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CoB supported on Ag-activated TiO_2 as a highly active catalyst for hydrolysis of alkaline $NaBH_4$ solution

Xiaochen Shen [a], Qing Wang [a], Qingquan Wu [a], Siqi Guo [a], Zhengyan Zhang [a], Ziyang Sun [a], Baishu Liu [a], Zhibin Wang [b], Bin Zhao [a, *], Weiping Ding [a]

[a] Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China
[b] State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China

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ABSTRACT

In this study, a series of TiO_2 (activated by Ag) supported CoB catalysts were synthesized using electroless deposition method. Compared to the unsupported CoB catalyst, the CoB/Ag–TiO_2 catalysts showed much better catalytic activity and higher stability on hydrolysis of $NaBH_4$ in alkaline aqueous solution and the catalysts were insensitive to air oxidation. The optimistic loading amount of CoB was 2.8 wt% and its hydrogen generation rate reached 6294 mL min^{-1} (g Co)$^{-1}$ in 1 wt% $NaBH_4$ + 5 wt% NaOH solution at 293 K. The catalytic activity was comparable to some noble catalysts and could retain nearly 70% after 5 cycles. The catalysts were studied by varies techniques and the results revealed that the dispersion of CoB was improved and the CoB/Ag–TiO_2 catalysts possessed distinct porous structure which could promote the diffusion of reactants/products. The surface composition and the electron transfer effects between the Co^0 with B^0 and Ag^0 could also affect the catalytic activity. Under the current experimental conditions, the specific activation energy of 2.8CoB/Ag–TiO_2 catalyst was determined as 44 kJ mol^{-1} and the kinetic equation was also deduced.

1. Introduction

The high development of economy leads to booming energy needs in today's world. Fossil fuels are depleting and their combustion cause serious pollution and greenhouse emissions. Therefore, renewable energies are keenly concerned by the scientists, the development and application of renewable energies become hot research issues currently [1]. As a kind of renewable energy carrier, hydrogen displays diverse advantages over the traditional fuels, such as high energy density and zero emission, etc [2,3]. However, the utilization of hydrogen energy is restricted severely by how to acquire and store hydrogen safely and conveniently [4]. Compared to pressurized tanks and cryogenic liquid hydrogen, reversible hydrogen storage materials such as metal/alloy hydrides [5–7], carbon materials [8], and complex hydrides [9–11] have greater promise owing to their high volumetric hydrogen capacity, favorable energy efficiency, and safety advantage. Among the chemical hydrides of interest, sodium borohydride ($NaBH_4$) receives widely concerns due to high hydrogen capacity (with a theoretical value of 10.6 wt%), good storability, reaction controllability, low reaction-initiating temperature. Furthermore, the hydrolysis product of $NaBO_2$ is environmentally benign [12,13]. These advantages are very conductive to obtaining hydrogen for fuel cells used in portable equipments.

$NaBH_4$ can be hydrolyzed according to the following reaction:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2\uparrow \quad \Delta H^0 = -216.7\ \mathrm{kJ\ mol^{-1}}$$

In order to restrain the self-hydrolysis of $NaBH_4$, NaOH is often added into the $NaBH_4$ solution as stabilizer. The hydrolysis reaction is greatly accelerated using catalysts at ambient temperature [14]. A number of catalysts based on metals/alloys have been developed toward the reaction, including Pt, Ru [15,16], Raney Ni and Co [17,18], Co and Ni borides [19–21], etc. Among the catalysts, Co and Ni based catalysts are widely concerned due to their relative high catalytic activity, low cost, broad source and easy preparation.

Metal borides such as CoB, NiB, NiCoB, RuB, etc. are commonly used catalysts in selective hydrogenation, hydrogen generation etc. A lot of work had been done on the synthesis of metal boride and their catalytic properties were also studied [22–24]. These catalysts

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* Corresponding author. Tel.: +86 25 83596749; fax: +86 25 83317761.
E-mail address: binzhao@nju.edu.cn (B. Zhao).

