Catalytic activity of nickel nanoparticles in hydrogenation of *p*-nitrophenol to *p*-aminophenol

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ABSTRACT

Nickel nanoparticles with different sizes and different structures were prepared by reducing nickel oxalate with hydrazine hydrate in the presence of citric acid, sodium dodecyl sulphonate, Tween 80, PEG 6000, and D-sorbitol as organic modifiers. The type of organic modifiers affected the size and the structure of the resultant nickel nanoparticles. The catalytic activities of the nickel nanoparticles increased with decreasing the particle size in the hydrogenation of *p*-nitrophenol to *p*-aminophenol. All the as-prepared nickel nanoparticles showed higher catalytic activity and selectivity than conventional Raney Ni catalyst.

1. Introduction

Recently, metal nanoparticles have been attracting great attention because of their remarkable catalytic performance in hydrogenation, oxidation, and reduction reactions [1–3]. It was reported that Pd, Pt, Rh, Ru, Au, and Ni nanoparticles exhibited higher catalytic activity than conventional supported metal catalysts in hydrogenation [4,5] and oxidation reactions [6–8]. The catalytic activity and selectivity of metal nanoparticles are strongly dependent on their size and shape [4,9,10]. Direct hydrogenation of *p*-nitrophenol catalyzed by nickel catalyst is considered as an alternative green process for the production of *p*-aminophenol [6,11]. However, the catalytic performance of nickel nanoparticles in the hydrogenation of *p*-nitrophenol to *p*-aminophenol was seldom investigated [12–14]. In particular, the effect of particle sizes on the catalytic activity of nickel nanoparticles was not investigated in detail.

Generally, nickel nanoparticles can be prepared by a variety of methods, such as wet chemical reduction in aqueous solution [15–18] or in organic medium [19–23], microemulsion [24], and hydrothermal [25,26] methods. Among these preparation routes, wet chemical reduction is a versatile and economic method. However, it is difficult to prepare phase pure nickel nanoparticles in aqueous medium because nickel nanoparticles are easily oxidized in water [17,25–27], which limits their application. On the other hand, organic modifiers, such as sodium carboxyl methyl cellulose

[9], tetrabutylammonium bromide [10,15], sulfonated polybutadiene [16], and cetyltrimethylammonium bromide [17], were used in the size-controlled synthesis of nickel nanoparticles. But the effect of organic modifiers on the crystal structure of the resultant nickel nanoparticles was not discussed in detail until now.

Our present work describes the synthesis of phase pure nickel nanoparticles with different sizes and different crystal structures via a simple chemical reduction route starting from nickel oxalate and hydrazine hydrate in anhydrous ethanol. In this process, citric acid, sodium dodecyl sulphonate, Tween 80, PEG 6000, and D-sorbitol were used as organic modifiers, which play an important role in deciding the size and the crystal structure of the resultant nickel nanoparticles. The catalytic performance of the nickel nanoparticles in the hydrogenation of *p*-nitrophenol to *p*-aminophenol was investigated and compared with that of conventional Raney Ni catalyst.

2. Experimental section

2.1. Synthesis of nickel nanoparticles

Nickel nanoparticles were prepared by reducing nickel oxalate ($NiC_2O_4 \cdot 2H_2O$, 98.5%) with hydrazine hydrate ($N_2H_4 \cdot H_2O$, 85%) in the presence of organic modifiers with different functional groups, such as citric acid, sodium dodecyl sulphonate, Tween 80, PEG 6000, and D-sorbitol. Typically, the organic modifier (0.37 g) and nickel oxalate (2.49 g) were dissolved in the anhydrous ethanol solution (70 mL) by ultrasonic dispersion for 30 min. While the mixture was heated to 60 °C, an ethanol solution of NaOH (1 M,

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20 mL) was added dropwise into it to adjust the pH of the reaction solution to 12. After that, hydrazine hydrate ethanol solution (7.5 mL in 10 mL anhydrous ethanol) was added dropwise into the mixture and heated up to 80 °C for 8 h under stirring. The resultant nickel nanoparticles were cooled to room temperature and kept in anhydrous ethanol solution. Nickel nanoparticles were centrifuged and washed with anhydrous ethanol when they were used as catalysts in the hydrogenation of *p*-nitrophenol.

2.2. Preparation of Raney Ni catalyst

Raney Ni catalyst was prepared by the following procedure: 1.0 g of Ni–Al alloy with a weight ratio of 47:53 was added to an aqueous solution of NaOH (6.0 M, 10 mL) under stirring at 50 °C. After that, the reaction solution was heated to 80 °C and stirred for 1 h. The resultant black precipitate was washed with distilled water to neutrality and then washed with anhydrous ethanol to re-place water. The as-prepared Raney Ni catalyst was kept in anhy-drous ethanol. The particle sizes of the as-prepared Raney Ni were analyzed on a scanning electron microscope (JSM 7001F) operating at 10 kV. The average particle size of the as-prepared Ra-ney Ni was 13 μm, which was calculated by a weighted average method according to the individual particle sizes of the all counted particles.

