Hydrogen generation by hydrolysis of sodium borohydride on CoB/SiO$_2$ catalyst

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ABSTRACT

Generation of hydrogen by hydrolysis of alkali metal hydrides has attracted attention. Unsupported CoB catalyst demonstrated high activity for the catalytic hydrolysis of NaBH$_4$ solution. However, unsupported CoB nanoparticles were easy to aggregate and difficult to reuse. To overcome these drawbacks, CoB/SiO$_2$ was prepared and tested for this reaction. Cobalt (II) acetate precursor was loaded onto the SiO$_2$ support by incipient-wetness impregnation method. After drying at 100 °C, Co cations were deposited on the support. The dried sample was then dispersed in methanol/water solution and then fully reduced by NaBH$_4$ at room temperature. The catalyst was characterized by N$_2$ sorption, XRD and XPS. The results indicated that the CoB on SiO$_2$ possessed amorphous structure. B and Co existed both in elemental and oxidized states. SiO$_2$ not only affected the surface compositions of CoB, but also affected the electronic states of Co and B. B^0 could donate partial electron to Co^0. The structure effect caused by the SiO$_2$ support helped to prevent CoB nanocluster from aggregation and therefore the activity increased significantly on hydrolysis of alkaline NaBH$_4$ solution. The CoB/SiO$_2$ catalyst showed much higher activity than the unsupported CoB catalyst. At 298 K, the hydrogen generation rate on CoB/SiO$_2$ catalyst was 4 times more than that on the unsupported CoB catalyst. The hydrogen generation rate was as high as 10,586 mL min^{-1} g^{-1} catalyst at 298 K. CoB/SiO$_2$ is a very promising catalyst for this reaction.

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1. Introduction

Hydrogen is considered as a promising alternative energy in the next generation due to its non-toxic, environmental-friendly, a variety of sources to obtain and the relatively low cost. Many researchers have devoted to the work of hydrogen generation. There are many methods to produce hydrogen. Among them, the most attractive one is the generation of hydrogen by hydrolysis of alkaline metal hydrides. Sodium borohydride shows the superior qualities for providing a safe and practical way to generate hydrogen. Generating hydrogen by hydrolyzing NaBH$_4$ aqueous solution has many advantages [1] high hydrogen storage capacity (10.7 wt.%); stability under alkaline state; hydrogen generation occurs only in the presence of selected catalysts; the reaction byproduct, sodium borate (NaBO$_2$), can be recycled, and the other byproduct in gas stream is water; reaction rate is easy to control; hydrogen can be generated even at 273 K, and the hydrogen generated has high purity.

At room temperature and without a catalyst, only a negligible amount of hydrogen is released in aqueous solution of NaBH$_4$, especially for the instance for adding alkali as NaOH into the solution. By adding a suitable catalyst, the hydrogen

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generation rate is significantly enhanced. The hydrolysis reaction is exothermic and proceeds according to the following equation [2]:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \uparrow \Delta_r H_m^\theta = -300 kJ\, mol^{-1} \quad (1)$$
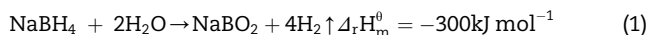
Recently, more and more efforts have been made on research of the catalysts on hydrolysis of $NaBH_4$. Many different metals or alloys have been reported to show good catalytic activities on this hydrolysis reaction. Schlesinger et al. [3] reported that colloidal platinum, platinized asbestos, platinum oxidation catalyst, copper-chromic oxide, activated charcoal supported the fact that Raney nickel could accelerate the hydrolysis reaction apparently. Noble metals including Ru [4] and Pt [5] are widely employed as catalysts due to the high catalytic activities, but the scarcity and the high cost of these noble metals limited their application. Appropriate substitute materials for the noble metals based catalysts are keenly expected.

