

Graphene supported Ag@Co core-shell nanoparticles as efficient catalysts for hydrolytic dehydrogenation of amine boranes

Cheng Du^a, Jun Su^c, Wei Luo^{a,b,*}, Gongzhen Cheng^{a,**}

^a College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, Hubei 430072, PR China

^b Suzhou Institute of Wuhan University, Suzhou, Jiangsu 215123, PR China

^c Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, Wuhan, Hubei 430074, PR China

ARTICLE INFO

Article history:

Received 5 October 2013

Received in revised form

16 November 2013

Accepted 16 November 2013

Available online 24 November 2013

Keywords:

Amine borane

Graphene

Core-shell nanoparticles

Catalytic hydrolysis

ABSTRACT

Well-dispersed Ag@Co core-shell nanoparticles (NPs) supported on graphene with controlled compositions were synthesized by the reduction of silver nitrate, cobalt(II) acetate, and graphene oxide (GO) in the presence of hydrazine and ethylene glycol. These NPs were composition dependent catalysts for hydrogen generation from the hydrolysis of ammonia borane. Among all Ag@Co catalysts tested, the Ag_{0.5}@Co_{0.5}/graphene NPs exhibited the highest catalytic activity, with the turnover frequency (TOF) value of 10.5 mol H₂ min⁻¹ (mol catalyst)⁻¹, and activation energy value of 39.33 kJ/mol. Kinetic studies reveal that the catalytic hydrolysis of AB and MeAB are both first order with respect to the catalyst concentrations. Furthermore, the Ag_{0.5}@Co_{0.5}/graphene NPs show good durable stability and magnetically recyclability for the hydrolytic dehydrogenation of AB and MeAB, which makes the practical recycling application of the catalyst more convenient.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The search for safe and efficient hydrogen storage materials still remains one of the most challenging barriers in the “hydrogen economy” society [1,2]. Recently, boron–nitrogen containing compounds have attracted much attention in the chemical hydrogen storage materials probably due to their high gravimetric hydrogen densities and favorable kinetics of hydrogen release [3–5]. Among them, ammonia borane (NH₃–BH₃, AB), the parent amine borane, represents a leading material for hydrogen storage applications because of its high hydrogen content of 19.6 wt%, high stability under ambient condition, and environmental benignity [6–12]. With appropriate catalyst, hydrolysis of AB could release 3 mol hydrogen gas per mol AB under ambient condition, which appears to be the most convenient one for portable hydrogen storage application [13–30]. However, the methyl-substituted AB, methylamine borane (CH₃NH₂–BH₃, MeAB) with the 11.1 wt% hydrogen content, has not been widely studied [31–33]. Moreover, to the best of our knowledge, the hydrolysis of MeAB, which could also release 3 mol hydrogen per mol MeAB according to Eq. (1) has been rarely reported [34]. Therefore, exploring new strategy to develop suitable

catalysts that meet efficient, economical, and stable requirements toward hydrogen generation from the amine borane systems under moderate condition is crucial for their practical applications.



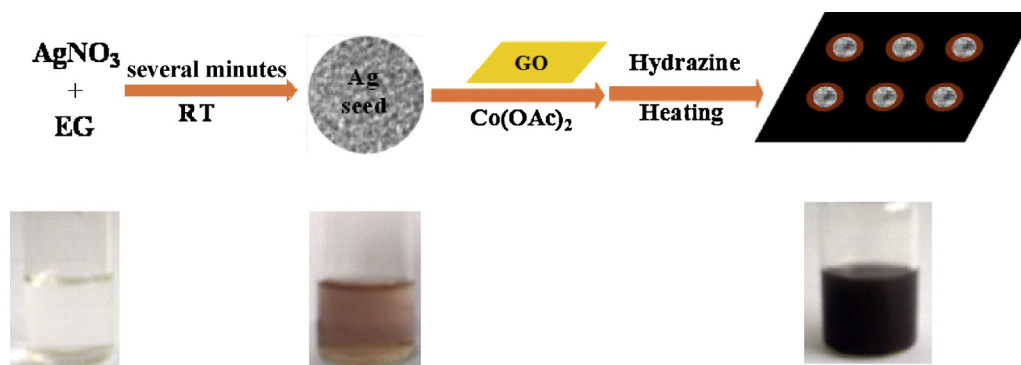
So far, not only noble and non-noble metal based NPs but also their composites have shown high catalytic activity toward hydrolytic dehydrogenation of AB. However, their catalytic performance is highly dependent on the dispersion of the active metals. To avoid the aggregation, various stabilizers have been applied as capping agents to stabilize the metal NPs. Graphene as a novel carbon material with high thermal conductivity, large theoretical surface areas, and excellent mobility of charge carriers could be an ideal substrate for growing and anchoring metal NPs for potential applications [35–40].

