Hydrogenation of nitrophenols catalyzed by carbon black-supported nickel nanoparticles under mild conditions

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ABSTRACT

A carbon black (CB) supported nano-Ni catalyst is prepared by a facile method using nickel chloride as the nickel source and hydrazine hydrate as the reducing agent. TEM observation shows that Ni nanoparticles have a good dispersion with a narrow size distribution on the surface of carbon black. The catalyst exhibits significantly high catalytic activity for hydrogenation of nitrophenols even at 30 °C. The high performance obtained here can be attributed to the specific characteristics of the nanostructure of the catalyst and the synergistic effect of nano-Ni and carbon black, including plenty of oxygen-containing groups of carbon black for anchoring Ni atoms, strong adsorption ability for organic molecules and good conductivity for electron transfer from the carbon black to Ni nanoparticles. Moreover, the Ni-based catalyst is relatively cheap and magnetically separable, thus achieving a low-cost hydrogenation of nitrophenols to aminophenols.

1. Introduction

Nitroaromatic compounds are being widely used in industrial processes, including the manufacture of dyes, pharmaceuticals, pigments, pesticides, wood preservatives and rubber chemicals [1–4]. Therefore, nitroaromatic compounds are often presented as water pollutants due to the release in industrial effluents. These pollutants pose significant health risks due to their carcinogenicity and may leave residues in animal products such as meat and eggs. Among various nitroaromatic compounds, nitrophenols are listed as one of top 114 organic pollutants by the United State Environmental Protection Agency (USEPA) [5,6], and especially, they have been implicated in carcinogenesis, teratogenesis and mutagenesis [5–7]. On the other hand, it is hardly inevitable that nitrophenols are a kind of important byproducts for the synthesis of nitro compounds, such as nitrobenzene, which can be produced through benzene nitration in the presence of mixed acid. Moreover, apart from mono-nitrophenols, di- and tri-nitrophenols (DNP and TNP) with stronger toxicity, carcinogenicity, mutagenicity and teratogenicity, are also significant byproducts in industrial processes [5,8,9]. Besides, the nitrophenols can also be produced in the air through the atmospheric photochemical reactions of nitrobenzene, bromobenzene and aromatic hydrocarbons with hydroxyl radicals and nitrogen oxides [10]. It is known that the reduction products of nitrophenols, aminophenols with lower toxicity are widely used as intermediates for the synthesis of pesticides, medicine, dyes and other fine chemicals [11,12]. As a typical example, p-aminophenol (p-AP) is less poisonous than p-nitrophenol (p-NP), and has become an important intermediate for the production of analgesic and antipyretic drugs such as phenacetin, paracetamol and acetanilide [3,13,14]. Therefore, for the sake of industrial mass production and the construction of environment-friendly society, it is of great significance to implement cost-effective strategy for the reduction of nitrophenols to aminophenols.

Several approaches for the reduction of nitrophenols to aminophenols have been reported so far, such as iron-acid reduction [1,2,15], electrolytic reduction [16], catalytic hydrogenation [17–21], etc. Iron-acid reduction requires strong acidic medium with low selectivity in general. In the meantime, a large amount of metal oxides is produced during the process, resulting in environmental problems. The electrolytic reduction is usually carried out in acidic or alkaline media and requires high energy consumption. Among all practicable routes mentioned above, only catalytic hydrogenation is a cost-effective process because this route can achieve high conversion efficiency with low emission under mild reaction conditions [22–24].

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Undoubtedly, the precious metal-based catalysts are still remain the leading catalysts for hydrogenation such as palladium [25–27], platinum [28–30], rhodium [31,32], ruthenium [33,34] and aurum-based [35–37] systems, even though their widespread applications are limited by their low earth-abundance and high cost. In order to solve these problems, various non-precious metal catalysts [38–40], especially nickel-based catalysts [3,39–41] have been developed as economical alternatives in hydrogenation reactions. However, compared with precious metal-based catalysts, the nickel-based systems usually exhibit relatively low activity, require higher temperatures and consume more energy in the process. Up to now, much less attention has been paid to the reduction of nitrophenols to aminophenols with nickel-based catalysts at lower temperatures [16,19].

Carbon black (CB), such as Vulcan XC-72, is one of the most commonly used supports for metal-based catalysts in many studies and commercial applications due to its turbostratic structures with high surface area and conductivity, especially, its lower cost when compared with nanocarbons [37,42]. Nevertheless, Vulcan XC-72 also suffers from the disadvantages such as its relatively lower content of oxygen-containing groups for anchoring precursor metal ions or metal nanoparticles and deep micropores or recesses which trap the metal nanoparticles making them difficultly accessible to reactants. It is known that the performance of XC-72 supported catalysts can be enhanced through modification, for instance, using acidification of XC-72 to produce more oxygen-containing groups.

Hence, it is of great interest to develop a carbon black supported nano-Ni catalyst for the hydrogenation reactions of nitrophenols under mild conditions. If that can be accomplished, then it may be possible to achieve the cost-effective hydrogenation of nitrophenols to aminophenols. Herein, we report a facile strategy for the preparation of Ni/CB system as an advanced catalyst for hydrogenation of nitrophenols to aminophenols. It is found that the Ni nanoparticles (Ni NPs) are well dispersed on the surface of carbon black and have a narrow size distribution. The Ni/CB catalyst exhibits significantly high catalytic activity for hydrogenation of nitrophenols at lower temperatures, thus its performance is impressively higher than that of recently reported nickel-based nanocatalysts [1,2,18]. Compared with noble metal-based catalysts, this catalyst is much cheaper and magnetically separable. Such a catalyst facilitates achieving the cost-effective hydrogenation of nitrophenols to aminophenols.