Since the 1980s, metal boride amorphous alloy catalysts prepared by reduction of metal salts with borohydride have attracted much attention in catalyzing the hydrolysis reaction owing to their unique properties, such as the isotropic structure and the high concentration of the coordination of unsaturated sites. It has been reported that cobalt boride catalyst showed the competitive activities with Pt and Ru based catalysts. In our lab, amorphous CoB, NiB catalysts have been used for the hydrolysis reaction. The results showed that CoB catalyst illustrated higher activity than NiB catalyst in $NaBH_4$ hydrolysis reaction, which is in good accordance with the literature. Dai et al. [6] synthesized nickel foam-supported cobalt–boron catalysts by hydrogenation with sodium borohydride. These catalysts showed similar catalytic activities as Ru and Pt-based catalysts. The stability of the catalyst is one of the most important factors to limit the application of these kind of catalysts. It was improved apparently on the supported catalysts. There are several papers on these that support hydrogen production. Xu et al. [7] prepared γ-alumina-supported Co catalysts, which exhibited excellent activities on hydrolysis of $NaBH_4$. Simagina et al. [8] found that the Rh/TiO_2 catalysts showed the best performance for $NaBH_4$ hydrolysis. Demirci et al. [9] studied the Ru-promoted sulphated zirconia (ZrO_2-SO_4^{2-}) catalyst and investigated the kinetics of the $NaBH_4$ hydrolysis. Unsupported CoB catalyst demonstrated high activity for the catalytic hydrolysis of $NaBH_4$ solution. However, unsupported CoB nanoparticles were easy to aggregate and difficult to reuse.

In this study, SiO_2-supported CoB catalyst was prepared. Unsupported CoB was prepared for comparison. It is known that CoB has a very strong interaction with Al_2O_3. SiO_2 is inert and was chosen as the support in this study. The samples were characterized by N_2 sorption, XRD, TEM and XPS. The catalysts were tested for hydrogen generation by hydrolysis of sodium borohydride in a batch reactor.

2. Experimental

2.1. Chemicals

Cobalt acetate tetrahydrate (>98%) was supplied by Showa Chemicals (Tokyo, Japan). Sodium borohydride (>98.5%) was purchased from Sigma–Aldrich. SiO_2 was obtained by Hayashi Pure Chemical Industries. Methanol (>99.9%) was from Tedia. Double distilled water was used in the preparation.

2.2. Catalysts preparation

All the reagents used in this research were analytical grade without further purification. Double distilled water was used for the catalysts' preparation. CoB/SiO_2 catalysts were prepared by a two-step impregnation-reduction method. 0.21 g (0.001 mol) Cobalt (II) acetate tetrahydrate (Co($CH_3COO)_2 \cdot 4H_2O$) was dissolved in distilled water. A suitable amount of SiO_2 support was put into the solution under magnetic stirring at room temperature for about 30 min, and then the material was dried in an oven at 373 K for 4 h. The dried powder was put into a conical flask. 5 mL 1 mol L^{-1} sodium borohydride solution (methanol–water mixture as solute, volume ratio = 1:1) was added into the conical flask in a dropwise manner using micro-tubing pump to reduce Co^{2+}. The suspension was kept under magnetic stirring. The reduction was conducted under nitrogen stream, which was used as a shelter gas to purge out oxygen in solution. The loading of CoB was 5 wt. %. Excess amount of borohydride ($NaBH_4/Co^{2+}$ molar ratio = 3/1) was used in order to fully reduce cobalt cations. The resultant black particles were centrifuged and washed with water and methanol thoroughly. Since CoB nanocluster on support was easily to be oxidized, it was kept in methanol solution.

For comparison, an unsupported CoB catalyst was also synthesized using similar method without SiO_2 support. Since unsupported CoB was very fine and would catch fire in dry form due to rapid oxidation by air, it was also kept in methanol for further use.

2.3. Catalyst characterization

The morphology, crystalline structure, surface compositions and the electronic states of the corresponding elements were characterized by various techniques.

N_2 sorption isotherms were measured at 77 K using a Micromeritics ASAP 2010. Prior to the experiments, the samples were degassed at 393 K until the vacuum pressure was below 10^{-4} Pa. The specific surface areas of the samples were calculated by Brunauer–Emmett–Teller (BET) method for relative pressures in the range $p/p_0 = 0.05-0.2$.