Herein, we report a facile synthesis of magnetically recyclable graphene supported Ag_x@Co_{1-x} (x = 0.32, 0.50, 0.60, 0.68) core-shell NPs. The properties of the as-synthesized NPs were investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM) equipped with energy dispersive X-ray (EDX), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), FTIR, Raman, and X-ray photoelectron spectroscopy (XPS) measurements. The results show that the Ag@Co/graphene core-shell NPs exhibit high catalytic activity and recyclability toward hydrolysis of AB and MeAB.

* Corresponding author at: College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, Hubei 430072, PR China. Tel.: +86 02787467716.

** Corresponding author.

E-mail addresses: wluo@whu.edu.cn (W. Luo), gzcheng@whu.edu.cn (G. Cheng).



Scheme 1. Schematic illustration of the formation of Ag@Co/graphene core-shell nanoparticles and corresponding color evolution.

2. Experiment

2.1. Chemicals and materials

Ammonia borane ($\text{NH}_3\text{-BH}_3$, AB, Aldrich, 90%), sodium borohydride (Sinopharm Chemical Reagent Co., Ltd., $\geq 96\%$), methylamine hydrochloride ($\text{CH}_3\text{NH}_2\cdot\text{HCl}$, Sinopharm Chemical Reagent Co., Ltd., $\geq 96\%$), potassium permanganate (KMnO_4 , Shanghai Chemic Co., Ltd., $\geq 99.5\%$), hydrogen peroxide (H_2O_2 , Sinopharm Chemical Reagent Co., Ltd., $\geq 30\%$), sulfuric acid (H_2SO_4 , Sinopharm Chemical Reagent Co., Ltd., 95–98%), phosphoric acid (H_3PO_4 , Sinopharm Chemical Reagent Co., Ltd., $\geq 85\%$), hydrazine hydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, Sinopharm Chemical Reagent Co., Ltd., $\geq 85\%$), tetrahydrofuran ($\text{C}_4\text{H}_8\text{O}$, Sinopharm Chemical Reagent Co., Ltd., $\geq 99\%$), dimethyl ether anhydrous ($\text{C}_4\text{H}_{10}\text{O}$, Sinopharm Chemical Reagent Co., Ltd., $\geq 99.7\%$), graphite power (Sinopharm Chemical Reagent Co., Ltd., $\geq 99.85\%$), silver nitrate (AgNO_3 , A.R.), ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$, Sinopharm Chemical Reagent Co., Ltd., $\geq 99\%$), cobalt(II) acetate ($\text{Co}(\text{OAc})_2$, Sinopharm Chemical Reagent Co., Ltd., $\geq 99\%$). Graphene oxide (GO) and methylamine borane were prepared by the methods reported in the literatures [41–43]. All chemicals were used as obtained. We use ordinary distilled water as the reaction solvent.

