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Fabrication of Pt-loaded NiCo nanochains with superior catalytic dehydrogenation activity

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ABSTRACT

A new magnetic Pt-loaded NiCo nanochain, with the diameter from 80 nm to 120 nm, has been prepared through microwave-induced assembly process followed by the galvanic displacement performance. Pt nanoparticles are distributed on the surface of NiCo nanochains. The products are investigated as hydrolytic dehydrogenation catalyst for potential hydrogen energy applications. Compared with NiCo nanochains, the Pt-loaded NiCo nanochains present exceedingly high catalytic activity toward the hydrolytic dehydrogenation of ammonia borane aqueous under ambient atmosphere at room temperature, where the $Ni_{16}Co_{80}/Pt_4$ nanochains exhibit high catalytic activity with a lower activation energy of 45.72 kJ mol^{-1} and a superior dehydrogenation rate of 1.17×10^4 mL min^{-1} g^{-1}, suggesting the potential application in hydrogen fuel and chemical industry.

1. Introduction

Hierarchically structured multimetallic nanocatalysts with high catalytic activity and low activation energy are highly demanded for various chemical processes, such as catalytic reforming, hydrogenation, dehydrogenation, fuel-cell electrocatalysis and so on [1–5]. Through the cooperation of electron structure mediated by composition and active site arrangement, the catalytic performance of hierarchically structured multimetallic nanocatalysts can be finely tuned [6–10] to improve the catalytic activity.

On the other side, considering a clean fuel of hydrogen and its application obstacles in safe efficient storage, various researches have been performed for the development of new materials that can store or deliver hydrogen at acceptable rates [11–17]. So far, no single material investigated meets all of the necessary transportation requirements, such as volumetric and gravimetric hydrogen capacities, handling pressure and temperature, and recycling of byproducts. Recent explorations in chemical hydrogen storage materials have suggested that ammonia borane (H_3NBH_3, AB) is an active candidate owing to its low molecular weight (30.7 g/mol) and high hydrogen capacity (19.6%) [18,19]. Furthermore, AB has good water solubility (33.6 g AB/100 g water)[20] and higher stability in aqueous solution at room temperature [21]. Meanwhile, it is nontoxic [22] and has an exothermic hydrolysis reaction ($\Delta H_0 = -155.97$ kJ/mol) [23].

In order to avoid deactivation caused by the aggregation of nanoparticles, the fabrication of noble metal-alloy hierarchical structures is a good way for preparing catalysts with better catalytic activity. Numerous Ni and Co compounds, including bimetallic nanoparticles and their noble metal containing composite catalysts, such as Pt–Ni, Ag–Ni, Ag–Co, Au–Co, Ru–Ni, Rh–Ni–graphene core shell and alloy catalysts, have been reported for use in the hydrolysis reaction of AB [7,8,24–26,15]. However, the stability and efficiency of catalysts are still obstacles need to be overcome. Recently, we have noticed that the microwave-assisted route offers a clean, cheap, and convenient heating strategy that usually results in higher yields and shorter reaction time [27,28]. This way, we can heat the materials rapidly by the energy transmitted from microwave which is generated by resonance or relaxation. Microwave technology with high evenness and small temperature gradient is proved to be a selective heating method, and it can be an approach to the formation of noble metal-alloy hierarchical structures.

For the purpose of developing high-performance catalysts toward AB dehydrogenation under moderate conditions, we concentrate our research on the fabrication of Pt-loaded NiCo nanochains, which serve as catalysts through microwave-induced assembly process followed by the galvanic displacement performance. In the resultant, Pt nanoparticles were well dispersed on the surface of NiCo nanochains. Compared with NiCo nanochains, the catalytic activity and stability toward AB hydrolytic dehydrogenation can be remarkably enhanced by Pt-loaded NiCo nanochains under ambient atmosphere at room temperature, which will be promising for the application in energy fuel and chemical industry.

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2. Experimental section

2.1. Materials

Nickel chloride ($NiCl_2{\cdot}6H_2O$, 99%), cobalt acetate ($Co(Ac)_2{\cdot}4H_2O$, 99%), chloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$, 99%), hydrazine hydrate ($N_2H_4{\cdot}H_2O$, 85%), polyvinyl pyrrolidone K-30 (PVP, $(C_6H_9NO)_n$, Mw: av. 40,000), ethylene glycol (EG, $C_2H_6O_2$, 99%), and ethanol (C_2H_5OH, 99%) were purchased from Shanghai Lingfeng Chemical Reagent Co., LTD, ammonia borane (AB, NH_3BH_3, 90%) was purchased from Aldrich, and all the reagents were used without further purification.

2.2. Synthesis

2.2.1. Preparation of NiCo nanochains

NiCo nanochains were prepared by microwave-induced routine on MAS-II system (Shanghai XinYi Instrument Co., LTD). The system can operate at 2450 MHz frequency and work at 0–1000 W power. The reaction temperature and time were programmed according to Table S1 in Electronic Supplementary Material (SM). In a typical procedure, $NiCl_2{\cdot}6H_2O$ (120 μmol), $Co(A_C)_2{\cdot}4H_2O$ (120 μmol) and PVP (100 mg) were added to 20 mL of EG at room temperature, the mixture was vigorously stirred for 20 min under ultrasonic, and then 200 μL of $N_2H_4{\cdot}H_2O$ (80 wt%) was added. Finally, the above solution was transferred into a 100-mL three-neck flask within a series molar ratio of Ni^{2+} to Co^{2+} at 100/0 (S1), 90/10 (S2), 80/20 (S3), 50/50 (S4), 20/80 (S5), 10/90 (S6), and 0/100 (S7). Under microwave irradiation for 3 min according to the program in Table S1, the products were cooled to room temperature. After it has been cooled, the black products were collected, washed with distilled water and ethanol three times under ultrasonic and dried in a vacuum oven at 60 °C for 5 h.

