原位生成非晶纳米钴高效催化氨硼烷的醇解制氢

陈 浩 俞哲健 徐丹丹 李 洋 王明明 夏良敏 罗书平*

(浙江工业大学绿色化学合成技术国家重点实验室培育基地,杭州 310014)

摘要:用金属钴配合物和过渡金属(Cu,Ni,Co 等)原位生成的非晶纳米粒子作为均相、多相催化剂,研究氨硼烷的醇解放氢反应, 结果发现原位生成的非晶钴纳米粒子展现出优异的产氢性能。通过 10 次的催化循环测试,钴纳米粒子放氢催化转换数 (TON)可达 6 000,最高催化产氢速率(TOF)达 515 $mol_{H_2} \cdot mol_{metal}^{-1} \cdot h^{-1}$。该催化剂制备方便,且产氢稳定性好。此外,对钴纳米粒子催化氨硼烷放氢实验做动力学研究,计算其催化活化能为 20.00 $kJ \cdot mol^{-1}$,低于大多数已经报道的其他纳米催化剂催化氨硼烷放氢反应的活化能。通过硼谱的跟踪检测,发现钴纳米催化氨硼烷的醇解反应产物是硼酸三甲酯,并对此催化反应机理进行了初步的解释和讨论。

In-Situ Formed Amorphous Co Nanoparticles for Efficiently Catalytic Hydrogen Production from the Methanolysis of Ammonia Borane

CHEN Hao YU Zhe-Jian XU Dan-Dan LI Yang
WANG Ming-Ming XIA Liang-Min LUO Shu-Ping*

(*State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology,*
Zhejiang University of Technology, Hangzhou 310014, China)

Abstract: Amorphous Co nanoparticles formed in-situ displayed high catalytic activity for hydrogen generation from the methanolysis reaction of ammonia borane, among many homogeneous catalysts and heterogeneous catalysts of cobalt. Its turnover number (TON) was up to 6 000 for ten cycles and its turnover frequency (TOF) was up to 515 $mol_{H_2} \cdot mol_{metal}^{-1} \cdot h^{-1}$. Moreover, the easily preparation and the great recycling performance made it have good application in future. After the kinetics studies, its catalytic activation energy (E_a) for the methanolysis reaction was measured as 20.00 $kJ \cdot mol^{-1}$, which was lower than most of the reported values for other nano-sized catalysts. Through the ^{11}B NMR, trimethylborate was the only product. Furthermore, the catalytic reaction mechanism was preliminarily explained and discussed.

Keywords: *in-situ* synthesis; ammonia borane; methanolysis; hydrogen generation

0 Introduction

In order to solve the problems of over consuming fossil fuels and the accompanied environmental pollution of our earth, there is an urgent need to search for efficient, clean, renewable and rich energy resources[1-4]. Hydrogen is considered to be the ideal candidate of clean energy due to it is easily obtained

and burning cleanly[5-9]. However, the search for safe and efficient hydrogen storage materials is a key challenging issue in the development of the "hydrogen economy"[10-11]. The ammonia borane complex (AB) is considered as a promising candidate for on-board hydrogen applications because of its high hydrogen density (19.6%(w/w)) and high stability[12-14].

Generally, there are two primary ways to release hydrogen from AB, catalytic thermolysis and catalytic hydrolysis (include methanolysis) respectively. The former usually requires high temperature and the rate of dehydrogenation of AB is low, while the latter can release 3.0 equivalents of hydrogen in the presence of a suitable catalyst. Moreover, the comparison between catalytic hydrolysis and catalytic methanolysis of AB is whether ammonia is liberated. The catalytic methanolysis of AB release hydrogen gas without ammonia evolution and yield the recyclable methanolysis by-product ammonium tetramethaoxyborate[15-17].

Due to the advantages of nano-catalysis, the current research has been concentrated on the development of some metal nanoparticles possessing high activity and reusability in the hydrolytic or methanolic dehydrogenation of AB. Rh[18], Pd[19], Co-Ni[20], Co-GO[21], Co-Cu[22] and Co-Ag[23] nanoparticles exhibited excellent catalytic activity. Although the active metal nanoparticles-catalyzed hydrolysis or methanolysis of AB possessed high hydrogen production efficiency, sometimes the preparation was cumbersome. Although the homogeneous catalysts for the methanolysis of AB was generally higher efficient than the heterogeneous catalysts, people tended to nano-catalysis. Few of the studies of homogeneous catalysis for the methanolysis or hydrolysis of ammonia borane were done. However, many hydrogen transfer reactions of ammonium borane as an additive have been investigated[24-25].

