



Full Length Article

Synthesis of novel platinum-on-flower-like nickel catalysts and their applications in hydrogenation reaction



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ABSTRACT

Without any capping agent, surfactant or external magnetic field, hierarchical nickel was successfully prepared via a simple hydrothermal reduction method by using hydrazine hydrate as reducing agent. The structure and morphology of the products (for instance, flower-like, column-like and spherical-like) were controlled by adjusting hydrothermal conditions including reaction temperature and solvent. The morphology transformation mechanism was proposed and discussed. Corresponding platinum/nickel catalysts (Pt/Ni) were obtained by the galvanic replacement reaction method. And the catalytic activity of the platinum/nickel samples was evaluated by using selective hydrogenation of nitrobenzene. It was found that platinum/flower-like nickel showed the most excellent catalytic performance among the as-synthesized catalysts in this work, with good stability as well. Moreover, reasons for the enhancement of platinum/flower-like nickel for nitrobenzene hydrogenation were investigated.

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1. Introduction

Many research literatures have reported the nanomaterials with a variety of morphologies and structures were obtained by controlling the synthesis conditions [1–5]. And the performance of the nanomaterials, such as catalytic activity, magnetic properties, electronic behaviors and memory function, are very dependent on their shapes and nanostructures [6–9]. For example, the investigation of the relationship between morphology and catalytic performance of the nanomaterials catalysts has attracted more and more attention of the researchers [10,11]. As-reported methods of preparing nanomaterials mainly included liquid phase reducing methods (such as hydrothermal reduction [12], solvothermal synthesis [13], sol-gel [14], micro-emulsion [15] and precipitation [16]), chemical vapor deposition (CVD) [17], electrodeposition [18], microwave synthesis [19] and some other physical methods. The metallic crystal with dif-

ferent morphologies and structures could be obtained via the above methods, taking nickel crystal as an instance to discuss.

It is well known that nickel is widely used in the catalytic and magnetic field [20,21]. The rational design of its morphology and nanostructure is essential to realize ideal properties. Such morphologies as sea-urchin-like, snow-flake-like architectures, chain-like, sphere-like, column-like, nanowires, dendritic-like, fiber-like and prick-like hierarchical nickel have been prepared [22]. In the published work of Pal' group, the prickly nickel nanowires were synthesized at ~80 °C via hydrazine hydrate reducing method under magnetic field, using polyethylene glycol *p*-(1,1,3, 3-tetramethylbutyl)-phenyl ether (TX-100) as surfactant [21]. Fu et al. prepared the hierarchical nickel with the dendritic-like morphology at 160 °C by a simple hydrothermal synthesis, adding cetyltrimethylammonium bromide (CTAB) as surfactant. And this dendritic-like nickel exhibited ferromagnetic characteristics [23]. Nickel crystals with various morphologies, such as superfine nanoparticles, urchinlike chains, smooth chains and rings, were synthesized via a liquid phase chemical reduction method by adjusting the reaction conditions (reaction temperature, synthesis time, sequence of adding chemicals and addition of PVP) [24]. With the assistance of silver seeds, the flower-like nickel materials have been synthesized at 60 °C by the hydrazine hydrate reducing method in the presence of different capping agents

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(triethanolamine-TEA, diethanolamine-DEA, ethylene glycol-EG) [25]. And the controlled synthesis of Ni fibers, nanospheres, nanowires, and nanoflowers was performed under the external magnetic field [26,27]. But most of the above-mentioned nickel crystals with different morphologies were prepared by using surfactant or capping agent, or with the aid of magnetic field.

For the hydrogenation of nitrobenzene, the reported catalysts mainly consist of noble metal (eg. Pt, Au, Ag, Pd, Ru, Rh), non-noble metal (eg. Ni, Co) and bimetallic catalysts (eg. Pb-Pt) [28,29]. The hierarchical nickel has outstanding magnetic property, high heat conductivity coefficient and monolith feature, which is beneficial to be separated with reaction liquid and improve reaction rate [30]. To improve the Pt dispersion of Pt-based catalyst and its catalytic performance, the nickel crystal, as catalyst support, was prepared at different temperatures via hydrothermal synthesis method in this work, without addition of any surfactant or capping agent. The effect of synthesis temperature and solvent on the morphology of nickel crystal was investigated. Then platinum supported on the nickel crystal (Pt/Ni catalysts) were obtained by galvanic replacement reaction method. Finally, the relationship between the morphologies of the Pt/Ni catalysts and their catalytic performance for the selective hydrogenation of nitrobenzene was established.

2. Experimental section

The chemicals used in this work were analytical grade without further purification, which were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All reagents were used as received. Deionized water was obtained by using a Milli-Q system.