X-ray diffraction (XRD) patterns were obtained using a Siemens D500 powder diffractometer. The XRD patterns were collected using Cu K_α radiation (0.15405 nm) at a voltage and current of 40 kV and 30 mA, respectively. The samples were scanned in the range of $2\theta = 20 - 70°$ at a scanning rate of $0.05°\, s^{-1}$.

The morphology of the samples was investigated by transmission electron microscopy (TEM) using a JEOL JEM-2000 FX II microscope operated at 160 kV. The sample was dispersed in methanol and then dipped onto a carbon coated copper grid (300 #) (Ted Pella Inc., CA, USA), and dried in vacuum over night.

XPS spectra were collected using Al K_α radiation at a voltage and current of 20 kV and 30 mA, respectively. The base pressure in the analyzing chamber was maintained on

the order of 10^{-7} Pa. The spectrometer was operated at 23.5 eV pass energy. The surface composition of the samples was determined from the peak areas multiplied by the corresponding sensitive factor of each element. All the spectra were deconvoluted using XPSPEAK software with a Shirley type background. The peak type was Lorenz–Gaussian (30: 70).

2.4. Catalytic activity

0.500 g NaBH$_4$ and 1.875 g NaOH were dissolved in 50 mL deionized water. The concentrations of the solution were 1% NaBH$_4$ and 3.75% NaOH. The pH of solution was 13. This aqueous solution was used for the hydrolysis reaction. The activity test setup is illustrated in Fig. 1. Firstly, 0.2 g catalyst was loaded into a flask which was sheltered by N$_2$ gas, and 12 mL of the above solution was fed into the reaction flask under magnetic stirring. The temperature of the reaction system was maintained by a water bath. The hydrogen generated was collected by an inverted and water-filled cylinder. Hydrogen volume was measured by monitoring the water displacement from the cylinder as the reaction proceeded. The relative error for the H$_2$ volume measurement was within 2%.

A comparison experiment was also conducted using unsupported CoB catalyst under similar conditions except that the amount of CoB was changed to 0.010 g (the same amount of CoB in 0.200 g CoB/SiO$_2$).

3. Results and discussion

XRD

The XRD patterns of SiO$_2$-supported CoB, unsupported CoB and SiO$_2$ are shown in Fig. 2. No distinct peak could be observed in XRD patterns of the unsupported CoB and CoB/SiO2, indicating that the CoB possessed amorphous structure on SiO$_2$. This result is in accordance with the literature. Wu et al. [10] have reported that CoB was amorphous after vacuum-dried at 90 °C and CoB diffraction could not be distinguished from the baseline. If the temperature increased from 90 to 300 °C, CoB diffraction peaks could be detected due to the crystallization or agglomeration of the small particles. In this study, the supported catalysts were dried in the
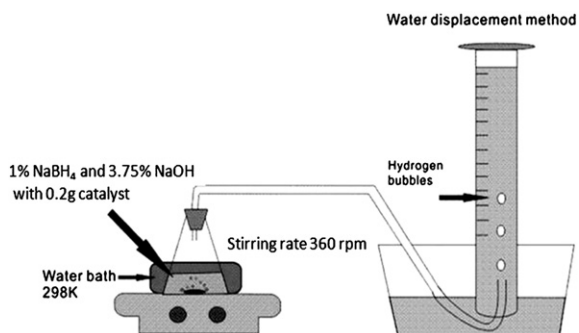
vacuum oven at room temperature. The mild condition successfully sustained the amorphous state of CoB catalyst. The SiO$_2$ was also amorphous. The XRD patterns did not show characteristic peaks of CoB in CoB/SiO$_2$ sample. In conclusion, both samples should not be heated at high temperature to prevent from sintering.

