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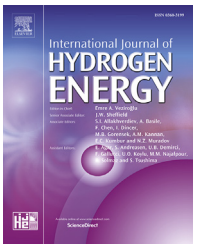

Polydopamine-coated halloysite nanotubes supported AgPd nanoalloy: An efficient catalyst for hydrolysis of ammonia borane

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ABSTRACT

AgPd alloy nanoparticles (NPs) supported on halloysite nanotubes (HNTs) coated polydopamine (PDA) successfully synthesized by one-pot hydrothermal route. XRD, TEM and XPS were employed to verify the alloy structure of the obtained AgPd NPs. The HAADF-STEM result revealed that the thickness of PDA coating was ~10 nm, which could be formed on the surface of HNTs, and the existence of PDA was beneficial to deposit AgPd alloys with high dispersibility on the surface of HNTs. AgPd/PDA-HNT nanocomposites were effective catalysts for the hydrolysis of ammonia borane at room temperature, and the reaction was completed within 160 s using Ag_3Pd_2/PDA-HNT as catalysts, with a high total turnover frequency (TOF) value of 90 mol_{H2} $mol^{-1}_{catalyst}$ min^{-1} and a low apparent activation energy (Ea) of 22.7 kJ mol^{-1}. After the sixth cycle, Ag_3Pd_2/PDA-HNT catalyst retained 72% of its initial activity and 100% conversion. The excellent catalytic properties, good durability and reusability, enabled Ag_3Pd_2/PDA-HNT to be an ideal catalyst in the practical applications.

Introduction

Hydrogen is regarded as one of the best alternative energy because of its abundance, high energy density, and cleanliness. However, the large-scale utilization of hydrogen is hindered by the lack of safe and efficient hydrogen storage methods. Hydrogen generation from chemical hydrogen storage materials in a catalytic process is a convenient and effective approach to apply hydrogen energy in a practical fashion. Typical hydrogen storage chemicals include formic acid (HCOOH), hydrous hydrazine ($N_2H_4{\cdot}H_2O$), methanol (CH_3OH), and ammonia-borane (NH_3BH_3, AB), with hydrogen contents of 4.4, 8.0, 18.8, and 19.6 wt.%, respectively [1]. NH_3BH_3, as the simplest B–N compound, exhibits many advantages of high hydrogen content, low molecular weight (30.7 g mol^{-1}) and high stability in solutions, making it a highly promising candidate for hydrogen storage. When proper catalysts are used, hydrogen release can occur from AB hydrolysis at ambient condition, therefore, efficient, economical and easily prepared catalysts are highly desired. Numerous transition metal catalysts have been tested for the hydrolysis of AB, such as noble metal-based catalysts, including Pt, Rh, Ru, Ag, and Pd, display high activities [2–6]. Their bimetallic components have also attracted widespread attention due to the synergistic effect between components that can enhance

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catalytic performance, such as AgPd, PtPd and RuPt et al. [7–10]. The catalytic activity can be adjusted by selecting different compositions, controlling of the electronic structure and surface metal sites. However, small metal particles, especially on the nanoscale, are frequently subjected to the aggregation problem, because of their high surface energy, which usually leads to a decrease of their catalytic activity. To avoid this issue, various types of support materials have been employed to uniformly disperse the metal NPs [11–13].

Halloysite nanotubes (HNTs), $Al_2Si_2O_5(OH)_4 \cdot nH_2O$, are composed of gibbsite (Al-OH) octahedral sheet groups on the internal surface and siloxane (Si-O-Si) groups on the external surface and have a predominantly hollow tubular structure [14,15]. The different surface chemistry at each side of nanotubes offers the opportunity for selective modification with organic molecules to make hybrid materials. Compared with other nano sized materials, naturally occurring HNTs are easily obtained and much cheaper than other nanotubes such as carbon nanotubes (CNTs) and boron nitride nanotubes [16,17]. Owing to all of these features, HNTs have great potential applications for catalytic fields. Moscow Gubkin University group has studied that HNTs were used as template for synthesis core-shell composite catalysts, enhancing metal ions loading, and the catalytic performance was markedly improved [18–22]. Although origin HNTs show the richness of surface hydroxyl groups and charges, they still have a relatively weak adhesion with catalyst NPs due to the absence of chemical interaction, leading to the catalyst particles easily leaching from the support surface during the reactions. To overcome this problem, one method is the effective surface functionalization of nanotubes, which makes it possible to improve adhesive capacity of catalyst NPs on HNTs [23,24]. Our group has extensively studied the use of different methods to modify the HNTs surface, including organic silanes functionalization, polymer modification method and alkali etching method et al. [25–29]. PDA exhibits good biocompatibility and stability, which can be easily introduced by the self-polymerization of dopamine at weakly alkaline pH, and this polymerization procedure of dopamine offers a convenient means for surface modifications and has been widely used, like TiO_2 NPs, graphene oxide, and clay materials [16,17,30].

