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The Hydrogen Generation from Hydrolysis of Ammonia Borane via Zeolitic Imidazolate Frameworks Co-ZIF-9

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Abstract: Crystalline zeolite imidazolate framework ZIF-9 has been prepared via solvothermal method, and used as an efficient heterogeneous catalyst for the hydrolytic dehydrogenation of ammonia borane(AB) complex to generate a stoichiometric of hydrogen at room temperature. Co-ZIF-9 exhibited much higher catalytic activity than the bare Co nanoparticles(NPs) for hydrogen generation from the hydrolysis of AB, duo to that the porous structure of Co-ZIF-9 play an important role in the catalytic hydrolysis of AB. Additionally, the activation energy for Co-ZIF-9 was measured to be approximately of 40.8 kJ · mol^{-1}, being lower than most of reported activation energy values for the same reaction using many different catalysts, indicating the superior catalytic performance of Co-ZIF-9.

Key words: ammonia borane; Co-ZIF-9; solvothermal method; hydrolysis; hydrogen generation

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0 Introduction

Hydrogen, owing to its clean burning nature, high calorific value, environmentally benign, has been considered as one of the new energy carriers for heating, transportation, mechanical power and electricity generation. The storage and separation of hydrogen are the major problems that must be overcome on the way to a hydrogen-powered society [1-2]. In the last few decades, different storage solutions have been developed, such as metal hydrides [3], sorbent materials [4] and chemical hydride systems [5]. Among the various kinds of solid hydrogen storage materials, ammonia borane ($NH_3 \cdot BH_3$, AB) has recently been considered as a promising candidate for chemical hydrogen storage application due to its high hydrogen content, low molecular weight, and environmentally friendly nature [5-9]. There are several methods for the release of hydrogen from AB, which can be broadly divided into categories, namely solid thermolysis and solvolysis (hydrolysis or methanolysis). However, thermal dehydrogenation process requires high temperature and power consumption. In contrast, AB is able to release hydrogen via at room temperature hydrolysis reaction in the presence of a suitable catalyst. Thus, the catalysts are the predominant factor for the hydrolytic dehydrogenation of AB. So far many metals such as noble metals Rh [10], Ru [11-12], Pd [13], Pt [14], Au [15], and non-noble metals Fe [16], Co [17-18], Ni [19-20], Cu [21-22] have been investigated for this reaction, among which noble metal catalysts provide significant catalytic activities in the hydrolysis of AB. For the practical application of this system, it is important to develop cost effective catalysts.

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Recently,a new class of porous materials known as metal organic frameworks (MOFs)[24-26],especially, the family of zeolitic imidazolate frameworks (ZIFs), has been currently attracted significant attention[18-19]. ZIFs have ordered porous structures,with high specific surface area and chemically flexible frameworks,consisting of inorganic metal ions(eg.,Zn,Co,Cu) coordinated with organic imidazole or imidazolate ligands. However,since first discovery of the ZIF sample,research efforts have been mostly aimed in preparing new ZIFs and investigating their applications in gas storage and separation. Actually,using ZIFs as catalysts or catalyst supports have been reported very limited in the literature[27-28].

In this work,for the first time,the crystalline zeolite imidazolate framework Co-ZIF-9 has been used as highly efficient catalyst for hydrogen generation from NH_3NH_3 for chemical hydrogen storage. Compared with the Co NPs,the Co-ZIF-9 showed higher performance for the dehydrogenation of NH_3NH_3 at convenient temperature for chemical hydrogen storage.

1 Experimental

1.1 Chemicals

All chemicals were commercially obtained and used without further purification. Ammonia borane (NH_3BH_3, AB, Aldrich, 90%), sodium borohydride ($NaBH_4$, Sigma-Aldrich, 99%), cobalt (II) nitrate hexahydrate($Co(NO_3)_2 \cdot 6H_2O$, Sinopharm Chemical Reagent Co. Ltd., > 99%), benzimidazole (H-PhIM, Sigma-Aldrich, 98%), *N*, *N*'-dimethylformamide (DMF) 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.