Herein, a series of pincer Co complexes have been designed and synthesized in our previous work[26]. Then using them as catalysts, the methanolysis of ammonia borane was investigated in homogeneous system. Later, the *in-situ* formed amorphous Co nanoparticles was discovered and studied for the methanolysis of ammonia borane in heterogeneous system. Importantly, the Co-NPs possessed highest activity and reusability in the methanolic dehydrogenation of AB. Proposed catalytic mechanism was put forward based on the amorphous Co-NPs were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transform infrared spectra (FT-IR) and X-ray photoelectron spectroscopy (XPS). What was more, we also studied the kinetics of methanolysis of AB. Especially, the activation energy of the methanolysis of ammonia borane towards amorphous Co nanoparticles was calculated to be 20.00 kJ·mol^{-1}, which was close to that of some noble metal-based catalysts[27-28].

1 Experimental

1.1 Chemicals

A series of Co-complexes were synthesized from our previous work[26]. The chemicals used in the experiment were purchased from Energy Chemical. Methanol was an analytical level and was used after heavy steaming with non-aqueous anaerobic treatment. All pieces of glassware were washed several times with aqua regia and ordinary distilled water. Unless otherwise noted, all manipulations were carried out under an inert atmosphere.

1.2 *In-situ* preparation for amorphous Co nanoparticles and its characters

To a 100 mL round bottom flask was added CoCl$_2$ (0.390 g, 3 mmol) and NH$_3$BH$_3$ (0.930 g, 30 mmol) in the glovebox. MeOH (10 mL, 250 mmol) was added dropwisely and slowly to avoid a strong hydrogen production reaction. The mixture was stirred at room temperature until no gas was generated. After the completion of the reaction, the Co NPs was obtained in vacuo. Other metal nanoparticles were prepared in the same way. The morphology and microstructure of the samples were characterized by TEM on a FEI TECBAI G2 F30 instrument operated at 300 kV. The XRD patterns were obtained with a PANalytical X, Pert PRO diffractometer with Cu $K\alpha_1$ radiation in the 2θ scan range from 10° to 80° at room temperature (40 kV and 100 mA). The FT-IR spectra were obtained with a nicolet 670 FT-IR spectrometer using

a KBr pellet technique. The XPS was performed with a Thermo Fisher (Escalab 250Xi) using Al $K\alpha$ X-rays as an excitation source (1 486.8 eV).

1.3　Evaluation of the catalytic activity

To assess the catalytic activity of the amorphous Co nanoparticles for methanolysis of AB, the classic water-displacement method involving determining the rate of hydrogen generation was performed. The experimental apparatus used in this study was identical to that reported by Matthias Beller[29].

2　Results and discussion

Initially, the Co NPs was characterized with TEM, XRD, FTIR and XPS. Firstly, the TEM images of sample was proved to be the Co NPs (Fig.1(a,b)). The morphology of the sample could be clearly observed. The particles were mainly spatially discrete