2.3. Characterization

The as-prepared nickel nanoparticles were characterized by X-ray diffraction (XRD) on a Rigaku, D-max 2200 X-ray diffractome-ter with Cu Kα radiation at λ = 1.5406 Å. High resolution transmis-sion electron microscopy (HRTEM) images and the corresponding selected area electron diffraction (SAED) patterns were obtained on a microscope (JEM-2100) operated at an acceleration voltage of 200 kV to characterize the morphologies and the crystal struc-tures of the as-prepared nickel nanoparticles. The average particle sizes of the samples were calculated by a weighted average meth-od according to the individual particle sizes of the all counted particles.

2.4. Catalytic hydrogenation of p-nitrophenol to p-aminophenol

The hydrogenation of *p*-nitrophenol was carried out in a 1000 mL capacity stainless steel autoclave fitted with a magneti-cally driven impeller. The autoclave was charged with 3.0 g of *p*-nitrophenol dissolved in 150 mL anhydrous ethanol and 0.09 g of the as-prepared nickel nanoparticles or Raney Ni catalyst. Firstly, the autoclave was purged with nitrogen for 10 min. Then hydrogen from a cylinder was introduced and raised to 0.8 MPa. Under stir-ring at 600 rpm, the reaction was carried out at a temperature of 100 °C for different time. The liquid phase sample was analyzed by high-performance liquid chromatography (HPLC, Varian ProStar 210) equipped with an ultraviolet detector set at a wavelength of 254 nm and a C18 column (5 μm, 4.6 mm × 250 mm). A mixture of methanol and acetic acid (0.2 wt.%) aqueous solution (3:2 v/v) was used as a mobile-phase at a flow rate of 1 mL/min.

3. Results and discussion

3.1. XRD analysis

The XRD patterns of the samples are shown in Fig. 1. The XRD diffraction peaks appearing at 2θ = 44.5, 51.9, and 76.5° correspond to the (1 1 1), (2 0 0), and (2 2 2) planes of the face-centered-cubic (fcc) nickel (JCPDS 04-0850), respectively. No impurity diffraction
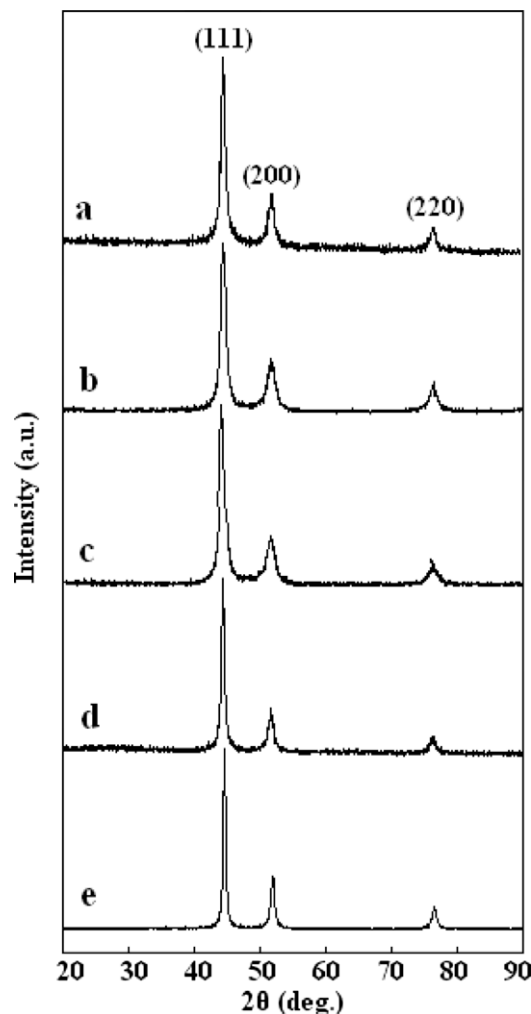

Fig. 1. XRD patterns of the nickel nanoparticles prepared by reducing nickel oxalate with hydrazine hydrate and using (a) citric acid, (b) sodium dodecyl sulphonate, (c) Tween 80, (d) PEG 6000, and (e) D-sorbitol as organic modifiers, respectively.

peaks were detected, indicating that phase pure metal nickel was prepared under the present experimental conditions.

3.2. HRTEM analysis

Fig. 2 shows the TEM and HRTEM images of the nickel nanopar-ticles prepared by reducing nickel oxalate with hydrazine hydrate in the presence of citric acid, sodium dodecyl sulphonate, Tween 80, PEG 6000, and D-sorbitol as organic modifiers, respectively. The insets in the TEM images show the corresponding SAED pat-terns by directing the incident electron beam perpendicular to one of the nanoparticles. The diffraction rings are indexed to fcc nickel metal and indicate that all the resultant nickel nanoparticles are of a polycrystalline structure. TEM images show that all the as-prepared nickel nanoparticles are spherical in shape. The ability of the organic modifiers on decreasing particle size of nickel nanopar-ticles is in an order of citric acid (9 nm) > sodium dodecyl sulpho-nate (60 nm) > Tween 80 (178 nm) > PEG 6000 (184 nm) > D-sorbitol (339 nm).

When citric acid was used as an organic modifier, the resultant primary nickel nanoparticles with an average diameter of 9 nm loosely aggregated to form secondary spherical particles with an average diameter of 254 nm, giving a large surface area. The forma-tion of secondary nanoparticles could be ascribed to the synergistic