Synthesis of nickel nanoparticles supported on metal oxides using electroless plating: Controlling the dispersion and size of nickel nanoparticles

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ABSTRACT

Nickel nanoparticles supported on metal oxides were prepared by a modified electroless nickel-plating method. The process and mechanism of electroless plating were studied by changing the active metal (Ag) loading, acidity, and surface area of metal oxides and were characterized by UV–vis spectroscopy, transmission electron microscopy, scanning electron microscopy, and H_2 chemisorption. The results showed that the dispersion of nickel nanoparticles was dependent on the interface reaction between the metal oxide and the plating solution or the active metal and the plating solution. The Ag loading and acidity of the metal oxide mainly affected the interface reaction to change the dispersion of nickel nanoparticles. The use of ultrasonic waves and microwaves and the change of solvents from water to ethylene glycol in the electroless plating could affect the dispersion and size of nickel nanoparticles.

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1. Introduction

Interest in clusters or nanoparticles with properties distinct from those of individual atoms and molecules or bulk matter has been widespread [1]. Supported nickel nanoparticles have been reported frequently in magnetic science and catalysis science. In particular, nickel nanoparticles supported on metal oxides with unique chemical and physical properties have been widely used as catalysts for many hydrorelated reactions, such as the hydrogenation, hydrogenolysis, and hydrotreating reactions [1–6]. Such supported nickel nanoparticles are mostly synthesized by the impregnation/deposition of nickel complexes from an aqueous solution onto the supports [4]. Metal oxide in aqueous suspension is generally electrically charged, as shown in Fig. S1 (the scheme of the adsorption of metal ions by metal oxides in aqueous suspension with different pHs) [2], and an "equilibrium deposition filtration" (EDF) method is widely used for the synthesis of supported nickel nanoparticles [1–3]. The dispersion of nickel nanoparticles is very high, as the nickel loading on supports is low (below 5 wt%, mostly) [4,5]. But the EDF method cannot be applied in such cases when a higher nickel loading (e.g., >15 wt%) or a controllable particle size of nickel nanoparticles is required. Incipient wetness impregnation, wet impregnation, pore volume impregnation, dry impregnation, and nondry impregnation without filtration have been extended to increase the nickel loading and the particle

size, although the dispersion of nickel nanoparticles is relatively lower [4]. Indeed, a new method for the synthesis of supported nickel nanoparticles with high dispersion as well as high nickel loading is significant for their further catalytic application. The electroless nickel-plating method should be a suitable choice because it has been proved to control the nickel loading, particle size, and dispersion of nickel nanoparticles [4–6].

The electroless nickel plating should first be activated by active substrates preloaded with Ni, Ag, Au, Pd, or Pt metal. The plating occurs by the reduction of nickel ions at the surface of the active substrate immersed into the plating solution and continues to deposit on the substrate through a catalytic action of the deposit itself [7–9]. Two mechanisms of electroless plating with borohydride as reductant have been reported by Gorbunova (Scheme S1) and Mallory (Scheme S2) [5,6,10–13]. Three routes for the activation of electroless nickel plating are proposed based on the two mechanisms and the work of Hwang and Lin as shown in Fig. 1 (a description in detail can be found in the supporting materials) [7,13–15]. Three routes for the generation of new nuclei for the continuous deposition are as follows: (i) the nuclei are separated from the Ag metal and diffuse into the plating solution, and then are adsorbed/deposited by supports (Fig. 1a); (ii) the nickel ions preadsorbed by supports are reduced by the generating electrons or H atoms (Figs. 1b and 1c); and (iii) the nickel ions near the supports are reduced by the generating electrons or H atoms and adsorbed by the supports (Figs. 1b and 1c). These routes are related to the interface reaction/interaction between the support and the plating solution or the active metal and the plating solution. Little work on the relation has been reported, although the dis-

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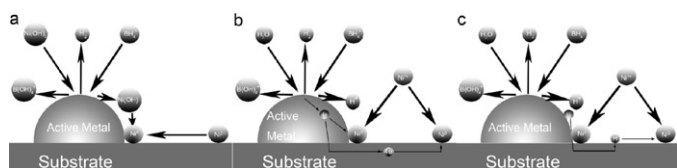
Fig. 1. Processes of nickel deposition on substrates based on (a) hydrolyzed nickel mechanism, (b) electrochemical mechanism, and (c) hydrogen atom mechanism.

persion and size of nickel nanoparticles are mainly affected by the generation of new nuclei [16].

In this paper, the interface reaction/interaction between the support and the plating solution or the active metal and the plating solution in the electroless nickel plating was studied. The mechanism of electroless plating was first studied to point out the factors affecting the dispersion and size of nickel nanoparticles on metal oxides. The changes of the acidity and area of supports and the microwave or ultrasonic wave technique were used to promote the dispersion of nickel nanoparticles. The as-prepared supported nickel nanoparticles were also evaluated in the catalytic hydrogenation of sulfolene and hydrodechlorination of chlorobenzene (see Supporting materials).

## 2. Materials and methods

2.1. Materials

Nickel(II) sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$), potassium borohydride (KBH_4), ethylenediamine (en) ($H_2NCH_2CH_2NH_2$), sodium hydroxide (NaOH), silver nitrite ($AgNO_3$), 25 wt% ammonia ($NH_3 \cdot H_2O$), formaldehyde (HCHO), and various metal oxide supports, such as TiO_2, MgO, Fe_3O_4, SiO_2, γ-Al_2O_3, and ZrO_2, were of reagent grade. Doubly distilled water was used in all the experiments.

