Short communication

Room temperature hydrolytic dehydrogenation of ammonia borane catalyzed by Co nanoparticles

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ABSTRACT

Amorphous and well dispersed Co nanoparticles (less than 10 nm) have been *in situ* synthesized in aqueous solution at room temperature. The as-synthesized Co nanoparticles possess high catalytic activity ($1116 \, L \, mol^{-1} \, min^{-1}$) and excellent recycling property for the hydrogen generation from aqueous solution of ammonia borane under ambient atmosphere at room temperature. The present low-cost catalyst, high hydrogen generation rate and mild reaction conditions (at room temperature in aqueous solution) represent a promising step toward the development of ammonia borane as a viable on-board hydrogen-storage and supply material.

1. Introduction

Nowadays, the search for effective and safe hydrogen-storage materials is one of the most difficult challenges toward hydrogen powered society as a long-term solution for a secure energy future. Ammonia borane (NH_3BH_3, AB), which is a stable solid at room temperature, has a hydrogen capacity of 19.6 wt.%, exceeding that of gasoline and making itself an attractive candidate for chemical hydrogen-storage applications [1–14]. AB can release hydrogen gas through pyrolysis, methanolysis, and hydrolysis routes with some transition metal-based catalysts [15–20].

Recently, the first-row transition metals, such as Fe, Co, Ni, etc. are very attractive in catalytic applications, including the catalytic dehydrogenation of AB, because such catalysts advantageously combine both the high reactivity and low cost [21–28]. For instance, Baker and co-workers applied 10 mol.% Ni-NHC (N-heterocyclic carbine) complexes to catalyze the thermal dehydrogenation of AB at 60 °C, and about more than 2.5 equiv. of H_2 could be generated over 4 h [29]. In addition, Manners and co-workers reported that 1 mol.% colloidal Co(0) can catalyze the complete hydrolysis of AB in 60 min at room temperature [30]. Those works have successfully expanded the catalyst materials for hydrogen generation from AB to more abundant and economical first-row metals over than the noble elements such as Pt and Rh, etc. However, the reaction rate is still quite depressed. Shall we find a simple method to highly

elevate the catalytic activity of the first-row metals?

In this paper, we successfully synthesized the amorphous Co nanoparticles in aqueous solution under ambient atmosphere at room temperature *via* a very facial *in situ* synthesis method. The amorphous Co nanoparticles obtained are found to be highly active for the hydrolysis reaction of AB. When the Co catalyst to AB molar ratio is 4 mol.%, the hydrolysis of AB can be completed in only 1.7 min. To the best of our knowledge, this is the fastest rate attained to date using a first-row transition metal catalyst for the hydrolysis of AB. More interesting, the present Co nanoparticles can keep their high catalytic activity almost unchanged even after 5 recycling test under ambient atmosphere at room temperature.

2. Experiment

2.1. Chemicals

Ammonia–borane (NH_3BH_3, Aldrich, 90%), cobalt (II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, Wako Pure Chemical Industries, Ltd., >98%), and sodium borohydride ($NaBH_4$, Aldrich, 99%) were used as received. Ultrapure water with the specific resistance of 18.3 MΩ cm was obtained by reversed osmosis followed by ion-exchange and filtration (Yamato-WQ 500, Millipore, Japan).

2.2. In situ synthesized Co nanoparticles and their catalytic activities to the hydrolysis of AB

A mixture of appointed amount of NH_3BH_3 and $NaBH_4$ was kept in a two-necked round-bottom flask. One neck was connected to a

gas burette, and the other was connected to a pressure-equalization funnel to introduce aqueous solution of $CoCl_2$ (0.26 M, 10 mL). The molar ratio of catalyst to reactant (Co/AB) was changed with several values (1, 2, 3, 4, and 5 mol.%), and the $CoCl_2$ salt to the reduction agent ($NaBH_4$) molar ratio was kept for a constant of 1:1.4. The reactions were started when the aqueous $CoCl_2$ solution was added to the mixture of $NaBH_4$ and NH_3BH_3 with vigorous shaking. The evolution of gas was monitored using the gas burette. The reactions were carried out at room temperature under ambient atmosphere.

