Hydrogen generation by sodium borohydride hydrolysis on nanosized CoB catalysts supported on TiO$_2$, Al$_2$O$_3$ and CeO$_2$

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ABSTRACT

A series of nanosized CoB catalysts supported on TiO$_2$, Al$_2$O$_3$, and CeO$_2$ were prepared. The catalysts were prepared by incipient-wetness impregnation. The sample was dried at 100 °C and then dispersed in water and reduced by an aqueous solution of sodium borohydrate at room temperature. An unsupported CoB cluster was used for comparison. The activities of the supported CoB catalysts were higher than that of unsupported one. The reaction rates of these supported CoB catalysts decreased in the order: CoB/TiO$_2$ > CoB/Al$_2$O$_3$ > CoB/CeO$_2$ > unsupported CoB. The reaction kinetics on various catalysts was also investigated.

1. Introduction

Hydrolysis of sodium borohydride (NaBH$_4$) has been reported to be a good way to generate hydrogen [1]. The reaction is

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \quad \Delta H = -300 \text{ kJ/mol} \quad (1)$$
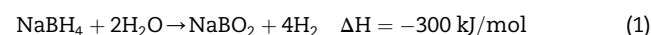
This reaction has been extensively studied [2–5]. It has been reported [2,6] that metal alloy such as NiB and CoB are good catalysts for this reaction. There are many literatures on CoB catalysts for this reaction. Patel et al. [7] reported the effect of electron transfer between metallic Co and B. Co acted as an electron acceptor, and boron acted as an electron donor. Jeong et al. [8] showed that CoB is active for this reaction. Noble metals such as Ru and Pt are active for this reaction, but they are expensive [2,9–16].

Nanoalloy material, such as NiB and CoB, has drawn attention due to its short-range order and long-range disorder in structure [17]. It has isotropic structure and many unsaturated active sites [17]. Some researchers [18–20] reported that crystalline CoB had higher activity than the amorphous one. With increasing heat-treating temperature, the Co–B precursor changed from an amorphous phase to a mixture of CoB and metal Co; and finally got a pure metal Co phase. Hydrogen generation rate of CoB calcined under 500 °C was the highest, up to 2970 ml/g min. In contrast, Jeong et al. [21] reported that the best calcination temperature for CoB was 250 °C. However, these results are questionable, because crystalline CoB had a very small surface area and less uncoordinated active sites [22,23]. Theoretically, it should result in lower activity than the amorphous CoB.

Although unsupported CoB is active for hydrolysis of sodium borohydride [24–27], it is not stable and difficult to reuse and operate. Therefore supported CoB catalyst is better for practical application. In a previous paper [17], one of the

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authors has reported that CoB is active for hydrolysis of sodium borohydride. CoB/SiO$_2$ is more active than CoB. It is interested to investigate the effect of other supports for CoB on hydrolysis of sodium borohydride solution.

In this study, several kinds of supported CoB catalysts were tested, i.e. CoB/TiO$_2$, CoB/Al$_2$O$_3$ and CoB/CeO$_2$. An unsupported CoB catalyst was included for comparison. The catalysts were tested for the hydrolysis of sodium borohydride solution at pH 13 to generate hydrogen.

2. Experimental

2.1. Materials

Cobalt acetate tetrahydrate [Co(CH$_3$COO)$_2$·4H$_2$O] (>98%) was purchased from Showa Chemicals (Tokyo, Japan). Titania and ceria (>99.8%) were obtained from Evonik-Degussa (Germany). Alumina was obtained from Strem Chemicals (Newburyport, USA). Sodium borohydride (NaBH$_4$) (>98.5%), was purchased from Sigma–Aldrich (USA). Sodium hydroxide (NaOH) (>98.5%) and methanol (CH$_3$OH) (>99.9%) were supplied by Tedia Co. (Ohio, USA). Double distilled water (H$_2$O) was used in the preparation of the catalysts.

2.2. Catalysts preparation

2.2.1. Preparation of unsupported CoB nanocluster
Unsupported CoB catalyst was prepared by chemical reduction method. Cobalt acetate was reduced by sodium borohydride solution at room temperature. The CoB catalyst was prepared by dissolving cobalt acetate in 50 vol.% absolute methanol (20 ml, 0.1 M) at room temperature and under vigorous stirring. It was reported by Liu et al. [6] that nanosized CoB could be formed by using 50 vol.% methanol in water as the solvent. The solution of sodium borohydride (6 ml, 1 M) was added dropwisely with a micro-tubing pump into the mixture under the nitrogen stream which was used as a shelter gas. In the starting materials, the molar ratios of Co: B was fixed at 1: 3. Excess amount of borohydride was used in order to fully reduce cobalt cation to metal. The resultant CoB powder was washed with double distilled water two times, then rinsed by methanol.