1.2 Instrumentation

Powder X-ray diffraction(XRD) studies were performed on a Rigaku RINT-2200 X-ray diffractometer with a $Cu_{K\alpha}$ source (40 kV,20 mA). The morphologies and sizes of the samples were carried out using cold field emission scanning electron microscope (SEM, SU8020). FTIR spectra were collected at room temperature by using a Thermo Nicolet 870 instrument using KBr discs in the 500 ~ 4 000 cm^{-1} region.

1.3 Preparation of crystalline zeolite imidazolate framework Co-ZIF-9

The Co-ZIF-9 was synthesized using cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$ and benzimidazole (H-PhIM) by a solvothermal method in DMF,according to a literature procedure[29]. Briefly,1.05 g $Co(NO_3)_2 \cdot 6H_2O$) and 0.3 g H-PhIM were mixed into 90 mL DMF. After stirring,the transparent solution was transferred into a Teflon autoclave. The autoclave was closed and heated at a rate of 5 ℃ · min^{-1} to 130 ℃ in drying oven and held at this temperature for 48 h,then cooled to room temperature at 0.4 ℃ · min^{-1}. After crystallization,the as-prepared purple ZIF-9 crystals were filtered and then washed with DMF three times. Finally,ZIF-9 was conducted with vacuum drying at 80 ℃ for 10 h to obtain ZIF-9 catalyst.

1.4 Preparation of cobalt NPs (Co NPs)

The cobalt NPs were preparedby in situ synthesis method. $Co(NO_3)_2 \cdot 6H_2O$ was dissolved in 6 mL of distilled water,and kept in a 25 mL two necked round-bottomed flask. Then 4 mL of aqueous solution containing 55 mg of AB and 10 mg $NaBH_4$ were added into the flask with shaking.

1.5 Hydrolytic dehydrogenation of AB

In a typical experiment,15 mg Co-ZIF-9 were dispersed in 6 mL distilled water,and kept in a two-necked round-bottomed flask. A burette filled with water was connected to the reaction flask to measure the volume of hydrogen. The reaction started when 4 mL of aqueous solution containing 55 mg of AB and 10 mg $NaBH_4$ were added into the flake with vigorous shaking. The reaction was completed when there was no more gas generation. The reactions were carried out at different temperatures (298,303,308,313 K) under ambient atmosphere.

1.6 Reusability of Co-ZIF-9 in the hydrolysis of AB

For the durability test of the catalysts,after the first run of hydrogen generation reaction was completed,another equivalent of NH_3BH_3(55 mg) was subsequently added to the reaction system and the released gas was monitored by the gas burette. The reactions were repeated 5 times under ambient atmosphere at room temperature. After cycle test,the catalysts were

separated from the reaction solution by centrifugation, washed with water for three times and dried in vacuum oven at 313 K overnight.

2 Result and discussion

Crystalline zeolite imidazolate framework Co-ZIF-9 was prepared using cobalt nitrate hexahydrate and benzimidazole by a solvothermal method, and used as cost effective catalyst for the hydrolytic dehydrogenation of ammonia borane(AB) complex to generate a stoichiometric of hydrogen at room temperature. Fig. 1 shows the time course of the hydrogen generation from AB (0.16 mol · L^{-1}, 10 mL) in the presence of the Co-ZIF-9 and Co catalysts. The catalytic results demonstrated that the reaction rate and the amount of hydrogen evolution significantly depended on the catalysts. As shown in Fig. 1, a stoichiometric amount of hydrogen was evolved in 5.55 min and 9.55 min, respectively, in the presence of the Co-ZIF-9 and bare Co catalysts. Obviously, the as-synthesized Co-ZIF-9 exhibited superior performance, in comparison to bare Co NPs, for the hydrolytic dehydrogenation of AB at convenient temperature for chemical hydrogen storage. In the present reaction system, hydrogen is evolved via the following two reactions:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \quad (1)$$

