Available online at www.sciencedirect.com

ScienceDirect

Journal of Natural Gas Chemistry 21(2012)488–494

Journal of Natural Gas Chemistry

www.elsevier.com/locate/jngc

Hydrogen generation from methanolysis of sodium borohydride over Co/Al_2O_3 catalyst

Dongyan Xu[1*], Lin Zhao[1], Ping Dai[2], Shengfu Ji[3]

1. College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, Shandong, China;
2. College of Electromechanical Engineering, Qingdao University of Science and Technology, Qingdao 266061, Shandong, China;
3. State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

[Manuscript received March 8, 2012; revised April 13, 2012]

Abstract

Co/Al_2O_3 catalyst is prepared with an impregnation-chemical reduction method and used to catalyze the methanolysis of sodium borohydride ($NaBH_4$) for hydrogen generation. At solution temperature of 0 °C, the methanolysis reaction can be effectively accelerated using Co/Al_2O_3 catalyst and provide a desirable hydrogen generation rate, which makes it suitable for applications under the circumstance of low environmental temperature. The byproduct of methanolysis reaction is analyzed by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The characterization results indicate that methanol can be easily recovered after methanolysis reaction by hydrolysis of the methanolysis byproduct, $NaB(OCH_3)_4$. The catalytic activity of Co/Al_2O_3 towards $NaBH_4$ methanolysis can be further improved by appropriate calcination treatment. The catalytic methanolysis kinetics and catalyst reusability are also studied over the Co/Al_2O_3 catalyst calcined at the optimized temperature.

Key words

hydrogen generation; sodium borohydride; methanolysis; cobalt

1. Introduction

The commercialization of fuel cell-based portable devices puts forward an urgent demand for an efficient and safe medium for hydrogen storage and generation. Chemical hydrides, particularly $NaBH_4$, have attracted worldwide interest as a source to supply pure hydrogen for fuel cells, because it is non-flammable and non-toxic in nature, with high theoretical hydrogen storage gravimetric capacity as well as one among the very few non-hydrocarbon, non-greenhouse-gas-producing materials [1]. The most advantage of this kind of material is easy to generate hydrogen by hydrolysis of $NaBH_4$ at room temperature using catalysts to control the reaction rate [2−5].

Stoichiometrically, the hydrolysis for 1 mol $NaBH_4$ would require 2 mol H_2O:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \qquad (1)$$

The hydrogen storage density based on this reaction stoichiometry is 10.8 wt%, which meets well the DOE target of 9.0 wt% H_2 (2015). However, the actual hydrolysis of $NaBH_4$ is typically conducted in the aqueous phase where large quantities of excess water are required:

$$NaBH_4 + (2+x)H_2O \rightarrow NaBO_2 \cdot xH_2O + 4H_2 \qquad (2)$$

Two main issues cause the utilization of excess water for the practical application of $NaBH_4$ hydrolysis. The first one is that the thermodynamically stable forms of the byproduct are hydrated [6], which inevitably decreases the gravimetric hydrogen storage capacities from 10.8 to 7.3 and 5.5 wt% for $x = 2$ and 4, respectively. The second one concerns the low solubility of metaborate byproduct (28 g per 100 g H_2O) [7,8]. Therefore, the concentration of $NaBH_4$ at 25 °C should be lower than 16 g per 100 g H_2O to keep the liquid state of $NaBO_2$, leading to a drastic reduction of the gravimetric hydrogen storage capacity from 10.8 to 2.9 wt%. Although many basic continuous-flow systems have been proposed, none of them could overcome the inherent solubility limitations imposed by the byproduct ($NaBO_2$) which prevents $NaBH_4$ concentration from being high enough to meet the DOE target of 9.0 wt% H_2 (2015) [9].

---

[*] Corresponding author. Tel: +86-532-84022506; Fax: +86-532-84022757; E-mail: xdy0156@sina.com.cn

The work was financially supported by the Key Project of Chinese Ministry of Education (No. 208076), Shandong Provincial Natural Science Foundation, China (No. ZR2010EM069) and the Open Project of State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology.

doi:10.1016/S1003-9953(11)60395-2

Recently, an alternative process based on non-aqueous system, in which water was displaced with alcohol, particularly methanol, has been proposed [10−12]. The overall reaction between methanol and $NaBH_4$ can be described as follows:

$$NaBH_4 + 4CH_3OH \rightarrow NaB(OCH_3)_4 + 4H_2 \qquad (3)$$

The gravimetric hydrogen storage capacity of the system of $NaBH_4$-$4CH_3OH$ is 4.9 wt%. Like the hydrolysis system, this methanolysis system is also a potential candidate for portable fuel cells in spite of its low hydrogen storage capacity. Compared to a hydrolysis system, the methanolysis system possesses some favorable advantages. First, the spontaneous methanolysis reaction has been proved to exhibit rapid reaction kinetics at 273 K. The rate constant for the non-catalytic methanolysis reaction at 273 K has been estimated to be greater than that of the hydrolysis reaction [13,14]. Second, unlike the sticky hydrated byproduct of the hydrolysis reaction, the byproduct of methanolysis reaction, $NaB(OCH_3)_4$, does not have the tendency of plugging the reactor. Furthermore, the low freezing point of methanol is a significant advantage for generating hydrogen at subzero temperatures.