2.2.2. Preparation of supported CoB catalysts
Supported CoB catalysts were prepared by incipient-wetness impregnation method. Cobalt acetate was used as the starting material. The Co metal loadings in catalyst were all 5 wt. %. The samples were then reduced by NaBH$_4$ solution at room temperature, instead of H$_2$ gas at high temperature. Using this method, very small CoB particles on the support could be obtained. Titania (Evonik-Degussa P25), ceria (Evonik-Degussa) and alumina (Strem Chemicals) were used as the supports. The aqueous solution of cobalt acetate was impregnated onto supports, and then dried in an oven at 100 °C for 4 h. The powder sample was then dispersed in water. 50 vol. % methanol in water solution of sodium borohydride (5 ml, 1 M) was then added dropwisely with a micro-tubing pump into the mixture under a nitrogen stream as a shelter gas to purge air. The molar ratio of Co/B in the starting material was fixed at 1/3. Excess amount of NaBH$_4$

Table 1 – Hydrogen generation rates on different catalysts at 30 °C (Batch system, 30 °C, 1 wt. % NaBH4, 3.75 wt.% NaOH, 0.2 g catalyst, stirring rate 480 rpm, pH = 13).

Catalyst	H$_2$ generation rate (ml/min g CoB)
Unsupported CoB	3349
5 wt.% CoB/TiO$_2$	12,503
5 wt.% CoB/Al$_2$O$_3$	11,649
5 wt.% CoB/CeO$_2$	10,389

was used in order to fully reduce cobalt cations to metal. The resultant powder was washed with double distilled water, and then rinsed by methanol. The sample was dried in the vacuum oven at room temperature for 12 h.

2.3. Reaction test

The catalytic activities of the as-prepared catalysts were tested by hydrolysis of sodium borohydride. In a 50 ml volumetric flask, 0.4965 g NaBH$_4$ and 1.875 g NaOH were dissolved in 50 ml de-ionized water. The concentrations of reaction solution were 1.0% NaBH$_4$ and 3.75% NaOH. 20 ml of the reaction mixture was injected into the reaction flask, which contained 0.2 g catalyst. The pH value was 13 and the stirring rate was 480 rpm. Water bath was used to keep the system in isothermal condition. The amount of hydrogen generation was measured by water replacement method. Hydrogen was collected by a cylinder through a plastic tube attached on the reaction flask.

3. Results and discussion

Unsupported CoB nanocluster is easy to ignite in air due to rapid oxidation. It is very unstable and easy to aggregate. When CoB was supported on the support, it became stable. It should be noted that the unsupported CoB particles were
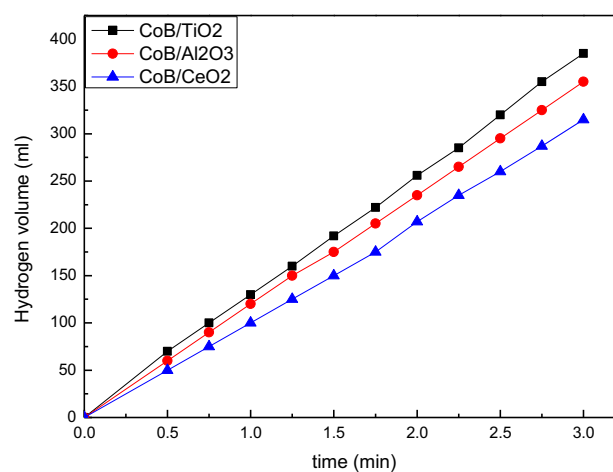

Fig. 1 – Hydrogen generation of sodium borohydride using supported CoB catalysts. (Batch system, 30 °C, 1 wt. % NaBH$_4$, 3.75 wt.% NaOH, 0.2 g catalyst, stirring rate 480 rpm, pH = 13).

Table 2 – Hydrogen generation rate (ml/min g CoB) on supported CoB catalysts at various reaction temperatures. (Batch system, 1 wt. % NaBH4, 3.75 wt.% NaOH, 0.2 g catalyst, stirring rate 480 rpm, pH = 13).

Catalyst	Temperature (°C)			
	10	20	30	40
CoB/TiO_2	2944	6738	12,503	24,057
CoB/Al_2O_3	2174	5495	11,649	22,132
CoB/CeO_2	2094	4717	10,389	19,591

Fig. 3 – **Hydrogen generation of sodium borohydride using supported CoB catalysts. (Batch system, 20 °C, 1 wt. % NaBH$_4$, 3.75 wt.% NaOH, 0.2 g catalyst, stirring rate 480 rpm, pH = 13).**

ferromagnetic and were attached on magnetic stirring bar during reaction.