In order to find an optimized reaction condition for hydrogen generation from AB, the concentration of AB was changed with several values (0.5, 1.0, 2.6, 4.0, 7.0, and 10.0 mmol), while the molar ratio for AB:$CoCl_2$:$NaBH_4$ was kept a constant of 1:0.04:0.06. The reactions were started when the aqueous $CoCl_2$ solution was added to the mixture of $NaBH_4$ and NH_3BH_3 with vigorous shaking. The evolution of gas was monitored using the gas burette. The reactions were carried out at room temperature under ambient atmosphere.

### 2.3. Recycle/stability test of the Co nanoparticles

After the hydrogen generation reaction was completed (Co/AB = 4 mol.%), another equivalent of AB (90 mg) was added to the reactor which contained the mixture of the reaction solution and the Co catalyst. The released gas was then monitored by the gas burette. Such recycling experiments were repeated for 5 times under ambient atmosphere at room temperature.

2.4. Catalyst characterization

Powder X-ray diffraction (XRD) was performed on a Rigaku RINT-2000 X-ray diffractometer with Cu Kα for the *in situ* synthesized Co nanoparticles after removed from the reaction solution and dried in argon atmosphere. A glass substrate holding the powder sample was covered by an adhesive tape on the surface to prevent the sample from exposure to air during the measurements. Transmission electron microscope (TEM, Hitachi H-9000NA) and select area electron diffraction (SAED) were applied for the detailed microstructure information of the Co sample. X-ray photoelectron spectroscopy analysis (XPS) was carried out on a Shimadzu ESCA-3400 X-ray photoelectron spectrometer using an Mg Kalpha source (10 kV, 10 mA) for the Co nanoparticles after washing with water and drying in argon atmosphere.

3. Results and discussion

Fig. 1 demonstrates that the hydrogen generation from AB catalyzed by *in situ* synthesized Co particles (Co/AB = 4 mol.%) under ambient atmosphere. At the first 10 s, the black Co particles were rapidly generated. The *in situ* synthesized Co catalyst exerts quite excellent catalytic activity, with which the hydrolysis reaction of AB is completed within only 1.7 min. The hydrolysis reaction can be expressed as the following equation [8]:

$$NH_3BH_3 + 2H_2O \rightarrow NH_4^+ + BO_2^- + 3H_2$$
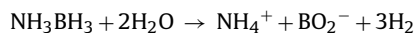
The molar ratio of hydrolytically generated H_2 to the initial AB is close to 3.0, thereby indicating that the dehydrogenation is completed.

With lowering the Co content from 4 to 1 mol.%, the reaction rate is slightly decreased, as seen from Fig. 1(inset). The hydrolysis reactions can be completed in approximately 3.6, and 5.0 min at the Co/AB ratios of 3 and 2 mol.%, respectively. Notably, even at Co/AB = 1 mol.%, the evolution of the approximately total hydrogen gas can be finished within 10 min.

To find an optimized reaction condition for hydrogen generation from AB, the concentration of AB has been changed for several
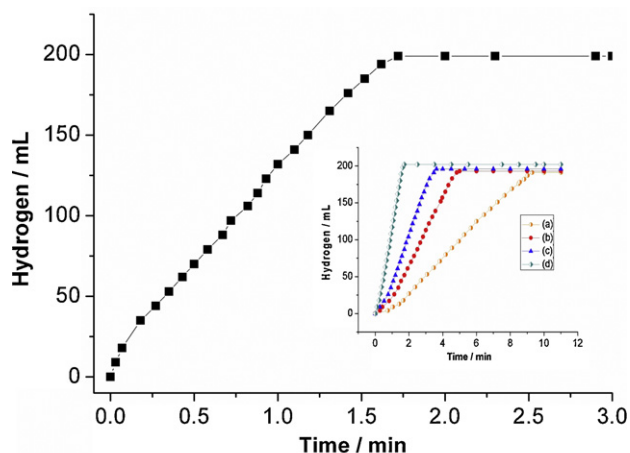

