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Short communication

Influence of M–B (M = Fe, Co, Ni) on aluminum–water reaction

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HIGHLIGHTS

- The chainlike Fe–B catalyst forms a network structure.
- The catalytic activity in the initial Al/H_2O reaction at 45°Cis Fe–B > Ni–B > Co–B.
- Aluminum is rapidly corroded after consecutive additions of Al batches.
- The high concentrations of OH^- in the local domain triggers the corrosion of Al.

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ABSTRACT

In this work, the aluminum–water reaction induced by Fe–B, Co–B and Ni–B particles was studied. The catalysts were mixtures of the metal boride and metallic particles. The chainlike Fe–B catalyst forms a network structure under the influence of an external magnetic field and has a large specific surface area. Aggregated particles of Co–B and Ni–B catalyst have small specific surface area. Catalytic activity in the initial corrosion of aluminum increases with increasing Fe–B content because of the large specific surface area and the formation of a micro galvanic cell. However, the amount of hydrogen generated slowly decreases with increasing amount of Co–B and Ni–B. The activity of Fe–B, Co–B and Ni–B in the initial Al/H_2O reaction decreases in the order Fe–B > Ni–B > Co–B. The calculated apparent activation energies in the presence of Fe–B, Co–B and Ni catalysts are 38.2, 39 and 29.6 kJ mol^{-1}, respectively. Aluminum is rapidly and completely corroded in a weakly alkaline solution (pH < 10) after consecutive additions of Al batches because of high concentrations of OH^- in the local domain and an increase in the amount of $Al(OH)_3$ precipitate.

1. Introduction

Hydrogen generation though reaction of aluminum in water and aqueous alkaline solution is extensively being studied because of its safety, cheapness and simplicity. This is one of the mild and easily controlled reactions for the sustainable production of pure hydrogen for use-on-demand systems. However, an inert alumina film that is spontaneously formed on Al surface is stable and prevents the Al/H_2O reaction at neutral pH. This oxide film, which has a thickness of 4–10 nm, is composed of a compact layer of Al_2O_3 and a thin layer of boehmite [γ-AlOOH] or bayerite $Al(OH)_3$ [1].

Several methods have been used to break the alumina film to accelerate hydrogen generation. Soler observed that the addition of $NaSnO_2$ or $NaAlO_2$ to a NaOH solution stimulated the corrosion of Al at high pH or formation of an Al/Sn micro galvanic cell [2,3]. Fan and coworkers studied the hydrogen generation by use of an Al metal mixture with Ga, Bi, In, Sn, Li, Mg or Hg prepared by ball milling [4–6]. They proposed that the improvement of the rate of hydrogen generation rate is related to the formation of a micro galvanic cell or to the production of a soluble hydroxide. Deng investigated the effect of the addition of γ-Al_2O_3 on the corrosion of Al and explained by the uniform corrosion model [7,8]. Dreizin reported that a mixture of Al and oxide (Bi_2O_3, MoO_3, CuO or MgO) prepared by ball milling reacted with water to produce hydrogen via pitting corrosion [9].

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Amorphous Fe–B, Co–B and Ni–B catalysts have been used in powdered form in studies on $NaBH_4$ hydrolysis in a wide range of conditions. These catalysts, which were prepared through in situ reduction, show high catalytic activity in the hydrolysis of $NaBH_4$ because of their amorphous structure and high surface area [10,11]. Their catalytic activity in alkaline solution decreases in the order: Co–B > Ni–B > Fe–B, as the surface of Co is more favorable for the conversion of $BH_3(OH)^-$ to $B(OH)_4^-$ and for the release of the molecular hydrogen [12]. However, no studies on the catalytic activity of Fe–B, Co–B and Ni–B on the Al/H_2O reaction have been reported. In this work, Fe–B, Co–B and Ni–B were prepared through hydrolysis of $NaBH_4$ in deionized water. Their behavior in Al/H_2O reaction at 45 °C were examined. The effect of Fe–B, Co–B and Ni–B on the initial Al/H_2O reaction was found to decrease in the order Fe–B > Ni–B > Co–B.

2. Experimental

2.1. Preparation of catalyst

Raw aluminum powder (99.0% purity, Tianjin Damao Chemistry Reagent Factory, China, Tianjin), 99.0% $NaBH_4$, and 99.0% $CoCl_2 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ (Tianjin Bodi Chemical Co., China) were used in this study.

Fe–B, Co–B and Ni–B catalysts were synthesized through the conventional wet chemical reduction method. These catalysts were typically obtained by adding 0.2 g of borohydride solution to a 20 mL solution containing 0.5 g Fe^{3+}, Co^{2+} or Ni^{2+} ions without stirring. A magnetic stirring bar was used to provide an external magnetic field to collect magnetic particles. Fe–B and Co–B particles, which are strongly ferromagnetic, are attracted to the magnetic stirring bar. Ni–B particles, on the other hand, were separated by filtration because of their weak magnetic property. To remove remaining Na^+ and Cl^- ions, Fe–B, Co–B and Ni–B particles were washed with water and ethanol. Then, it was dried at room temperature.