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are commonly synthesized by chemical-reduction method and their catalytic properties are closely related to the specific non-crystalline structure which endows them several intrinsic characteristics, including short-range order, long-range disorder, and more surface coordinatively unsaturated sites [25,26]. The hydrolysis of $NaBH_4$ is a strong exothermic reaction and hydrogen generated rapidly from the surface of catalysts. In addition, the solution is always with strong basicity. These factors raise very strict requirements on the stability of the catalysts. Due to the non-crystalline nature, the stability and reusability of metal borides always could not satisfy the practical demands for hydrogen generation from alkaline $NaBH_4$ aqueous solution. To support the non-crystalline metal borides on some supports such as Ni foam, TiO_2, SiO_2 might be an effective way to solve this problem. Dai et al. [27] prepared the nickel foam supported CoB catalyst and the supported CoB catalyst had good catalytic activity for hydrolysis of $NaBH_4$ due to a significantly increased surface area. Su et al. [28] synthesized a porous Co/SiO_2 catalyst and the highest hydrogen generation rates of 49% Co/SiO_2 catalysts were 2513 mL min^{-1} g^{-1}. The particle size, dispersion, and the combination of metal borides with the support are sensitive to the preparation method, conditions of synthesis including concentration, stirring speed, temperature, etc [29,30].

Though there are many methods to prepare supported catalysts, the electroless deposition method shows apparent significance due to the convenience, low-cost, improved combination of active species with the support, etc. Zhang et al. [31] studied the nickel nanoparticles supported on metal oxides that prepared by a modified electroless deposition method and the catalytic activity and stability were improved in the hydrogenation of sulfolene and the hydrodechlorination of chlorobenzene. They also prepared supported NiB catalysts using electroless deposition method under microwave irradiation [32]. Compared to NiB nanoparticles, the catalytic activity and selectivity in the hydrogenation of acetophenone were promoted. Rakap et al. [33] also found similar improvements in Co–Ni–P/Pd–TiO_2 catalyst prepared by electroless deposition approach for the hydrolysis of $NaBH_4$. The maximum H_2 generation rate reached ~3780 mL H_2 min^{-1} (g catalyst)$^{-1}$ at 55 °C and retained 86.4% of initial activity at the fifth run. At present, to prepare supported CoB catalysts by using electroless deposition method was rarely reported.

In this paper, a series of supported CoB catalysts on Ag activated TiO_2 supports were fabricated by electroless deposition method. The catalytic properties on hydrolysis of alkaline $NaBH_4$ aqueous solution (1 wt% $NaBH_4$ + 5 wt% NaOH) were investigated. The morphology, structure, existing states and surface composition of the catalysts were studied to understand the factors that affected the activity and the stability of CoB/Ag–TiO_2 catalysts. In addition, the effects of reaction temperature and the concentrations of catalysts, $NaBH_4$, NaOH on the catalytic activities were also studied to obtain the specific activation energy and the corresponding kinetic equation under the current conditions.

2. Experimental

2.1. Synthesis of Ag-activated TiO_2 support

The TiO_2 support was synthesized by sol–gel method [34,35]. The procedures were simplified as follows: 2.0 mol L^{-1} aqueous ammonia was added drop-wisely into 0.25 mol L^{-1} $TiCl_4$ solution till the pH value of the solution reached 9.0. 30 min later, the precipitate was filtered and washed with water thoroughly. Then the residue was dried under vacuum at 393 K for 24 h and calcined at 773 K for 3 h to get the TiO_2 support.

3 g TiO_2 was added into 200 mL Ag-activation solution which was composed of 0.0471 g L^{-1} $AgNO_3$, 0.0882 g L^{-1} $NH_3 \cdot H_2O$, 0.0118 g L^{-1} NaOH, 0.0047 g L^{-1} HCHO. The suspension was magnetic-stirred at 313 K for 4 h. Then filtered and washed with water and then dried under vacuum at 323 K for 4 h. Finally, the Ag activated TiO_2 support with light purple color was obtained.

