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Short Communication

Size-controlled synthesis of a supported Ni nanoparticle catalyst for selective hydrogenation of p-nitrophenol to p-aminophenol

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1. Introduction

Nickel nanoparticles, especially supported nickel nanoparticles on various carriers, have been extensively studied as heterogeneous catalysts [1–3]. These supported nickel nanoparticles are generally prepared by reducing nickel cations impregnated on supports with H₂ at a high temperature (e.g. 400 °C) [1–3]. This conventional reduction method usually leads to large nickel aggregates and broad size distributions when preparing catalysts with high nickel loading (>5 wt.%) [4–7]. As a result, the aqueous reduction of nickel cations impregnated/adsorbed on supports with a strong reducing agent (e.g. hydrazine) at ambient conditions earns increasing interest because of its advances on controlling particle morphology, size, and dispersion [6,7]. In our previous work, we succeeded in controlling the synthesis of Ni-B nanoparticles (e.g. metal loading, particle morphology, size and dispersion, etc.) using a modified electroless plating technique with borohydride as a reductant [8–13]. However, the resulted Ni–B nanoparticles possess unstable amorphous structure adverse to the recycle of catalysts in many practical reactions. Here, we attempted to synthesize supported crystalline nickel nanoparticles by a modified electroless plating method using hydrazine hydrate as a reductant, in order to obtain stable and controllable supported nickel particles.

ABSTRACT

We reported a general strategy of size-controlled synthesis of supported nickel nanoparticle catalysts using electroless plating technique. The synthesis conditions (e.g. compositions of plating solution and plating temperatures) were optimized to promote plating rate, and nickel nanoparticles with 9 nm diameter and a narrow size distribution were highly dispersed on TiO₂. The as-prepared Ni/TiO₂ catalyst showed high activity, selectivity and stability in the selective hydrogenation of p-nitrophenol to p-aminophenol.

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The reduction of p-nitrophenol (PNP) to p-Aminophenol (PAP) is a model reaction which has been widely used for the quantification and comparison of the catalytic activity of metal nanoparticles [14]. Nitrophenol compounds are among the most common organic pollutants in industrial and agricultural waste waters, but the PAP is an important intermediate for the manufacture of analgesic and antipyretic drugs [15]. The nickel catalysts have been widely used in the hydrogenation of PNP to PAP [16,17]. Chen et al. found that the unsupported nickel nanoparticle catalyst yields good hydrogenation activity and selectivity [18,19], but sintering of nickel nanoparticle occurs after hydrogenation [18]. Here, a Ni/TiO₂ catalyst with small and uniform nickel particles for PNP hydrogenation was synthesized by an electroless plating method, in which TiO₂ served as supports to disperse and stabilize nickel particles.

2. Experimental

2.1. Preparation of Ni/TiO₂ catalyst

2.1.1. Seeding 1 wt.% Ni(nuclei)/TiO₂

2.1.1.1. Synthesis of 0.1 wt.% Ag/TiO₂ per Refs. [8–13]. 12 g TiO₂ (anatase, 18 m²/g, 70–120 nm) 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⁻¹ AgNO₃, 8.82×10^{-2} g L⁻¹ ammonia, 1.18×10^{-2} g L⁻¹ NaOH, and 4.71×10^{-3} g L⁻¹ HCHO. The resulting Ag/TiO₂ was collected and washed with distilled water, and then dried at 363 K for 4 h.

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Seeding 1 wt.% Ni(nuclei)/TiO₂ via electroless nickel plating catalyzed by Ag/TiO₂ [8,11,13]: 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 catalytic action of the deposit itself [8,13]. For the electroless nickel plating catalyzed by Ag metal, we have confirmed that the nickel nuclei are simultaneously generated by the growth of nickel clusters on Ag metals [8–13] and the reduction of nickel ion aggregates adsorbed by supports [13] at the beginning of plating. In a typical synthesis, 1.66 g H₂N-CH₂CH₂-NH₂ was dissolved in 80 mL distilled water under stirring, and 0.71 g NiSO₄·6H₂O and 4.0 g NaOH was dissolved in the above solution respectively. Then, 0.55 g KBH₄ dissolved in 20 mL distilled water was mixed to compose the plating solution containing 7.1 g L^{-1} NiSO₄·6H₂O, 16.6 g L^{-1} H₂N–CH₂CH₂–NH₂, 5.5 g L⁻¹ KBH₄ and 40.0 g L⁻¹ NaOH. For plating, 2 g Ag/TiO₂ was added into 20 mL Ni-B plating solution at 80 °C for 5 min, and then the Ni(nuclei)/TiO₂ was separated without washing.