globular particles with sizes on the nanoscale (approximately 4 nm in diameter) (Fig.1c). Because of its strong magnetism, the Co NPs prepared tended to aggregate to some extent. Secondly, according to the standard card (PDF No.73-0365), the XRD patterns of the Co NPs (Fig.S1a) was ammonium chloride. The result showed that there was the formation of ammonium ion in the process of catalytic reaction. After washed by the degassed water, as could be seen in Fig.S1b, there might be amorphous Co NPs. Then, FTIR was used to detect surface chemical information of the sample (Fig.S2). The Co NPs had two broad absorption bands in the infrared spectrum. The broad absorption band centered at 3 400 cm^{-1} could be assigned to the vibration of the surface residual NH and OH groups[30]. The framework bands in the range 500~1 300 cm^{-1} was Co NPs, which was similar to the
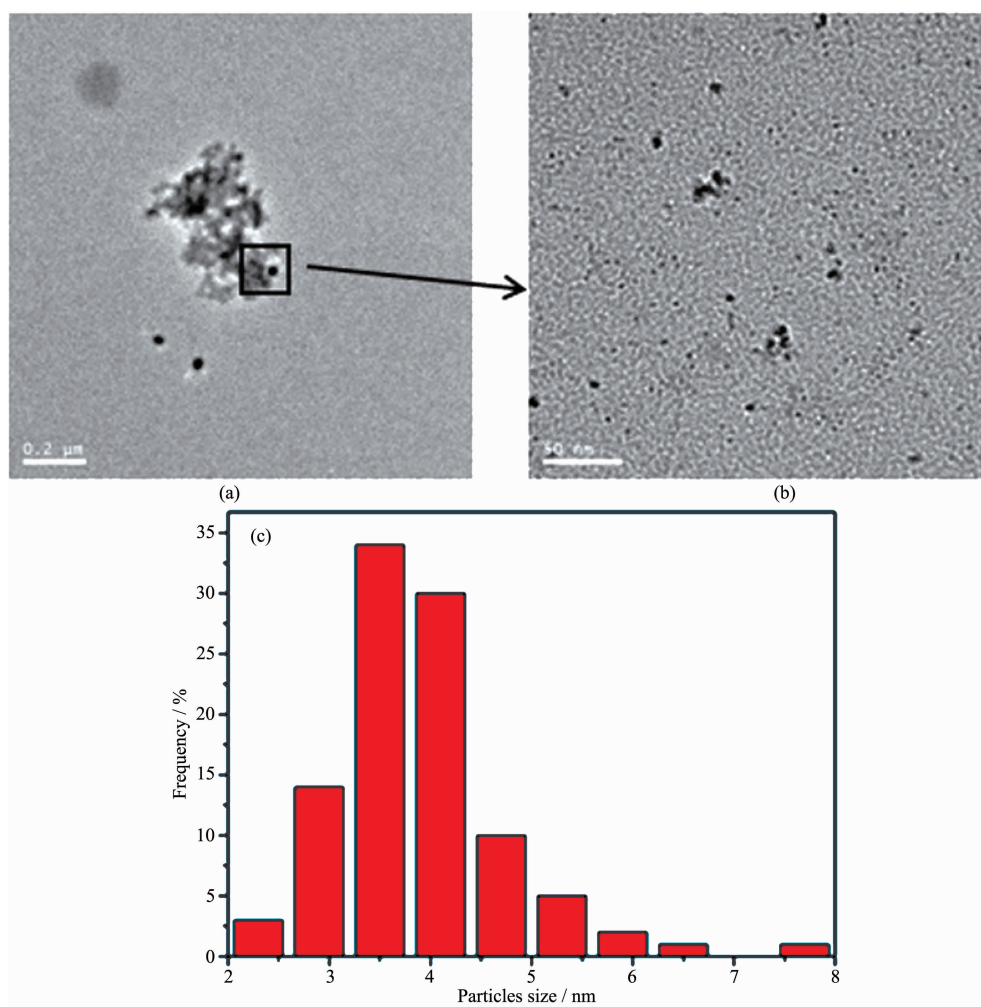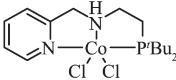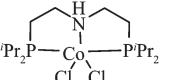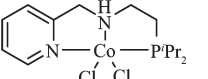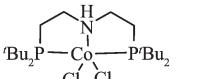

Fig.1　TEM images (a, b) and particle size histogram (c) of Co NPs (washed by the degassed water)

characteristic absorption band of nano alumina [31]. Finally, XPS was used to further investigate the localized valence orbitals of the transition metal composite (Fig.S3). As could be seen in Fig.S3b, the peak of Co composite could be deconvoluted into three peaks at binding energy 782.1, 780.1 and 778.5 eV. The first two peaks were related to Co^{2+} and Co^{3+}, and the last peak could be assigned to the metallic $Co^{[32]}$. This suggestion that Co was formed by the reduction of Co(Ⅱ) with AB during the methanolysis process possibly. There were also three peaks located at 529.3, 530.8 and 532.4 eV in the O1s spectrum (Fig.S3c) which were attributed to the cobalt oxide and other substances.