and

$$NH_3BH_3 + 2H_2O \rightarrow NH_4BO_2 + 3H_2 \quad (2)$$

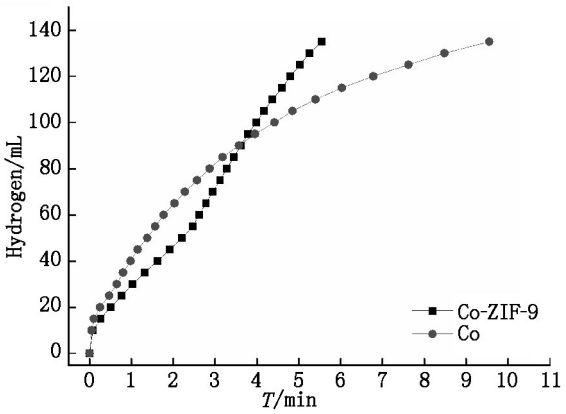

Fig. 1 Hydrogen generation from the hydrolysis of AB (0.16 mol · L^{-1}, 10 mL) with $NaBH_4$ (10 mg) in the presence of (a) Co-ZIF-9, (b) Co at 298 K (catalyst: 15 mg)

Under the present reaction condition, the total amount of hydrogen via reaction (1) and (2) is about 135 mL. Moreover, the turnover frequency (TOF) of the Co-ZIF-9 and bare Co catalysts were measured to be 9.74 and 5.61 mol H_2 · mol^{-1} Co · min^{-1}, respectively, for the hydrogen generation from the hydrolysis of AB.

Fig. 2 shows the volume of hydrogen generated versus time during the catalytic hydrolysis of AB (0.16 mol · L^{-1}, 10 mL) solution in the presence of Co-ZIF-9 catalysts with different contents (5, 10, 15, 20, 25, 30 mg) at room temperature. As shown in Fig. 2, when the catalyst content increased, the reaction time decreased obviously from 20.2 min to 2.1 min. The hydrogen generation rate is determined from the linear portion of each plot for different cobalt content. The inset of Fig. 3 shows the plot of hydrogen generation rate vs. cobalt contents, both in logarithmic scale. The slope of the obtained line is 1.04, which is closed to 1.00, indicating that the hydrolytic dehydrogenation of AB catalyzed by the Co-ZIF-9 is a first-order reaction with respect to the catalyst concentration.

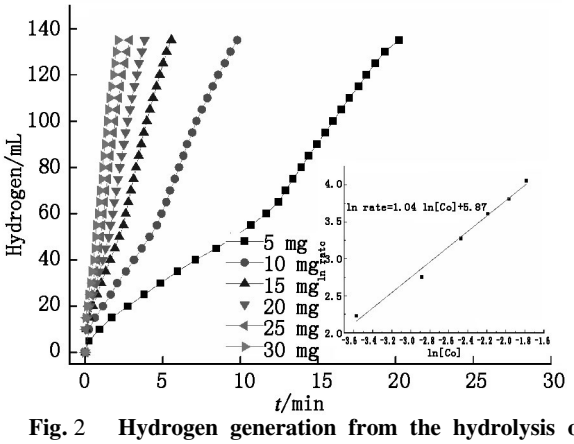

Fig. 2 Hydrogen generation from the hydrolysis of AB (0.16 mol · L^{-1}, 10 mL) with $NaBH_4$ (10 mg) in the presence of Co-ZIF-9 with different contents at 298 K. The inset shows the plot of hydrogen generation rate vs. the contents of Co, both in logarithmic scale