2.2. Preparation of supported nickel nanoparticles

The Ag/support was synthesized per Refs. [16,17]. From 1.0 to 6.3 g support was added to 425-ml solutions with stirring at 313 K for 4 h. The solution was composed of 4.71×10^{-2} g/L $AgNO_3$, 8.82×10^{-2} g/L ammonia, 1.18×10^{-2} g/L NaOH, and 4.71×10^{-3} g/L HCHO. The resulting Ag/support was collected and washed with distilled water, and then dried at 363 K for 4 h. The electroless nickel plating was performed by adding the Ag/support to the plating solution with the following composition: $NiSO_4 \cdot 6H_2O$, 12.0 g/L; KBH_4, 5.5 g/L; en, 10 g/L; and NaOH, the amount needed to reach pH 13.5. No reactant was added to hold the pH and the concentrations of Ni^{2+} ions and borohydride constant during the plating, and the pH and the concentration of Ni^{2+} decreased with plating time. The reaction lasted until no significant bubbles were observed (about 20–40 min). The product was collected and washed thoroughly with distilled water, and then washed and stored with ethanol. The plating was carried out under conventional heating (water bath) or microwave irradiation (60 W, 2455 MHz) at 323 K. The theoretical nickel loading was controlled between 15 and 20 wt%. The solvents of the plating solution were water and ethylene glycol (EG). An ultrasonic wave (80 W, 40 kHz) was also introduced in some electroless plating experiments. The metal oxides TiO_2, MgO, γ-Al_2O_3, Fe_3O_4, SiO_2, and ZrO_2 were of 200 mesh.

2.3. Instrumentation

The chemical compositions of samples were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) on an IRIS Intrepid spectrometer. Transmission electron microscope
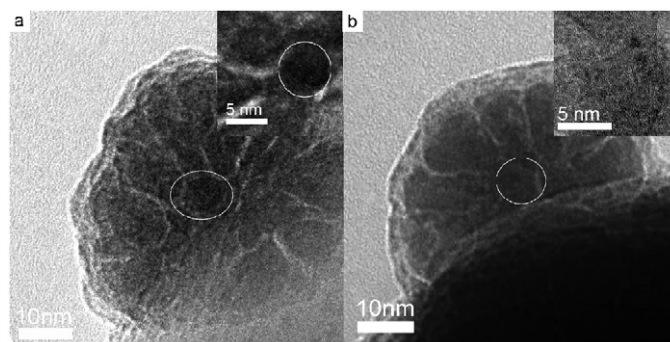
Fig. 2. HRTEM images of nickel nanoparticles in Ni/TiO_2 with 0.16 wt% Ag loading.

(TEM) images were acquired using a JEOL-2010 FEF high-resolution transmission electron microscope equipped with an EDX system (EDAX) and a Philips EM400ST transmission electron microscope. Scanning electron microscope (SEM) images were obtained on a LEO 1530VP field emission instrument. The surface area of the sample was measured using the BET method by N_2 physisorption at 373 K on an automatic surface area and pore size analyzer (Autosorb-1-MP 1530 VP). The UV–vis spectra were recorded on a Cary-100 spectrometer (Varian) equipped with an integration sphere. Barium sulfate was used as a reference. The spectra of solutions were recorded in the range 200–800 nm. The isoelectric point (IEP) was measured as in Ref. [1]. The active nickel surface area (S_{Ni}) of sample was determined by hydrogen chemisorption using a dynamic pulse method [18].

3. Results and discussion

3.1. The processes of new nucleus generation and nickel deposition

Electroless metal plating is frequently rethought to proceed by an electrochemical mechanism such as simultaneous of cathodic metal deposition and anodic oxidation of reductant [7,10,15]. The electrochemical conditions for carrying out electroless plating are as follows: The oxidation potential of the reductant is less noble to the reversible potential of the metal to be deposited and the active metal has enough catalytic activity for the anodic oxidation to take place at a reasonable rate [15]. The activation of the plating means that the active metal preloaded on the support catalyzes the anodic oxidation of reductants and induces a potential shift negative to the reversible potential of the metal to be deposited [7,15]. The anodic oxidation of the reductants proceeds mainly by the hydrogen evolution mechanism on copper, silver, and gold and the hydrogen ionization mechanism on cobalt, nickel, palladium, and platinum [15]. The nature and distribution of new active nuclei/species formed during the activation process by the active metal greatly affect the deposition behavior and the properties of the deposit [16].

In our previous work, the nickel nanoparticles were found to be deposited selectively on the TiO_2 or MgO support, rather than formed as a continuous film [17–19]. Fig. 2 shows the HRTEM images of two typical nickel nanoparticles in the Ni/TiO_2 sample with 0.16 wt% Ag loading. One has a dark ellipse in the center of the particle, which is highlighted with a white circle in the insert of Fig. 2a. Its EDX result in Fig. S2a indicates that some Ag elements are observed in the nickel nanoparticle. Because Ag atoms exhibit much higher atomic weight than Ni atoms and the nickel nanoparticle shows an amorphous structure [16–18], the Ag core can be distinguished obviously in the TEM image [18]. This means that the dark ellipse is ascribed to the Ag nuclei. It shows that this type of nickel nanoparticles are formed by the continuous deposition of nickel on the active Ag metal. During the TEM characteriza-