Next, the methanolysis dehydogenation of AB catalyzed by homogeneous and heterogeneous cobalt catalysts was researched. Cobalt complexes **1~4** were chosed because they displayed high catalytic activity in the reduction reaction by AB. Co NPs and other metal NPs were easy prepared by the metal reduction by AB *in-situ* method. As was shown in Table 1, the Co NPs and complex **1** displayed higher performance

for hydrogen production. The generated hydrogen was measured by a drainage method, using a burette to observe the volume of hydrogen. The volume of hydrogen produced versus time was plotted in Fig.2. We have proceeded the twice experiments with the methanolysis of AB catalyzed by Co NPs and complex **1** respectively. Due to the similar rate and amount of hydrogen evolution, it showed good reproducibility. As the reaction gone, the structure of the complex **1** might be destroyed by the AB which leaded to the decrease of hydrogen production rate. However, in-situ formed amorphous Co NPs exhibited high activity all the time and its turnover frequency (TOF) was calcul- ated to be 515 $mol_{H_2} \cdot mol_{metal}^{-1} \cdot h^{-1}$ during the first hydrogen release process (Fig.2). Compared with some noble metal-based catalysts[27-28,33], the catalytic perfor- mance of Co NPs was poor. However, the value of TOF was much higher than those of Cu-based catalysts, which could only reach up to 19 $mol_{H_2} \cdot mol_{metal}^{-1} \cdot h^{-1}$ [34]. Moreover, Sun et al.[35] and Filiz et al.[36] demonstrated that metallic Co was very active towards the methanolysis of AB.

Table 1　Rate of hydrogen production by catalysts

Entry	Catalyst	TOF[a] / ($mol_{H_2} \cdot mol_{metal}^{-1} \cdot h^{-1}$)
1		437
2		220
3		39
4		46
5	Fe-NPs	24
6	Co-NPs	515
7	Ni-NPs	286
8	Cu-NPs	65
9	Zn-NPs	77

[a] Reaction condition: Reaction of anhydrous catalyst (1.2 mg) in methanol (4 mL), with addition of anhydrous AB (2 mmol) to system; TOF=TON$_{H_2}$/t, where t is the reaction time (h); Entire system remains 298 K.
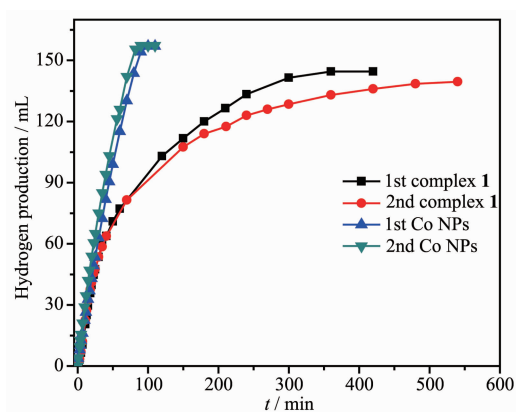
Fig.2　Twice hydrogen production of ammonia borane (2 mmol) by complex **1** (1.2 mg) and Co NPs (1.2 mg) in methanol (4 mL)
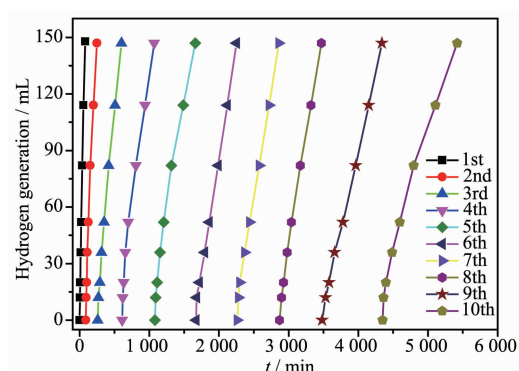

Fig.3　Recycling of Co NPs (1.2 mg) in methanol (4 mL), with addition of aqueous AB (2 mmol) to system in each cycle (the entire system remained 298 K)

Subsequently, the stability of Co NPs catalyzing AB was measured by adding another equivalent (2 mmol) of AB into the mixture after the previous cycle (Fig.3). The 10th cycles were tested. The turnover number for hydrogen production (TON) could reach 6 000 in the 10th process. It was worth pointing out that the rate of hydrogen generation by Co NPs was highest in the first cycle and then decreased very slowly in other cycles, which identified with the catalytic activity of Co NPs. The decrease of catalytic activity was mainly attributed to the Co containing active species adsorbed on the surface of the trimethylborate and a slight aggregation of the Co NPs during the reaction[37]. The Co NPs dispersed in solution or supported on suitable solid materials with large surface area could catalyze AB more quickly, suggesting its good stability. Additionally, the surface electronic properties and geometrical structure of the

nanoparticles determine the catalytic activity, selectivity and stability[38].

