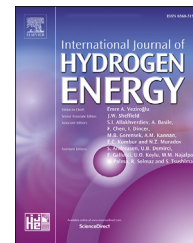




ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

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

Ultrafine palladium nanoparticles anchoring graphene oxide-ionic liquid grafted chitosan self-assembled materials: The novel organic-inorganic hybrid catalysts for hydrogen generation in hydrolysis of ammonia borane

Hang Jia, Xin Chen, Chun-Yan Liu, Xue-Jian Liu, Xiu-Cheng Zheng*,
Xin-Xin Guan, Pu Liu**

College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, China

ARTICLE INFO

Article history:

Received 4 February 2018

Received in revised form

17 April 2018

Accepted 21 April 2018

Available online 30 May 2018

Keywords:

Graphene oxide-ionic liquid chitosan

Self-assembly

Palladium nanoparticles

Organic-inorganic hybrid catalysts

Ammonia borane

Hydrogen generation

ABSTRACT

The novel graphene oxide-ionic liquid grafted chitosan composites (denoted as GO-ILCS) are firstly prepared via a self-assembly process. Then, they are used to anchor ultrafine palladium nanoparticles by the in-situ reduction of palladium chloride with sodium borohydride. The resultant Pd(0)/GO-ILCS organic-inorganic hybrid catalysts are characterized by various techniques and used to catalyze the hydrolytic dehydrogenation of ammonia borane (NH_3BH_3 , AB) under ambient conditions. The results reveal that the palladium nanoparticles are highly dispersed on GO-ILCS and the Pd(0)/GO-ILCS catalysts exhibit high catalytic activity and excellent reusability in the reaction. The turnover frequency (TOF) is as high as $25.6 \text{ mol}_{\text{H}_2} \cdot \text{mol}_{\text{Pd}}^{-1} \cdot \text{min}^{-1}$ and the catalytic activity does not decrease obviously after six runs. The orders of palladium and AB concentrations are 1.00 and 0.33 in the catalytic reaction, respectively. Notably, the activation energy of the reaction ($E_a = 38 \text{ kJ mol}^{-1}$) over the resultant catalysts is obviously lower than most of the palladium-based catalysts reported previously. It is expected the Pd(0)/GO-ILCS catalysts are of exciting potential in the field of hydrogen energy.

© 2018 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

As a clean energy, hydrogen is considered to play an important role in energy supply because of its high energy density, non-toxicity, high abundance and environmental sustainability [1–4]. However, secure storage of hydrogen faces

enormous challenges and the researchers focus on the solid hydrogen storage materials [5]. Ammonia borane (NH_3BH_3 , AB), which has high hydrogen content (19.6 wt%), good stability, nontoxicity and high solubility in water, has been considered as one of the most promising solid hydrogen storage materials [6–8]. Hydrogen can be released from AB via the solvolysis or thermolysis processes [9,10]. As for the

* Corresponding author.

** Corresponding author.

E-mail addresses: zhxch@zzu.edu.cn (X.-C. Zheng), liupu@zzu.edu.cn (P. Liu).

<https://doi.org/10.1016/j.ijhydene.2018.04.156>

0360-3199/© 2018 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

hydrolytic procedure, AB can release hydrogen at ambient temperature over suitable catalyst (Eq. (1)) [11].



Transition metals, such as Co [12,13], Ni [14,15], Ru [16], Rh [17,18], Pd [19] and Pt [20,21] have been used as active catalysts for the hydrolytic dehydrogenation of AB. However, these metal nanoparticles are easily aggregated to large particles during the catalytic reaction, which decreases the activity [22]. Therefore, it is crucial to select a suitable support to stabilize these nanoparticles [23]. Currently, various materials have been used as supports such as graphene [24,25], carbon black [26], zeolites [27], polymers [28,29], hydroxyapatites [30] and ZSM-5 [31]. Among them, graphene has developed rapidly due to its remarkable physicochemical properties including large surface area, strong mechanical strength, excellent electronic property, superior electrical conductivity and low toxicity [32]. As a kind of derivative of graphene, graphene oxide (GO) has similar carbon network with graphene. What's more, GO is a negatively charged material containing various oxygen functional groups (-OH, -C-O-C, -C=O and -COOH) on the surface and edge, which facilitate to assemble on a solid surface with positively charged material through interfacial interaction process [33,34].