The effect of temperature on the hydrogen generation rate by Co-ZIF-9 was also studied, and a series of experiments were carried out by varying the temperatures. Fig. 3 shows the volume of hydrogen generated versus reaction time in the hydrolysis of AB (0.16 mol · L^{-1}, 10 mL) catalyzed by Co-ZIF-9 catalysts at various temperatures in the range of 293-308 K. Clearly, with the increase of the reaction temperature, the catalytic activity of the Co-ZIF-9 improves remarkably. The reaction rate constant k at different

temperatures was estimated from the slope of the linear part of each plot in Fig. 3. The Arrhenius plot of ln$k$ versus 1/T for the catalyst is plotted in Fig. 3 (inset), from which the activation energy (E_a) for the hydrolytic dehydrogenation of AB is measured to be 40.8 kJ·mol^{-1}, being lower than most the reported activation energy values (Table 1), indicating the superior catalytic performance of the Co-ZIF-9 catalyst.

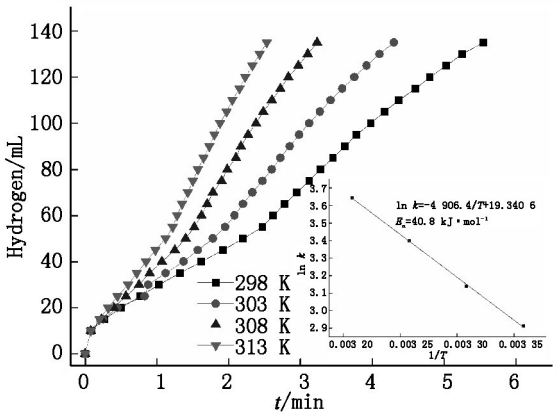

Fig. 3　Hydrogen generation from the hydrolysis of AB (0.16 mol·L^{-1}, 10 mL) with $NaBH_4$ (10 mg) in the presence of Co-ZIF-9 (15 mg) at 293 ~ 308 K. The inset shows the Arrhenius plot (ln$k$ vs. 1/T)

Table 1　The values of activation energy (E_a) for hydrogen generation from aqueous AB at room temperature

Catalyst	E_a/(kJ·mol^{-1})
$Co/\gamma\text{-}Al_2O_3$ [30]	62.0
$RuCo/\gamma\text{-}Al_2O_3$ [31]	47.0
Zeolite-confined Cu [32]	51.8 ± 1.8
$Cu_{0.2}@Co_{0.8}$/rGo [33]	51.3
CoB/MCM-41 [33]	51.0 ± 3.0
$Cu_{0.33}Fe_{0.67}$ [34]	43.2
CoB/SBA-15 [35]	43.0 ± 2.0
Co-ZIF-9	40.8
$Ru@SiO_2$ [12]	38.2
$Pt/\gamma\text{-}Al_2O_3$ [14]	21.0

The reusability of the Co-ZIF-9 catalyst was tested under ambient atmosphere at room temperature. After complete hydrolysis of AB, kept the catalyst of Co-ZIF-9 in the reaction solution under ambient conditions, and a new AB (55 mg) was added to the reaction system. Fig. 4 shows the productivity of hydrogen versus reaction time for the generation of hydrogen from an aqueous AB (0.16 mol·L^{-1}, 10 mL) solution catalyzed by the Co-ZIF-9. After five runs of the catalytic reaction for dehydrogenating aqueous AB, the productivity of hydrogen remained almost unchanged, indicating that the Co-ZIF-9 shows good durability/stability for hydrogen generation from the aqueous of AB at room temperature.

