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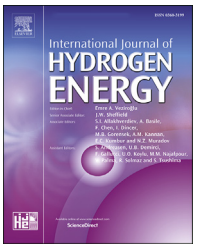

Monodisperse PtCu alloy nanoparticles as highly efficient catalysts for the hydrolytic dehydrogenation of ammonia borane

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ABSTRACT

Pt-M alloy nanoparticles (NPs) with well-defined size and compositions exhibit dramatically catalytic performance in chemical reactions. In this work, monodisperse PtCu NPs with controlled size and compositions were synthesized by the co-reduction method in the presence of oleylamine. These NPs have excellent catalytic activities in the hydrolytic dehydrogenation of ammonia borane (AB) and their activities were composition dependent. Among the different-composition PtCu NPs, the $Cu_{50}Pt_{50}$ NPs exhibit the highest catalytic activity with an initial turnover frequency of 102.5 $mol_{(hydrogen)} \cdot mol^{-1}_{(catalyst)} \cdot min^{-1}$ and an apparent activation energy of 36 $kJ \cdot mol^{-1}$, which demonstrate the validity of partly replacing Pt by a first-row transition metal on constructing high performance heterogeneous nanocatalysts for the hydrolytic dehydrogenation of AB.

Introduction

As a promising clean energy source, hydrogen (H_2) has drawn much attention due to its merits for replacing non-renewable energy [1]. Especially, H_2 is considered as an environmentally friendly candidate with only water as by-product for its application in the proton exchange membrane fuel cells (PEMFC) [1,2]. However, one of the barriers to realize the H_2 energy society is the efficient and safe storage of H_2 under mild conditions [1–4]. To meet the requirement for the practical application, one conceptual solution is to search for efficient hydrogen storage materials which have the advantages of high gravimetric and volumetric hydrogen storage capacity. According to the up-to-date targets for on-board hydrogen storage systems set by the U.S. Department of Energy (DOE), the minimum gravimetric and volumetric capacities are 5.5 wt% and 40 $g \cdot L^{-1}$ for the year 2020, ultimately increasing to 7.5 wt % and 70 $g \cdot L^{-1}$, respectively [5]. In order to fulfill this criterion, a large amount of research has been performed on hydrogen storage materials.

Ammonia borane (AB), as the simplest B–N compound, exhibits the advantages of low molar molecular weight (30.7 $g \cdot mol^{-1}$), high hydrogen density (19.6 wt%), and high stability in solutions, making it a highly promising candidate for hydrogen storage [6–11]. Numerous studies has been carried out on the AB dehydrogenation which has two major

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ways, that is, the thermolysis dehydrogenation and hydrolytic dehydrogenation. Usually, the former needs high temperature and the rate of hydrogen released from AB was relatively low [12]. In contrast, the AB can release three equivalents of H_2 rapidly by hydrolysis reaction at room temperature when the proper heterogeneous catalysts are used [13]. This interesting character has driven lots of efforts to develop novel catalysts to improve the hydrolysis efficiency of AB.

Nowadays, Pt-based nano-catalysts have attracted extensive interest because of its superior catalytic properties [14–18]. Since Xu et al. first reported Pt nanoparticles (NPs) as catalyst for AB dehydrogenation by the hydrolysis reaction [19], numerous Pt-based nanomaterials have been employed to catalyze the hydrolysis of AB [20–31]. Guler group prepared 3D TiO_2 nano-network decorated with Pt NPs by atomic layer deposition, which effectively promoted the hydrolysis of AB [27]. And Dong et al. reported the easily prepared Pt NPs modified on carbon fibers which exhibited high catalytic activity with an initial TOF of 35 min^{-1} [28]. Xu group prepared PtCu alloy nanoflowers with hierarchical nanoporous structure, which showed superior catalytic performance in the hydrolysis of AB [29]. To date, many efforts have been devoted to developing efficiently Pt nanocatalysts for AB hydrolysis, however, due to the rarity of Pt in the earth and the growing demand, Pt costs are extremely high, which is the greatest challenge for its widespread applications. Recent research has shown that Pt-based bimetallic NPs (alloy, intermetallic, core-shell) which contained Pt and a first-row transition metal can not only reduce the amount of Pt but also obtain the same or better catalytic activity [29,32]. As a low-cost transition metal, Cu nanoparticles catalysts have showed high AB hydrolysis activities [33–59]. Wang group prepared Cu NPs supported on rGO by a facile in situ procedure, which exerted satisfactory catalytic activity with an initial TOF of 3.61 min^{-1} [34]. Kaya et al. employed magnetic $SiO_2/CoFe_2O_4$ particles supported Cu nanoparticles as an effective catalyst, which showed efficient performance in AB hydrolysis with an initial TOF of 40 min^{-1} [35]. Xu group reported that Cu/Ru nanoparticles embedded in porous carbon showed significant activity for catalytic AB hydrolysis due to the synergistic effect between the two mental [49]. To date, the catalytic activity gap between Cu and Pt-based catalysts still exists, but Cu would be a very good dopant mental in preparing Pt-based alloyed nanoparticles. Therefore, these bimetallic PtCu alloy NPs may provide an effective method for the future catalysts design and synthesis to optimize the catalytic activity of AB hydrolysis and H_2 generation.