Furthermore, the kinetics studies for the methanolysis reaction of AB have been explored. More specifically, the amounts of catalyst, the concentrations of AB and the temperatures were experimented on the methanolysis of AB, respectively. The effect of the amount of catalyst on the hydrogen generat rate of the catalytic reaction was first studied, where the concentration of AB was maintained at 2 mmol at 298 K and the catalyst amounts were divided into 1.0, 1.2, 1.5 and 2.0 mg (Fig.4).The initial rate of hydrogen generation was determined from the initial nearly linear portion of each plot. As was seen in Fig.4a, the rate of hydrogen production was improved with an increased amount of the catalyst in a certain range, because a larger dosage of the catalysts could provide more active sites for catalytic reaction. In addition, the number of catalysts and the rate of hydrogen
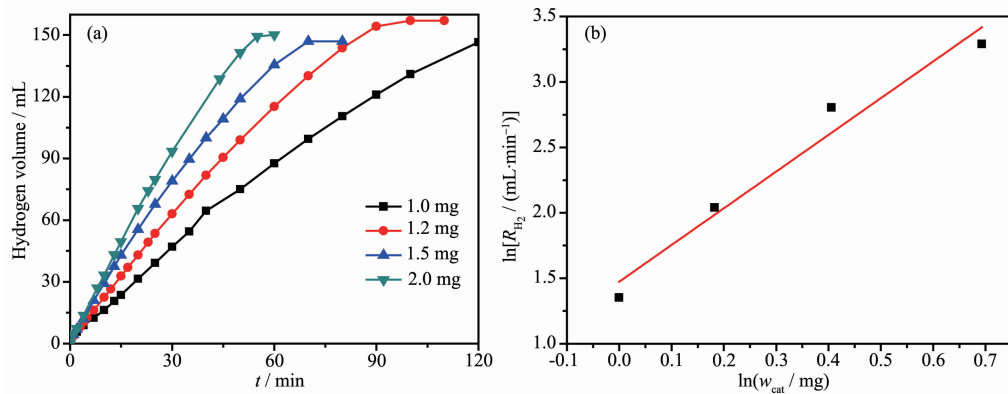

Fig.4　(a) Influence of catalyst amount on hydrogen generation rate; (b) Fitting plot of hydrogen generation rate (R_{H_2}) vs catalyst amount (w_{cat})

production were linearly correlated (Fig.4b). The results showed that the catalytic methanolysis reaction of AB was first-order with respect to the catalyst amount, which was consistent with a relevant report by Özkar et al.[16].

The influence of AB concentration on the hydrogen evolution rate was also evaluated (Fig.5). The hydrogen generation rate barely changed with the different amounts of AB (0.5, 1.0, 1.5 and 2.0 mmol), using Co NPs catalyst (1.2 mg) at 298 K. The studies suggested that the methanolysis reaction of the AB complex was zero-order with respect to the AB amounts. Thus we could infer that the methanolysis reaction of the AB complex on the catalyst surface was a rate-limiting step[39].

In order to get activation energy (E_a) for the methanolysis reaction, the effect of various temperatures (288, 298, 303 and 313 K) was also discussed

(Fig.6a). According to Arrhenius plot and response characteristics indicating that the reaction was quasi zero-order with respect to the AB concentration[40], the E_a was calculated to be 20.00 kJ·mol⁻¹. Although the H₂ evolution rate for the amorphous Co nanoparticles was lower than that of the Pt-based catalysts, the activation energy for amorphous Co nanoparticles was close to that of some Pt-based catalysts.