2.1.1.2. Synthesis of 15 wt.% Ni/TiO₂. The electroless nickel plating should first be activated by active substrates preloaded with Ni, Ag, Au, Pd, or Pt metal [8–13]. For our present plating using N₂H₄·H₂O as reductant, the Ni metal is found to possess better catalytic activation than Ag metal in which 3–4-fold plating time was shortened. Thus, the 1 wt.% Ni(nuclei)/TiO₂ was used as the catalyst for the plating.

For composing plating solution, 15.0 g Ni(CH₃COO)₂·4H₂O dissolved in 40 mL distilled water was mixed with 40 mL N₂H₄·H₂O (containing 7.5–30.2 g N₂H₄·H₂O) under stirring. After that, 20 mL NaOH (2–6 g NaOH) solution was added into the above mixture with stirring. To synthesize Ni/TiO₂, 2 g Ni(nuclei)/TiO₂ was added into 100 mL nickel plating solution. The suspension was maintained at 60–90 °C for 10– 15 min, and then cooled to room temperature. The black product was filtered and washed with distilled water until pH = 7–8, then washed with ethanol to remove water and kept in ethanol.

2.2. Characterizations

X-ray diffraction patterns (XRD) were collected on the Rigaku D/ max-2500 diffractometer employing Cu K\alpha radiation ($\lambda = 1.5418$). Transmission electron microscopy (TEM) images were acquired using a Philips Tecnai G² high-resolution transmission electron microscope. The surface-area-weighted cluster diameter, d_{TEM}, was calculated using d_{TEM} = $\sum n_i d_i^3 / \sum n_i d_i^2$ [20].

Chemisorption experiments were carried out in a pulse chromatographic microreactor. ~200 mg catalyst was treated by flowing 100 mL min⁻¹ Ar gas from room temperature to 300 °C (5 °C min⁻¹ ramping rate) and kept for 2 h. Then, the sample was cooled down to 30 °C, and 1% H₂/Ar was injected every 5 min until the calculated areas of consecutive pulses were constant. The dispersion and surface area of active Ni (S_{Ni}) was calculated assuming H/Ni_(surf) = 1 stoichiometry and a surface area of 6.5×10^{-20} m² per Ni atom [20]. Mean cluster sizes (d_{chem}) were also estimated as Ref. [20].

2.3. Hydrogenation of PNP

The hydrogenation of PNP was carried out in a high-pressure stainless steel autoclave. In a typical experiment, 0.4 g catalyst was dispersed in 40 mL ethanol and 20 mL distilled H_2O , and 8 g p-nitrophenol was transferred to the solution. The reaction was performed at 100 °C and 1.5 MPa H_2 pressure with stirring at 800 rpm. The hydrogenation was monitored by the hydrogen mass flow meter, and the hydrogenation products were analyzed by a High Performance Liquid Chromatography (HPLC), and their structures were confirmed by LC–MS. 4-aminocyclohexanol was detected as a by-product from the further hydrogenation of PAP.

Blank experiments containing the reactant and solvent (ethanol and water) without metal catalysts have been carried. No conversion of PNP (under the detection limit of HPLC) was found, suggesting that there is no contribution on hydrogenation from autoclave or solvent (ethanol and water). The initial hydrogenation rate was calculated as a turnover rate (TOR) of PNP hydrogenation as molar hydrogenation rates per surface Ni atom.

3. Results and discussion

3.1. Characterizations

Fig. 1 shows the XRD pattern of Ni/TiO₂ catalyst prepared with ratios of $[N_2H_4]/[Ni^{2+}]=5$ and $[OH^-]/[Ni^{2+}]=1.25$ at 80 °C. Two new reflection peaks (Fig. 1) at $2\theta = 44.59^{\circ}$ and 51.90° corresponding to Ni (111) and (200) crystal plane respectively are observed, suggesting an fcc structure of metallic nickel particles. Also, the XRD pattern presents broad peaks corresponding to Ni metal with low intensities. This indicates a small crystalline size of nickel nanoparticles on TiO₂.

The morphology of Ni/TiO₂ was observed by TEM (Fig. 2). Spherical nickel nanoparticles are homogeneously dispersed on the external surface of TiO₂. The Ni dispersion of Ni/TiO₂ is 0.13 corresponding to a mean particle diameter (d_{chem}) of 9.1 nm. The d_{chem} is consistent with that measured by TEM characterization (d_{TEM} = 9.5 nm in Fig. 2), suggesting a narrow size distribution of Ni nanoparticles. Therefore, we calculated the nickel nanoparticle size based on hydrogen chemisorptions in the following discussion.

