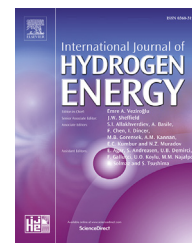




ELSEVIER

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

ScienceDirect

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

# Carbon-supported small Rh nanoparticles prepared with sodium citrate: Toward high catalytic activity for hydrogen evolution from ammonia borane hydrolysis

Jiaqin Chen, Min Hu, Mei Ming, Caili Xu, Yi Wang, Yun Zhang<sup>\*\*</sup>,  
Jiangtao Wu, Daojiang Gao, Jian Bi, Guangyin Fan<sup>\*</sup>

College of Chemistry and Materials Science, Sichuan Normal University, Chengdu 610068, PR China

## ARTICLE INFO

### Article history:

Received 11 October 2017

Received in revised form

11 December 2017

Accepted 12 December 2017

Available online xxx

### Keywords:

Rhodium

Catalytic hydrolysis

Ammonia borane

Sodium citrate

## ABSTRACT

Hydrogen generation from the hydrolysis of ammonia borane (AB) over heterogeneous catalysts is essential for practical applications. Herein, efficient hydrogen evolution from AB hydrolysis over the carbon-supported Rh nanoparticles synthesized with sodium citrate (Rh/C-SC) was achieved at 25 °C. The turnover frequency value of Rh/C-SC was 336 mol H<sub>2</sub> (mol<sub>Rh</sub> min)<sup>-1</sup>, whereas that of Rh/C catalyst only yielded a value of 134 mol H<sub>2</sub> (mol<sub>Rh</sub> min)<sup>-1</sup>. The improvement of the catalytic performance of Rh/C-SC catalyst could be attributed to the small Rh particles with highly active surface areas, which were prepared by using sodium citrate as the stabilizing agent. This result indicates that sodium citrate can be applied as a useful stabilizing agent for synthesizing active metal nanoparticles, thus highly promoting the practical application of AB system for fuel cells.

© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

## Introduction

Hydrogen is particularly attractive as an alternative to fossil fuels because of its high energy density, environmental benignity, and clean burning nature [1]. Nevertheless, the safe storage and transport of hydrogen remains a tremendous challenge toward the hydrogen energy based economy [2,3]. Chemical hydrides have attracted considerable attention as attractive and promising hydrogen storage materials for portable hydrogen storage applications. Ammonia borane (AB) has been considered as one of the leading contenders in

promising chemical hydrides for various applications because it presents a high hydrogen content (19.6 wt%), high stability, and superior solubility under ambient conditions [4,5]. Therefore, hydrogen evolution from AB catalytic hydrolysis is increasingly believed to be an efficient technique to address energy and environmental concerns [6–8]. Recently, AB hydrolysis catalyzed by heterogeneous catalysts under mild conditions has been identified as a potential approach for hydrogen evolution.

Noble metal-based materials are state-of-the-art catalysts for AB hydrolysis [5,9–24]. Metal nanoparticles have been immobilized on different supports to enhance the AB

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [zhangyun@sicnu.edu.cn](mailto:zhangyun@sicnu.edu.cn) (Y. Zhang), [fanguangyin@sicnu.edu.cn](mailto:fanguangyin@sicnu.edu.cn) (G. Fan).

<https://doi.org/10.1016/j.ijhydene.2017.12.079>

0360-3199/© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

hydrolysis reaction to generate hydrogen [25–27]. Specifically, Rh-based catalysts have captured increasing research interest because of their superior catalytic property toward AB hydrolysis [10,20,28–38]. Considering their high cost and limited availability, researchers have assigned significant importance to the development of highly efficient Rh catalysts for AB hydrolysis. One of the promising techniques is to control the Rh size. Small metal nanoparticles (NPs) mean that more surface-active sites are available, thus resulting in an enhancement of catalytic activity [10,39,40]. Given their high surface energies, metal NPs with ultrafine sizes are unstable and tend to aggregate, resulting in the decrease of active sites for reactants [3,41,42]. Considering on this problem, researchers added stabilizing agents to prohibit the aggregation of the metal NPs and promote their size and morphology [43,44]. However, normal stabilizing agents can strongly bind to the surface of the metals and induce low catalytic activity [3,39,43,45,46]. To obtain a high catalytic activity, researchers exerted additional effort to remove the stabilizing agent, which strongly binds to the metal NPs [3,39]. Nowadays, new types of stabilizing agents that can efficiently reduce particle size, prohibit aggregation, and improve stability of metal NPs are highly desirable.