A series of supported CoB catalysts were prepared by incipient-wetness impregnation, and then dried at 373 K. The drying temperature was high enough to anchor cobalt cations on the support, but not too high to cause sintering. The sample was then reduced by NaBH$_4$ at very mild condition, instead by flowing hydrogen gas at high temperature. This special technique could produce well-dispersed supported CoB catalysts.

The catalytic activities of the as-prepared catalysts were tested by hydrolysis of sodium borohydride. The hydrogen generation rates of different catalysts at 30 °C are shown in Table 1. It shows that the hydrogen generation rates of supported CoB catalysts were higher than that of unsupported CoB catalyst.

The volumes of hydrogen generation on various supported CoB catalysts at 30 °C are shown in Fig. 1. Among these supports, CoB/TiO$_2$ demonstrated the highest catalytic activity. CoB/Al$_2$O$_3$ and CoB/CeO$_2$ also had higher activities than the unsupported CoB catalyst. The hydrogen generation rates of CoB/TiO$_2$, CoB/Al$_2$O$_3$ and CoB/CeO$_2$ at 30 °C were 12,503, 11,649 and 10,389 ml/min/g CoB, which were three to four times higher than that of unsupported CoB catalyst.

TiO$_2$ from Evonik-Degussa Company had a primary particle size of 27 nm, specific surface area of 57.4 m^2/g, and the phase

composition of 80% anatase and 20% rutile. Al$_2$O$_3$ had a surface area of 275 m^2/g, average pore diameter 2.8 nm, pore volume 0.15 ml/g and bulk density 0.5 g/ml. CeO$_2$ from Evonik-Degussa had a surface area of 40 m^2/g. It is a nonporous nanoparticle. The results did not show any correlations between the activities of supported CoB catalysts and the pore structure and surface acidities of these supports.

The hydrogen generation rates of supported catalysts at various reacting temperature are listed in Table 2. The reaction rates of these supported CoB catalysts decreased in the order: CoB/TiO$_2$ > CoB/Al$_2$O$_3$ > CoB/CeO$_2$ > unsupported CoB.

The hydrogen generation rate on all supported CoB catalysts increased with increasing temperature, as expected. The volumes of hydrogen generation on the supported CoB catalysts at various temperatures are shown in Figs. 2–4. The results show that the amounts of hydrogen generation
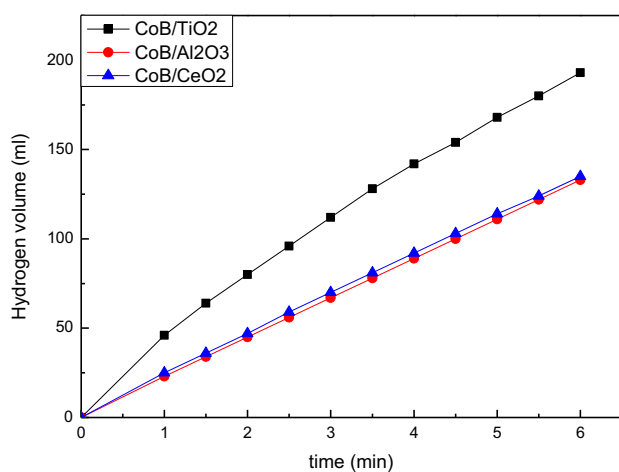