2.1. Synthesis of nickel crystal

Typically, the green transparent aqueous nickel(II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) solution of 30 mL was obtained by dissolving 0.4500 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 30 mL of deionized water. Then 5 mL of anhydrous ethanol was added to the above solution under magnetic stirring for ten minutes. Subsequently, 1.8130 g of NaOH was dissolved in deionized water (5 mL), forming aqueous NaOH solution, and it was added into the as-obtained solution. After vigorous agitation for 10 min, 5 mL of reducing agent (85 wt% hydrazine hydrate- $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) was injected and maintained for 10 min. Then the above mixture was sealed into a 100 mL Teflon-lined stainless-steel autoclave, followed by hydrothermal synthesis at X °C for 1 h in an electric oven; where X = 60, 90, 120, 150 or 180 °C. After the reaction finished, the autoclave was cooled down to room temperature (RT) naturally. And the black products were deposited on the bottom of the Teflon cup and collected by filtration, repeatedly washed with distilled water and absolute ethanol. The final samples were obtained after dried under vacuum at 60 °C for 6 h, signed as Ni-X, X representing synthesis temperature = 60, 90, 120, 150 or 180. With the purpose of investigating the effect of solvent on the morphology of Ni, the aqueous $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ solution of 30 mL was replaced with ethanol $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ solution of 30 mL, with other reaction conditions kept unchanged. This hierarchical nickel was prepared at 150 °C, denoted as Ni-ethanol.

The platinum/nickel catalysts were prepared by the galvanic replacement reaction method [30–35]: 0.1000 g of nickel crystal was dispersed in a certain amount of aqueous H_2PtCl_6 solution (1.0000 g $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ dissolved in 250 mL deionized water) by ultrasonication at RT for 2 h. And the solid was obtained by filtration, thoroughly washed with deionized water and anhydrous ethanol, and dried in a vacuum oven at 60 °C for 6 h. The Pt loading in the catalysts was determined with inductively coupled plasma atomic mass spectrometry (Agilent ICP-MS 4500-300) –2.0 wt%.

2.2. Characterizations

X-ray diffraction (XRD) analysis was carried out to obtain the crystallite structures of the samples, using a Rigaku Ultima IV X-ray diffractometer equipped with high-speed array detection system and Cu *K* α radiation (40 kV and 30 mA) as the X-ray source. The 2 θ Bragg angles was varied from 10° to 90°. The scanning electron microscopy (SEM) images and energy dispersive X-ray spectrum (EDS) of the samples were obtained by using MLA650F scanning electron microscope. And the samples were supported on conducting resin prior to test. Transmission electron microscope (TEM) and high resolution transmission electron microscope (HRTEM) measurements for the catalysts were performed on a FEI TECNAI F20 high-resolution transmission electron microscope operated at 200 kV. Before TEM and HRTEM tests, the samples were dispersed in ethanol under ultrasound. The suspension containing catalysts was dropped onto a copper grid supported with a thin holey carbon film. XPS measurements were performed on PHI Quantum 2000 Scanning ESCA Microprobe equipment with monochromatic Al *K* α radiation to gain the chemical states and composition of Pt and Ni element on the surface of the catalysts. The high-sensitivity low-energy ion scattering (HS-LEIS) tests were conducted on IonTOF Qtac100 low-energy ion scattering analyzer. $^4\text{He}^+$ ions with a kinetic energy of 3 keV were applied at a low ion flux equal to 1325 pA cm⁻². $^{20}\text{Ne}^+$ ions with a kinetic energy of 5 keV were applied at a low ion flux of 1600 pA cm⁻². The scattering angle was 145°.

The catalytic performance of the catalysts in the selective hydrogenation of nitrobenzene was obtained by using high-pressure autoclave (Parr 4848) as reactor. 40 mL of ethanol nitrobenzene solution (nitrobenzene = 11.15 mmol) and 0.0300 g of catalyst were placed into the reactor. Air in the reactor was replaced with H₂, and H₂ was continuously added into the autoclave until the pressure reached 4.5 MPa. The reaction was carried out at 80 °C for 1 h at the mechanical stirring speed of 500 rpm. After the reaction was over, the reactor was quickly cooled down to about 5 °C. Subsequently, the liquid was separated from the catalyst by magnetic separation. The liquid products were analyzed by gas chromatography (GC) on a Shimadzu GC 2010 instrument furnished with a DB-35 60 m × 0.32 mm capillary column and a flame ionization detector (FID), and gas chromatography–mass spectrometry (GC–MS) on a Shimadzu GC–MS 2010. The rate of nitrobenzene hydrogenation (*r*) was determined on the basis of the following equation:

$$r = n_{\text{conversion of nitrobenzene}} / (n_{\text{total platinum}} \times t)$$

where $n_{\text{conversion of nitrobenzene}}$, t and $n_{\text{total platinum}}$ represent mols of conversing nitrobenzene, reaction time (h) and total mols of platinum in the catalysts. The unit of *r* is mol_{Pt}⁻¹ h⁻¹.

3. Results and discussions

3.1. Effect of hydrothermal temperature on the shape of the hierarchical nickel

Fig. 1 shows the XRD patterns of the hierarchical nickel prepared at various temperatures. It is obvious that only three diffraction peaks (2 θ at 44.5°, 51.9° and 76°) are ascribed to Ni face-centered cubic (fcc) structure (JCPDS card No. 04-0850). It indicates that purified Ni metallic state crystal has been successfully obtained when the hydrothermal temperature varied from 180 °C to 60 °C, fixing the amount of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ –0.4500 g, reaction time 1 h and hydrazine hydrate 5 mL. The XRD patterns of the platinum/nickel catalysts are depicted in Fig. 2. It can be seen that the XRD patterns for the hierarchical nickel samples are very similar to those for the platinum/nickel catalysts. And no any diffraction peak due

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