INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2017) 1–5

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Short Communication

Co_3O_4 hollow fiber: An efficient catalyst precursor for hydrolysis of sodium borohydride to generate hydrogen

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ARTICLE INFO

Article history:
Received 9 October 2017
Received in revised form
14 November 2017
Accepted 17 November 2017
Available online xxx

Keywords:
Hydrogen generation
Sodium borohydride
Co_3O_4 hollow fiber
Combustion method
Template

ABSTRACT

Sodium borohydride ($NaBH_4$) is one of promising hydrogen storage materials for practical application, and the development of high-efficient catalysts for $NaBH_4$ hydrolysis to generate hydrogen is of critical importance. In this communication, Co_3O_4 hollow fiber composed of nanoparticles array was served as catalyst precursor and facilely prepared by combustion method with template of the absorbent cotton. For characterization, FE-SEM, HRTEM, EDS, XRD, FTIR and ICP were applied, respectively, and typical water-displacement method was performed to evaluate the catalytic activity. Using a solution composed of 10 wt% $NaBH_4$ and 2 wt% NaOH, hydrogen generation rate was up to 11.12 L min^{-1} g^{-1} (25 °C), which is much higher than that of the commercial cobalt oxides and similar catalyst precursors reported in literature.

Introduction

As one kind of promising hydrogen storage materials, sodium borohydride ($NaBH_4$) provides high storage density up to 10.6 wt%, which is much higher than the requirements of US Department of Energy for board hydrogen storage systems in light-duty vehicles. Hydrogen generation technology based on the catalytic hydrolysis of $NaBH_4$ attracts increasing attention because of its advantages including simple process, easy control, no CO_x impurities and so on [1,2].

In general, alkaline $NaBH_4$ solution acted as liquid fuel can release hydrogen using professional catalysts. Among these, cobalt-based catalysts are low-cost and popular, which have been reviewed by Demirci et al. [3] and Brack et al. [4]. Cobalt oxides, an efficient catalyst precursor, can be reduced by $NaBH_4$, and the resulting active Co_xB compounds will further catalyze the hydrolysis of $NaBH_4$ to generate hydrogen [5]. Krishnan et al. [6] found that the catalytic activity of Co_3O_4 nanoparticles synthesized by thermal decomposition method was higher than that of some noble metal catalysts like Pt/C, Ru/C and PtRu/C, etc. As reported by Groven et al. [7], Co_3O_4

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https://doi.org/10.1016/j.ijhydene.2017.11.113

nanofoam created by solution combustion process presented higher activity than commercial Co_3O_4 and metallic Co powders. In addition, hydrothermal method was also applied by Lu and co-workers for the preparation of CoO nanocrystals as catalyst precursor [8].

As we know that the aggregation phenomenon of nanoparticle catalysts is regarded as one of the major problems for their practical utilization. To solve that and provide enough active sites, supported and self-supported nano-array structures are preferable and effective [9–14]. For instance, Sun et al. [9] developed 3D hierarchical CuO/Co_3O_4 core-shell nanowires array on copper foam for $NaBH_4$ hydrolysis, and the catalyst precursor exhibited a maximum hydrogen generation rate of 6.16 L min^{-1} g^{-1} (25 °C), good durability and favorable reusability.

In general, fiber-like materials have high specific surface area and are relatively convenient for filtration and recycling. Herein, Co_3O_4 hollow fiber composed of nanoparticle array was facilely prepared by combustion method with the template of absorbent cotton, and corresponding catalytic activity for $NaBH_4$ hydrolysis was contrasted with commercial cobalt oxides and literature results.

Experimental

All chemical reagents purchased from Sinopharm were of analytical grade and used as received. Briefly, 1.00 g common absorbent cotton was impregnated into 0.10 mol L^{-1} cobalt acetate solution. After repeated impregnation and drying treatments, the loading of cobalt acetate on the absorbent cotton was about 0.85 g. As shown in Fig. 1, the resulting purple sample was transferred into watch glass, following with igniting and complete combustion. Finally, loose and black product was thoroughly cleaned with deionized water and dried at 80 °C overnight.

