

Development of Al₂O₃ carrier-Ru composite catalyst for hydrogen generation from alkaline NaBH₄ hydrolysis

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ABSTRACT

A recyclable and reusable Ru/Al₂O₃ catalyst is prepared for hydrogen generation from the hydrolysis process of alkaline sodium borohydride (NaBH₄) solution. The hydrogen generation rate by the hydrolysis and methanolysis of alkaline NaBH₄ was explored as a function of NaOH concentration. Meantime, the byproducts derived from the spent alkaline NaBH₄ solution were characterized by X-ray diffraction (XRD), scanning electro microscope/energy dispersive spectrometer (SEM/EDS) and NMR (Nuclear Magnetic Resonance). The effect of NaOH concentration on the hydrogen generation from the hydrolysis of NaBH₄ significantly depends on the type of catalysts. With increasing NaOH concentration, the hydrogen generation rates decrease when using ruthenium (Ru) composite as a catalyst. The hydrogen generation rate of the methanolysis of NaBH₄ is significantly inhibited in the presence of NaOH as compared with the hydrolysis of NaBH₄. The durability test of the Ru/Al₂O₃ catalyst shows that the hydrogen generation rate decreases with recycling and reuse. The XRD and NMR analysis results show that the borate hydrate (NaBO₂ · H₂O) was derived from the hydrolysis of 20 wt% and 30 wt% NaBH₄.

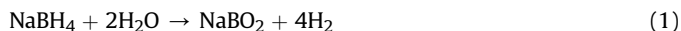
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1. Introduction

Hydrogen is an environmentally friendly energy source. In the future, hydrogen will be used to replace current fossil fuels. Hydrogen can provide energy through internal combustion engines or through proton exchange membrane (PEM) fuel cells by converting the chemical energy of hydrogen gas into electrical energy. Nowadays, the subject of fuel cells is attracting great interest. Fuel cells with high conversion efficiency are used in transportation and personal electronic applications [1]. When hydrogen is used in a fuel cell, water is the only product. Hydrogen can be stored in tanks of compressed or liquefied hydrogen, carbon nanotubes, metal hydrides and chemical compounds. Among the methods of hydrogen storage, chemical hydrides (NaBH₄, KBH₄, LiBH₄ etc.) have been studied intensively [2–5] as hydrogen sources for portable PEM fuel cells.

Sodium borohydride (NaBH₄) is a type of borohydride which has drawn much attention due to its large theoretical hydrogen content of 10.8%. Solutions of NaBH₄ are nonflammable, the rate of hydrogen generation is easily controlled, the reaction byproduct NaBO₂ can be recycled and hydrogen can be generated even at low

temperatures [6]. NaBH₄ has strong reduction ability. It is not only applicable for organic chemicals and inorganic chemicals, but it can also act as a catalyst and reductant for dye and pharmaceutical products. The self-hydrolysis of NaBH₄ in aqueous solution can release hydrogen through the following process:



The hydrogen generation of NaBH₄ is inhibited in the presence of high pH solution. The alkali acts as a stabilizer to prevent the self-hydrolysis of NaBH₄ in aqueous solution. Normally, NaOH is chosen as the hydrogen generation inhibitor for the hydrolysis of NaBH₄. In the presence of a suitable catalyst, the alkaline NaBH₄ solution can rapidly release hydrogen. Researches are done to find these suitable catalysts. Different catalysts such as ruthenium (Ru) [7–9], rhodium (Rh) [10], platinum (Pt) [11], PtRu [3], nickel (Ni) [12,13], cobalt (Co) [14–17], Co–B [18–21], Co–B/Pd [22], Ni–B [23] and Fe–Co–B/Ni [24] have been extensively studied. Among the above metal compositions, the Ru metal exhibits the most effective catalytic activity.

According to previous studies [25–27], the type of byproduct in spent NaBH₄ solution depends on experimental conditions, such as reaction time, amount of water, temperature and catalytic agents. Stepanov et al. [25] explained that phase transitions of byproducts occur as NaBH₄ hydrolyzes due to absorption of air humidity.

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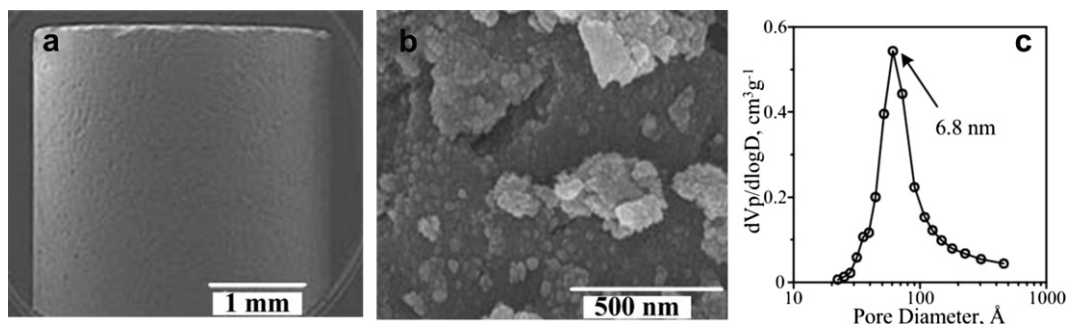


Fig. 1. Scanning electron microscope of the Ru/Al₂O₃ catalysts: (a) 25 $\times$, (b) 100,000 $\times$ and (c) pore size distribution of Ru/Al₂O₃.

