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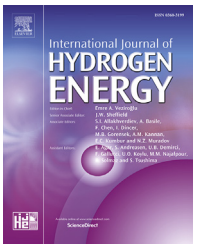

Efficient catalytic properties of SO_4^{2-}/M_xO_y (M = Cu, Co, Fe) catalysts for hydrogen generation by methanolysis of sodium borohydride

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ABSTRACT

The SO_4^{2-}/M_xO_y (M = Cu, Co, Fe) catalysts were prepared and applied to hydrogen production from methanolysis of sodium borohydride for the first time. The morphologies and properties of the as-prepared catalysts were characterized by XRD, BET, FT-IR, TEM and SEM-EDX techniques. Under our experimental conditions, SO_4^{2-}/CuO exhibits much higher catalytic activity than those of SO_4^{2-}/CoO and SO_4^{2-}/Fe_2O_3 catalysts and follows the order of SO_4^{2-}/CuO > SO_4^{2-}/CoO > SO_4^{2-}/Fe_2O_3, which is opposite to order of BET surface area, implying that the methanolysis of sodium borohydride is not a structure-sensitive reaction. It can be inferred that both acidic and metallic sites are responsible for the high catalytic performance of the SO_4^{2-}/M_xO_y catalysts towards $NaBH_4$ methanolysis. In addition, the effects of the concentrations of $NaBH_4$ and methanol, catalyst dosage, and reaction temperature on the hydrogen generation rate have been investigated using SO_4^{2-}/CuO as catalyst. The SO_4^{2-}/CuO-catalyzed methanolysis reaction follows a power law, *i.e.* $r = A \cdot \exp(-13135/RT) \cdot [NaBH_4]^{1.01} \cdot [CH_3OH]^{1.60} \cdot [Catalyst]^{0.52}$. The apparent activation energy was calculated to be 13.13 kJ/mol.

Introduction

In most cases, hydrogen is regarded as attractive energy carrier and preferred fuel to use for the present generation of fuel cells being developed for commercial applications [1–3]. However, the use of hydrogen as a fuel is still largely hindered by the lack of safe and efficient technology for hydrogen generation, storage and transportation. Sodium borohydride ($NaBH_4$, SB) is viewed as one of the most promising chemical hydrides for supplying hydrogen to portable fuel cells due to its high hydrogen content, easily controllable hydrolysis reaction, and nontoxicity [4]. The hydrogen generation can be initiated on demand by adding a catalyst to aqueous solution of SB that was stabilized with bases to inhibit the spontaneous hydrolysis reaction during the period of storage. Therefore, many efforts have been dedicated to the hydrolysis of SB with special attention to the catalyst exploration during the past decade [5].

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Recently, alcohols as alternative solvolytic agents to water have gradually attracted attention because the alcoholysis reaction can eliminate the freezing problem associated with $NaBH_4$–H_2O reaction system operated at subzero temperatures. Until now, methanol [6], ethanol [7], glycol [8] and glycerol [9] have been mainly investigated for hydrogen generation from SB alcoholysis. Based on these research results, the spontaneous reaction kinetics of hydrolysis and alcoholysis can be concluded to follow the order of methanolysis > glycolysis > glycerolysis > hydrolysis > ethanolysis.

As confirmed, methanolysis of SB (Eq. (1)) exhibits the most rapid reaction kinetics in the absence of catalyst at ambient temperature. The reaction byproduct of SB methanolysis, sodium tetramethoxyborate ($NaB(OCH_3)_4$), does not have a tendency toward plugging the reactor and can be regenerated easily to methanol through hydrolysis (Eq. (2)) [10,11].

$$NaBH_4 + 4CH_3OH \rightarrow NaB(OCH_3)_4 + 4H_2 \quad (1)$$

$$NaB(OCH_3)_4 + 2H_2O \rightarrow NaBO_2 + 4CH_3OH \quad (2)$$

Until now, both metal-based and non-metal-based catalysts have been explored to improve the kinetics of SB methanolysis. Like in the hydrolysis system, the supported metal catalysts have been demonstrated to be active in the methanolysis reaction. Fe–B supported on porous Ni foam with a relative low activation energy of 7.02 kJ/mol in the SB methanolysis has been reported by Ocon et al. [11]. Yan et al. [12] reported that the Ni_2P/SiO_2 prepared by solution-phase method shows a unique high activity for SB methanolysis compared with that by conventional temperature-programmed reduction or sol-gel method. Surprisingly, it was found that the non-noble Co–TiO_2 catalyst shows higher catalytic activity than that of noble Ru–TiO_2 in catalyzed methanolysis of SB at 20 °C [13].