3.2. N$_2$ sorption

In order to understand the high activity of SiO$_2$-supported CoB catalyst in the hydrolysis of alkaline NaBH$_4$ solution, two aspects should be considered. First, the texture features including the CoB dispersion, porous structure etc. originated from SiO$_2$ support favored the catalysis reaction. The electronic states of Co and B on surface also played key roles in the metal boride related reaction.

The texture properties of the CoB and CoB/SiO$_2$ were characterized by N$_2$ sorption measurements. The specific surface area of CoB was 17 m^2 g^{-1}, which was much smaller than that of CoB/SiO$_2$ (277 m^2 g^{-1}). CoB was highly dispersed on SiO$_2$ support, as expected. The highly dispersion of active species provided more chances for the reactants to adsorb on the active species.

The N$_2$ adsorption-desorption isotherm of CoB/SiO$_2$ catalyst is illustrated in Fig. 3. This sample showed a type IV isotherm and there was an H1 type hysteresis loop in the relative pressure range between 0.60 and 0.95. The N$_2$ sorption property was similar with the SiO$_2$ support (not shown here). The pore size distribution inset in Fig. 3 showed that there were two main pore sizes existed at 8.0 nm and 16.0 nm, indicating the mesoporous nature of CoB/SiO$_2$ sample. The characteristics is attributed to the SiO$_2$ support.

3.3. TEM

The TEM images of CoB and CoB/SiO$_2$ are shown in Fig. 4. Both samples were aggregated by nanoparticles due to very strong van der Waals force. The primary particle of CoB was about 3 nm. When it was exposed to air, it ignited immediately due to high oxidation rate. Therefore, the sample should be kept in methanol solvent to prevent from oxidation. The size of the
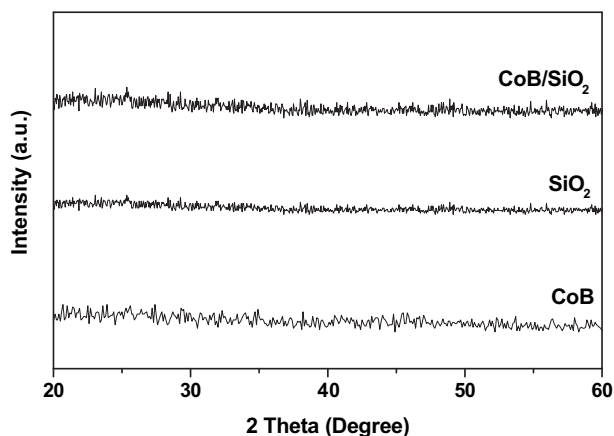

Fig. 1 – The reaction setup.

Fig. 2 – XRD patterns of CoB and CoB/SiO$_2$ catalyst and the SiO$_2$ support.

secondary particles of CoB in solvent was about 30–40 nm. For CoB/SiO$_2$ sample, the CoB particle size was about 3 nm. These results are in accordance with the XRD results. CoB/SiO$_2$ sample could be exposed to air without ignition. In other words, it was more stable than the unsupported CoB, and it was also easier to separate from solvent.

3.4. XPS

The XPS spectra of CoB and CoB/SiO$_2$ catalysts are shown in Fig. 5. The corresponding surface compositions calculated using XPS peak areas are listed in Table 2. The atom ratio of Co: B was 52.89: 47.11 for CoB. The Co/B ratio increased to 11.75 : 6.01 for CoB/SiO$_2$, indicating the surface enrichment of Co species on the supported sample. Fig. 5A illustrates the Co 2p$_{3/2}$ level of these two samples. There were two peaks in each spectrum. The peak of 778.4 eV for CoB was attributed to metallic Co which was close to the standard value (778.3 eV) [12]. The peak at 781.2 eV was ascribed to Co^{2+}. For SiO$_2$-supported CoB, these two peaks shifted to 779.7 and 782.5 eV, respectively. The binding energy of Co^0 on CoB/SiO$_2$ was 1.3 eV higher than the standard value.