Marrero-Alfonso et al. [26] suggested that the solid byproducts of the reaction are unknown mixtures of hydrated sodium metaborates. Few studies have explored the byproducts from the hydrolysis of alkaline NaBH₄ solution.

Ru salt alone is not feasible for hydrogen generation, because control of the reaction and the separation of the catalyst from the spent solution are not easy to perform. Supported catalysts have

been used to solve the problem. In this study, alumina (Al₂O₃) was selected as the support material for the preparation of the Ru/Al₂O₃ catalyst because of its hardness and low cost. Using the synthesized catalyst, the effects of NaOH concentration, catalyst loading and durability test on the hydrogen generation were investigated. This study also characterized the hydrolysis byproducts of NaBH₄ at various concentrations of NaOH.

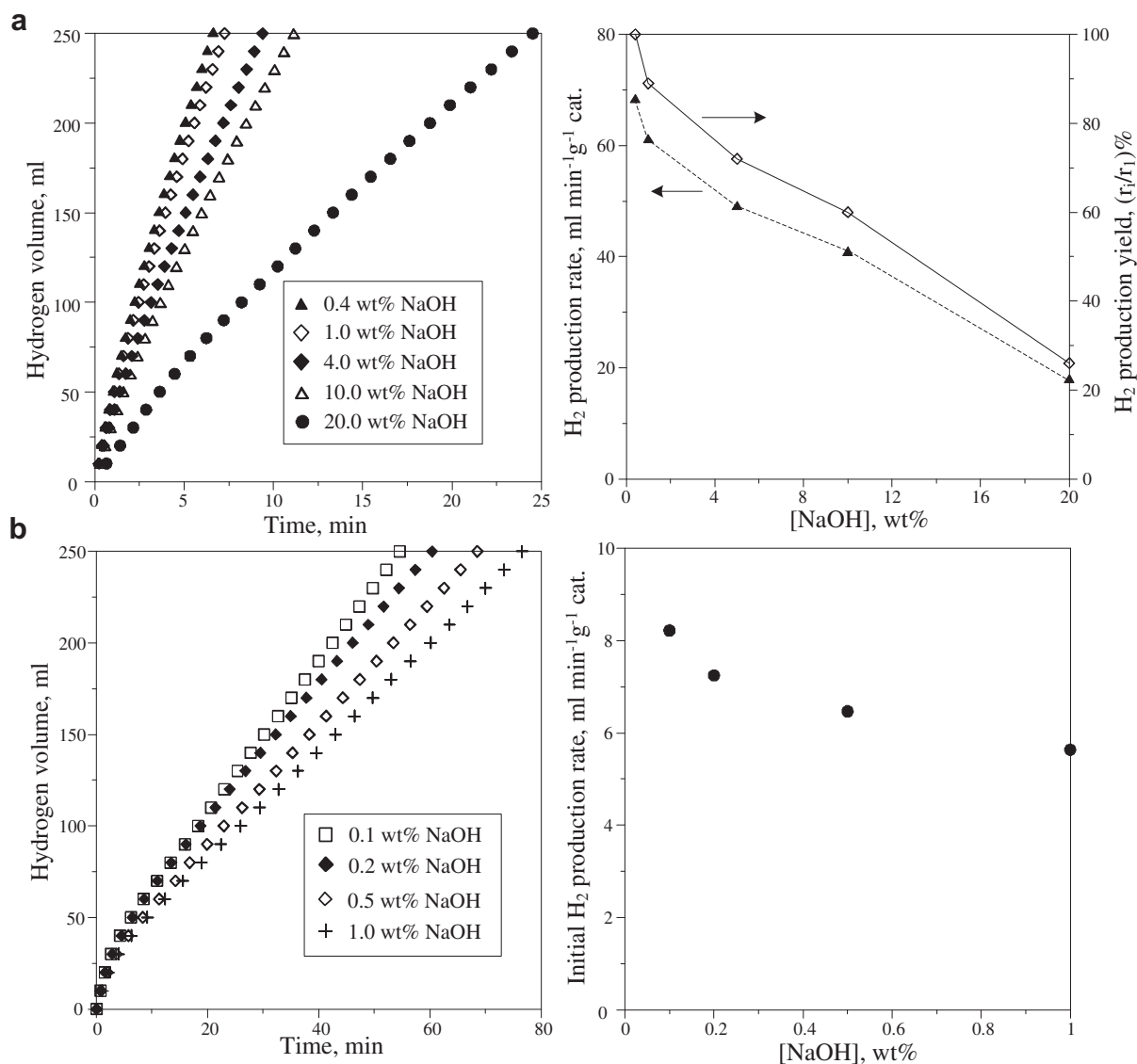


Fig. 2. Effect of concentrations of NaOH on hydrogen generation from the (a) hydrolysis and (b) methanolysis of 12.5 wt% NaBH₄ at 298 K using 0.5 g Ru/Al₂O₃ catalysts.

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