Journal of Power Sources 224 (2013) 304–311

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

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

Evaluation of a cobalt–molybdenum–boron catalyst for hydrogen generation of alkaline sodium borohydride solution–aluminum powder system

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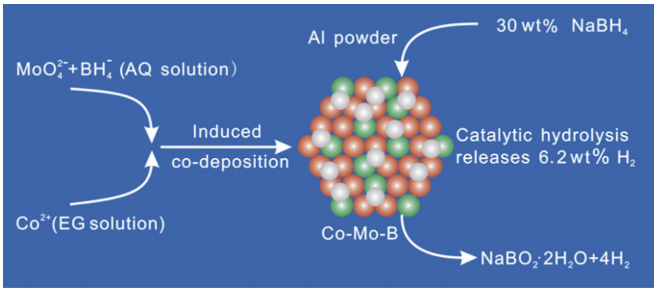
HIGHLIGHTS

- ► A newly synthesized Co–Mo–B catalyst is reported.
- ► The catalyst exhibits remarkably catalytic activity to hydrolysis reaction of $NaBH_4$.
- ► A hydrogen generation system is composed of $NaBH_4$ solution, catalyst and Al powder.
- ► This system can yield >6 wt% H_2 with fast kinetics and high fuel conversion.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 July 2012
Received in revised form
25 September 2012
Accepted 27 September 2012
Available online 11 October 2012

Keywords:
Hydrogen generation
Sodium borohydride
Cobalt–molybdenum–boron catalyst
Aluminum powder

ABSTRACT

Catalyst study is a central issue in the development of sodium borohydride ($NaBH_4$)-based hydrogen generation systems. Here, we report the preparation, characterization and utilization of a novel cobalt–molybdenum–boron (Co–Mo–B) catalyst. Our study found that the Co–Mo–B catalyst prepared by chemical reduction method using an ethylene glycol solution of cobalt chloride exhibits remarkably higher catalytic activity than the Co–B and Co–Mo–B catalysts prepared in aqueous solution. On the basis of the phase, microstructure and elemental chemical state analyses, the mechanistic reasons for the improved performance of the newly prepared Co–Mo–B catalyst were discussed. Our study demonstrated that the combined usage of concentrated $NaBH_4$ solution, Co–Mo–B catalyst and a small amount of Al powder constitutes a high-performance hydrogen generation system, which can yield >6 wt% hydrogen with fast kinetics and high fuel conversion.

1. Introduction

The widespread implementation of hydrogen fuel cell technology requires advanced hydrogen storage materials that can store and deliver large amounts of hydrogen at moderate temperatures with fast kinetics. Extensive studies on interstitial metal hydrides and complex hydrides have led to no viable material that can reversibly store over 6 wt% hydrogen at relevant conditions to the practical operation of proton exchange membrane fuel cell [1]. Considerable recent efforts were therefore directed toward the development of H-rich chemical hydrides as potential hydrogen carriers for vehicular and portable applications [2–7].

$$NaBH_4 + (2+x)H_2O \xrightarrow{\text{Catalyst}} NaBO_2 \cdot xH_2O + 4H_2\uparrow + 210\ \text{kJ} \qquad (1)$$

Sodium borohydride ($NaBH_4$) is a representative chemical hydride [3–6], which reacts with water to generate H_2 and sodium

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http://dx.doi.org/10.1016/j.jpowsour.2012.09.106

metaborate ($NaBO_2$) following Eqn. (1), where x denotes the number of water of hydration. In the past decade, significant progress has been made in developing $NaBH_4$-based hydrogen generation (HG) system. A number of noble or non-noble transition metals/alloys/salts [8–30] have been identified to be catalytically active toward the hydrolysis reaction of $NaBH_4$. Concurrently, a series of prototype HG generators/systems have been demonstrated that possess power levels ranging from a few watts to kilowatts [9–11,17]. In addition, evolutionary advances have been achieved in regeneration chemistry [31,32], which may potentially allow efficient recycle of spent fuel back to borohydride. But in spite of these technological advances, $NaBH_4$-based HG systems are still limited for vehicular applications [33,34]. This is primarily due to the low effective hydrogen capacity of the system and the prohibitively high hydrogen cost. The former originates from the solubility limitation of $NaBO_2$ in aqueous solution [34,35] and the presence of "dead weight" water of hydration. The latter should be essentially ascribed to the lack of energy-efficient and cost-effective regeneration route [33].

The negative judgment made by US Department of Energy in 2007 [33] frustrated the efforts in developing $NaBH_4$ as a transportation fuel, but it did not extinguish the research interest in the $NaBH_4$-based HG system [34]. Recently, several strategies have been employed to address the key problems of the $NaBH_4$-based HG system. Use of solid $NaBH_4$ to react with water can alleviate the solubility limitation [12,15,36,37], yielding higher hydrogen capacity than the conventional solution-based hydrolysis systems. Combined usage of $NaBH_4$ and aluminum (Al) can effectively improve the HG performance and meanwhile, reduce the hydrogen cost [38–40]. Quite recently, our study further found that using highly active catalyst makes it possible to obtain high hydrogen capacity from the aqueous solution containing high concentration of $NaBH_4$. Since the hydrolysis reaction of $NaBH_4$ is highly exothermic, the rapid proceeding of the hydrolysis reaction will cause rapid temperature rising of the fuel solution, and thereby increasing the solubility of $NaBO_2$ in the aqueous solution.