2.2. Measurement of the amount of generated hydrogen

Fresh catalyst and 0.2 g Al were mixed manually for <5 min. The resulting mixture was transferred to 30 mL dionized water and sealed in a 50 mL flask with stirring. Initial reaction of the mixture was allowed to proceed for 400 min, and then consecutive batches of pristine Al were added to the same flask individually in succession. The byproduct $Al(OH)_3$ was accumulated in this reaction. The flask was heated in a water bath to maintain constant temperature during the entire reaction. The hydrogen produced by the reaction was collected in an inverted burette completely filled with tap water. The volume of hydrogen produced within 400 min was recorded at 10 min intervals from the water-level change in the inverted burette.

2.3. Characterization

The structure of the product was determined on a Bruker D8 Advance X–ray diffractometer (XRD) with Cu Kα radiation at a voltage and current of 40 kV and 40 mA. Surface electronic states and valence state were studied by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD multi-technique). The morphology of the products was investigated by means of an S-4800 field–emission scanning electron microscope (FE-SEM). In order to examine the specific area of the byproducts, Brunauer–Emmet–Teller (BET) surface area measurement was performed at −196 °C on NOVA 4000, Quantachrome Corporation.

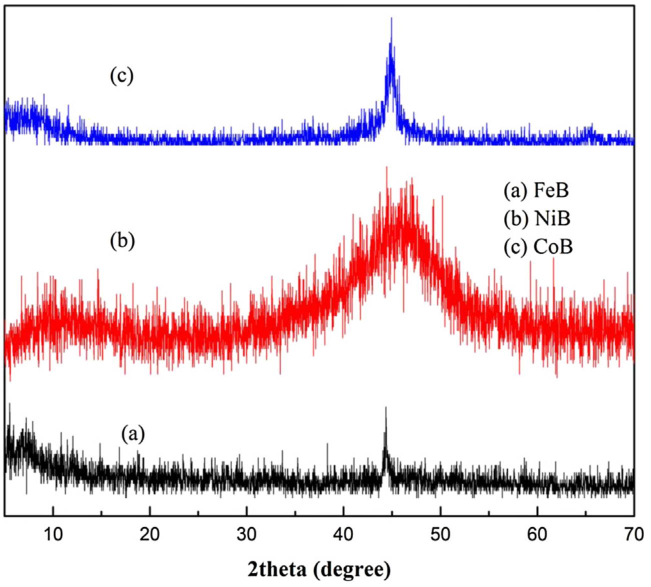

Fig. 1. Typical XRD profiles of Fe–B, Co–B and Ni–B.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 shows the typical XRD profiles of the fresh Fe–B, Co–B and Ni–B. Typically, they were amorphous. However, the appearance of a peak at 2θ of 45° in the patterns of the Fe–B, Co–B and Ni–B suggests the presence of small amounts of metal Fe, Co and Ni. That is, the catalysts consisted of a mixture of M–B particles (M = Fe, Co, Ni) and reduced metal. The XPS results show that Fe, Co and Ni in the Fe–B, Co–B and Ni–B were in their oxidized state, as evidenced by their binding energies of 711 eV, 782 eV and 853 eV (Fig. 2). No metallic Fe, Co and Ni were detected because of long time storage in the air. This result suggests that the metallic Fe, Co and Ni are not stable in air and are easily oxidized.

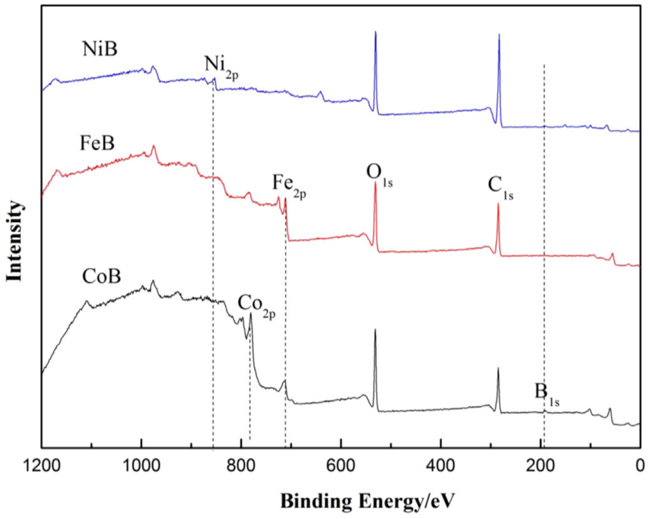

Fig. 2. X-ray photoelectron spectra for Fe–B, Co–B and Ni–B.