



Short communication

Spectrophotometric analysis of nickel colloid performances as catalysts for hydrogenation of nitro-phenol: Influence of the stabilizing agents

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ABSTRACT

Nickel nanoparticles are prepared through thermolysis or polyol procedures and they are fully characterized through TEM and XRD. The catalytic efficiencies are tested toward the hydrogenation reaction of 4-nitrophenol, which was spectrophotometrically detected. A significant improvement of the reaction rate and turnover number (TON) and frequency (TOF) is observed using alkyl amine-stabilized nanoparticles, likely due to their reduced surface steric hindrance. However, the polymer stabilized-nanocatalysts show a better selectivity for product formation, since only hydrogenation products are observed, while azo-benzene derivatives are detected when alkyl amine-stabilized nanoparticles are used. The findings indicate an important impact of surface properties of colloids on the catalysed reaction.

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1. Introduction

Metal nanoparticles have attracted increasing attention due to their electronic and surface properties [1–3]. Catalysis research using nanoparticles is a rapidly growing field fostered by the progress in materials research [4–6]. It has been reported that the size reduction is generally beneficial for a catalyst since it increases the number of thermodynamically high-energy active surface atoms and it lowers the reduction potential of the metal on the surface. The control of the material growth and shape is usually reached by the use of specific stabilizers [2]; however, their presence also strongly affects the properties of the nanocatalyst surface [4,7–8].

Nickel catalysis plays a central role in many synthetic transformations including the reduction of electron rich carbon bonds. More recently, nickel nanocolloids have been tested as catalysts in reactions occurring in suspension [9–11]. The preparation of Ni-based nanocatalysts arouses particular interest since this metal is more abundant and cheaper than others, which are widely used in catalysis, thus enabling the development of cost-effectiveness chemical protocols.

In the last few years, different preparation procedures have been proposed for colloidal nickel nanoparticles (Ni-NPs) [11–13] in order to optimize their catalytic performances. Jiang et al. [10] have shown that size and morphology of nickel nanoparticles can be modified

using different capping agents and an impact on the catalytic performances of the colloids has been observed; Blosi et al. [11] prepared highly crystalline nanoparticles in the 80–200 nm size range using a microwave-assisted synthetic procedure, which displayed good catalytic efficiencies.

In this context, it has been observed that for metal NPs the capping agents control the growth and stability of colloids, but they also adhere to the nanoparticle surface establishing specific interactions; Borodko et al. [14] have observed charge transfer between PVP and Pt nanoparticles, which could interfere in the catalytic reactions especially if an electron transfer mechanism is involved. More recently, it has been reported that in PVP-stabilized gold colloids the capping agent induces a shielding effect, reducing the catalytic activity of gold nanoparticles in alcohol oxidation reactions [4].

The hydrogenation reaction of nitroarenes to give aromatic amine is a model reaction widely used to test the performances of different catalysts [15]. The hydrogenation of 4-nitrophenol to give 4-aminophenol has a good industrial impact since the product is an important starting raw material for several fine chemicals in the field of dyes and pharmaceuticals [16]. Recently the mechanism of hydrogenation of nitroaromatics in the presence of heterogeneous catalysts and the role of intermediates have been deeply discussed [17,18].

In this work, Ni-NPs are prepared with different synthetic approaches to investigate the effects of dimensions, structure, and surface features (in terms of capping agents) on the catalytic properties of the resulting materials; also, the use of spectrophotometric detection

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enables working at low concentrations (10^{-5} M) of reagents with excellent sensitivity compared to other analytical techniques.

2. Experimental details

2.1. Materials

Acetone ($\geq 99.5\%$), methanol ($\geq 99.8\%$), ethanol (absolute, $\geq 99.8\%$), ethylene glycol (EG, $\geq 99.0\%$), and triethylene glycol (TEG, $\geq 99.0\%$) from Sigma-Aldrich and ultrapure water (≤ 18.0 M Ω) obtained with a Millipore Milli-Q gradient system were used as solvents. Nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\geq 98.0\%$), nickel(II) acetylacetonate ($\text{Ni}(\text{acac})_2$, 95%), sodium borohydride (NaBH_4 , $\geq 98.0\%$), dioctylamine (DOA, 98.0%), trioctylphosphine (TOP, 97%), polyvinyl pyrrolidone (PVP, MW 40,000), and 4-nitrophenol (4-NPh, $\geq 99.5\%$) were purchased from Sigma-Aldrich and used without any further purification.

2.2. Preparation of the catalytic nanoparticles

All the preparations are carried out in a de-aerated atmosphere achieved by vigorously bubbling nitrogen in the solvent at least for 30 min.

2.2.1. Ni-NP prepared through the thermolysis method

Nickel nanoparticles are synthesized by a modified procedure involving the thermal decomposition of $\text{Ni}(\text{acac})_2$ in the presence of capping agents [13]. In a typical synthesis, 1.0 g $\text{Ni}(\text{acac})_2$ is dissolved in DOA (41.4 mmol) containing TOP (3.1 mmol). Under nitrogen stream the solution is stirred and heated at 383 K with a heating rate of 5 K/min. After 30 min, the temperature is quickly raised to 493 K (constant heating rate of 15 K/min) and the obtained dark brown mixture is kept under stirring for 2 h. After cooling to room temperature, the nanoparticles are recovered by precipitation with 10.0 mL ethanol and washed three times by centrifugation and dispersion in ethanol. After the final washing step, the supernatant is discarded and the precipitate is collected and dried at room temperature for 24 h (sample Ni-NPs1).