Herein, we report a simple method to prepare monodisperse PtCu alloy NPs and their catalysis for hydrolysis of the AB in aqueous solution under mild conditions. The PtCu alloy NPs display highly catalytic activity for AB hydrolytic dehydrogenation with a composition dependent. The optimum catalyst is $Pt_{50}Cu_{50}$ NPs with an initial turnover frequency (TOF) of 102.5 $mol_{(hydrogen)} \cdot mol^{-1}_{(catalyst)} \cdot min^{-1}$ and an apparent activation energy of 36 $kJ \cdot mol^{-1}$. These experimental results demonstrate the validity of partly replacing Pt by a first-row transition metal on designing heterogeneous nanocatalysts with high catalytic activity for the AB hydrolytic dehydrogenation.

Experimental

Chemicals

Platinum (II) acetylacetonate ($Pt(acac)_2$, 97%), Copper (II) acetylacetonate ($Cu(acac)_2$, 97%) and oleylamine ($CH_3(CH_2)_7CH = CH(CH_2)CH_2NH_2$, OAm) were all purchased from Aladdin. All the chemicals were used as received without further purification. Deionized water was used for all the experiment.

Synthesis of monodisperse PtCu NPs

In a typical synthesis of 4 nm $Pt_{50}Cu_{50}$ NPs, 0.25 mmol $Pt(acac)_2$ and 0.25 mmol $Cu(acac)_2$ were mixed with 10 mL OAm by stirring for 40 min under a mild N_2 flow. The mixture was heated to 280 °C at a heating rate of 4 °C min^{-1} and kept at 280 °C for 60 min before it was cooled to room temperature. Then the product was separated by centrifugation at 9500 rpm for 10 min and washed three times with a mixture of hexane/ethanol. The product was then dispersed in hexane.

By keeping $Pt(acac)_2$ amount constant, we can easily synthesize Pt, $Pt_{70}Cu_{30}$ and $Pt_{30}Cu_{70}$ NPs by changing the $Cu(acac)_2$ amount from 0 to 0.58 mmol.

Synthesis of PtCu/C catalyst

In a typical procedure, 10 mg PtCu NPs were dissolved in 10 mL hexane and 20 mg Ketjen carbon was dissolved in 20 mL ethanol before they were mixed. Then the mixture sonicated for 60 min to ensure the complete adsorption of the NPs onto the Ketjen carbon. After centrifugal separation and desiccation, the mixture was dissolved in 10 mL acetic acid and then heated at 70 °C overnight. The reaction mixture was cooled down to room temperature and then centrifuged at 9500 rpm for 10 min. The obtained mixture was washed twice with ethanol. The PtCu/C NPs were weighed and suspended in deionized water by sonication at least 20 min.

Hydrolysis of AB catalyzed by PtCu/C

The experimental setup for the hydrolysis of AB was similar to that described in a previous report [60]. The volume of hydrogen gas was measured by a typical water-filled gas burette system. In a typical procedure, 5 mL PtCu/C NPs suspension (1 mg/mL) was transferred to a two-necked jacketed reaction flask, which was thermostated to 25 °C under magnetic stirring. Then 31.9 mg AB was added into the catalyst solution and the volume of hydrogen gas was measured by recording the displacement of water level every time.

Characterization

X-ray diffraction (XRD) patterns were collected on a PAN analytical X'Pert powder with Cu Kα radiation (λ = 1.5418 Å). Transmission electron microscopy (TEM) images were acquired on a JEM-1400 operating at 100 kV (JEOL Ltd). High-resolution TEM (HRTEM) images were obtained on a Talos F200X with an accelerating voltage of 200 kV.

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