Single cobalt sites in mesoporous N-doped carbon matrix for selective catalytic hydrogenation of nitroarenes

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ABSTRACT

A supported cobalt catalyst with atomically dispersed Co-N_x sites (3.5 wt% Co) in a mesoporous N-doped carbon matrix (named Co@mesoNC) is synthesized by hydrolysis of tetramethyl orthosilicate (TMOS) in a Zn/Co bimetallic zeolitic imidazolate framework (BIMZIF(Co,Zn)), followed by high-temperature pyrolysis and SiO_2 leaching. A combination of TEM, XRD XPS and X-ray absorption spectroscopy studies confirm the absence of cobalt nanoparticles and indicate that these highly dispersed cobalt species are present in the form of Co-N_x. The exclusive formation of Co-N_x sites in the carbon matrix is attributed to the presence of a large amount of Zn and N in the BIMZIF precursor together with the presence of SiO_2 in the pore space of this framework, extending the initial spatial distance between cobalt atoms and thereby impeding their agglomeration. The presence of SiO_2 during high-temperature pyrolysis is proven crucial to create mesoporosity and a high BET area and pore volume in the N-doped carbon support (1780 m^2 g^{-1}, 1.54 cm^3 g^{-1}). This heterogeneous Co@mesoNC catalyst displays high activity and selectivity (>99%) for the selective hydrogenation of nitrobenzene to aniline at mild conditions (0.5–3 MPa, 343–383 K). When more challenging substrates (functionalized nitroarenes) are hydrogenated, the catalyst Co@mesoNC displays an excellent chemoselectivity to the corresponding substituted anilines. The presence of mesoporosity improves mass transport of reactants and/or products and the accessibility of the active Co-N_x sites, and greatly reduces deactivation due to fouling.

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1. Introduction

The reduction of nitroarenes to their substituted anilines is of great importance in organic synthesis and applied on large scale for the production of dyes, pharmaceuticals, pigments, and agrochemicals [1–4]. Hydrogen is attractive because it is one of the cleanest reductant [5–7]. Despite the development of a large number of molecular catalysts [8–12], in general these homogeneous catalysts suffer from difficulties in recycling and separation from products. Hence, heterogeneous catalysts containing supported metal nanoparticles (NPs) are more attractive [13–18]. Platinum-group metals have been proposed as alternative and are industrially used in the direct hydrogenation of nitroarenes [19–23]. Although they are highly efficient in the activation of nitro groups, these catalysts are also highly active for hydrogenolysis of carbon-halogen bonds (i.e. —F, —Cl, etc.) and hydrogenation of other reducible groups (i.e. C=O and C=C, etc.), which usually leads to poor chemoselectivity [24–28]. Thus, the exploration for advanced materials that catalyze the hydrogenation of nitroarenes maintaining high activities and without compromising chemoselectivity remains challenging.

Recently, tremendous efforts have led to the development of cheaper first-row transition-metal-based hydrogenation catalysts (i.e. Fe, Co, and Ni) [15,29–41]. Among these catalysts, N-doped carbon supported cobalt materials prepared by the carbonization of metal-organic-frameworks (MOFs) or a mixture of cobalt salts and organic complex exhibited good activity and chemoselectivity in the hydrogenation of nitroarenes [29–32,36,39–46]. There is a general agreement that cobalt plays an indispensable role in enhancing the hydrogenation activity of the catalysts. Yet, the heterogeneity of the cobalt species (i.e. accessible and inaccessible cobalt nanoparticles encapsulated by graphite shells, single cobalt atoms coordinated with nitrogen (Co-N_x), etc.) raises debate on what is the real active site in the hydrogenation process, and therefore greatly hinders the rational design and development of highly active and durable catalysts. Very recently, by one-step pyrolysis of

a cobalt-containing MOF (ZIF-67) under N_2 atmosphere followed by a subsequent acid treatment, we proved that the accessible cobalt nanoparticles in that system exhibit a high activity for this reaction [36]. Surprisingly, after acid leaching, the sample still shows outstanding hydrogenation activity. Although highly dispersed cobalt species (i.e. Co-N_x) are considered to exist in the acid-leached sample, the presence of those acid-resistant cobalt nanoparticles, fully encapsulated by multilayer graphitic carbon shells largely impedes further exploration of the structure-activity relation in this reaction. Hence, a rational design strategy that can preferentially produce active Co-N_x sites should be explored.

In view of the similar coordination of Co^{2+} and Zn^{2+} with 2-methylimidazole in ZIF-67 and ZIF-8 [47–49], a series of Zn/Co bimetallic zeolitic imidazolate framework (BIMZIF(Co,Zn)) have been recently reported, where the spatial distribution of Co and Zn in the framework is largely dependent on sequential addition of the metal precursors during synthesis [50–54]. Remarkably, when the precursors are added together, a homogeneous distribution of Zn and Co in the BIMZIF(Co,Zn) can be obtained. The presence of Zn^{2+} effectively separates Co atoms in the framework, and, to some extent, precludes their agglomeration into cobalt NPs during the high-temperature pyrolysis [52,53]. The carbon matrix generated using this strategy exhibits high surface area but normally microporosity [52,53], which can lead to significant internal mass transport limitations during the catalytic process, and therefore catalytic activity and stability can be severely inhibited [55,56].