3.2. Formation of Ni nanoparticles

The control of metal particle size is of the utmost importance for the performance of any industrial supported metal catalyst. Here, we used TiO_2 with low surface area (18 m²/g [9]) to disperse 15 wt.% Ni. Consequently, it is difficult to prepare small Ni particles by using the conventional impregnation–reduction method [6,7]. The following discussion clearly shows our success in the synthesis of small Ni particles with high metal loading using the electroless nickel plating technique.

In our previous work [11,13], the control synthesis of Ni–B particles by electroless plating has been achieved by designing dispersion and size of Ni(nuclei). We found that the formation of highly dispersed Ni–B particles is dependent on the generation of highly distributed nuclei on supports, because the growth of nickel particles occurs via selective deposition of nickel metal on the nuclei [13]. Because the electroless nickel plating with different reductants possesses the similar process [20], we regarded that the role of Ni



Fig. 1. XRD pattern of Ni/TiO₂ catalyst.



Fig. 2. (a) TEM image and (b) Ni particle size distribution of Ni/TiO₂ sample; and TEM images of Ni/TiO₂ catalyst (c) before and (d) after 10-time hydrogenation.

 $(nuclei)/TiO_2$ in plating and the plating process are similar with that in Ni–B plating shown in previous work [8–13]. Thus, the plating rate was referred to the key factor for size control of Ni particles.

In the present work, when Ni(nuclei)/TiO₂ was added to the plating solution, a mass of nickel particles was deposited through autocatalysis of seeded nickel nuclei and the plating rate was drastically accelerated. More than 180 min for the plating process was required if there were no nuclei in the initial plating solution, which was two-fold or ten-fold time extension compared to the plating using Ag/TiO₂ (60 min) [21] or Ni(nuclei)/TiO₂ (10–15 min), respectively. A high plating rate favors generating large amount of nuclei during inducing period and leads to small and uniform nickel nanoparticles [8,13], which was also confirmed by the following study of plating conditions (e.g., temperature, $[N_2H_4]/[Ni^{2+}]$ and $[OH^-]/[Ni^{2+}]$



Fig. 3. Effect of plating conditions on the particle size and turnover rate (at ~30% conversion of PNP) of resulting Ni/TiO₂ samples. (a) change of molar ratios of $[OH^-]/[Ni^{2+}]$ with $[N_2H_4O]/[Ni^{2+}]=5$ at 80 °C, (b) change of molar ratios of $[N_2H_4O]/[Ni^{2+}]=1.25$ at 80 °C, and (c) change of temperatures with $[N_2H_4O]/[Ni^{2+}]=5$ and $[OH^-]/[Ni^{2+}]=1.25$.

ratios). Here, we achieved the size-controlled synthesis of Ni nanoparticles (9–20 nm), which are much smaller than our previous reported Ni particles (~45 nm) using Ag/TiO₂ as support [21].

3.2.1. Effect of $[OH^{-}]/[Ni^{2+}]$ ratio

The reduction of nickel ions by hydrazine in basic solution is often described as [6,7]:

$$2Ni^{2+} + N_2H_4 + 4OH^- \rightarrow 2Ni^0 + N_2 + 4H_2O.$$
(1)

A high pH value facilitates the reduction of nickel ions by hydrazine, and enhances the reduction rate. However, excess OH^- ions lead to a fast precipitation of $[Ni(N_2H_4)_3]$ (OH_2 to large nickel hydroxide precipitates on TiO_2 and then large nickel particles after reduction (Fig. 3a). Therefore, the particle size increases by increasing pH values ($[OH^-]/[Ni^{2+}]$ ratios), and a suitable alkalinity of solution was required to avoid fast precipitation of nickel hydroxides. Here, a molar ratio of $[OH^-]/[Ni^{2+}]$ equal to 0.8–1.3 is optimized to obtain small nickel nanoparticles (Fig. 3a).

