



ELSEVIER

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

journal homepage: [www.elsevier.com/locate/hydro](http://www.elsevier.com/locate/hydro)

# In situ facile synthesis of Rh nanoparticles supported on carbon nanotubes as highly active catalysts for H<sub>2</sub> generation from NH<sub>3</sub>BH<sub>3</sub> hydrolysis

Qilu Yao, Zhang-Hui Lu\*, Yushuai Jia, Xiangshu Chen\*, Xin Liu

Jiangxi Inorganic Membrane Materials Engineering Research Centre, College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang, 330022, China

## ARTICLE INFO

### Article history:

Received 22 September 2014

Received in revised form

27 November 2014

Accepted 14 December 2014

Available online 7 January 2015

### Keywords:

Hydrogen generation

Ammonia borane

Hydrolysis

Carbon nanotubes

Rhodium nanoparticles

## ABSTRACT

In this work, carbon nanotubes (CNTs) supported rhodium nanoparticles (Rh NPs) (Rh(0)/CNTs) have been successfully prepared via a very simple in situ method and used as the catalysts for hydrogen generation from the hydrolysis of ammonia borane (AB, NH<sub>3</sub>BH<sub>3</sub>) under ambient atmosphere at room temperature. The as-synthesized nanocatalysts were characterized by XRD, SEM, TEM, EDX, ICP, and XPS measurements. The characterized results revealed that ultrafine Rh NPs of about 1.1–3.4 nm were well-dispersed on CNTs. Compared with free Rh(0) NPs and Rh(0)/activated charcoal, the Rh(0)/CNTs showed higher catalytic activity for the hydrolysis of NH<sub>3</sub>BH<sub>3</sub> with a total turnover frequency (TOF) value up to 706 mol H<sub>2</sub> (mol Rh min)<sup>-1</sup>, which was among the highest of all the heterogeneous catalysts ever reported for the same reaction. The recyclability tests revealed that the Rh(0)/CNTs are still active after five runs of hydrolysis of NH<sub>3</sub>BH<sub>3</sub> providing 100% conversion and retaining 61% of their initial catalytic activity (TOF = 431 mol H<sub>2</sub> (mol Rh min)<sup>-1</sup>). In addition, the activation energy for the hydrolysis of NH<sub>3</sub>BH<sub>3</sub> catalyzed by Rh(0)/CNTs was measured to be 32 ± 1 kJ/mol, which was lower than most of the values reported for other catalysts.

Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

## Introduction

Hydrogen, owing to its clean burning nature, high calorific value, and environmentally benign, has been considered as one of the new energy carriers for heating, transportation, mechanical power and electricity generation [1]. Development of safe and efficient hydrogen storage materials is one of the major problems that must be overcome on the way to a hydrogen-powered society. In the last few decades, different

storage solutions have been developed, such as metal hydrides [2], sorbent materials [3], and chemical hydride systems [4]. Among the various kinds of solid hydrogen storage materials, ammonia borane (AB, NH<sub>3</sub>BH<sub>3</sub>) has recently been attracted considerable attention as a potential chemical hydrogen storage material due to its high hydrogen content (19.6 wt%), low molecular weight, and environmentally friendly nature [5–9]. There are several methods for the release of hydrogen from NH<sub>3</sub>BH<sub>3</sub>, which can be broadly divided into two categories, namely solid thermolysis [10,11]

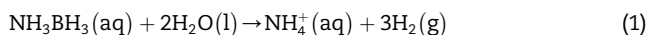
\* Corresponding authors.

E-mail addresses: [luzh@jxnu.edu.cn](mailto:luzh@jxnu.edu.cn) (Z.-H. Lu), [cxs66cn@jxnu.edu.cn](mailto:cxs66cn@jxnu.edu.cn) (X. Chen).

<http://dx.doi.org/10.1016/j.ijhydene.2014.12.047>

0360-3199/Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

and solvolysis (hydrolysis or methanolysis) [12–16]. However, thermal dehydrogenation process requires high temperature and power consumption. In the presence of a suitable catalyst, catalytic hydrolysis of  $\text{NH}_3\text{BH}_3$  can release as much as 3 mol of  $\text{H}_2$  per mol  $\text{NH}_3\text{BH}_3$  under ambient atmosphere at room temperature (Eq. (1)). Thus, the catalysts are the predominant factor for the hydrolytic dehydrogenation of  $\text{NH}_3\text{BH}_3$ .



So far, lots of catalysts have been tested for  $\text{NH}_3\text{BH}_3$  hydrolysis, including noble metals Rh [17–23], Pt [17,18,24–26], Au [13,18,27], Pd [18,28–30], Ru [18,31–35] and non-noble metals Fe [36–38], Co [39–41], Ni [42–45], Cu [46–49]. However, the development of catalysts with high performance is still remained a considerable challenge [7–9]. Many efforts were performed in the attempt to obtain efficient and economical accessible non-noble metal-based catalysts, but the definition of the optimal compromise between costs and catalytic performances are still important challenges to overcome. Although noble metal NPs, such as Rh, Ru, and Pt, have limited resources and high price tags, they show higher catalytic activity than that of non-noble metal nanocatalysts even at a very low metal concentration [23–25,32]. Therefore, the use of noble metal NPs as catalysts for the hydrolysis of  $\text{NH}_3\text{BH}_3$  still has great significance. However, metal NPs in nano-size are easily aggregated into clumps during the catalytic processes, resulting in the heavy loss of catalytic active and even inactivation [23]. The prevention NPs agglomeration is a challenging task in the area of nanocatalysts. Carbon nanotubes can be considered as cylindrical hollow microcrystals of graphite. In recent years, CNTs has attracted tremendous attention as a catalyst support material for nanoscale metal catalysts owing to their high specific surface area, good thermal and chemical stability, and superior electrical conductivity [24,32,50–52]. In particular, CNTs can offer beneficial interactions between metal NPs and support which substantially enhance the catalytic activity.

