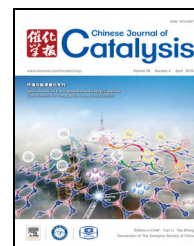


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Cobalt nanoparticles encapsulated in nitrogen-doped carbon for room-temperature selective hydrogenation of nitroarenes

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ABSTRACT

Here, we report cobalt nanoparticles encapsulated in nitrogen-doped carbon (Co@NC) that exhibit excellent catalytic activity and chemoselectivity for room-temperature hydrogenation of nitroarenes. Co@NC was synthesized by pyrolyzing a mixture of a cobalt salt, an inexpensive organic molecule, and carbon nitride. Using the Co@NC catalyst, a turnover frequency of $\sim 12.3 \text{ h}^{-1}$ and selectivity for 4-aminophenol of $>99.9\%$ were achieved for hydrogenation of 4-nitrophenol at room temperature and 10 bar H_2 pressure. The excellent catalytic performance can be attributed to the cooperative effect of hydrogen activation by electron-deficient Co nanoparticles and energetically preferred adsorption of the nitro group of nitroarenes to electron-rich N-doped carbon. In addition, there is electron transfer from the Co nanoparticles to N-doped carbon, which further enhances the functionality of the metal center and carbon support. The catalyst also exhibits stable recycling performance and high activity for nitroaromatics with various substituents.

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1. Introduction

Selective hydrogenation of nitroarenes is a promising approach to produce aromatic amines and aminocyclohexanes [1,2]. Aromatic amines are important bulk chemicals in many fields, including production of fine chemicals, commercial products, and polymers [3,4]. Along with the products of hydrogenation of the nitro groups, some byproducts are also produced, such as nitroso and azo compounds. For substituted nitroarenes with reducible groups (e.g., $-\text{Cl}$, $-\text{C}=\text{O}$, and $-\text{CHO}$ groups), selective hydrogenation of the nitro group is a great challenge. Noble-metal-based catalysts have been used for the chemical transformation of nitrobenzene to aniline, and excellent selectivities and activities have been achieved under mild

conditions [5–13]. However, noble-metal-free catalysts are preferred in industry because of their low cost and abundance. In this case, transition-metal- [14–22] and carbon-based [23–28] catalysts show potential for selective hydrogenation of nitrobenzene, but they suffer from low activity and require harsh reaction conditions. To achieve high activity and selectivity under mild conditions, both the H_2 molecules and nitro groups must be effectively activated, which is difficult to achieve with a catalyst containing only a single type of active site.

For bifunctional catalysts composed of a carbon-based material loaded with a transition-metal-based catalyst, the support material can not only confine the metal atoms, but it can also modify the electronic environment of the metal nanoparti-

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cles (in a way similar to homogeneous catalysts with organic ligands), which increases the catalytic activity. Recently, earth-abundant metals (e.g., Co) have been used for hydrogenation of nitrobenzene [14,20]. Reduced cobalt can act as a hydrogen acceptor owing to the electron-deficient state of its surface, which promotes cleavage of H–H bonds. However, it suffers from low chemoselectivity because of coadsorption of two or more nitroarenes. In this case, catalytic coupling of azo compounds can occur. Heteroatom-doped carbon with an adjustable electron structure and chemical stability can stabilize metal nanoparticles [29–33]. Doping N atoms into the carbon matrix can cause charge delocalization [34–36] and a high positive charge density on the carbon atoms next to the doped N atoms, which are beneficial for adsorption of compounds containing a nitro group. N-doped carbon has been used as a catalyst for hydrogenation of nitrobenzene because of the strong interaction between nitrobenzene and carbon catalysts [37], but its activity is still very low owing to its poor ability for H₂ activation. Metal catalysts can also be activated by carbon-nitride-based materials [38–40], where the electron density of the metal centers changes because in-lattice N atoms act as electron-accepting groups. Therefore, using N-doped carbon as a support for metal-based nanocatalysts is expected to enhance their catalytic activity.