Fig. 5B shows the B 1s level for CoB and CoB/SiO$_2$. The spectra of B 1s were very different between these two samples. There were two peaks located at 188.2 eV and 192.5 eV on unsupported CoB, corresponding to B^0 and B^{3+} states, respectively. But for CoB/SiO$_2$ sample, the peaks shifted to 188.0 eV and 191.7 eV, respectively. It should be noticed that the binding energy of B^0 for these samples were much higher than that of standard value (187.1 eV) [12]. It has been reported [13] that boron in metal borides acted as an electron donor and contributed partial electrons to Co. Consequently, the increase of the binding energy of B^0 should be attributed to this reason. Some researchers have reported that boron did not donate electrons to metal [14,15]. The present results support the conclusion that boron donates electrons to nickel. The discrepancies are possibly due to different starting materials and different solvents used in preparation. The particle size of CoB in this study was much smaller than those in the literature. The change of binding energies of Co was not as much as that of B. There are two explanations for this.
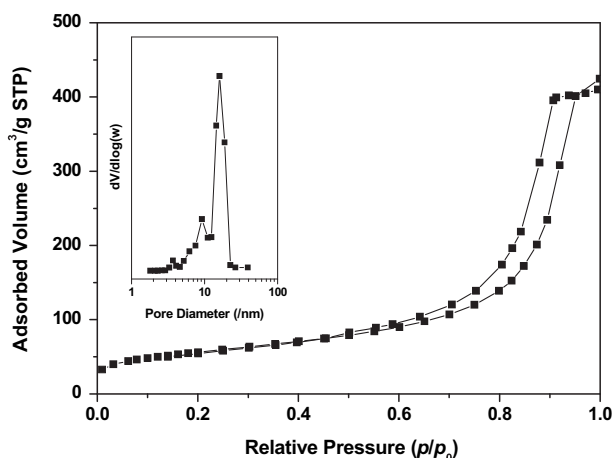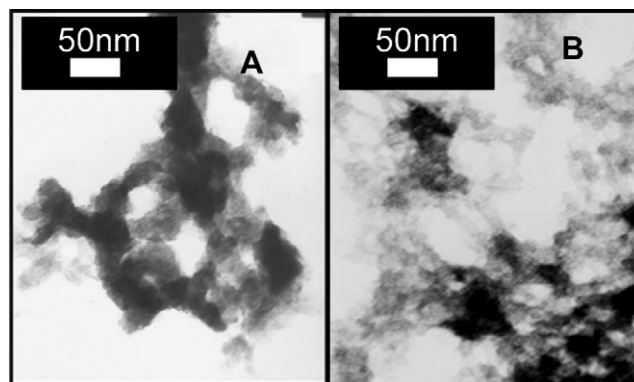

Fig. 4 – TEM images of (A) CoB and (B) CoB/SiO$_2$ catalysts.

Firstly, the amounts of Co were greater than that of B in the CoB catalyst. Secondly, the atomic weight of Co was greater than that of B, so the binding energy of Co was not as sensitive as that of B.

Surprisingly, the binding energy of Co^0 on CoB/SiO$_2$ increased apparently. This could be explained by the following results. From the surface concentrations of Co and B
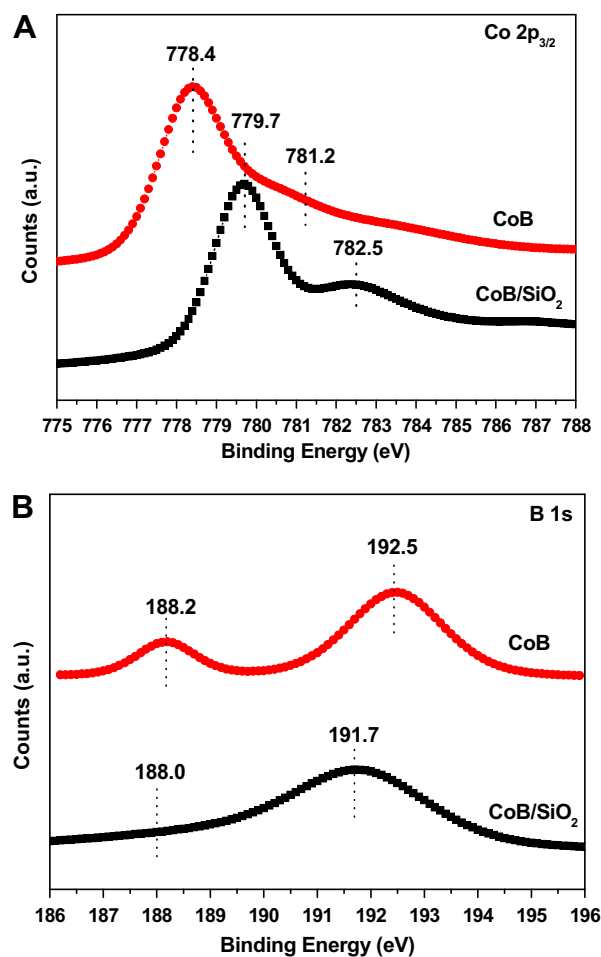