In the present study, we employed a combination of catalysis and dual-fuel strategies to improve the HG performance of the $NaBH_4$-based system. Our study found that the Co–Mo–B catalyst prepared by a chemical reduction method using an ethylene glycol solution of cobalt chloride ($CoCl_2$) is highly active toward the hydrolysis reaction of $NaBH_4$. Even for a concentrated fuel solution containing 30 wt% $NaBH_4$, the usage of Co–Mo–B catalyst enabled a 100% fuel conversion. When the Co–Mo–B catalyst was used in combination with a small amount of Al powder, the constituted system can rapidly release 6.2 wt% hydrogen within around 5 min. The favorable combination of high hydrogen capacity, fast HG kinetics, high fuel conversion and safe fuel storability, makes the newly developed system very promising for portable hydrogen storage applications.

2. Experimental

2.1. Chemicals and preparation of the catalysts

$NaBH_4$ (96% purity), sodium hydroxide (NaOH, 96%), cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, 99%) sodium molybdate dihydrated ($Na_2MoO_4 \cdot 2H_2O$, 99%) and ethylene glycol (99%) were purchased from Sinopharm. Al powder (−325 mesh, 99%), Co powder (99.9%), Mo powder (99.9%), CoO powder (95%), MoO_2 powder (99.5%) and MoO_3 powder (99.95%) were purchased from Alfa Aesar. All reagents were used as received. Deionized water was used in preparation of all the aqueous solutions.

The Co–Mo–B catalysts were prepared by chemical reduction method using two solutions: the aqueous or ethylene glycol solution A containing 0.25 M $CoCl_2$; the aqueous solution B containing 1 M $NaBH_4$, 0.25 M NaOH and 0–0.05 M Na_2MoO_4. Here, the concentration of Na_2MoO_4 was varied to adjust the Mo content of the catalyst. The addition of Na_2MoO_4 in solution B instead of solution A was to minimize the formation of MoO_3 precipitate via the reaction between Na_2MoO_4 and $CoCl_2$. In a typical run, 50 mL of solution A was first added in a beaker, followed by dropwise addition of equal volume of solution B using a pressure-equalizing dropping funnel. The solution was kept undisturbed under magnetic stirring until the gas bubbling ceased. After the reaction completed, the black precipitate was magnetically separated from the solution, and then washed thoroughly with deionized water and ethanol to remove the residual Na^+, BH_4^-, BO_2^-, MoO_4^{2-} and Cl^- ions. For comparison, the Co–B catalyst was prepared following the same procedure. The catalyst samples were finally dried at 40 °C under dynamic vacuum for 48 h. The chemical reactions involved in the catalyst preparation process can be described by Eqns. (2)–(5).

$$BH_4^- + 2Co^{2+} + 4OH^- \rightarrow BO_2^- + 2Co\downarrow + 2H_2\uparrow + 2H_2O \quad (2)$$

$$2BH_4^- + 2H_2O \rightarrow 2B\downarrow + 2OH^- + 5H_2\uparrow \quad (3)$$

$$3BH_4^- + 2MoO_4^{2-} + 2H_2O \overset{Co}{\rightarrow} 3BO_2^- + 2Mo\downarrow + 6H_2\uparrow + 4OH^- \quad (4)$$

$$BH_4^- + 2H_2O \rightarrow BO_2^- + 4H_2\uparrow \quad (5)$$

2.2. Characterization and HG performance testing

The catalyst samples were characterized by powder X-ray diffraction (XRD, Rigaku D/MAX-2500, Cu $K\alpha$ radiation), transmission electron microscopy (TEM, FEI Tecnai F20) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Al $K\alpha$ X-ray source). In preparation of the TEM sample, the catalyst powder was first dispersed in ethanol solution by ultrasound and then deposited on a holey carbon film supported on a copper grid. In the XPS measurements, high-resolution scans of elemental lines were recorded at 50 eV pass energy of the analyzer. All the binding energies were calibrated using the C 1s peak (at 284.6 eV) of the adventitious carbon as an internal standard. The curve fitting was performed using XPS PEAK 4.1 software. After being degassing at 463 K for 12 h, the catalyst samples were measured by N_2 adsorption at 77 K using the Brunauer–Emmett–Teller (BET) method in a Micromeritics ASAP 2010 apparatus to determine the specific surface areas (SSA). Element analyses of the catalyst samples were conducted in an inductively coupled plasma-atomic emission spectrometry (ICP-AES, Iris Intrepid). The magnetization measurements were made in a Quantum Design MPMS-7DC magnetometer under a magnetic field of 0–10,000 Oe at 298 K.

The HG performance testing was conducted in a 250 mL three-neck flask. Unless specified otherwise, the flask was placed in a thermostat that was equipped with a water circulating system to maintain the reaction temperature, typically within ±0.5 °C. In a typical measurement run, the $NaBH_4$ aqueous solution was preheated and held at the designated temperature, and then the powdery catalyst attached on a magnetic stirring bar was dropped into the solution to initiate the hydrolysis reaction. In the case of the system using Al powder as additional solid fuel, Al powder was added together with the catalyst. The generated hydrogen gas passed through a trap/heat exchanger to cool to room temperature followed by contacting with a silica drier to remove water vapor.