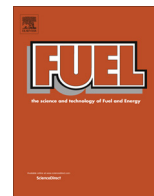




Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel



Enhanced hydrogen generation by methanolysis of sodium borohydride in the presence of phosphorus modified boehmite

Dongyan Xu*, Yusong Zhang, Fei Cheng, Lin Zhao

College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, Shandong, China

HIGHLIGHTS

- Phosphorus (P) modified boehmite catalyst was prepared.
- Methanolysis of NaBH₄ was effectively accelerated by using P/boehmite catalyst.
- Catalytic activity of P/boehmite was improved by appropriate calcination treatment.
- First-order kinetic model was proved to be the suitable kinetic model.

ARTICLE INFO

Article history:
Received 22 February 2014
Received in revised form 23 May 2014
Accepted 23 May 2014
Available online xxxxx

Keywords:
Hydrogen generation
Sodium borohydride
Methanolysis
Boehmite
Phosphorus

ABSTRACT

Phosphorus (P) modified boehmite catalysts were prepared with wet impregnation method using phosphoric acid (H₃PO₄) as the P source. The P/boehmite catalysts with different P loadings ranging from 0 to 6.4 wt% were obtained by regulating the concentration of H₃PO₄. These catalysts were characterized by BET surface area and FTIR spectroscopy measurements and their catalytic performance for hydrogen generation by methanolysis of sodium borohydride at 0 °C was evaluated. The results show that the as-prepared non-metallic P/boehmite catalyst exhibited high catalytic activity toward the methanolysis reaction under the circumstance of low environmental temperature. Appropriate calcination treatment can enhance the catalytic activity of P/boehmite catalyst to some extent. To understand the kinetic behavior of the methanolysis reaction in the presence of these catalysts, the experimental data were fitted to both zero-order and first-order kinetic models using the integral method.

© 2014 Published by Elsevier Ltd.

1. Introduction

Proton exchange membrane fuel cells, also known as polymer electrolyte membrane fuel cells (PEMFCs), are a type of fuel cell being developed for transportation applications as well as for stationary and portable applications. Basically, the fuel cell technology converts an energy carrier, mostly hydrogen, into electricity. However, its widespread use is severely limited by the lack of a safe, convenient, efficient hydrogen storage and infrastructure system [1]. To overcome these major barriers, much effort has been made to convert various fuels into hydrogen in situ [2].

Chemical hydrides have attracted wide attentions as a novel approach to provide pure hydrogen for fuel cells due to some advantages including stability, nonflammable in alkaline solution, convenience of H₂ release via hydrolysis at ambient conditions,

and recyclability of byproducts [3]. During the past decade, considerable efforts have been made to generate hydrogen by the hydrolysis of NaBH₄, most of which focus on catalysts, reactors, and hydrolysis kinetics [4–7]. Although the hydrogen storage density based on this hydrolysis reaction stoichiometry is 10.8 wt%, the actual hydrolysis of NaBH₄ is typically conducted in the aqueous phase where large quantities of excess water are required to facilitate mass transfer of reactant and ensure complete dissolution of hydrated byproduct (NaBO₂·xH₂O), resulting in a significant reduction of the gravimetric hydrogen storage capacity from 10.8 to 2.9 wt% [8–10].

Recently, the reaction of methanol rather than water with NaBH₄ has been successfully demonstrated for the generation of hydrogen [11–13]. Compared to the hydrolysis system, the methanolysis system is more attractive because of some additional advantages. The rate constant for the methanolysis reaction at 273 K has been suggested to be greater than that of the hydrolysis reaction [14]. The byproduct, NaB(OCH₃)₄, has less tendency of

* Corresponding author. Tel.: +86 532 84022506; fax: +86 053288723931.
E-mail address: xdy0156@sina.com.cn (D. Xu).

plugging the reactor. In addition, the low freezing point of methanol makes the methanol–NaBH₄ system to be suitable to generate hydrogen at subzero temperatures. Most of all, the hydrolysis of NaB(OCH₃)₄ by-product liberate the consumed methanol efficiently, which thus can be continuously recycled and reused in methanolysis reaction [15].

To facilitate the application in cold weather condition, it is critical to improve the kinetics of the methanolysis reaction at low solution temperatures. Hannauer et al. [16] found that Co–TiO₂ shows higher catalytic performances than those of Ru–TiO₂ toward methanolysis of NaBH₄. Lo et al. [11] have investigated the methanolysis of NaBH₄ over 45 to –20 °C using metal chlorides and platinum-coated lithium cobalt oxide as catalysts. The results showed that the rate of methanolysis was enhanced by more than 110 times at –20 °C in the presence of 10 wt% CoCl₂ catalyst. NiCl₂, Ni₂B and RuCl₃ were also found to be effective in improving the kinetics of alcoholysis reaction in non-stabilized NaBH₄ [17].