Fig. 1. Hydrogen evolution for the hydrolysis of AB (0.26 M, 10 mL) in the presence of the *in situ* synthesized Co with Co of 4 mol.%, and inset (a) 1 mol.%, (b) 2 mol.%, (c) 3 mol.% and (d) 5 mol.% under ambient atmosphere at room temperature.

values, while the molar ratio for AB:$CoCl_2$:$NaBH_4$ is kept a constant of 1:0.04:0.06. Therefore, the concentration of the $CoCl_2$ and $NaBH_4$ in each experiment was inevitably changed with the change of the concentration of AB. The concentrations for the starting materials of AB, $CoCl_2$, and $NaBH_4$ in the experiments were listed in Table 1, along with the resultant hydrogen generation rate which is described as the ratio of the volume of H_2 gas to the molar content of Co catalyst in a specific reaction time ($L\,mol^{-1}\,min^{-1}$). It is obvious that the starting molar concentrations of AB/$CoCl_2$/$NaBH_4$ have an obvious effect to the hydrogen generation rate. With the increase in the concentration of AB/$CoCl_2$/$NaBH_4$ from 0.05/0.002/0.003 to 0.26/0.0104/0.0156 M, the hydrogen generation rate is increased obviously from 559 to 1116 $L\,mol^{-1}\,min^{-1}$. However, with further increasing, the H_2 generation rate decreases gradually. For example, when the concentration of AB/$CoCl_2$/$NaBH_4$ is elevated up to 1.00 M/0.04 M/0.06 M, the H_2 generation rate is lowered to 824 $L\,mol^{-1}\,min^{-1}$.

Based on the results of Fig. 1 and Table 1, the best Co/AB ratio and the most suitable AB, $CoCl_2$ and $NaBH_4$ concentrations for the present catalytic hydrolysis reaction of AB is 4 mol.% and 0.26, 0.0104 and 0.0156 M, respectively, with which the hydrolysis reaction can complete within only 1.7 min and the reaction rate can reach a value as high as 1116 $L\,mol^{-1}\,min^{-1}$.

It has been reported by our previous work that, in the presence of the crystalline Co particles supported on γ-Al_2O_3 with a Co to AB ratio of 1.8 mol.%, the hydrolysis of AB is completed in about 60 min [31]. Obviously, the present *in situ* synthesized Co particles are much more catalytically active than that of the previous one. Considering the factor of the catalyst to AB molar ratio, the activity of the present Co particles (Co/AB = 4 mol.%) is approximately 15 times higher than that of the previous crystallized one. This excellent catalytic activity might result from the amorphous state of the Co catalyst (*vide infra*). Pt-based materials, such as Pt/C, PtO_2, Pt black, K_2PtCl_4 are reported to exhibit the highest activities to the hydrolysis of AB with the completion time ranging from 2 to 15 min [9]. Therefore, the *in situ* synthesized Co catalyst here holds a Pt-like high catalytic activity in aqueous solution under ambient atmosphere at room temperature.

Fig. 2 shows the XRD pattern of the *in situ* synthesized Co catalyst (Co/AB = 4 mol.%) after washing with water and drying in argon atmosphere. It is clear that no obvious diffraction pattern was found in this sample, which implies that the *in situ* prepared Co particles are in an amorphous phase. Compared with its crystalline counterpart, the amorphous catalyst is considered to possess much

Table 1
Concentrations of AB, $CoCl_2$ and $NaBH_4$, and H_2 generation rate in each experiment.