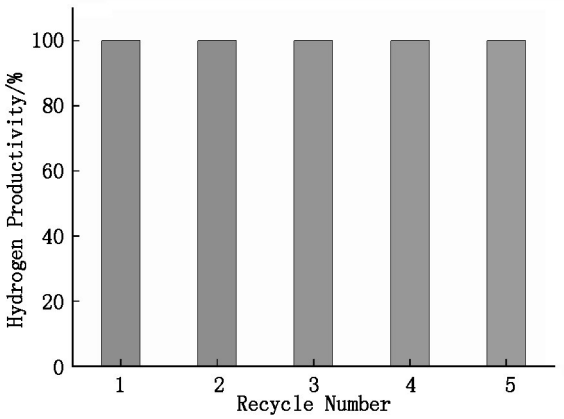

Fig. 4　Hydrogen productivity vs. recycle number for hydrogen generation from the hydrolysis of AB (0.16 mol·L^{-1}, 10 mL) in the presence Co-ZIF-9 (15 mg) at sequential runs by the addition of equivalent amounts of AB

Powder X-ray diffraction (XRD) was performed on Co-ZIF-9 before and after hydrolysis of AB. As shown in Fig. 5(a), several sharp peaks were observed on the XRD profile for the fresh Co-ZIF-9. The positions of diffraction peaks indicated that Co-ZIF-9 was highly crystalline material and the recorded pattern corresponds well with the previous reports [26,29]. Moreover, Compared with the fresh and used catalyst revealed that the Co-ZIF-9 could maintain its basic structure and crystallinity after the hydrolytic dehydrogenation of AB.

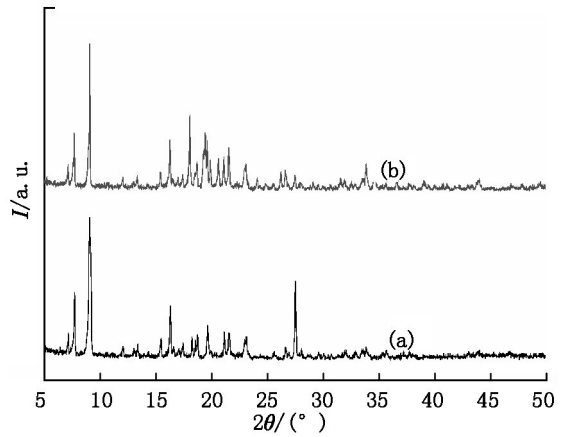

Fig. 5　Powder X-ray diffraction patterns for the (a) reused and (b) fresh of Co-ZIF-9

As expected, the SEM micrograph showed that a crystalline material was achieved (Fig. 6). The morphology of Co-ZIF-9 shows no significant changes be-

fore and after catalytic reaction. Meanwhile, FTIR spectrum showed the same nature, namely, the catalyst of Co-ZIF-9 has not changed much before and after hydrolysis reaction (Fig. 7). These characteristic results reveal that the catalyst of Co-ZIF-9 has high stability during the hydrogen generation from the hydrolysis of AB.