Recently, Ru immobilized Al₂O₃ pellets were synthesized as a catalyst for hydrogen generation from the methanolysis of NaBH₄ in alkaline solution [13]. In our previous study, Co/Al₂O₃ was proven to be an effective catalyst for the methanolysis of NaBH₄ [18]. Up to now, only several supported transitional metal catalysts have been demonstrated to exhibit high performance for this methanolysis reaction, and the literatures for the methanolysis of NaBH₄ with non-metallic catalysts remain scarce. Boehmite (AlOOH) is an important material which can be utilized industrially as the catalyst or the precursor of the catalysts. In the present work, we report for the first time the application of boehmite and phosphorus modified boehmite as catalysts for hydrogen generation by methanolysis of NaBH₄.

2. Experimental

2.1. Catalyst preparation

Commercial boehmite (Shandong Aluminium Co., Ltd. China) was used as the catalyst precursor. Different weight percentages of phosphorus (0.4, 2.0, 3.9, and 6.4) were doped into boehmite by the wetness impregnation method using phosphoric acid solution as a source of P. The phosphorus-doped boehmite was then calcined in air at 300 °C for 2 h. The as-prepared catalysts are denoted as xP/boehmite, where x indicates the nominal amount of phosphorus present in the samples.

2.2. Catalyst characterization

The specific surface area (Brunauer–Emmett–Teller, BET), pore size (Barrett–Joyner–Halenda, BJH), and pore volume (V_p) of the catalysts were measured by the N₂ adsorption–desorption method at liquid nitrogen temperature (–196 °C) using an ASAP 2010 apparatus (Micromeritics). Fourier transform infrared (FTIR) spectra of the samples were recorded on a TENSOR27 FTIR spectrophotometer (Bruker) in the range of 400–4000 cm^{–1}.

2.3. Catalyst testing

Methanol (99.5% purity, Yantai Sanhe Chemical Reagent Co., Ltd, China) and sodium borohydride (NaBH₄, 98.0% purity, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) were used as received in this work. The kinetic studies were carried out with the same method and apparatus as described in [18]. The conversion of hydrogen volume into number of moles was done by applying the ideal gas law at room temperature (20 °C).

3. Results and discussion

3.1. Textural properties

Fig. 1 provides the N₂ adsorption/desorption isotherms measured at 77 K and pore-size distributions for the unmodified and phosphorus modified boehmite catalysts. As shown in Fig. 1a, the shapes of adsorption/desorption isotherms are those of typical “type IV” isotherms with H3 hysteresis loops according to the IUPAC classification. These significant hysteresis loops at relative pressure P/P₀ above 0.50 indicate the presence of non-uniform slit-like mesopores in the samples [19,20], which is parallel to the observation of pore size distributions in Fig. 1b based on the pore volumes of the BJH (Barrett–Joyner–Halenda) desorption branch in the measurement of nitrogen isotherms. As shown, these pore size distributions are broad and mainly range from 4 to 30 nm.

Table 1 summarizes the textural properties of the boehmite and P/boehmite catalysts employed in this work. As shown in Table 1, the BET surface areas and pore volumes of P/boehmite catalysts decrease with phosphorus loading, implying the progressive blockage of the boehmite pores by phosphorus oxide species. It was also suggested that the decrease in the surface areas and pore volume at higher phosphorus loadings can be ascribed to the formation of polymeric phosphates species, especially at the entrance of pore channels in phosphorus modified H-ZSM-5 catalysts [21].

3.2. FTIR spectra

FTIR spectra of the boehmite and P/boehmite catalysts are shown in Fig. 2. In the case of boehmite, the intensive peak centered at 3478 cm^{–1} and weak band centered at 1630 cm^{–1} are

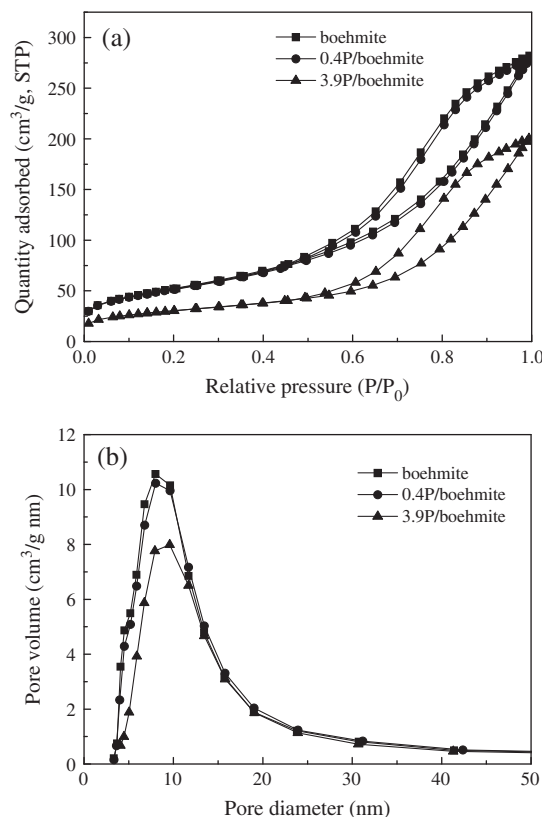


Fig. 1. N₂ adsorption/desorption isotherms (a) and BJH pore size distributions (b) of boehmite and P/boehmite samples.

Download English Version:

<https://daneshyari.com/en/article/6637073>

Download Persian Version:

<https://daneshyari.com/article/6637073>

[Daneshyari.com](https://daneshyari.com)