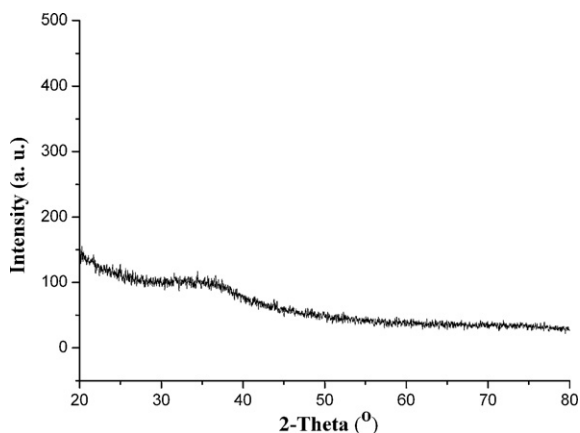| Composition	Expt. 1	Expt. 2	Expt. 3	Expt. 4	Expt. 5	Expt. 6
Concentration (M)						
AB	0.05	0.1	0.26	0.4	0.7	1
$CoCl_2$	0.002	0.004	0.0104	0.016	0.028	0.04
$NaBH_4$	0.003	0.006	0.0156	0.024	0.042	0.06
H_2 generation rate ($L\,mol^{-1}\,min^{-1}$)	559	859	1116	1002	874	824

Fig. 2. X-ray diffraction patterns of the *in situ* synthesized Co nanoparticles (Co/AB = 4 mol.%).

more structure distortion and hold much more catalytic active sites [32,33]. Thus it can be considered that the excellent catalytic activity of the present Co particles may be attributed to its amorphous state.

To investigate the microstructure and further confirm the crystallinity of the as-synthesized Co catalyst, we have applied TEM and SAED on the Co sample (Co/AB = 4 mol.%). As seen from Fig. 3, the sizes of Co particles are approximately <10 nm, moreover, these nanoparticles are well dispersed without any dispersion agent. The related SAED pattern (Fig. 3, inset) for the Co sample demonstrates the diffuse diffraction rings of an amorphous phase which is well consistent with the XRD result.
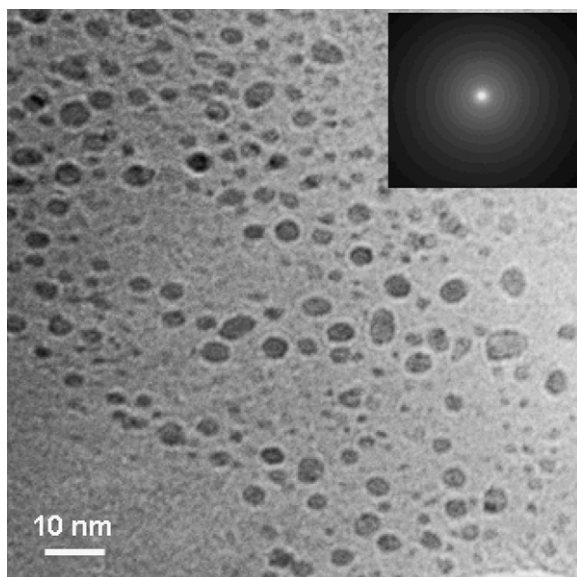

Fig. 3. TEM micrograph and the corresponding selected area electron diffraction (SAED) pattern of the *in situ* synthesized Co nanoparticles (Co/AB = 4 mol.%).

Normally, syntheses of magnetic nanoparticles often require the use of toxic and/or expensive precursors and, additionally, most of the preparation procedures reported to date rely heavily on the organic solvents but not an aqueous phase, mainly due to the hydrophobicity of the dispersing/capping agent used, as well as high temperature and high dilution conditions [34–36], and thus inevitably resulting in high production cost and serious environmental issue while addressing industrial production. Herein, we have successfully synthesized Co nanoparticles by using a very low-cost inorganic Co salt as the metal precursor, and the as-synthesized Co nanoparticles have the good dispersion without any additional dispersing agent in aqueous solution at room temperature. The facile synthesis method completely avoids the use of volatile organic solvents and expensive organometallic precursors, which is of pivotal importance from a "green" synthetic strategy and industrial scale manufacture perspective. It has been reported that amine containing material (stearylamine) could act as the protection (or dispersion) agent for synthesis of Co–Fe/Cr metal coordination nanoparticles [37]. In this sense, ammonium in the present system might has the positive effect for the well dispersion of the Co nanoparticles.

