reduced transition metals as catalysts to catalyze the hydrolysis of AB, and observed accelerated rates of hydrogen release rate. Cao[14] et al. spread AB on boron and nitrogen modified carbon cryogels and lowered the activation energy for dehydrogenation. However, most of those approaches inevitably bring additional weight (supports or solvents, etc.) to the system and thus considerably reduce the overall hydrogen content. Increasing activities have been given to chemical modification to AB recently. Through replacing H of NH_3 in AB by alkali or alkaline earth metals, lithium amidoborane, sodium amidoborane, and calcium amidoborane have been synthesized successfully.[15−18] The advantages of the newly developed amidoboranes lie in the lowered dehydrogenation temperature (i.e., 90 °C for alkali metal amidoboranes), more usable hydrogen (i.e., 10.9 wt % at 90 °C) and depression of Borazine.[16a] The pending issues are catalytically controlled dehydrogenation, regeneration of used fuel, and elimination of unwanted byproducts, such as NH_3 and NH_2BH_2, etc. In this study, we report a newly developed “co-precipitation”

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method in introducing 2.0 mol % nanosized Co- and Ni-based catalysts to AB in solid form. Our experimental results show that the catalyst-doped AB samples can release ca. 5.8 wt % H_2 rate at a temperature as low as 59 °C. Moreover, the dehydrogenation does not bring any detectable borazine and sample foaming.

2. Experimental Section

2.1. Coprecipitation Method. NH_3BH_3 (97% Sigma-Aldrich), $CoCl_2$ (99.9% Alfa-Aesar), $NiCl_2$ (98% Alfa-Aesar), and tetrahydrofuran (THF; 99.8% J&K Chemical) were used as received. All sample handlings were conducted in an MBraun 200 glovebox filled with purified argon. The introduction of catalyst additives to AB follows, in principle, the typical incipient wetness method. In a typical experiment, 0.0002 mol of $CoCl_2$ or $NiCl_2$ was put into 10 mL of THF at room temperature and sonicated for 20 min. Then, 0.01 mol AB were added into that THF solution containing $CoCl_2$ or $NiCl_2$. Immediately after, the resulting solution or blending was distilled at room temperature and under a reduced pressure in a rotary evaporator. Most of THF was removed within 3 min and samples were continuously vacuumed overnight to eliminate the rest THF. After that, samples were preserved at ~10 °C to avoid self-decomposition.

2.2. Characterizations. A homemade temperature-programmed desorption (TPD)−mass spectrometer (MS) combined system was employed to detect the gaseous products during AB decomposition. Volumetric release for quantitative measurements of hydrogen desorption from samples were carried out on a homemade Sievert type apparatus. X-ray diffraction (XRD) measurements were conducted on a PANalytical X'pert diffractometer (Cu Kα, 40 kV, 40 mA). To avoid sample contamination by air, the sample holder was covered by a piece of shielding film. Morphologies of samples were observed on a transmission electron microscope (TEM) (JEM-2000EX, JEOL Co. Ltd., Japan). EPR measurements were carried out on a Bruker A200 spectrometer at room temperature. Differential scanning calorimeter (DSC) data were obtained from STA449C thermal analysis system provided by the Netzsch Company.