Fig. 2 – **Hydrogen generation of sodium borohydride using supported CoB catalysts. (Batch system, 10 °C, 1 wt. % NaBH$_4$, 3.75 wt.% NaOH, 0.2 g catalyst, stirring rate 480 rpm, pH = 13).**
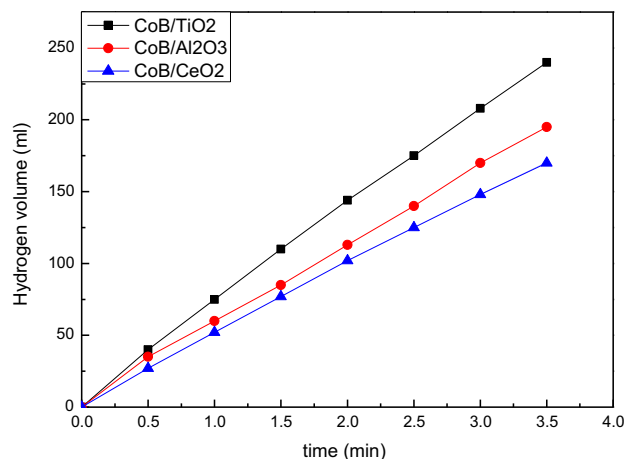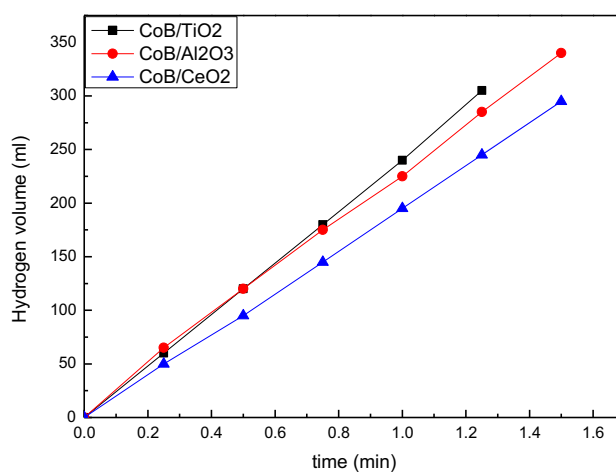

Fig. 4 – **Hydrogen generation of sodium borohydride using supported CoB catalysts. (Batch system, 40 °C, 1 wt. % NaBH$_4$, 3.75 wt.% NaOH, 0.2 g catalyst, stirring rate 480 rpm, pH = 13).**

Table 3 – Kinetics data of supported CoB catalysts.

Catalyst	CoB/TiO$_2$	CoB/Al$_2$O$_3$	CoB/CeO$_2$
$E_{act.}$ (kJ/mol)	51.0	56.8	55.3
k_0 (ml/g min)	7.8×10^{12}	7.0×10^{13}	3.5×10^{13}

increase linearly with reaction time, indicating that the reaction is zeroth order with respect to the concentration of sodium borohydride. The reaction rate of zeroth order reaction can be expressed as:

$$r = k_0 \exp(-E_{act}/RT) = k_{NaBH_4} \qquad (2)$$

The activation energy (E_{act}) of this reaction can be obtained by plotting ln k_0 versus 1/T. The activation energies of CoB/TiO$_2$, CoB/Al$_2$O$_3$ and CoB/CeO$_2$ are 51.0, 56.8 and 55.3 kJ/mol, respectively, as shown in Table 3. These values are smaller than that of unsupported CoB catalyst [17]. Ye et al. [23] reported that the activation energy of unsupported CoB catalyst is 64.87 kJ/mol. Our result is in agreement with their result. The value of pre-exponential factors, k_0, of CoB/TiO$_2$, CoB/Al$_2$O$_3$ and CoB/CeO$_2$ are 7.8×10^{12}, 7.0×10^{13}, 3.5×10^{13} ml/g min, respectively. The activation energies and pre-exponential factors of various catalysts are listed in Table 3. The pre-exponential factor (k_0) means total collision times of reactant to active sites. Higher k_0 indicates that the dispersion of CoB is better. The lower $E_{act.}$ indicates the faster reaction rate. As a result, the value k_0 of CoB/TiO$_2$ was the lowest, but the value $E_{act.}$ of CoB/TiO$_2$ caused its high activity. In addition, the activation energies of CoB/Al$_2$O$_3$ and CoB/CeO$_2$ had only slight variation, so the pre-exponential factor (k_0) determined the reaction rate.

4. Conclusions

A series of supported CoB catalysts were prepared by incipient-wetness impregnation, dried at 373 K and then reduced by NaBH$_4$ solution. This special technique could produce well-dispersed supported CoB catalysts. An unsupported CoB catalyst was prepared by chemical reduction method. These catalysts were used for hydrolysis of sodium borohydride solution at pH 13. Supported CoB catalysts demonstrated higher catalytic activities than the unsupported CoB catalyst. CoB/TiO$_2$ had the highest activity. The reaction rates of these supported CoB catalysts were CoB/TiO$_2$ > CoB/Al$_2$O$_3$ > CoB/CeO$_2$ > CoB.

The volumes of hydrogen generation on all supported CoB catalysts increased linearly with reacting time, suggesting zeroth order reaction with respect to NaBH$_4$ concentration. The activation energy and pre-exponential factor for different supported CoB catalysts on hydrolysis of sodium borohydride were also investigated. The low activation energy of CoB/TiO$_2$ caused its high activity.

In conclusion, the supported CoB catalysts are promising for hydrolysis of sodium borohydride. They are more active and more stable than the unsupported catalyst. They are also easier to separate and reuse after reaction than the unsupported CoB.

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