2.2. Synthesis of $\text{Ag}_x\text{@Co}_{1-x}$ /graphene ($x=0, 0.32, 0.5, 0.6, 0.68, 1$) catalysts

In a typical synthesis of $\text{Ag}_{0.5}\text{@Co}_{0.5}$ /graphene, 0.1 mmol silver nitrate was dissolved in ethylene glycol (EG, 10.0 mL). The colorless solution was turned to reddish brown under sonication for several minutes. Then 0.2 mmol cobalt(II) acetate and 50 mg GO were added into the solution. Under vigorously stirring, the resulting solution was then slowly heated up to a temperature of 110°C directly and kept under a flow of high-purity nitrogen gas for 1 h to remove oxygen. Next 5 mL hydrazine hydrate was quickly injected into the solution. The mixture was kept at 110°C for 1 h and then cooled to room temperature. Ethanol was added to precipitate the NPs, and the product was collected by centrifugation at 8500 rpm for 10 min. The obtained NPs were further washed twice in ethanol and dried by oil pump vacuum at 50°C for 3 h to give Ag@Co (1:1, molar ratio)/graphene as a dark gray powder. By changing the precursor ratio between cobalt(II) acetate and silver nitrate, the core-shell NPs of different compositions were prepared, with nominal Ag/Co ratios 1:2, 1:1, 1:4 and 2:1, which respectively led to catalysts with $\text{Ag}_{0.5}\text{@Co}_{0.5}$ /graphene, $\text{Ag}_{0.6}\text{@Co}_{0.4}$ /graphene, $\text{Ag}_{0.68}\text{@Co}_{0.32}$ /graphene and $\text{Ag}_{0.32}\text{@Co}_{0.68}$ /graphene compositions. The Ag/graphene and Co/graphene compositions were prepared by the same method.

2.3. Catalytic hydrolysis of AB and MeAB

Water (5 mL) was added to the $\text{Ag}_{0.5}\text{@Co}_{0.5}$ /graphene (20 mg, $[\text{Ag}] + [\text{Co}] = 0.06$ mmol) powder. Since the NPs and graphene are both hydrophobic, ultrasonication was required to get a uniform dispersion. The hydrolysis of ammonia borane was carried out at $25 \pm 0.2^\circ\text{C}$. To start the reaction, 5 mL AB (31 mg) aqueous solution was introduced into the aqueous dispersion of catalysts under vigorous stirring. The volume of hydrogen gas evolved was measured by recording the displacement of water level in an inverted and graduated water-filled buret. Hydrolysis of MeAB was used the same method.

2.4. Kinetic studies of hydrolytic dehydrogenation of AB and MeAB catalyzed by $\text{Ag}_{0.5}\text{@Co}_{0.5}$ /graphene NPs

Sets of experiments with different concentrations of $\text{Ag}_{0.5}\text{@Co}_{0.5}$ /graphene ($[\text{Ag}] + [\text{Co}] = 0.04, 0.05, 0.06, 0.07$ mmol) were performed at room temperature ($25 \pm 0.2^\circ\text{C}$) while the AB (or MeAB) concentration was kept the same (1 mmol) to determine the rate law of the catalytic hydrolysis of AB (or MeAB). Temperature was varied at $25 \pm 0.2^\circ\text{C}$, $30 \pm 0.2^\circ\text{C}$, $35 \pm 0.2^\circ\text{C}$ and $40 \pm 0.2^\circ\text{C}$ while keeping the molar ratio of catalyst/AB or catalyst/MeAB as 0.06 to obtain the activation energy (E_a).

2.5. Recycle stability test

For recycle stability test, catalytic reactions were repeated 5 times by adding another equivalent of AB (or MeAB) (1 mmol) into the mixture after the previous cycle.

2.6. Characterization

TEM images were obtained using a FEI Tecnai G20 U-Twin TEM instrument operating at 200 kV. Powder X-ray diffraction (XRD) patterns were measured by a Bruker D8-Advance X-ray diffractometer using Cu K α radiation source ($\lambda = 0.154178$ nm) with a velocity of 6°min^{-1} . FTIR spectra were collected at room temperature by using a Thermo FTIR-iS10 instrument using KBr discs in the $400\text{--}4000 \text{ cm}^{-1}$ region. Raman spectra were carried out using a confocal Raman microscope (Renishaw, RM-1000) at 514.5 nm excitation. X-ray photoelectron spectroscopy (XPS) measurement was performed with a Kratos XSAM 800 spectrophotometer. The inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was performed on IRIS Intrepid II XSP (Thermo Fisher Scientific, USA).

Download English Version:

<https://daneshyari.com/en/article/65584>

Download Persian Version:

<https://daneshyari.com/article/65584>

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