Finally, the product was probed after the reaction was completed. In the previous work, ammonium tetramethoxyborate was the only product in methanolysis reaction of AB[15-17]. The B-containing product was monitored by the ¹¹B NMR spectrum in the process of reaction (Fig.7). When the reaction was over or the reaction was going half an hour, the ¹¹B NMR (18.69) revealed the formation of trimethylborate, which disagreed with the ammonium tetramethoxy-borate (8.7).
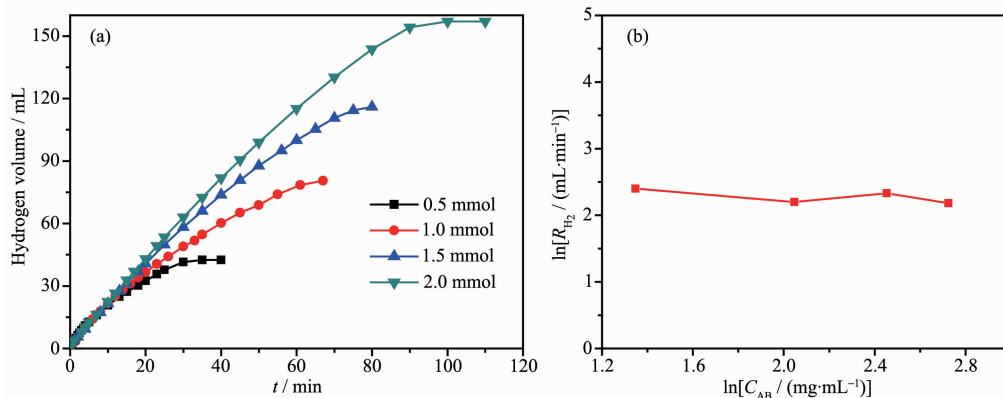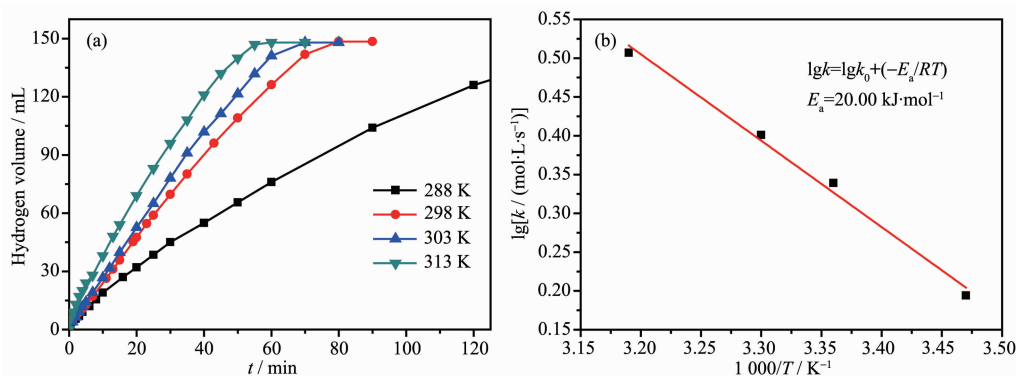

Fig.5　(a) Effect of amounts of AB on the hydrogen generation rate; (b) Fitting plot of the hydrogen generation rate (R_{H_2}) vs concentration of AB (C_{AB}) in 4 mL methanol

k_0 and k are the reaction rate constant, E_a is the activation energy for the reaction, R is the gas constant and T is the reaction temperature

Fig.6　(a) Plot of time vs volume of hydrogen generated from methanolysis of AB (2 mmol) catalyzed by Co NPs (1.2 mg) at different temperatures; (b) Corresponding Arrhenius plot

Fortunately, the plausible mechanism of the AB methanolysis reaction was predicted (Fig.8). Cobalt dichlorotetrakis (methanol)-coordination compound, formed by cobalt chloride in methanol solution, was reduced to metallic Co by AB and then reunited together. In the process of first step, there might be the formation of ammonium ion, which was consistent with the XRD of Co NPs. As pointed out by Xu et al. [41], AB interacted with the surface of metal to form an active complex, which might be the rate-determining step. The active complex was then attacked by a CH_3OH molecule, which readily leaded to dissociation of the BN bonds to produce the trimethylborate along with the release of H_2 and NH_3[26].
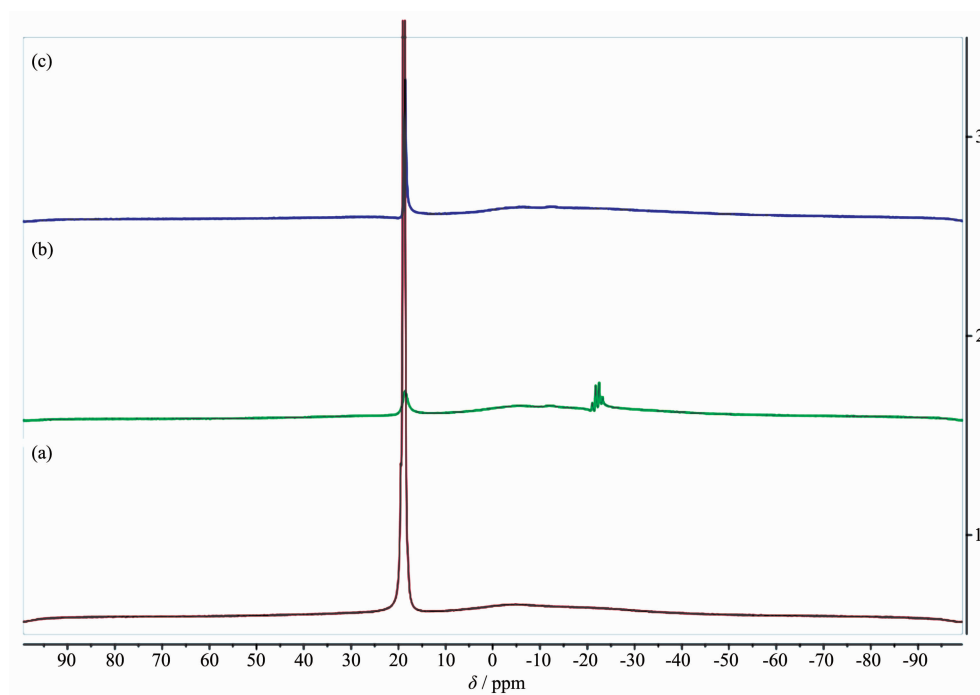