2. Experimental

2.1. Materials

Ethylene glycol (EG, 99.0%), nitric acid (HNO$_3$, 65–68%), hydrazine hydrate (N$_2$H$_4$·H$_2$O, 50%), nickel chloride (NiCl$_2$·6H$_2$O, 98%), *o*-nitrophenol (*o*-NP, 98%), *m*-nitrophenol (*m*-NP, 99%) and *p*-nitrophenol (*p*-NP, 99.0%) were all of analytical grade and supplied by Sinopharm Chemical Reagent Co., Ltd. Sodium borohydride (NaBH$_4$, 98%), sodium hydroxide (NaOH, BP. 98–100.5%) were obtained from Aladdin Industrial Cooperation. Vulcan XC-72 carbon black (CB) was purchased from Cabot Corporation. All chemicals were used without further purification and all solutions used in this study were prepared by using deionized water.

2.2. Synthesis of Ni and Ni/CB catalysts

Vulcan XC-72 carbon black used as the support was first acidized with nitric acid to gain better hydrophility and better adsorptivity for metallic ions. The acidification procedure is as follows: 3.0 g of carbon black and 300 mL of concentrated nitric acid were mixed uniformly in a 500 mL round-bottom flask. The mixture was heated to 100 °C under continuously stirring and constant reflux for 12 h. The resulting carbon black was centrifuged and washed with deionized water until neutral, and then dried for further use.

Ni/CB catalysts with differing Ni content were synthesized by a facile soft chemistry method. In a typical experimental procedure for the preparation of Ni/CB catalyst with 22 wt% Ni content is as follows: 0.05 g of CB was dispersed in 70 mL of EG, followed by adding 30 mL of EG solution of NiCl$_2$·6H$_2$O (0.0122 mol L^{-1}). Then the resulting mixture was heated to 60 °C under mechanical stirring for 20 min. Finally, 8 mL of hydrazine hydrate (50%) and 5 mL of NaOH/EG (1 mol L^{-1}) solution were added into the above mixture. After 30-minute reaction, the suspension was centrifuged, washed and vacuum freeze–dried. The product was labeled as Ni$_{0.22}$/CB (the subscript represents the actual Ni loading amount determined by ICP analysis). A series of Ni/CB catalysts with differing Ni content were prepared via the same method by varying the feeding ratio and marked as Ni$_{0.002}$/CB, Ni$_{0.11}$/CB, Ni$_{0.33}$/CB, Ni$_{0.41}$/CB and Ni$_{0.49}$/CB, respectively. The above procedure was also used to synthesize pure nano Ni catalyst without CB for comparison.

2.3. Characterization

Several characterization measurements were performed on the as-prepared catalysts. The morphologies of the catalysts were characterized by transmission electron microscope (TEM, JEOL JEM-2100, 200 kV). Samples for TEM analysis were prepared by dropping the ethanol suspension of catalysts onto the 300 mesh Cu grids coated with a carbon layer. The crystal structures of as-prepared catalysts were characterized by powder X-ray diffraction (XRD) analyses using a Bruker D8 Advanced diffractometer with Cu Kα radiation (λ = 0.15406 nm), and the scanning angle ranged from 10° to 80° (2θ) at the scanning speed of 0.05 ° s^{-1}. X-ray photoelectron spectroscope (XPS) measurements were performed on a RBD-upgraded PHI-5000C ESCA system (Thermo ESCALAB 250) with Al Kα radiation (hν = 1486.6 eV). Magnetic measurements were carried out with a vibrating sample magnetometer (VSM, Lakeshore7300) from −5000 Oe to +5000 Oe at room temperature (300 K). Inductively coupled plasma atomic emission spectrometry (ICP, Shimadzu ICPS-7510) was applied to determine the exact amounts of Ni in catalysts.

2.4. Catalytic hydrogenation reactions of nitrophenols

Catalytic hydrogenation reactions of nitrophenols in the presence of excess NaBH$_4$ were conducted in aqueous solution at atmospheric pressure and 30 °C, which can be served as the model reaction to assess the performance of Ni/CB catalysts with differing Ni content. In a typical experiment, aqueous solution of *p*-NP (0.5 mM) was freshly prepared and 5 mg of catalyst were dispersed in 10 mL of deionized water under ultrasonic radiation for several minutes until uniformly dispersed, then 2 mL of the dispersion were taken out and injected into 50 mL of *p*-NP solution under continuous stirring for 1 h to reach the adsorption-desorption equilibrium. After that, 0.1 g of NaBH$_4$ was put into the mixture with stirring. The reaction progress was evaluated by taking a small portion of the reaction mixture (diluted five times with deionized water) at specified time intervals and measuring the UV–vis spectra on PERSEE TU-1900. After the reaction, the catalyst can be easily removed from the solution phase under an external magnetic field, washed with ethanol and then reused 10 times in succession. In addition, the hydrogenation reactions of *o*-NP and *m*-NP were carried out under the same conditions. For comparison, CB and nano Ni catalyst were also participated in the hydrogenation reactions. Moreover, catalytic hydrogenation of *p*-NP was conducted at four different temperatures (20, 30, 40 and 50 °C) to evaluate the impact of the temperature on the reaction. In order to investigate the effect of sol-