Fig. 1 – Combustion process of the absorbent cotton impregnated with cobalt acetate.

To evaluate the activity of catalyst precursor, 0.0100 g product was added into 3.0 mL reaction solution consisting of 10 wt% $NaBH_4$ and 2 wt% NaOH. In a typical measurement, water-displacement method was performed to record the hydrogen generation volume as a function of reaction time, as described elsewhere [14]. Commercial chemical reagents of CoO, Co_2O_3 and Co_3O_4 (AR, Shanghai Macklin Biochemical Co., Ltd, China) were used as contrast samples. For material characterization, field-emission scanning electron microscopy (FE-SEM, ZEISS SUPRA 55), high-resolution transmission electron microscopy (HRTEM, FEI Tecnai G2 F20), energy

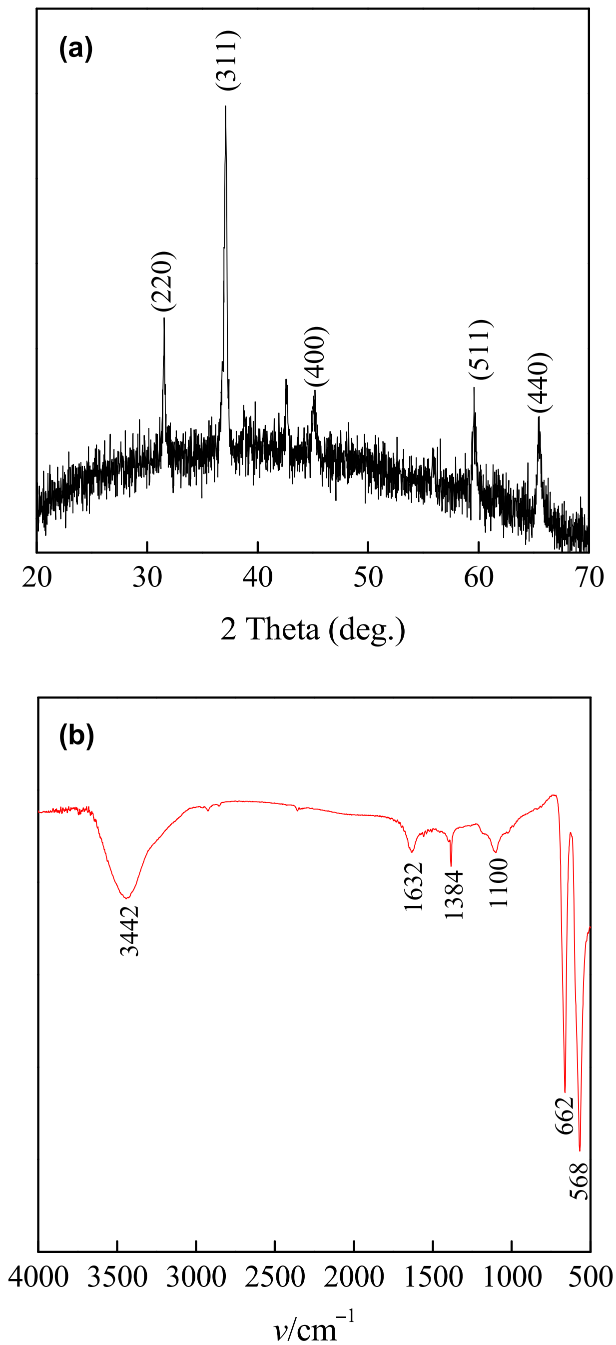

Fig. 2 – XRD and FTIR patterns of the resulting product.

Please cite this article in press as: Wei L, et al., Co_3O_4 hollow fiber: An efficient catalyst precursor for hydrolysis of sodium borohydride to generate hydrogen, International Journal of Hydrogen Energy (2017), https://doi.org/10.1016/j.ijhydene.2017.11.113