Fig.7 ^{11}B NMR of (a) trimethylborate, (b) product when the reaction was going half an hour and (c) product when the reaction was complete
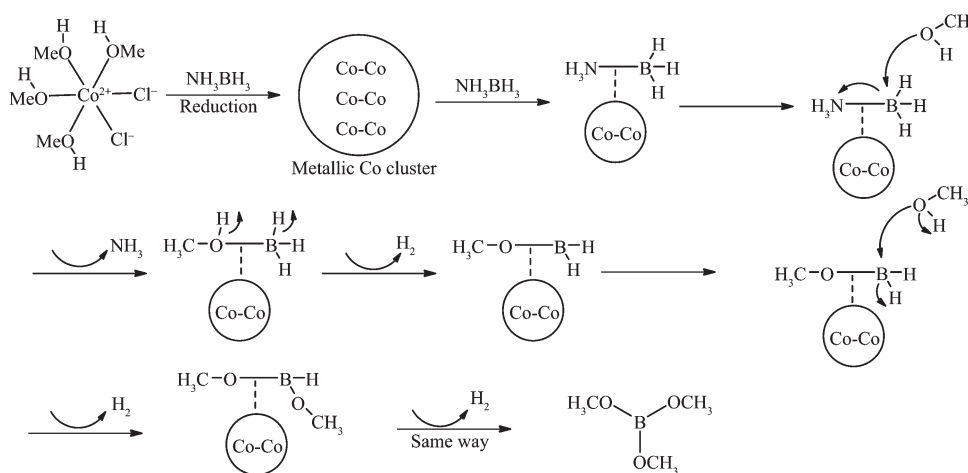

Fig.8   Plausible mechanism of the methanolysis of AB catalyzed by the Co NPs

3   Conclusions

In summary, we found that *in-situ* formed amorphous Co nanoparticles exhibited notable activity towards hydrogen generation from the methanolysis of AB at room temperature. The possible mechanism of

the AB methanolysis reaction was the surface catalysis of metals. Furthermore, we have investigated the kinetics of the methanolysis reaction of AB in detail. The activation energy was determined to 20.00 kJ·mol^{-1}. Their tunable catalytic properties shown here indicated that Co composite had great potential in developing AB as a hydrogen storage material for fuel cell applications. The results provided new insight into the enhanced performance of the Co hybrids and might help for the design of advanced catalysts.