In order to investigate the composition of the solid catalyst, XPS analysis is applied for the *in situ* synthesized Co nanoparticles (Co/AB = 4 mol.%) after washing with water and drying in argon atmosphere. The XPS results are shown in Fig. 4. It can be seen that the Co 2p3/2 and Co 2p1/2 are centered at approximately 778.6 and 793.6 eV, respectively, which meets the value of the metallic state of Co [38–41]. In addition, no boron element is found by XPS, corresponding to the sample is in a metallic state of Co but not in the alloy state of Co-B.

The stability or recycling ability is very important for the practical application of every catalyst. In this sense, the recycling stability of the Co nanoparticles is tested under ambient atmosphere. As shown in Fig. 5, even after 5 times of the recycling test, the activity of the as-prepared Co catalyst has no obvious decrease. This means
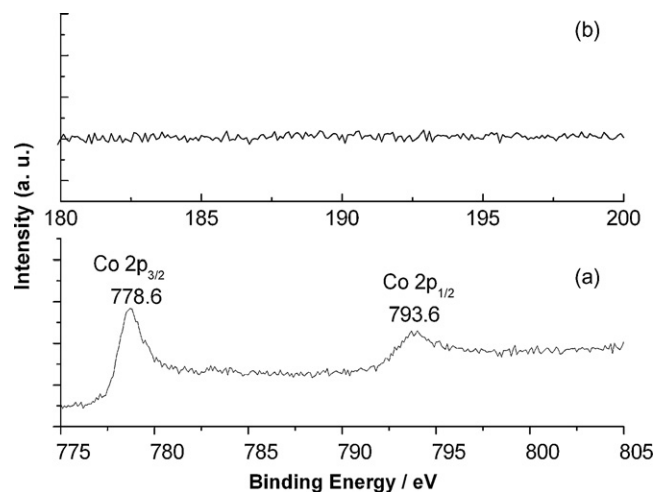

Fig. 4. XPS results for elements of (a) Co and (b) B of the *in situ* synthesized Co nanoparticles (Co/AB = 4 mol.%).
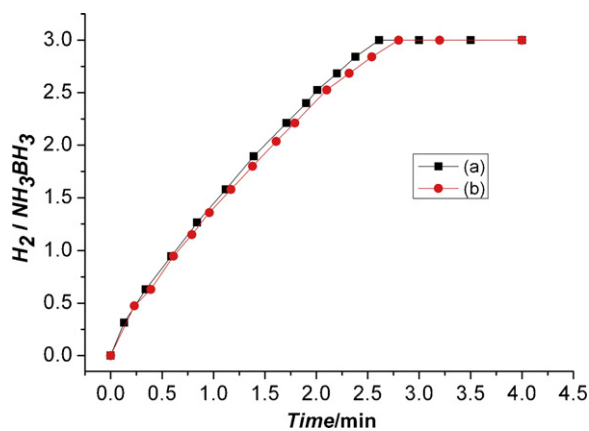
Fig. 5. The H_2/NH_3BH_3 molar ratio of hydrogen generated from aqueous solution (0.26 M, 10 mL) vs. reaction time catalyzed by *in situ* synthesized Co at (a) recycle number 1 and (b) recycle number 5 (Co/AB = 4 mol.%) under ambient atmosphere at room temperature.

that the *in situ* synthesized Co catalyst displays a good recycling stability in aqueous solution under ambient atmosphere. Moreover, the present Co catalyst could be effectively separated by an external magnet due to its magnetic property.

4. Conclusion

In summary, we have explored a simple, but very efficient, method to prepare amorphous and well dispersed Co nanoparticles without additional dispersing agent in aqueous solution at room temperature. The Co nanoparticles as-synthesized possess high catalytic activity and excellent recycling property for the H_2 generation from ammonia borane under ambient atmosphere at room temperature. Such amorphous catalyst is expected to be useful for fuel cells, metal–air batteries and electrochemical sensors. It would also provide excellent opportunities to study molecular mechanisms of heterogeneous catalysis. Moreover, the present low-cost catalyst, high hydrogen generation rate and mild reaction conditions (at room temperature in aqueous solution) represent a promising step toward the development of ammonia borane as a viable on-board hydrogen-storage and supply material.

Acknowledgments

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