Organic-inorganic hybrid materials are originated from the combination between organic and inorganic integrating parts at molecular level [35]. In recent years, they have received widespread attention in many fields including chemistry, biology and medicine because of their combined properties of the organic materials and inorganic materials [36]. Noticeably, as the supports of heterogeneous catalysts, the organic-inorganic materials have outstanding advantages such as hydrophilicity and porosity [37]. As a kind of natural biopolymer composed of 2-amino-2-deoxy-D-glucose and 2-acetamido-2-deoxy-D-glucose linked with β -(1–4) bond, chitosan (CS) has many advantages including nontoxicity, availability, good biodegradability and biocompatibility [38]. However, the solubility of CS restrains its utilization. Luckily, CS is a positively charged material that contains amine and hydroxyl groups which can be modified through chemical methods to offer new properties [39]. The main modification methods include O-substitution, N-substitution and free radical graft copolymerization [40]. It is interesting that the imidazole ionic liquid has excellent solubility in aqueous solution and it can react with CS to form ionic liquid grafted chitosan derivative (ILCS) through the N-substitution method [41]. Furthermore, ILCS is a positively charged material which can be used to prepare graphene oxide-ionic liquid grafted chitosan (GO-ILCS) composites with GO via the layer-by-layer (LBL) self-assembly method. In addition, owing to the π - π interaction between GO and CSIL, the distance between GO layers increases so that the LBL self-assembly composites have larger surface area and this is beneficial to anchor active metal particles.

Inspired by the understanding as mentioned above, an assumption is proposed that an assembly of GO and ILCS together may show superior behavior when used as supports. In this work, a novel GO-ILCS material is firstly synthesized via a self-assembly approach and then used as supports to anchor

palladium nanoparticles by in-situ reduction of PdCl₂ with NaBH₄. The resultant Pd(0)/GO-ILCS organic-inorganic hybrid catalysts are characterized by XRD, FT-IR, Raman, TEM-EDX and XPS. Their superior catalytic properties in hydrogen generation from the hydrolysis of AB at 30 °C are investigated. In addition, the reaction kinetics is also studied in details.

Experimental

Chemicals

Chitosan (CS, Zhejiang Golden Shell Pharmaceutical Co., Ltd, 2.0×10^5 Da), graphene oxide (GO, Nanjing XFNANO Materials Tech Co., Ltd), palladium chloride (PdCl₂, Aladdin), sodium borohydride (NaBH₄), ammonia borane (NH₃BH₃, Zhengzhou Boron Reagent Co., Ltd, 97%), sodium hydroxide (NaOH, Tianjin Kemiou Chemical Reagent Co., Ltd, > 96%), methanol (CH₃OH, Sinopharm Chemical Reagent Co., Ltd, > 99%), 1-methylimidazole (C₄H₆N₂, Aladdin, 99%), dichloromethane (CH₂Cl₂, Tianjin Kemiou Chemical Reagent Co., Ltd, > 99%), 1,6-dibromohexane (C₆H₁₂Br₂, Aladdin, 97%), hexane (C₆H₁₄, Tianjin Kemiou Chemical Reagent Co., Ltd, > 99%), ethanol (C₂H₆O, Tianjin Kemiou Chemical Reagent Co., Ltd, > 99%), anhydrous ethanol (C₂H₆O, Sinopharm Chemical Reagent Co., Ltd, > 99%), acetone (C₃H₆O, Yantai Gemini Chemical Co., Ltd, > 99%), hydrochloric acid (HCl, Luoyang Chemical Reagent Factory, 36–38%), and isopropyl alcohol (C₃H₈O, Sinopharm Chemical Reagent Co., Ltd, > 99%). All the chemical reagents were used as received without any further purification.

Synthesis of the high deacetylation chitosan (HCS)

Firstly, 20.0 g of CS was dispersed into 200 mL of NaOH aqueous solution (10 mol L⁻¹) and stirred for 1 h at 110 °C. Then, the solid was filtered and washed with deionized (DI) water for several times until the pH value of the filtered liquid was adjusted to 7. The above process was repeated for three times. Finally, the precipitation was washed with methanol and acetone for three times, respectively. The as-prepared HCS was dried at 60 °C under vacuum. According to the result of ¹H NMR, the deacetylation of HCS exceeded 99%.

Synthesis of 1-(6-bromohexyl)-3-methylimidazolium bromide (BHMIB)

The synthesis of BHMIB was according to the literature [42]. Firstly, 5 mL of 1-methylimidazole was dissolved into 53 mL of dichloromethane. Secondly, the solution was added dropwise into 37.6 mL of 1, 6-dibromohexane and stirred vigorously with a mechanical agitator at 47 °C for 10 h under nitrogen atmosphere. Thirdly, the product was obtained by removing dichloromethane using a rotary evaporator and extracting with hexane for three times. The product was purified by silica column chromatography (methanol: dichloromethane = 1: 4) to obtain BHMIB. ¹H NMR (400 MHz, D₂O, δ , ppm): 1.20 (q, J = 7.7 Hz, 2H, -CH₂-), 1.36 (m, J = 7.6 Hz, 2H, -CH₂-), 1.74 (m, 4H, -CH₂-), 3.38 (t, J = 6.6 Hz, 2H, -CH₂-), 3.80 (s, 3H, -CH₃), 4.11 (t, J = 7.2 Hz, 2H, -CH₂-), 7.34 (s, J = 1.4 Hz, 1H, -NCH-), 7.49 (s, J = 1.4 Hz, 1H, -NCH-), 8.63

Download English Version:

<https://daneshyari.com/en/article/7705538>

Download Persian Version:

<https://daneshyari.com/article/7705538>

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