In this work, for the first time, we reported a facile in situ one-step approach for the synthesis of CNTs supported Rh NPs (Rh(0)/CNTs) as the catalysts for catalytic hydrolysis of  $\text{NH}_3\text{BH}_3$  under ambient atmosphere at room temperature. In comparison to free Rh(0) NPs and Rh(0)/activated charcoal, the as-synthesized Rh(0)/CNTs nanocatalysts showed a better catalytic activity for the hydrolysis of  $\text{NH}_3\text{BH}_3$  with a total turnover frequency (TOF) of 706 mol  $\text{H}_2$  (mol Rh min) $^{-1}$ , which was among the highest of all the heterogeneous catalysts ever reported for the same reaction. Additionally, the kinetics of  $\text{NH}_3\text{BH}_3$  hydrolysis catalyzed by Rh(0)/CNTs NPs were further investigated under different catalyst concentrations, substrate concentrations, and reaction temperatures.

## Experimental

### Materials

Carbon nanotubes (inner diameter 4–8 nm and outer diameter 10–20 nm) were purchased from Chengdu Organic Chemicals. Ammonia borane ( $\text{NH}_3\text{BH}_3$ , AB, 90%), rhodium (III) chloride

trihydrate ( $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ , 38–42 wt% Rh basis) and sodium boron hydride ( $\text{NaBH}_4$ , 99%) were purchased from Aldrich. Ultrapure water with the specific resistance of 18.3  $\text{M}\Omega$  cm was obtained by reversed osmosis followed by ion exchange and filtration.

### Characterization

Powder X-ray diffraction (XRD) studies were performed on a Rigaku RINT-2200 X-ray diffractometer with a  $\text{Cu K}\alpha$  source (40 kV, 20 mA). The morphologies and sizes of the samples were observed by using a transmission electron microscope (TEM, JEM-2010) equipped with an energy dispersive X-ray detector (EDX) and selected area electron diffraction (SAED) for elemental analysis. The TEM samples were prepared by depositing one or two droplets of the nanoparticle suspensions on to the copper grids. Scanning electron microscope (SEM) images were carried out on a SU8020 cold field emission instrument. XPS spectra were measured on ESCALABMKLL X-ray photoelectron using an  $\text{Al K}\alpha$  source. The contents of Rh loading on the CNTs and leaching into the solution were analyzed by inductively couple plasma mass spectroscopy (ICP-MS, Agilent 7500CE). Fourier transform infrared (FTIR) spectra were measured by using a Thermo Nicolet 870 instrument using KBr discs in the 500–4000  $\text{cm}^{-1}$  region.

### In situ synthesis of CNTs supported Rh NPs and their catalytic activities toward the hydrolysis of $\text{NH}_3\text{BH}_3$

Carbon nanotubes were refluxed in a mixture of  $\text{HNO}_3$  (36 mL) and  $\text{H}_2\text{SO}_4$  (54 mL) at 80 °C for 6 h. The mixture was filtered and washed with distilled water until pH of the filtrate reached the value 7, followed by drying at 120 °C for 12 h in the oven. The functionalized CNTs (10 mg) were stirred in a two-necked round-bottom flask with 10 mL aqueous solution of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  (0.5 mM). The mixture was stirred for 12 h at room temperature. The catalytic reactions were started when  $\text{NH}_3\text{BH}_3$  (68.6 mg, 2 mmol) was added to the flask with vigorous stirring, and the evolution of gas was monitored using the gas burette. The reactions were carried out at room temperature under ambient atmosphere.

For comparison, activated charcoal supported Rh(0), free Rh(0) NPs, and CNTs toward the hydrolytic dehydrogenation of  $\text{NH}_3\text{BH}_3$  were synthesized by using the similar method.

### Kinetics of hydrolytic dehydrogenation of $\text{NH}_3\text{BH}_3$ catalyzed by Rh(0)/CNTs

In order to establish the rate law and obtain the activation parameters for the hydrolytic dehydrogenation of  $\text{NH}_3\text{BH}_3$  catalyzed by Rh(0)/CNTs, three different sets of experiments were performed. In the first set of experiments, the concentration of  $\text{NH}_3\text{BH}_3$  was held constant at 200 mM and the amount of Rh(0)/CNTs catalyst was varied in the range of 0.125, 0.25, 0.5, 1.0, and 1.5 mM, respectively, at 298 K. In the second set of experiments, the amount of Rh(0)/CNTs catalyst was kept constant at 0.5 mM while  $\text{NH}_3\text{BH}_3$  concentration was varied in the range of 100, 200, 300, 400, 500, 600, and 700 mM, respectively, at 298 K. Finally, the catalytic dehydrogenation of  $\text{NH}_3\text{BH}_3$  was performed at various temperatures in the range of 293–323 K in order to get the activation energy by keeping

Download English Version:

<https://daneshyari.com/en/article/7716348>

Download Persian Version:

<https://daneshyari.com/article/7716348>

[Daneshyari.com](https://daneshyari.com)