2.2.2. Preparation of Pt-loaded NiCo nanochains

The preparation of Pt-loaded NiCo nanochains was achieved through galvanic displacement process between Pt and Ni or Co based on NiCo nanochains in different composition using citric acid as capping agents. Briefly, $H_2PtCl_6{\cdot}6H_2O$ (6 μmol) and citric acid (12 μmol) were dissolved in deionized water (40 mL) and then added to 10.0 mg of the series of above as-synthesized NiCo nanochains under ultrasonic. After reaction was carried out for 30 min at room temperature, products were collected through centrifugation timely and washed by distilled water and ethanol several times under ultrasonic. Finally, products were dried for the following dehydrogenation catalysis investigation. The component analysis of resultant Pt-loaded NiCo nanochains in different molar ratios of Ni to Co were performed by inductively coupled plasma (ICP-AES) and confirmed by selected area energy dispersive X-ray spectroscopy (EDS). The products are proved to be Ni_{96}/Pt_4, $Ni_{87}Co_9/Pt_4$, $Ni_{78}Co_{18}/Pt_4$, $Ni_{47}Co_{49}/Pt_4$, $Ni_{16}Co_{80}/Pt_4$, Ni_9Co_{87}/Pt_4 and Co_{96}/Pt_4, respectively. The detailed data are listed in Table S2.

2.3. Evaluation of catalytic activity in dehydrogenation

To evaluate the catalytic properties of the synthesized catalysts, we measured their catalytic activities toward AB aqueous hydrolytic dehydrogenation. In a typical experiment, 20 mL of AB aqueous solution (0.13 M) was added to a three-neck flask (one neck was connected to a gas burette through soft rubber tube, and another was connected to temperature control device). Then, catalysts (5.0 mg NiCo nanochains and 5.0 mg Pt-loaded NiCo nanochains in different molar ratios of Ni to Co) were respectively added to the reaction solution rapidly and we kept every pipe orifice sealed. The reaction was started and carried out under constant electric stirring at room temperature. The volume of hydrogen gas generated from the hydrolysis reaction was measured using the water displacement method.

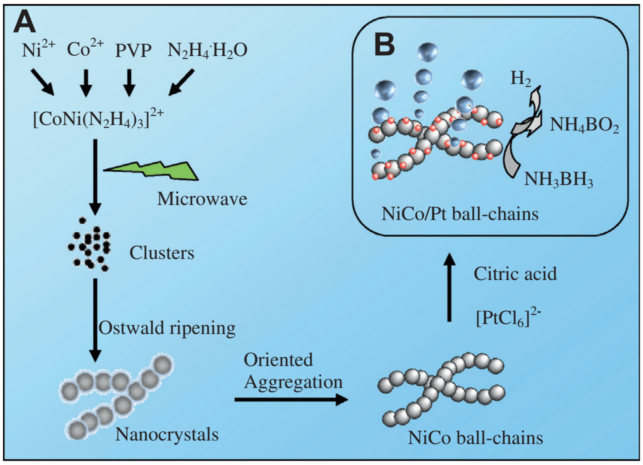
2.4. Characterization

The size and morphology of the products were obtained by using field-emission scanning electron microscopy (FE-SEM) of Hitachi S-4800. For the detailed study of microstructure, transmission electron microscopy (TEM) was taken on a JEOL JEM-1200EX microscope. Element analysis was measured by inductively coupled plasma (ICP-AES) on ICAP6300 (Thermo Fisher Scientific, USA) and was confirmed by selected area energy dispersive X-ray spectroscopy (EDS) conducted at 20 keV on a TN5400 EDS instrument (Oxford). The X-ray diffraction (XRD) measurements were performed on a Bruker D8 (German) using Cu Kα radiation source ($\lambda = 0.154$ nm). X-ray photoelectron spectroscopy (XPS) experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) using a Al Kα radiation ($h\nu = 1486.6$ eV). The whole spectra (0–1100 eV) and the narrow spectra of all the elements with quite high resolution were both recorded by using RBD 147 interface (RBD Enterprises, USA) through the AugerScan 3.21 software. Binding energies were calibrated by using the containment carbon (C1s = 284.6 eV, 288.174). The data analysis was carried out by using the RBD AugerScan 3.21 software provided by RBD Enterprises or XPSPeak4.1 provided by Raymund W.M. Kwok (The Chinese University of Hong Kong, China). The magnetization was measured on a LakeShore 7312 vibration sample magnetometer (VSM) (America), and the detailed data are summarized in Table S2.

3. Results and discussion

3.1. Preparation and mechanism

In order to improve the catalytic activity, Pt-loaded NiCo nanochains were designed and constructed, in which Pt nanoparticles (NPs) were dispersed on the surface of NiCo nanochains. The proposed formation mechanism of Pt-loaded NiCo nanochains is given in Scheme 1. Firstly, NiCo nanochains were prepared in a microwave-induced fabrication process which is driven by the "oriented attachment" mechanism associated with Ostwald ripening [29]. As a fact, the NiCo nanostructures are constructed in the anisotropic growth promoted by using PVP as directing agent. As displayed



Scheme 1. Schematic view: (A) Formation of Pt-loaded NiCo nanochains; (B) Catalytic hydrolysis dehydrogenation toward AB under ambient atmosphere at room temperature.