2.2. Preparation of the CoB/Ag–TiO_2 catalysts by electroless deposition method

CoB was supported on Ag–TiO_2 by using a one-step electroless deposition method [27,33]. The typical procedure was as follows (taking nominal loading of 3 wt% CoB/Ag–TiO_2 as an example): The calculated Ag–TiO_2 support was added into the electroless deposition solution (consisted of 9.42 g L^{-1} $Co(Ac)_2 \cdot 4H_2O$, 32.61 g L^{-1} $C_4H_6O_6$, 2.00 g L^{-1} $Na_2B_4O_7 \cdot 10H_2O$, 2.00 g L^{-1} NH_4Cl and 4.20 g L^{-1} $NaBH_4$, the pH of the solution was adjusted carefully to 12–13 with 1 mol L^{-1} NaOH). The electroless deposition was conducted at 318 K under magnetic stirring till no bubbles generated from the solution. The CoB/Ag–TiO_2 was collected by centrifugation, and washed with deionized water and pure methanol respectively before drying in the vacuum oven at 323 K for 12 h. The catalysts with nominal CoB loading of 1 wt%, 3 wt%, 5 wt%, 10 wt% and 15 wt% were synthesized with similar procedure and the actual loadings of CoB were 0.98 wt %, 2.8 wt%, 4.6 wt%, 7.5 wt% and 10.5 wt% respectively (determined by ICP). The catalysts were denoted XCoB/Ag–TiO_2, here X was the actual mass loading percentage of CoB.

For comparison, unsupported CoB was also prepared. Appropriate amount of $Co(Ac)_2 \cdot 4H_2O$ and $NaBH_4$ was dissolved separately in H_2O ($NaBH_4$: Co^{2+} = 3: 1, molar ratio). The $NaBH_4$ solution was added drop-wisely into the $Co(Ac)_2$ solution under vigorous stirring. During the solution preparation and the reduction process, the vessels and the reactor were placed in ice-water bath in order to reduce the hydrolysis of $NaBH_4$ and to maintain the reaction temperature to restrain the agglomeration of CoB nanoparticles. The black precipitate was centrifuged till no bubbles generated, and then washed with distilled water and absolute methanol several times, respectively. Finally, the precipitate was dried in the vacuum oven for 12 h at 323 K.

2.3. Catalyst characterization

The morphology of the CoB/Ag–TiO_2 catalysts was analyzed by a HITACHI S-4800 field emission scanning electron microscope (FE-SEM, 10 kV) equipped with an energy dispersive X-ray (EDX) analysis unit. The X-ray powder diffraction (XRD) patterns of the samples were recorded with a PHILIPS X'pert diffractometer operated at 40 kV and 40 mA (Cu K_α, $\lambda = 0.154184$ nm), the scanning was performed between 10 and 80°. Nitrogen adsorption-desorption test was measured with a Micromeritics ASAP 2020 physisorption analyzer. The specific surface areas of the catalysts were calculated from the N_2 adsorption-desorption isotherms by the BET method, while the pore volume and pore width were determined by BJH (Barrett–Joyner–Halenda) method using the desorption branch. X-ray photoelectron spectroscopy (XPS) of the catalysts was carried out on a PHI 5000 VersaProbe electron spectrometer using an Al K_α ($h\nu = 1486.6$ eV) X-ray source, the binding energy (BE) values were calibrated using C 1s = 284.6 eV as a reference.

2.4. Catalytic activity experiments

In a typical hydrogen generation experiment [36–38], CoB/Ag–TiO_2 catalyst containing 10.0 mg CoB catalyst equivalently was put into a sealed flask placed in the thermostatic water-bath maintained at 293.00 ± 0.05 K. Then 15.00 mL 1 wt% $NaBH_4$