In this work, we have for the first time fabricated highly dispersed AgPd alloy NPs immobilized on PDA-HNT nanocomposites through a facile one-pot hydrothermal route for the catalytic reaction of AB hydrolysis at ambient conditions. We demonstrated that the activity of the AgPd/PDA-HNT nanocatalysts could be enhanced by properly controlling the Ag/Pd molar ratio, and Ag_3Pd_2/PDA-HNT catalyst exhibited the best catalytic performance with TOF value of as high as 90 mol_{H2} $mol^{-1}_{catalyst}$ min^{-1} and Ea value of as low as 22.7 kJ mol^{-1}.

Experimental

Materials

All chemical reagents were obtained from commercial suppliers and used without further purification. The halloysite nanotubes (HNTs) mineral was obtained from clay minerals in Henan, China. Dopamine hydrochloride ($C_8H_{11}NO_2 \cdot 2HCl$, 98%), palladium nitrate dihydrate ($Pd(NO_3)_2 \cdot 2H_2O$, 39%), ammonia borane complex (NH3BH3, AB, 97%) were purchased from Aldrich. Tris (hydroxymethyl) aminomethane ($C_4H_{11}NO_3$, 99%), silver nitrate ($AgNO_3$, 99%), L-Ascorbic acid ($C_6H_8O_6$, L-AA, 99.7%) and trisodium citrate dehydrate ($C_6H_5Na_3O_7 \cdot 2H_2O$, 99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. The water was used deionized water.

Characterization

The surface morphology of the nanocatalysts was characterized by scanning electron microscopy (SEM, Hitachi S2400). The morphology and crystal structure of the samples were observed by high resolution transmission electron microscopy (HRTEM) and high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) on a FEI Talosf200s operating at an acceleration voltage of 200 kV. The crystal structures of the products were characterized by X-ray diffraction (XRD) on a D8ADVANCE in the range of 5–85°. N_2 adsorption/desorption isotherms and the distribution of pore size were recorded by Quantachrome NOVA4200 specific surface area and pore size distribution analyzer. The chemical compositions of the catalysts were analyzed by using ELAN 9000 inductively coupled plasma atomic mass spectrometer (ICP-MS). X-ray photoelectron spectroscopy (XPS) measurement was performed with a Thermo Scientific-ESCALAB 250XI multifunctional imaging electron spectrometer to study the surface properties of the nanocomposites. ^{11}B NMR spectra were recorded on an AVIII HD 400 with an operating frequency of 128.15 MHz D_2O was used as a lock. At the end of the catalytic reaction, the resulting solutions were filtered and the filtrates were collected for taking the ^{11}B NMR spectra.

Synthesis of AgPd/PDA-HNT catalyst

PDA-HNTs were prepared by pH-induced self-polymerization process under oxidizing conditions [26]. Firstly, 500.0 mg HNTs were dispersed in aqueous tris (hydroxymethyl) aminomethane solution (10 mM, pH = 8.5) with ultrasonically dispersing for 0.5 h to obtain HNTs suspensions (100 mL). Then 200.0 mg of dopamine hydrochloride powder was added into the obtained HNT suspensions being vigorously stirred for 6 h at 298 K. The PDA-HNTs were separated and washed by distilled water and dried under vacuum at 323 K overnight.

AgPd/PDA-HNT nanocatalysts were synthesized as follows in Fig. 1, 50.0 mg PDA-HNT was ultrasonically dispersed in 30 mL water and added to 275.0 mg $C_6H_5Na_3O_7 \cdot 2H_2O$. The solution was heated to 373 K with oil bath. Under a gentle nitrogen flow, 3.1 mL $AgNO_3$ (10 mM) and 2.1 mL $Pd(NO_3)_2 \cdot 2H_2O$ (10 mM) solutions were added into the above suspension with magnetic stirring. After that, 2.0 mL of aqueous solution containing 88.1 mg L-AA was added following stirring for 2 h during which the brown solution gradually turned to black. It was widely believed that oxygen-containing functionalities in PDA-HNT, hydroxy (–OH) groups, are necessary for supporting metal ions, which thus help to control the sizes and distributions of the formed metal

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