Fig. 3 – N$_2$ adsorption-desorption isotherms of CoB/SiO$_2$ catalyst (inset is the corresponding pore size distribution).

Fig. 5 – The XPS spectra of CoB and CoB/SiO$_2$ samples, (A) Co 2p$_{3/2}$ and (B) B 1s.

Table 1 – The hydrogen generation rate from hydrolysis of alkaline $NaBH_4$ solution.

Catalyst (with 10 mg active species)	Hydrogen generation rate (mL min^{-1} g^{-1} catalyst)
CoB	2450
CoB/SiO$_2$	10,586
SiO$_2$	0

listed in Table 2, one could find that after CoB was supported onto SiO$_2$, the surface content of Co^0 increased to 49.1% and that of B^0 decreased to 19.9%. The decrease of B^0 should affect the electron donation process of B. Furthermore, the atomic ratio of Co/B was increased, so the effect of B was further decreased.
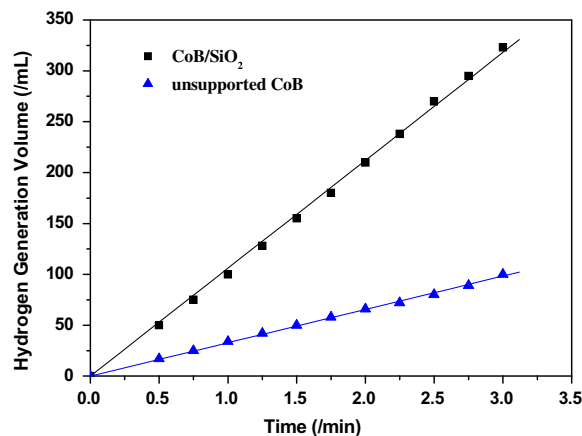
3.5. Hydrolysis reaction of NaBH$_4$

The catalytic activities of the as-prepared catalysts were evaluated by the hydrogen generation rate on hydrolysis of sodium borohydride. There are many literatures on the hydrolysis of sodium borohydride using CoB catalyst. Wu et al. [10] reported that crystalline CoB displayed better catalytic performance on this reaction than the amorphous CoB catalyst. Hydrogen generation rate of CoB calcined at 500 °C increased to 2970 ml g^{-1} min^{-1}. The results were questionable since CoB catalyst would sinter significantly at such a high temperature. Jeong et al. [11] also used crystalline CoB to catalyze the hydrolysis reaction. They found that the CoB catalyst treated at 250 °C showed the highest activity. The hydrogen generation rate was 2400 mL g^{-1} min^{-1}.

To our knowledge, the amorphous structure of the particles combining the following features favored the catalytic properties: a large number of surface coordinating unsaturated sites; more crystal defects, and the isotropic phase nature of the materials. The first two advantages always acted as the active sites during the catalysis reaction, the last one could provide the catalyst many special properties such as shape-selective catalytic property.