From a practical standpoint, it is very important to further improve the kinetics of the methanolysis reaction at low solution temperatures, which is particularly attractive in the applications under cold weather conditions. The present paper reports on the synthesis and characterization of Co/Al_2O_3 catalysts, which has been proved to exhibit high catalytic activity for hydrolysis of $NaBH_4$ in our previous study [15], and on its catalytic performance for methanolysis of $NaBH_4$ at 0 °C.

2. Experimental

2.1. Catalyst preparation

Boehmite (Chalco, 250 m^2/g) was chosen as the support. Analytical reagent grade cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$, 97.0 wt%), and sodium borohydride ($NaBH_4$, 98.0 wt%) from Shanghai Aibi Chemistry Preparation Co, Ltd. were used as received for catalyst preparation. All the catalysts were prepared with an impregnation-chemical reduction method. In a typical preparation procedure, the catalyst was prepared by impregnation of boehmite with an aqueous solution of cobalt nitrate. After drying, Co^{2+} was reduced by dropping a fixed amount of $NaBH_4$ solution into the catalyst precursor. Then, the sample was filtered, washed with distilled water for several times and dried for 10 h at 110 °C. Next, the catalyst was calcined under nitrogen atmosphere at different temperatures of 200 °C, 300 °C, 400 °C, 500 °C, 600 °C, and 700 °C for 2 h, respectively. The nominal Co loading of as-prepared Co/Al_2O_3 catalyst is 10 wt%.

2.2. Catalyst characterization

Powder X-ray diffraction patterns of the catalysts sample were obtained with a D8 ADVANCE X-ray diffractometer using Cu K_α radiation operating at 40 kV and 50 mA. The morphology and composition of the catalyst were investigated by scanning electron microscopy (SEM, JSM 6700F, operating at 8 kV) and energy-dispersive spectroscopy (EDS, INCA Energy). An FT-IR spectrometer (TENSOR27, Bruker) with an on-line cell was used to analyze the recovered byproduct.

2.3. Catalyst testing

Methanol (Laiyang Fine Chemical Factory, 99.5%) was used as received in this work. The kinetic studies were carried out in a 50 mL three-necked round-bottom flask. A thermometer was inserted into the solution to monitor the solution temperature. In a typical H_2 generation experiment, 0.5 g $NaBH_4$ and 0.20 g catalyst were initially put into the flask. The flask was immersed in an ice-water bath to maintain the temperature at 0 °C. The methanolysis reaction was initiated by injecting 10 mL methanol (or water, or the mixture of methanol and water) into the reactor. Because the evolved hydrogen could generate vigorous bubbles in the solution and enhance the contact between the reactant and the catalyst, no further stirring measure was taken during the reaction. A wet gas meter was used to measure the cumulative volume of the generated hydrogen over time.

3. Results and discussion

3.1. Uncatalyzed and catalyzed hydrolysis, methanolysis, and solvolysis (methanol-water mixture) of $NaBH_4$

Figure 1 shows the reaction kinetics of hydrogen evolution through both uncatalyzed and catalyzed hydrolysis, methanolysis, and solvolysis (a methanol-water mixture with different volumetric ratios of methanol to water) of $NaBH_4$ at a solution temperature of 0 °C, respectively. As shown in Figure 1(a), it is evident that the uncatalyzed hydrolysis of $NaBH_4$ is hardly initiated at 0 °C. With the increase of methanol/water ratio, i.e., the concentration of methanol in the mixture, the volume of generated hydrogen increases slowly, indicating that the reaction kinetics of the uncatalyzed methanolysis is faster than that of the uncatalyzed hydrolysis under the same experimental conditions. The effect of methanol/water molar ratio on the reaction kinetics may be related to the properties and structures of water-methanol mixture because the water-water interaction can play an important role in determining some of the properties of water-methanol solution [16]. Kusalik et al. [17] suggested that the water molecules appear most highly localized around the hydroxyl group of methanol solute in the water-rich solution whereas the local structure closely resembles that of pure methanol in the methanol-rich solution. Therefore, it can be speculated that the presence of water may restrain the reactivity of methanol with $NaBH_4$ owing to the interaction between water and methanol. It should be noted that although the hydrogen generation by uncatalyzed methanolysis of $NaBH_4$ in pure methanol solution at 0 °C is feasible, it still needs a relatively long induction period to begin the hydrogen evolution.