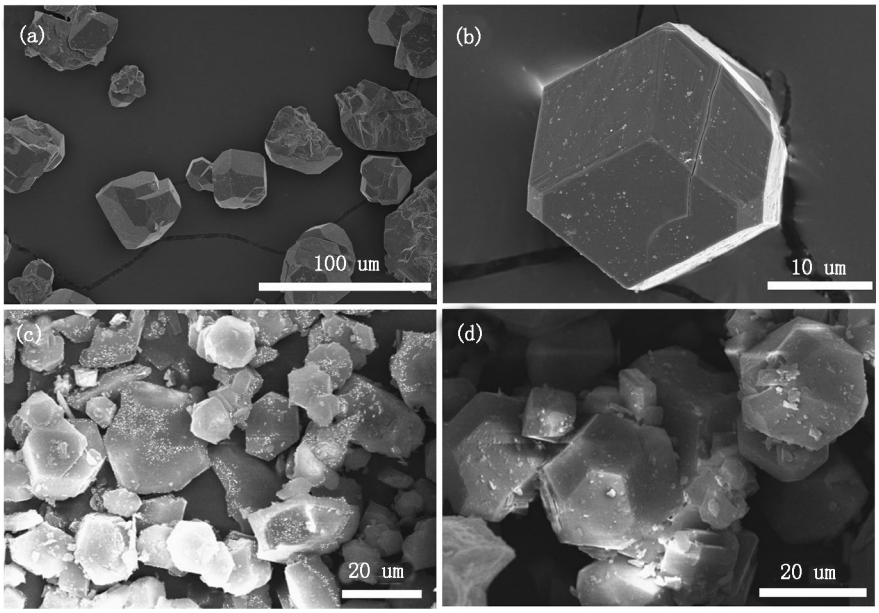

Fig. 6 SEM images of the (a) reused and (b) fresh of Co-ZIF-9

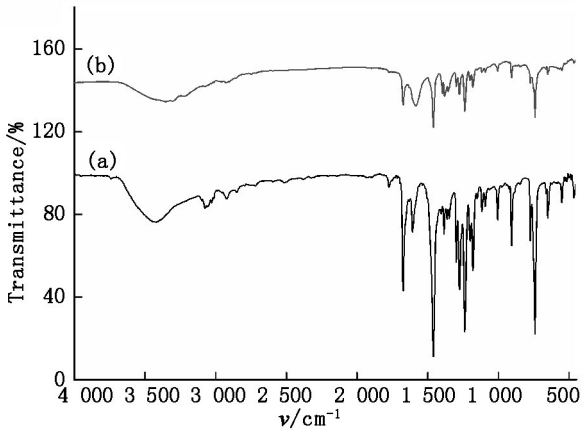

Fig. 7 FT-IR spectra of the (a) reused and (b) fresh of Co-ZIF-9

3 Conclusion

In summary, crystalline zeolite imidazolate framework Co-ZIF-9 has been successfully prepared by using the solvothermal method. The catalytic results demonstrated that the Co-ZIF-9 exhibit superior catalytic activity, in comparison to Co NPs, for the dehydrogenation of AB at convenient temperature for chemical hydrogen storage. The hydrolysis activation energy for Co-ZIF-9 was measured to be approximately of 40.8 kJ · mol^{-1}, which is lower than most the reported activation energy values for the same reaction using many different catalysts except for some noble-metal containing catalysts, indicating the superior catalytic performance of Co-ZIF-9. These results not only present an efficient catalyst for AB hydrolysis, but also provide new insight into the application of Co-ZIF-9 in the field of catalysis.

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沸石咪唑酯骨架结构材料 Co-ZIF-9 催化氨硼烷水解制氢

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摘要: 采用溶剂热方法合成了沸石咪唑酯骨架结构材料 Co-ZIF-9,并将其用于非均相催化氨硼烷水解放氢实验. 结果表明: 配位的 Co-ZIF-9 在室温下能够有效地催化氨硼烷放出氢气,且其催化活性远高于 Co 纳米粒子,Co-ZIF-9 的多孔结构在催化中起了很大的作用. 另外,Co-ZIF-9 催化水解氨硼烷的活化能约为 40.8 kJ mol^{-1},低于多数用于该催化实验的其他催化剂,表明所合成的沸石咪唑酯骨架结构材料 Co-ZIF-9 具有优越的催化性能.

关键词: 氨硼烷; 沸石咪唑酯骨架; 溶剂热法; 水解; 制氢 (责任编辑: 刘显亮)

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The GHSOM Network Cloud Classification Model of Stationary Satellite Infrared Cloud Images at Night

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Abstract: Aiming at the low accuracy of cloud classification at night,the features of FY-2E cloud images which include bright temperatures and split window values were extracted and selected based on the method of singular value decomposition. The neural network models of growing hierarchical self-organizing map (GHSOM) and self-organizing map (SOM) were built separately to classify cloud images at night,meanwhile,contrasting the classified effect of the two network models. The experiments results showed that GHSOM network can improve the distinguishing effect of cloud images at night greatly through hierarchical classified method,and the average accuracy of cloud classification results is higher than SOM.

Key words: growing hierarchical self-organizing map; self-organizing feature map; night cloud image: cloud classification (责任编辑: 冉小晓)