Supporting information is available at http://www.wjhxxb.cn

References:

[1] Esswein A J, Nocera D G. *Chem. Rev.*, **2007,107**:4022-4047

[2] Osterloh F E. *Chem. Soc. Rev.*, **2013,42**:2294-2320

[3] Yadav M, Xu Q. *Energy Environ. Sci.*, **2012,5**:9698-9725

[4] Hu C G, Chen X Y, Dai Q B, et al. *Nano Energy*, **2017,41**: 367-376

[5] Xu Y F, Mao N, Feng S, et al. *Macromol. Chem. Phys.*, **2017, 218**:1700049

[6] Xing Y L, Fang B Z, Bonakdarpour A, et al. *Int. J. Hydrogen Energy*, **2014,39**:7859-7867

[7] Zhang H, Cai J M, Wang Y T, et al. *Appl. Catal. B*, **2018, 220**:126-136

[8] Khalid N R, Liaqat M, Tahir M B, et al. *Ceram. Int.*, **2018,44**: 546-549

[9] Xu Y X, Chen R T, Li Z, et al. *ACS Appl. Mater. Interfaces*, **2017,9**:23230-23237

[10]Aw V D B, Areán C O. *Chem. Commun.*, **2008,6**:668-681

[11]Grewe T, Meggouh M, Tüysüz H. *Chem. Asian J.*, **2016,11**: 22-42

[12]Sun D H, Mazumder V, Metin Ö, et al. *ACS Nano*, **2011,5**: 6458-6464

[13]Chen W Y, Ji J, Duan X Z, et al. *Chem. Commun.*, **2014,50**: 2142-2144

[14]Zhang R Z, Zheng J L, Chen T W, et al. *J. Alloys Compd.*, **2018,763**:538-545

[15]Ramachandran P V, Gagare P D. *Inorg. Chem.*, **2007,46**: 7810-7817

[16]Özhava D, Özkar S. *Mol. Catal.*, **2017,439**:50-59

[17]Cui L, Cao X Y, Sun X P, et al. *ChemCatChem*, **2018,10**:1-7

[18]Özhava D, Özkar S. *Appl. Catal. B*, **2018,237**:1012-1020

[19]Karatas Y, Gülcan M, Çelebi M, et al. *ChemistrySelect*, **2017, 2**:9628-9635

[20]Kalidindi S B, Vernekar A A, Jagirdar B R. *Phys. Chem. Chem. Phys.*, **2009,11**:770-775

[21]Zhao B H, Liu J Y, Zhou L T, et al. *Appl. Surf. Sci.*, **2016, 362**:79-85

[22]Ke D D, Li Y, Wang J, et al. *Int. J. Hydrogen Energy*, **2016, 41**:2564-2574

[23]Bulut A, Yurderi M, Ertas E, et al. *Appl. Catal. B*, **2016,180**: 121-129

[24]Ramachandran P V, Drolet M P. *Tetrahedron Lett.*, **2018,59**: 967-970

[25]Korytiaková E, Thiel N O, Pape F, et al. *Chem. Commun.*, **2017,53**:732-735

[26]Fu S M, Chen N Y, Liu X F, et al. *J. Am. Chem. Soc.*, **2016, 138**:8588-8594

[27]Chandra M, Xu Q. *J. Power Sources*, **2007,168**:135-142

[28]Chen W Y, Ji J, Feng X, et al. *J. Am. Chem. Soc.*, **2014,136**: 16736-16739

[29]Luo S P, Mejia E, Friedrich A, et al. *Angew. Chem. Int. Ed.*, **2013,52**:419-423

[30]Paine R T, Narula C K. *Chem. Rev.*, **1990,90**:73-91

[31]Yu J, Bai H B, Wang J, et al. *New J. Chem.*, **2013,37**:366-372

[32]Surviliene S. *Solid State Ionics*, **2008,179**:222-227

[33]Dai H B, Kang X D, Wang P. *Int. J. Hydrogen Energy*, **2010, 35**:10317-10323

[34]Qiu X Q, Wu X, Wu Y W, et al. *RSC Adv.*, **2016,6**:106211-106217

[35]Sun D H, Mazumder V, Metin Ö, et al. *ACS Catal.*, **2012,2**: 1290-1295

[36]Filiz B C, Figen A K, Piskin S. *Appl. Catal. A*, **2018,550**: 320-330

[37]Cao S W, Jiang J, Zhu B C, et al. *Phys. Chem. Chem. Phys.*, **2016,18**:19457-19463

[38]Liu S, Li Y, Shen W J. *Chin. J. Catal.*, **2015,36**:1409-1418

[39]Li Y, Dai Y, Tian X K. *Int. J. Hydrogen Energy*, **2015,40**: 9235-9243

[40]Metin Ö, Özkar S. *Energy Fuels*, **2009,23**:3517-3526

[41]Xu Q, Chandra M. *J. Power Sources*, **2006,163**:364-370