Chemical Engineering Journal 210 (2012) 316–324

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

CoB/open-CNTs catalysts for hydrogen generation from alkaline $NaBH_4$ solution

Fang Li, Qiming Li, Hern Kim *

Energy and Environment Fusion Technology Center, Department of Environmental Engineering and Energy, Myongji University, Yongin, Kyonggi-do 449-728, Republic of Korea

HIGHLIGHTS

- Open multi-walled carbon nanotubes were obtained via oxidation method.
- CoB catalysts were effectively loaded in o-CNTs and c-CNTs supports.
- CoB/CNTs possess higher CoB loading than CoB/c-CNTs.
- CoB/o-CNTs exhibit higher activity than CoB/c-CNTs in NaBH4 hydrolysis.
- Activation energy of CoB/o-CNTs is much lower than that of CoB/c-CNTs.

ARTICLE INFO

Article history:
Received 21 June 2012
Received in revised form 23 August 2012
Accepted 30 August 2012
Available online 10 September 2012

Keywords:
Hydrogen generation
Sodium borohydride
o-CNTs
CoB catalyst

ABSTRACT

CoB catalysts supported on carbon nanotubes with open tips (o-CNTs) were successfully prepared and used in hydrogen production from $NaBH_4$ hydrolysis. The properties and morphologies of o-CNTs supports and CoB/o-CNTs catalysts were characterized by FT-IR, XRD, SEM–EDX and TEM, which showed that o-CNTs possess different organic functional groups and many open tips and CoB can be effectively loaded. Compared with CoB catalysts supported on carbon nanotubes with closed tips (c-CNTs), CoB/o-CNTs exhibit significantly higher hydrogen production rate of up to 3041 ml min^{-1} g^{-1} under the same conditions. In the experiment, the effect of CoB loading, catalyst supports, and operation temperature on hydrogen production rate was investigated in detail, which demonstrated that o-CNTs possess higher CoB loading than c-CNTs. It was shown that the apparent activation energy of CoB/o-CNTs is 37.63 kJ mol^{-1}, which is obviously lower than 44.43 kJ mol^{-1} of CoB/c-CNTs.

1. Introduction

In recent years, the increasing of energy demand has become a critical issue with the rapid economic development around the world. Highly efficient hydrogen production [1,2], hydrogen separation, and purification technologies [3–5] have attracted world-wild attention due to hydrogen is a potential material to meet the increasing demand for efficient and clean energy. Many types of chemical hydride have been demonstrated to be used as hydrogen generation materials such as lithium hydride (LiH) [6], sodium aluminum hydrogen ($NaAlH_4$) [7], lithium borohydride ($LiBH_4$) [8], and sodium borohydride ($NaBH_4$) [9]. Among them, $NaBH_4$ is more favorable due to its advantages of high hydrogen density (10.8 wt.%) and strong stability in alkaline solution [10]. The hydrolysis reaction of $NaBH_4$ is exothermic, and the reaction equation is given as the following equation:

$$NaBH_4 + 2H_2O = NaBO_2 + 4H_2 \quad \Delta H = -300\ \text{kJ/mol} \tag{1}$$

In order to enhance the hydrogen generation rate, more and more efforts have been made on the research of the catalysts for the hydrolysis of $NaBH_4$, for example, some noble metals such as platinum [11] and ruthenium [12] had been used as the catalysts and showed high catalytic activity in $NaBH_4$ hydrolysis, but they have many limitations in practical application such as high cost and relative scarcity. Therefore, some non-precious metal-based catalysts are more expected to be practical candidates in hydrogen generation from aqueous $NaBH_4$. Among them, CoB powder has been most studied as the catalysts for $NaBH_4$ hydrolysis. Amorphous CoB catalyst [13] was synthesized, which exhibited the hydrogen generation rate of 875 ml min^{-1} g^{-1} [14]. The hydrogen generation rate of 1640 ml min^{-1} g^{-1} can be achieved using CoB/Ni-foam catalyst. In our group, novel composites consisting of CoB catalyst and $NaBH_4$ implantation in polymers were prepared for portable hydrogen production, and a hydrogen production rate of 750 ml min^{-1} g^{-1} was reached when simply putting the composites into pure water [15]. Although unsupported CoB is very active for the hydrolysis of sodium borohydride, it is easy to aggregate and difficult to be recycled. Therefore, supported CoB catalyst is more feasible in practical application. In the published papers, some researchers reported that amorphous CoB/SiO_2 [16],

* Corresponding author. Tel.: +82 31 330 6688; fax: +82 31 336 6336.
E-mail address: hernkim@mju.ac.kr (H. Kim).

1385-8947/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cej.2012.08.102