3. Results and Discussion

3.1. Catalytic Dehydrogenation of AB. Two mole percent Co- or Ni-based catalyst was doped to AB following the "co-precipitation" method developed in this study, in which both AB and the precursors of Co or Ni catalyst were first added in THF and then coprecipitated by quickly removing THF from the solution. Through this method, catalyst dispersed well in the sample and could have good contact with the reactant (see below). Furthermore, the only added weight to AB is 2.0 mol % catalytic additives; therefore, the hydrogen capacity of the system does not have to be sacrificed significantly. Figure 1 shows the TPD curves of the pristine and the catalyst-doped AB samples, respectively. Identical to what was reported in the literature,[5,6] the pristine AB sample released the first equivalent of H_2 at temperatures above 100 °C and the second equivalent of H_2 at ~160 °C, whereas the catalyst-doped AB samples started to evolve H_2 at about 50 °C (see the Supporting Information) and gave broad desorption peaks centered at ca. 113 °C. The second-step desorption exhibits irregular pattern compared with that of the pristine AB indicating the formation of different products in the first step. Noted that "polymeric aminoboranes" (PAB in short), the general name of the product in first-step decomposition, is composed of oligomeric and polymeric linear, cyclic, branched aminoboranes.[8] The change in reaction conditions or mechanism is likely to bring the variation in product composition. Another important observation is that borazine was beyond the detection limit for those catalyst-doped AB samples (Figure 1b). Moreover, all these doped samples did not foam in the dehydrogenation. Figure 2 shows the photos of samples collected after being heated to 120 °C under identical conditions. The pristine AB sample expended severely and pushed up the lid of the sample pan. Contrastingly, the catalyst-doped samples did not exhibit any detectable foaming. We attribute this phenomenon to the feature that AB dehydrogenates catalytically prior to its melting point, i.e., ca. 100 °C[6] (see Figure 1a), where reacting species set up linkages with each other to form dimers or oligomers or polymeric aminoboranes, whose melting point is higher than the pristine AB. The DSC measurements confirm that the endothermic nature of AB melting (~100 °C) is hardly detectable when the catalyst-doped samples were heated to elevated temperatures at slower ramping rates (see Figure 4 below and the Supporting Information), which is clearly different from the pristine AB.

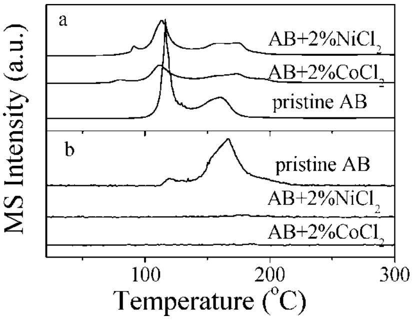

Figure 1. TPD-MS spectra of the pristine and 2.0 mol % Co- or Ni-doped AB samples, respectively. (a) H_2 signals and (b) borazine signals.

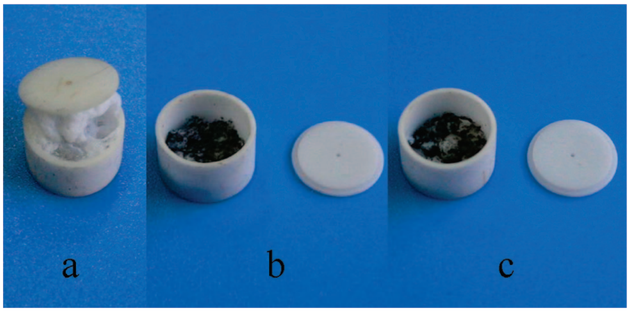

Figure 2. Photos of the (a) pristine, (b) 2.0 mol % Co-doped and (c) 2.0 mol % Ni-doped AB samples after being heated to 120 °C in argon at a ramping rate of 2 °C min^{-1}. Sample loading is ca. 2 mg.

Isothermal volumetric hydrogen release measurements present distinct features among the pristine and the doped AB samples. As shown in Figure 3, barely any hydrogen release was detectable from the pristine AB sample after being held at 59 °C for 1 day (Figure 3a), which is probably due to an extremely long induction period (for the formation of initiator, diammoniate of diborane, DADB in short) and/or high kinetic barrier in dehydrogenation at this tempera-

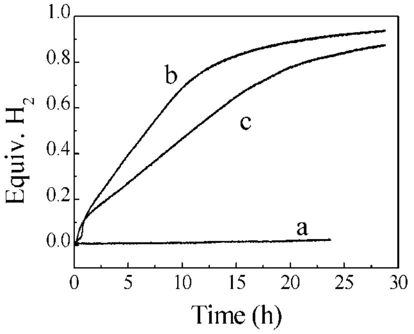

Figure 3. Volumetric hydrogen release measurements at 59 °C on the (a) pristine, (b) 2.0 mol % Co-doped, and (c) 2.0 mol % Ni-doped AB samples, respectively.