2.2.2. Ni-NP prepared through the polyol method

The synthetic route is adapted from a literature procedure [19]. Briefly, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.195 g) and PVP are dissolved (0.198 g) in 150.0 mL of EG under vigorous stirring. The resulting solution is heated to 413 K. At this temperature, 0.140 g of NaBH_4 is quickly added. The reaction mixture is maintained under stirring at 413 K for 2 h and then cooled to room temperature. The resulting Ni-NPs are precipitated by the addition of 50.0 mL of acetone and recovered by centrifugation at 4000 rpm. The precipitate is washed three times with a mixture of acetone/ethanol (50:50 v/v) and then dried at room temperature for 24 h (sample Ni-NPs2). The same procedure is also carried out in triethylene glycol using the same concentration of reagents in solution and setting the reaction temperature to 493 K (sample Ni-NPs3).

2.3. Ni NP characterization

TEM (Philips, model 208) operating at 80 kV of beam acceleration is used to obtain morphological information on the Ni nanoparticles. The sample suspensions are deposited in a 400 mesh copper-coated with a Formvar support grid. The size distribution histograms for the samples are obtained by analysing at least 100 nanoparticles in each sample.

The X-ray powder diffraction (XRPD) data are collected with a Philips X'PERT PRO MPD diffractometer operating at 40 kV and 40 mA, with a step size of 0.0170 2θ degree and step scan of 20 s, using $\text{Cu K}\alpha$ radiation and an X'Celerator detector. A. The sample (about 100 mg) is side-loaded onto an aluminium sample holder with an oriented quartz monocrystal underneath and pressed using a glass slide in order to minimize preferred orientations of the crystals.

UV-Vis spectra are collected with a Hewlett-Packard 8453 diode array spectrophotometer (a whole spectrum is recorded in 0.1 s). The kinetics of catalytic hydrogenation of 4-NPh is spectrophotometrically followed acquiring spectra at different reaction times. The optical response of nickel nanoparticles is analytically simulated using the Mie formulation and compared to the experimental UV-Vis spectra (see the Electronic supplementary material); in particular, literature data are used to reproduce the dielectric spectra of nickel [20] and nickel oxide [21].

2.4. Catalytic activity tests

Nickel nanoparticles are tested as catalyst for the hydrogenation of p-nitrophenol (4-NPh) to p-aminophenol (4-Aph) in the presence of NaBH_4 as source of H_2 . Briefly, 0.10 mg of Ni-NPs is mixed to 2.0 mL of a 0.09 mM aqueous solution of 4-NPh in a 1-cm path length quartz cuvette thermostated at 298 K. Immediately after, a fixed volume of an aqueous stock solution of NaBH_4 is added to give a final borohydride concentration of 0.1 M. The decrease in concentration of 4-NPh in solution is spectrophotometrically monitored following the decrease of the absorption band centred at 400 nm; an absorption coefficient value of $1.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 400 nm [22] is used to quantify 4-NPh concentration. The concentration of the catalyst in the reaction mixture is estimated from the mean diameter of NPs (through the analysis of TEM images), the amount of nickel salt precursor used in the NP preparation and the Ni atomic bulk density value of 8.91 g/cm³. The measurements are carried out in the presence of a large excess of NaBH_4 , compared to 4-NPh, so that the changes in the NaBH_4 concentration are negligible throughout the reaction. In these experimental conditions the hydrogenation reaction can be described with a pseudo-first order kinetic equation; the apparent rate constant (k_t), which is determined using the spectrophotometric data, gives information on the rate of the catalysed reactions and contains information on the catalytic efficiencies of the Ni-NPs.

TON (turnover number) and TOF (turnover frequency) of the catalysts are determined considering the disappearance of 4-NPh and the molar concentrations of the colloids. The molar concentration of Ni-NPs for each sample has been determined considering the amount of reduced metal and the average dimensions determined by TEM analysis. The determined TON and TOF can give information of the relative catalytic behaviour of the prepared colloids.

3. Results and discussion

3.1. Morphological and structural characterization of Ni-NPs

The nanoparticles prepared through the different synthetic procedures are characterized by TEM and X-ray diffraction measurements. TEM images are shown in Fig. 1 and demonstrate that spherical nanoparticles with a diameter below 10 nm are formed for all the samples. The size distribution analysis (Fig. 1), carried out on TEM images, enables the determination of average diameters of 7.7, 9.9 and 6.7 nm for Ni-NPs1, Ni-NPs2 and Ni-NPs3, respectively, with a different dispersion of dimensions for the three samples (Table 1). The comparison of the mean diameters of the Ni-NPs (Table 1) suggests that the synthetic conditions (such as solvent, temperature, and stabilizers) are crucial parameters. The synthesis conducted at the highest temperature (493 K) results in the sample (Ni-NPs3) with the smallest size and the narrowest size distribution, as indicated by the standard deviation in dimension (S.D. in Table 1).

For all the samples diffraction patterns are recorded (Fig. 2). Many well defined and sharp peaks are observed for sample Ni-NPs3 in the 35–80 2θ degree range, which are clearly attributed to the presence of hexagonal close-packed (hcp, JCPDS file no. 45-1027) and face-centred cubic (fcc, JCPDS file no. 04-0850) Ni phases (see Fig. 2 for the legend and the peak assignment to the Ni crystal planes); for the sample Ni-

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