Short communication

Room temperature hydrolytic dehydrogenation of ammonia borane catalyzed by Co nanoparticles

Jun-Min Yan, Xin-Bo Zhang, Hiroshi Shioyama, Qiang Xu*

National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

A R T I C L E   I N F O
Article history:
Received 25 June 2009
Received in revised form 25 August 2009
Accepted 26 August 2009
Available online 1 September 2009

Keywords:
Ammonia borane
Hydrolysis
Cobalt nanoparticles
Hydrogen generation
Catalysis

A B S T R A C T
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.

© 2009 Elsevier B.V. All rights reserved.

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 (NH₃BH₃, 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 H₂ 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 facile 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 (NH₃BH₃, Aldrich, 90%), cobalt (II) chloride hexahydrate (CoCl₂·6H₂O, Wako Pure Chemical Industries, Ltd., >98%), and sodium borohydride (NaBH₄, 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-WQ500, Millipore, Japan).

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

A mixture of appointed amount of NH₃BH₃ and NaBH₄ 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 CoCl2 (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 CoCl2 salt to the reduction agent (NaBH4) molar ratio was kept for a constant of 1:1.4. The reactions were started when the aqueous CoCl2 solution was added to the mixture of NaBH4 and NH3BH3 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:CoCl2:NaBH4 was kept a constant of 1:0.04:0.06. The reactions were started when the aqueous CoCl2 solution was added to the mixture of NaBH4 and NH3BH3 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 Kα 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]:

\[
\text{NH}_3\text{BH}_3 + 2\text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{BO}_2^- + 3\text{H}_2
\]

The molar ratio of hydrolytically generated H2 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 values, while the molar ratio for AB:CoCl2:NaBH4 is kept a constant of 1:0.04:0.06. Therefore, the concentration of the CoCl2 and NaBH4 in each experiment was inevitably changed with the change of the concentration of AB. The concentrations for the starting materials of AB, CoCl2, and NaBH4 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 H2 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/CoCl2/NaBH4 have an obvious effect to the hydrogen generation rate. With the increase in the concentration of AB/CoCl2/NaBH4 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 H2 generation rate decreases gradually. For example, when the concentration of AB/CoCl2/NaBH4 is elevated up to 1.00 M/0.04 M/0.06 M, the H2 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, CoCl2 and NaBH4 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-Al2O3 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, PtO2, Pt black, K2PtCl4 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, CoCl₂ and NaBH₄, and H₂ generation rate in each experiment.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Expt. 1</th>
<th>Expt. 2</th>
<th>Expt. 3</th>
<th>Expt. 4</th>
<th>Expt. 5</th>
<th>Expt. 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB (M)</td>
<td>0.05</td>
<td>0.1</td>
<td>0.26</td>
<td>0.4</td>
<td>0.7</td>
<td>1</td>
</tr>
<tr>
<td>CoCl₂ (M)</td>
<td>0.0002</td>
<td>0.004</td>
<td>0.0104</td>
<td>0.016</td>
<td>0.028</td>
<td>0.04</td>
</tr>
<tr>
<td>NaBH₄ (M)</td>
<td>0.003</td>
<td>0.006</td>
<td>0.0156</td>
<td>0.024</td>
<td>0.042</td>
<td>0.06</td>
</tr>
<tr>
<td>H₂ generation rate (L mol⁻¹ min⁻¹)</td>
<td>559</td>
<td>859</td>
<td>1116</td>
<td>1002</td>
<td>874</td>
<td>824</td>
</tr>
</tbody>
</table>

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.%).
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 H₂ 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

We gratefully thank AIST and NEDO for financial support.

References