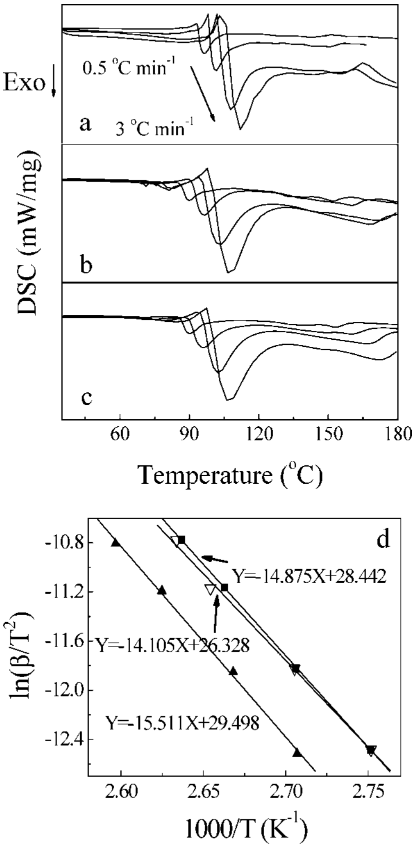

Figure 4. DSC profiles of dehydrogenation of (a) pristine, (b) Co-doped, and (c) Ni-doped AB samples at heating rates of 0.5, 1, 2, and 3 °C min^{-1}, respectively. (d) Kissinger plots of the pristine (▲), Co-doped (▽), and Ni-doped (■)AB samples at different heating rates.

ture.[19] The catalyst-doped AB samples, in contrast, evolved hydrogen vigorously at the same temperature (graphs b and c in Figure 3) without any observable induction period. Approximately one equivalent of H_2 can be released within 30 h. The overall feature of hydrogen release is clearly different from the sigmoidal kinetic behavior of pristine AB reported in literature,[7,20] which indicates that the mechanism of catalytic dehydrogenation may be different from the DADB initiated thermal decomposition. Such a hypothesis is further supported by the observations of different products in the first- and second-step (no borazine) dehydrogenation mentioned above.

Table 1. E_a, A, and k (at 80 °C) Calculated from Kissinger Equation and Arrhenius Equation

	E_a (kJ mol^{-1})	A (min^{-1})	k (80 °C) (min $^{-1}$)
pristine AB	129.0	1.00×10^{17}	8.14×10^{-3}
AB+2%Co	117.3	3.83×10^{15}	1.68×10^{-2}
AB+2%Ni	123.5	3.35×10^{16}	1.78×10^{-2}

3.2. Kinetic Analyses. To gain the insight of the enhanced kinetics, we determined the reaction kinetic parameters (activation energy E_a and the pre-exponential factor A) by using the Kissinger equation,[21−23] namely

$$\ln(\beta/T_p^2) = \ln(AR/E_a) - E_a/RT_p \qquad (1)$$

Here, T_p is the temperature at which the maximum reaction rate peaks, A the pre-exponential factor, β the heating rate, E_a the activation energy, and R the gas constant. DSC technique was applied to collect the temperatures of maximum reaction rate at various heating rates (shown in Figure 4). The dependence of $\ln(\beta/T_p^2)$ vs $1/T_p$ was plotted in Figure 4d. The activation energy E_a and the pre-exponential factor A were calculated from the slope ($-E_a/R$) and the intercept ($\ln(AR/E_a)$) of the fitted line, respectively. Once E_a and A are known, the specific rate constant k at a given temperature can be determined by the Arrhenius equation

$$k = A\exp(-E_a/RT) \qquad (2)$$

Table 1 presents E_a, A, and k (at 80 °C) for each sample. The E_a of the first dehydrogenation step of AB was reduced comparatively after doping with catalysts. At 80 °C the rate constant k of Co- or Ni-doped AB system is 2.06 or 2.19 times as that of the pristine AB. Reduction in kinetic barrier was also observed in the AB spread on nanoscalfold[7] and on the N−B modified carbon cryogel[14] systems. However, the reaction path of AB dehydrogenation in the Co- or Ni-catalyzed system and those spread systems should be different as discussed above.

3.3. Characterization of Catalysts. The identity of Co or Ni can hardly be observed by XRD because of the very low loading and/or poor crystallinity (see the Supporting Information). The morphologies of the Co- and Ni-doped AB samples were examined by TEM. As shown in images a and b in Figure 5, the majority of particles of Co and Ni catalysts are smaller than 3 nm, showing advantage of the “co-precipitation” method in making nanosized catalysts. Such a small size catalyst enables its fine dispersion and good contact with the reacting species. After volumetric release at 59 °C, the particles of Co and Ni catalysts are still in nanoscale (shown in images c and d in Figure 5). In the following part, those additives are characterized with a focus on the Co-doped system.