Fig. 6 shows the hydrogen generation amount as a function of time from the hydrolysis of alkaline NaBH$_4$ catalyzed by CoB and CoB/SiO$_2$. The hydrogen generation rate of SiO$_2$-supported CoB was much higher than that of the unsupported

Table 2 – Surface compositions of CoB and CoB/SiO$_2$ samples.

Sample		CoB	CoB/SiO$_2$
Surface Composition (Atomic ratio)		Co$_{52.89}$B$_{47.11}$	Co$_{11.75}$B$_{6.01}$/SiO$_2$
Co	Co^0	47.1%	49.1%
		778.4 eV	779.7 eV
	Co^{2+}	52.9%	50.9%
		781.2 eV	782.5 eV
B	B^0	51.3%	19.9%
		188.2 eV	188.0 eV
	B^{3+}	48.7%	80.1%
		192.5 eV	191.7 eV

Fig. 6 – Hydrogen generation volume as a function of reaction time on SiO$_2$-supported and unsupported CoB catalysts. (Catalyst amount: CoB/SiO$_2$: 0.20 g, CoB: 0.01 g, 298 K).

CoB. The rates calculated from Fig. 4 are listed in Table 1. The SiO$_2$ support did not show any activity in this reaction. Comparing with Jeong's work [11], the reaction solution they used was 20% NaBH$_4$ + 5% NaOH at 293 K. Our amorphous CoB catalyst showed comparable catalytic activity. The SiO$_2$-supported CoB catalyst showed very high activity on this hydrolysis reaction. For the equal amount of active species (CoB), the hydrogen generation rate of CoB/SiO$_2$ was 4 times more than that of the unsupported CoB catalyst.

The H$_2$ production from the metal-catalyzed hydrolysis of NaBH$_4$ is proposed to take place by following three kinetics steps [16–21]. In the first step, BH$_4^-$ ions are chemisorbed on the metallic cobalt atoms while in the second step the hydride ion H$^-$ is transferred from BH$_4^-$ ion to an unoccupied adjacent Co metal atom. In the last step, this negative charged hydrogen atom reacts with the water molecule to produce H$_2$ and OH$^-$ ion. The formed OH$^-$ ion reacts with electron deficient boron in BH$_3$ (absorbed on Co) to produce the BH$_3$(OH)$^-$ ion. The cycle of the aforementioned three steps till all the BH$_3$ groups converted to B(OH)$_4^-$. Molecular hydrogen is released during the full cycle. Looking at the mechanism mentioned above, the surface concentration of metal active sites was one of the key points to conduct the reaction. Although the binding energy of Co^0 in CoB/SiO$_2$ was much higher than that of CoB which indicating the electron density decreased in this sample, the high dispersion of active species, good pore structure provided by SiO$_2$ support and the high Co^0 surface content could compensate the higher binding energy. Consequently, compared to the CoB sample, the catalysis properties of CoB/SiO$_2$ was improved dramatically. The lower electron density of Co^0 also enhanced the stability of CoB catalyst to some extent.

4. Conclusions

SiO$_2$-supported CoB catalyst was synthesized by the impregnation-reduction approach. Compared to the unsupported CoB catalyst, the catalytic activity of CoB/SiO$_2$ for NaBH$_4$ hydrolysis reaction increased apparently. The supported CoB

catalyst had a higher Co^0 content on its surface and SiO_2 support provided higher CoB dispersion and prevent from sintering. The electron donation from B^0 to Co^0 was also observed. The structure effect of SiO_2 helped the CoB nano-clusters to have high dispersion and better thermal stability, resulting in high activity on hydrolysis of alkaline $NaBH_4$ solution. The CoB/SiO_2 catalyst showed much higher activity than the unsupported CoB catalyst. At 298 K, the hydrogen generation rate on CoB/SiO_2 catalyst was 4 times more than that on the unsupported CoB catalyst. The hydrogen generation rate was as high as 10,586 mL min^{-1} g^{-1} catalyst at 298 K. CoB/SiO_2 is a very promising catalyst for this reaction.

Acknowledgments

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