Herein, we report a facile and easily scalable method to construct an atomically dispersed cobalt catalyst with a 3.5 wt% Co loading in a mesoporous N-doped carbon for chemoselective hydrogenation of nitroarenes to their substituted anilines under mild conditions. The catalyst is synthesized in several steps: (i) hydrolysis of tetramethyl orthosilicate (TMOS) in the pores of a BIMZIF(Co,Zn), followed by (ii) high-temperature pyrolysis and (iii) silica leaching. We demonstrate that the high Zn/Co molar ratio in the parent BIMZIF together with the SiO_2-protection strategy is crucial to impede the formation of cobalt nanoparticles and preferentially generate atomically dispersed Co-N_x sites. At the same time, the SiO_2-templated approach maintains a high specific surface area and generates mesoporosity in the N-doped carbon matrix. These Co-N_x sites in the mesoporous N-doped carbon matrix exhibit superior hydrogenation activity and chemoselectivity, and good catalytic stability. This strategy opens a path for the rational designing of highly active non-noble catalysts for hydrogenation reactions.

2. Experimental

2.1. Materials

2-Methylimidazole (MeIm, purity 99%), zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, >98%), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, >99%), tetramethyl orthosilicate (TMOS ≥ 99%), and methanol (>99.8%) were purchased from Sigma-Aldrich Chemical Co. All the chemicals were used without further purification.

2.2. Catalyst synthesis

For the synthesis of BIMZIF(Co,Zn), a mixture of $Zn(NO_3)_2 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ with Zn^{2+}/Co^{2+} molar ratio of 25 was dissolved in 200 mL methanol. A mixture of MeIm (6.489 g) in 200 mL methanol was rapidly poured into the above solution with vigorous stirring for 24 h at room temperature [52]. The total molar amount of (Co^{2+} + Zn^{2+}) was fixed to be 10 mmol. Afterwards, the

products were collected by filtration, washed thoroughly with methanol, and dried overnight at 353 K under vacuum. For the synthesis of ZIF-8(Zn) and ZIF-67(Co), all the steps were the same except only $Zn(NO_3)_2 \cdot 6H_2O$ or $Co(NO_3)_2 \cdot 6H_2O$ and MeIm were used. Around 1 g ZIF materials can be produced from each batch.

1 g of the synthesized BIMZIF(Co,Zn) was suspended in 5 mL TMOS in an autoclave, and further transferred into a rotation oven and heated up to 333 K overnight. After the oven was cooled down to room temperature, the mixture was carefully washed with 0.5 mL ethanol by filtration. Then the obtained BIMZIF@TMOS material was placed in a cotton thimble of 22 mm diameter inside a glass tube of 25 mm diameter. The glass tube was fitted to a round bottom flask containing 500 ml of water. A needle to bubble 10 ml min^{-1} of N_2 flux into water was also fitted. The temperature was raised to 323 K to create a wet N_2 stream to hydrolyze the TMOS molecules for 24 h, after which the sample was collected and dried in an oven at 333 K overnight. The obtained sample was denoted as BIMZIF@SiO_2, with the yield of 1.2 g.

Co@NC-SiO_2 was prepared by pyrolysis of 1 g BIMZIF@SiO_2 at 1173 K for 4 h under N_2 at a ramp of 2 K min^{-1}, with the yield of 0.44 g. The obtained Co@NC-SiO_2 was further leached in 1 M NaOH solution for 24 h to remove the SiO_2 template, followed by washing with deionized water until the pH reached neutral, and dried at 323 K overnight under vacuum to afford Co@mesoNC sample, with the yield of 0.23 g.

For comparison, Co@NC and NC were prepared by pyrolysis of 1 g BIMZIF(Co,Zn) and ZIF-8 at 1173 K for 4 h under N_2 at a ramp of 2 K min^{-1}, respectively. The pyrolyzed ZIF-67 sample was obtained by pyrolysis of ZIF-67 at 1073 K for 8 h under N_2 using a temperature ramp of 2 K min^{-1}.

2.3. Characterization

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray diffractometer equipped with a Co-$K\alpha$ radiation (λ = 0.179026 nm). Transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) were performed by using a Talos F200X microscope (FEI, Hillsboro, OR, USA) at an acceleration voltage of 200 kV. Raman spectra were obtained with a commercial Renishaw in Via Reflex confocal microscope using a 532 nm laser. Measurements were carried out in samples without any pretreatment at ambient conditions. The N_2 adsorption-desorption measurements were performed by using a Micromeritics Tristar 3020 apparatus at 77 K [57]. Prior to measurement, samples were degassed under vacuum at 383 K overnight. The Co and N contents in the samples were measured by atomic adsorption spectroscopy (AAS) (Analyst 200, Perkin Elmer, USA) and elemental analysis (Vario EL, Elementar, Germany), respectively. XPS measurements were performed on a K-alpha Thermo Fisher Scientific spectrometer using monochromatic Al-K radiation at ambient temperature and chamber pressure of about 10^{-8} mbar. All the spectra measured were corrected by setting the reference binding energy of carbon ($1s$) at 284.8 eV.

X-ray absorption experiments were performed at DUBBLE beam line BM26A in ESRF, Grenoble. The materials were studied using Co K-edge. Energy calibration was achieved using metal foil as reference and the first peak in the first derivative of the metal foil XAS spectrum was calibrated to 7709 eV [58]. Calibration and data alignment was performed using Athena and reference compounds values were obtained from Hephaestus. After averaging, the spectra of the studied samples were normalized to a total absorption of unity and processed using the Athena data normalization and analysis package [59]. For normalization, the spline r-background parameter was set to 1.0. The background subtraction was carried using a pre-edge range of −200 to −30 eV and a post-edge linear range of 50–985 eV. A spline range of k = 0 to k = 14.8 A^{-1} and