Noting that AB is a reducing agent and the overall reaction environment is reductive, Co can hardly keep the Co^{2+} state. EPR was employed to identify the chemical state of Co doped in AB. An absorption at $g = 2.15$ was observed

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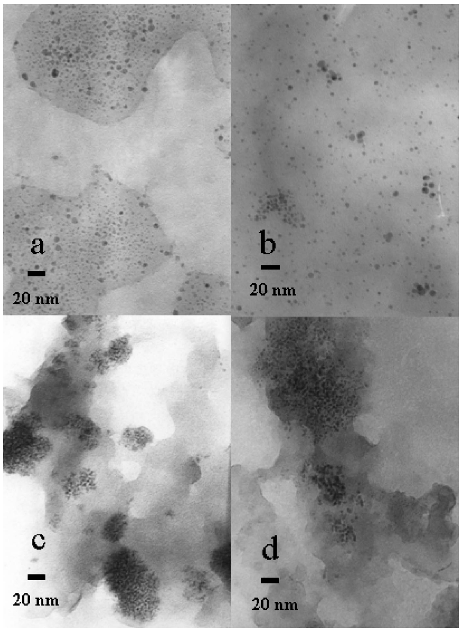

Figure 5. TEM images of the as-prepared (a) 2.0 mol % Co-doped, (b) Ni-doped AB samples, and the post-dehydrogenated (c) 2.0 mol % Co-doped, (d) Ni-doped AB samples.

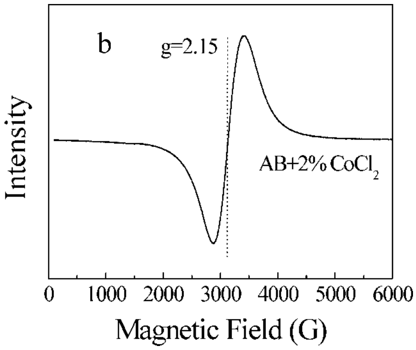

Figure 6. EPR curve of the 2.0 mol % Co-doped AB sample at room temperature.

(Figure 6), which is far from that of metallic cobalt ($g = 1.41$)[24] and close to that of Co^+ ($g = 2.16$).[24,25] It is worth noting that paramagnetic Co^{2+} could not give a spectrum because of fast spin−lattice relaxation at room temperature.[25] It is very likely that cobalt in its partially reduced state, i.e., Co^{1+}, is the active species. Previous reports on the Co- or Ni-catalyzed hydrolysis of $NaBH_4$ and AB suggested that a Co−B or Ni−B compound (such as Co_2B or Ni_3B) was the functional species.[26,27] As B is more electron negative than Co, Co should bear certain positive charge. Noted that in most cases, because of its poor crystallinity, Co−B or Ni−B compound was difficult to identify upon the in situ formation. Only when heated to elevated temperatures can crystalline compound be detected.[27] We believe there is a similarity between the Co-catalyzed dehydrogenation and that of the Co-catalyzed hydrolysis of AB, where the activation of B−H bond is essential in the reaction path.[10b] Indeed, when introducing Co_2B additive synthesized by reacting $CoCl_2$ and $LiBH_4$ in a molar ratio of 1/2 through ball milling, AB can also decompose at lower temperatures. However, further investigations on the chemical state of Co and the reaction mechanism are needed.

4. Conclusions

As a summary, the "co-precipitation" method was developed successfully in introducing nanosized catalytic additives, i.e., 2.0 mol % Co and 2.0 mol % Ni, to AB. Our experimental results show that the catalysts, less than 3 nm in size and in partially reduced chemical state, can catalyze solid-state AB dehydrogenation at a temperature as low as 59 °C. Moreover, the catalytic dehydrogenation does not have an induction period, detectable borazine, or sample foaming.

Supporting Information Available: XRD spectra of 2 mol % Co- or Ni-doped AB (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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