3.2.2. Effect of $[N_2H_4]/[Ni^{2+}]$ ratio

Fig. 3b shows that Ni nanoparticle size decreases by increasing ratios of $[N_2H_4]/[Ni^{2+}]$, and then remains constant when $[N_2H_4]/[Ni^{2+}]$ is higher than 5. For the reduction of nickel ions by hydrazine, the reduction rate plays a key role in the generation of high-dispersed nanoparticles [6,7]. A high reduction rate promotes the simultaneous deposition of nickel clusters on all nickel nuclei in a short time, leading to small and uniform nanoparticles. Here, the deposition rate is determined by concentrations of nickel ions and hydrazine around nickel nuclei. By increasing concentrations of hydrazine in solution, the concentration of reductant around nickel nuclei consequently increases and promotes deposition rate. When excess hydrazine (> $[N_2H_4]/[Ni^{2+}]=5$) is applied, the deposition process is controlled by consuming nickel ions around nuclei, and a further increase of hydrazine concentration could not influence the deposition rate. Consequently, the particle size decreases with increasing ratio of [N₂H₄]/[Ni²⁺], and attains practically constant size of ca. 9 nm at $[N_2H_4]/[Ni^{2+}] > 5$ (Fig. 3b).

3.2.3. Effect of plating temperatures

For electroless plating, the plating rate accelerates obviously by increasing plating temperatures [8–13], resulting in a small particle size (Fig. 3c). However, too high temperature (90 °C) leads to the decomposition of plating solution into nickel aggregates, which results in growth of particle sizes. Here, the optimal temperature is 80 °C (Fig. 3c).

3.3. Catalytic performance

Table 1 summarizes the catalytic performance of catalysts in selective hydrogenation of PNP to PAP. Because Raney Ni possesses the highest surface active nickel area per gram catalyst (S_{Ni}), the shortest hydrogenation time is required for a complete conversion of PNP. However, 4-aminocyclohexanol (5.4 mol%) as the by-product is detected. Unlike Raney Ni, Ni/TiO₂ and Ni–B/TiO₂ catalysts show



Fig. 4. The change of initial turnover rates and PAP selectivities for the hydrogenation on the recycled Ni/TiO_2 catalyst.

~100% selectivity of PAP, suggesting the lack of active sites to catalyze PNP hydrogenation to 4-aminocyclohexanol.

For supported nickel catalysts, Ni–B nanoparticles show two times turnover rate (TOR) higher than crystalline Ni nanoparticles (Table 1), which is consistent with the fact that amorphous Ni-B possesses higher hydrogenation activity than crystalline Ni metal [8–13]. However, the dilution of active Ni by B elements on Ni-B/TiO₂ results in a 60% lower S_{Ni} value than Ni/TiO₂. This leads to ~33% longer hydrogenation time to completely converse PNP, when the same Ni weight amount of catalysts is used (Table 1). As a result, the Ni/TiO₂ with a higher S_{Ni} value ensures a more economical choice to use it as PNP hydrogenation catalyst. Fig. 3 shows that TOR values are not affected by Ni particle sizes, indicating the structure-insensitive hydrogenation reaction and the requirement of small Ni particle size to promote S_{Ni} value for PNP hydrogenation. Again, the recycling experiments of Ni/TiO₂ (Fig. 4) show bit decrease of TOR values and selectivity, and the HRTEM images (Fig. 2c and d) indicate no change of particle size before and after 10 times hydrogenation. These results show the good stability of asoptimized Ni/TiO₂ for PNP hydrogenation.

4. Conclusions

The TiO₂-supported Ni nanoparticle catalyst was prepared by a modified electroless plating method using hydrazine hydrate as a reductant. The formation of small and uniform Ni nanoparticles requires a high plating rate by optimizing the ratios of $[N_2H_4]/[Ni^{2+}]$

Table 1

Hydrogenation performance of Ni/TiO2 and Raney Ni catalysts.

Samples	S _{Ni}	$\frac{\text{TOR}}{(\text{mol}(\text{s}\text{mol}_{\text{surf-Ni}})^{-1})}$	Hydrogenation time (min)	Conversion (%)	Selectivity (mol%)	
					PAP	4-aminocyclohexanol
Ni/TiO ₂	13.5	3.23	45	~100	~100	-
Raney Ni	20.8	3.25	37	~100	94.5	5.4
Ni-B/TiO ₂ ^a	5.4	6.05	60	~100	~100	-

^a The catalyst was prepared as Ref. [8].

and $[OH^-]/[Ni^{2+}]$ in plating solution and the plating temperature. The as-optimized Ni/TiO₂ with 9 nm particle size showed high activity, selectivity, and stability in hydrogenation of PNP to PAP. Comparing to Ni–B and Raney Ni catalyst, the Ni/TiO₂ is a more suitable choice for the PNP hydrogenation. Our investigation of the control of nickel nanoparticle size suggests a strategy to optimize metal catalyst for catalytic reactions.

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