Additionally, the non-metal catalysts have also received much attention due to good recoverable performance. Sahiner et al. have devoted a great deal of effort to develop a series of metal-free catalysts including halloysite nanotubes [14], polymeric microgels [15], natural microgranular cellulose [16], polymeric ionic liquid microgel [17], and tested their activities toward the methanolysis reaction. SiO_2 particles treated with various acids were found to exhibit excellent stability in the methanolysis of SB and approximately 80% of the high catalytic activity of the SiO_2–HCl nanoparticles is preserved after 10th cycles to use [18].

SO_4^{2-}/M_xO_y has been effectively demonstrated to catalyze organic synthesis as a group of solid catalysts [19,20]. To our best knowledge, SO_4^{2-}/M_xO_y has not been utilized for hydrogen generation by the controllable SB methanolysis so far. In this paper, a series of SO_4^{2-}/M_xO_y (M = Cu, Co, Fe) catalysts were prepared by precipitation method and applied to hydrogen generation from the catalytic methanolysis of SB. The obtained powders were characterized by XRD, BET, FTIR, SEM-EDX and TEM techniques. An optimal SO_4^{2-}/CuO catalyst was used to evaluate the effects of reaction temperature, reactant concentrations and catalyst dosage on the hydrogen generation rate. Moreover, the kinetics of the methanolysis reaction including activation energy and kinetic equation under the current conditions were also analyzed.

Experimental

Materials

Cupric nitrate ($Cu(NO_3)_2 \cdot 3H_2O$), 99.0 wt%), was purchased from Tianjin Dengke Chemical Reagent Co., Ltd. Iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), 98.5 wt%) was purchased from Sinopharm Chemical Reagent Co., Ltd. Cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$), 99.0 wt%) was purchased from Tianjin Bodi Chemical Reagent Co., Ltd. $NaBH_4$ (97.0 wt%) was used as hydrogen source and purchased from Chengdu Kelong Chemical Reagent Co., Ltd. CH_3OH (99.5 wt%) was used as solvolytic agent and purchased from Tianjin Fuyu Fine Chemical Co., Ltd. All reagents were used as received.

Catalyst preparation

The SO_4^{2-}/M_xO_y (M = Cu, Co, Fe) catalysts were prepared by precipitation method. Appropriate amount of metal precursor was weighted and dissolved in 50 mL deionized water in a flask, after 30 min of ultrasonic oscillation, ammonium hydroxide ($NH_3 \cdot H_2O$, 25–28 wt%) was used to obtain an appropriate pH around 9. The precipitates were filtered and rinsed thoroughly with deionized water after an aging process, and then dried at 110 °C. The obtained powders were then dipped with configured sulfuric acid (H_2SO_4, 1 mol/L) at 1:1.44 ratio of metal to sulphur after exhaustive grinding and drying. The achieved sediments were then dried at 110 °C for 6 h and calcined at 550 °C for 3 h.

Characterizations

The structures of the powdery catalysts were characterized by powder X-ray diffraction (XRD, D/max-2500/PC, Rigaku Corporation, Japan) operated at 40 KV with CuKα radiation. Brunauer-Emmett-Teller (BET) specific surface area and pore size were determined from N_2 adsorption at 77 K using a Micromeritics ASAP 2020 instrument. Fourier transform infrared spectroscope (FT-IR) experiments were performed by BRUKER-TENSOR 27 FTIR spectrometer (Germany) using KBr pellet with a scan range of 400–4000 cm^{-1}. The catalyst morphologies were investigated by transmission electron microscopy (TEM, JEM-1200EX, JEOL) at an accelerating voltage of 100 kV. The morphology analysis and chemical composition of the catalysts were obtained by scanning electron microscope (SEM, JSM-6700F, JEOL) and energy dispersive X-ray (EDX) unit fixed in the SEM equipment, respectively.

Hydrogen generation measurement

The catalytic methanolysis of SB was conducted in a batch system equipped with a thermometer. For a typical test, 5 mL of CH_3OH and 10 mg of catalyst were introduced into a three-neck flask which was immersed into a thermostatic water bath to maintain a constant ambient temperature at (20 ± 0.3) °C, followed by adding 100 mg of SB solid particles to initiate the reaction. An inverted, water-filled gas burette in a water-filled vessel was used to monitor the volume of the evolved H_2. Series of experiments were carried out to study the effects

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