Inspired by the above findings, we developed a synergetic catalyst composed of Co nanoparticles encapsulated in N-doped carbon (Co@NC) for room-temperature selective hydrogenation of nitroarenes. The N-doped carbon and cobalt center play roles in preferential adsorption of nitroarene and H₂ activation, so their synergetic effect leads to excellent activity and selectivity. The Co@NC catalysts were synthesized by calcining a mixture of a cobalt salt, an inexpensive organic molecule, and carbon nitride. The optimized Co@NC-1 catalyst shows excellent activity and selectivity at room temperature, which cannot be achieved using bare N-doped carbon or pristine-carbon-supported Co nanoparticle catalysts.

2. Experimental

2.1. Catalyst synthesis

To fabricate carbon nitride (g-C₃N₄), melamine was placed in a covered crucible, heated to 550 °C for 4 h under an inert environment, and then maintained at 550 °C for another 4 h. The as-synthesized yellow solid was ground into a powder, which was used to produce N-doped carbon. The homogeneous cobalt-containing precursor solution was prepared by dissolving cobalt nitrate hexahydrate (1.168 g) and triethylene diamine (1.92 g) in 40 mL of deionized water. g-C₃N₄ (1.0, 2.0, or 4.0 g for Co@NC-0.5, Co@NC-1, or Co@NC-2, respectively) was added to the aqueous solution under magnetic stirring. Owing to the effect of the Co–N bond, Co²⁺ ions can embed in the holes of carbon nitride and triethylene diamine molecules prevent excessive growth of Co particles during the following pyrolysis treatment. After the solvent was removed by vacuum freeze-drying, the solid powder was transferred to a covered crucible, heated to 900 °C at a rate of 2.5 °C/min under a N₂

atmosphere, and maintained at this temperature for 2 h. The as-obtained black solid samples were used for characterization and the catalytic reactions. To further investigate the role of N-doped carbon, Co@C was prepared by the conventional impregnation method using commercial carbon (VX720R) as the support. Pure N-doped carbon was also synthesized by pyrolysis of g-C₃N₄.

2.2. Characterization

Transmission electron microscopy (TEM) was performed with a Tecnai G2 F20 transmission electron microscope at 200 kV. The crystal structures were determined by a Rigaku D/max-2500 X-ray diffractometer (XRD) equipped with a Cu K_α irradiation source. Elemental analysis was performed with a Vario EL Cube equipped with a METTLER x86 instrument. The elemental composition and bonding information were obtained by X-ray photoelectron spectroscopy (XPS) at a pass energy of 187.85 eV (Physical Electronics PHI 1600 ESCA XPS system using a monochromated Al K_α X-ray source) using the C 1s peak at 284.6 eV as the internal standard. The nitrogen adsorption–desorption isotherms were determined with a ASAP 2020 physisorption analyzer at –196 °C, and the specific surface areas were calculated by the conventional Brunauer–Emmett–Teller (BET) method. The pore size distribution in the mesopore range was determined by the Barrett–Joyner–Halenda method. Before performing the measurements, all the samples were outgassed under vacuum at 200 °C for 12 h until the pressure was less than 0.66 Pa. The Fourier transform infrared spectroscopy (FTIR) spectra were recorded with a BioRad FTS 6000 spectrometer. Raman spectroscopy was performed with a Raman spectrometer (DXR Microscope) using a green semiconductor laser (532 nm) as the excitation source.

2.3. Catalytic hydrogenation of nitroarenes

Hydrogenation was performed in a 50-mL autoclave with a polytetrafluoroethylene lining using 0.5 mmol of the nitroarene, 5 mL of the solvent, and 30 mg of the catalyst. The autoclave was purged with N₂ and H₂ (15 bar) three times and then pressurized to 10 bar. After the reaction, the catalyst was separated by centrifugation, followed by analysis of the sample by gas chromatography (GC)–mass spectroscopy (MS) (Agilent 5975 equipped with a HP-5 capillary column) and GC (Agilent 7820 equipped with a flame ionization detector and AT-SE-54 capillary column).

3. Results and discussion

To enable large-scale production of Co@NC for possible use as a heterogeneous catalyst, we developed a freeze-drying method using cobalt nitrate as the metal salt and carbon nitride as the N precursor. The solid mixture was carbonized at 900 °C under an inert atmosphere (Fig. 1(a)). The X-ray diffraction (XRD) patterns indicate formation of metallic cobalt [41] (the peaks at about 44° and 51° are assigned to the (111) and (200) diffractions of Co nanoparticles) and graphitic carbon (the peak

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