Sodium citrate is an ideal stabilizing agent that is highly suitable for modifying small Rh NPs to catalyze the hydrolysis of AB. Herein, carbon-supported Rh NPs were synthesized by using sodium citrate as the stabilizing agent and NaBH<sub>4</sub> as the reducing agent (Rh/C-SC). Catalytic activity of the as-prepared Rh/C-SC sample was investigated for hydrogen generation from AB hydrolysis at room temperature. For comparison, the Rh catalysts synthesized without sodium citrate (Rh/C) and with L-ascorbic acid (Rh/C-LA) were also applied for the same reaction. Moreover, the kinetic studies of catalyst concentration, substrate concentration, and reaction temperature were conducted, followed by the investigation of reusability of Rh/C-SC. The Rh/C-SC exhibits a higher catalytic activity than that of Rh/C and Rh/C-LA catalysts. The maximum turnover frequency (TOF) value reaches 336 mol H<sub>2</sub> (mol<sub>Rh</sub> min)<sup>-1</sup> for Rh/C-SC, whereas only 134 mol H<sub>2</sub> (mol<sub>Rh</sub> min)<sup>-1</sup> and 60 mol H<sub>2</sub> (mol<sub>Rh</sub> min)<sup>-1</sup> are observed with Rh/C and Rh/C-LA catalysts, respectively. Moreover, the Rh/C-SC catalyst has a good recyclability in terms of being reused five times in the hydrolysis of AB. These results show that sodium citrate can be used as a suitable stabilizer for the preparation of small Rh NPs with improved catalytic performance toward AB hydrolysis.

## Experimental

### Chemicals and materials

RhCl<sub>3</sub>·xH<sub>2</sub>O with Rh content of 39 wt% was obtained from Kunming Institute of Precious Metals, China. AB complex (90%) and sodium borohydride were purchased from Sigma-Aldrich. Sodium citrate was obtained from Sinopharm Chemical Reagent Co. Ltd. Concentrated HCl was provided by Aladdin Industrial Inc., China. All chemicals were used without further purification. Carbon black (Vulcan XC-72R, Carbot Corp.) purchased from Sigma-Aldrich was applied as

a carrier without any modification. Ultrapure water was used in all tests.

### Catalyst preparation

The Rh/C-SC and Rh/C catalysts were prepared according to the procedures as shown in Scheme 1. For the synthesis of Rh/C-SC catalyst, a calculated amount of RhCl<sub>3</sub>·xH<sub>2</sub>O and 0.8 mmol sodium citrate were dissolved into 150 mL water in a 250-mL beaker. A 0.4 g sample of carbon black was then added into the container. After stirring for 1 h and followed by sonication for another 0.5 h, a uniform suspension was obtained. To reduce the Rh precursor, 15 mL of NaBH<sub>4</sub> aqueous solution (0.1 M) was added dropwise into the suspension under vigorous stirring at 5 °C for 8 h. After completing the reduction of Rh, the black solid was collected by centrifugation, and treated by wash cycles with water and ethanol several times to remove the weakly bound sodium citrate agent. The resulting black solid was then dried in a vacuum oven at 30 °C for 18 h before it was used for characterization and activity tests. For comparison, the Rh/C and Rh/C-LA catalysts with the same Rh loadings were also synthesized according to similar procedures. The nominal Rh loadings of Rh/C, Rh/C-LA, and Rh/C-SC were 2.58 wt%.

### Characterization

The morphology and particle size of the prepared samples were measured by transmission electron microscopy (TEM) with a JEOL JEM-2100F operated at an accelerating voltage of 200 kV. Powder X-ray diffraction (XRD) was conducted on a PANalytical X'Pert diffractometer with Cu K $\alpha$  radiation (40 kV and 40 mA) over the range at a scanning rate of 4° min<sup>-1</sup> in the 2 $\theta$  range from 10° to 80°. X-ray photoelectron spectroscopy (XPS) characterization was performed in a Thermo ESCALAB 250 Axis Ultra spectrometer with a monochromatic Al K $\alpha$  source (h $\nu$  = 1486.6 eV).

### Activity tests

The catalytic property of the Rh/C-SC catalyst was investigated for hydrogen generation from AB hydrolysis. Typically, the as-prepared Rh/C-SC (15.0 mg) and water (4.0 mL) were added into a 25-mL round-bottom-flask. After stirring the mixture for 30 min, followed by 30 min sonication, a fresh AB aqueous solution (34.2 mg dissolved in 1.0 mL H<sub>2</sub>O) was injected into the reactor to trigger the hydrolysis reaction. A water bath was used to maintain the reaction temperature constant at 25 °C. The volume of hydrogen evolution was detected using a water-displacement approach though calculating the volume of drained water. To determine the catalytic activity, the TOF was calculated according to the reported method [19].

The reusability of the Rh/C-SC catalyst for AB hydrolysis was studied as follows: Briefly, after the previous run of AB hydrolysis was finished, the solid catalyst was recovered from the reaction system by centrifugation and washed thrice with water. The isolated catalyst was re-dispersed in 4 mL of water under vigorous stirring for 30 min, and the next run of

Download English Version:

<https://daneshyari.com/en/article/7707977>

Download Persian Version:

<https://daneshyari.com/article/7707977>

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