



One-pot reductive amination of carbonyl compounds with nitro compounds with CO/H₂O as the hydrogen donor over non-noble cobalt catalyst



Peng Zhou^a, Changlin Yu^b, Liang Jiang^a, Kangle Lv^a, Zehui Zhang^{a,*}

^aKey Laboratory of Catalysis and Materials Sciences of the Ministry of Education, South-Central University for Nationalities, Wuhan 430074, PR China

^bSchool of Metallurgy and Chemical Engineering, Jiangxi University of Science and Technology, 86 Hongqi Road, Ganzhou 341000, PR China

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ABSTRACT

The one-pot reductive amination of carbonyl compounds with nitro compounds over heterogeneous non-noble metal catalysts was developed for the first time by transfer hydrogenation with CO/H₂O as the hydrogen donor. Nitrogen-doped carbon supported cobalt nanoparticles were observed to be active toward this reaction, affording structurally-diverse secondary amines with high yields. Kinetic studies revealed that the transfer hydrogenation of imines (C=N bonds) was the rate-determining step. Reaction mechanism studies indicated that both nitrogen and cobalt nanoparticles were important for the transfer hydrogenation with CO/H₂O to generate the proton (N–H⁺) and hydride (Co–H[−]) as the active species. Furthermore, the heterogeneous cobalt catalyst was highly stable without the loss of its catalytic activity during the recycling experiments.

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1. Introduction

Synthesis of amines and its derivatives represents one of the most active fields in synthesis chemistry. Nitro compounds as a type of readily available starting materials have been extensively studied for the synthesis of primary amines with fruitful results [1]. The as-formed primary amines can be further upgraded into many kinds of highly valuable chemicals such as secondary or tertiary amines, imines, azo compounds and other nitrogen-containing compounds, which are of great importance in the synthesis of pharmaceuticals, dyes, pigments, agrochemicals, and materials [2–6]. From the viewpoints of green and sustainable chemistry, it is highly attractive to perform the synthesis of their derivatives directly from nitro compounds by one-pot reaction strategies [7]. Compared with the methods by multiple steps, the one-pot method demonstrates higher atom efficiency by avoiding tedious purification steps and releasing fewer wastes.

Reductive amination, the coupling of carbonyl compounds with primary amines in the presence of a reducing reagent, has been considered to be one of the most efficient methods for the synthesis of secondary amines [8]. Although the reductive amination of carbonyl compounds with primary amines has enjoyed a huge success, the one-pot reductive amination directly from nitro com-

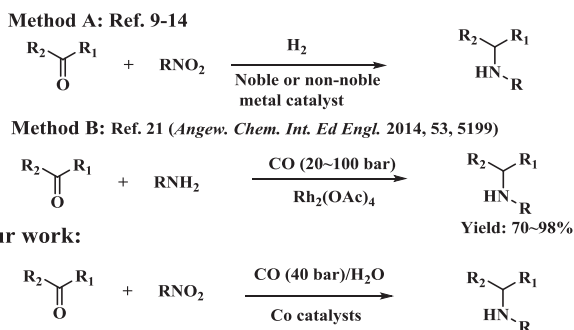
pounds has been less developed [9–15]. Methods for the one-pot reductive amination are mainly performed over noble metal catalysts with H₂ as the hydrogen source (Scheme 1, method A) [9–15]. The use of H₂ as the reducing reagent is environmentally friendly, as water was the oxidation product. Some noble metal catalysts were even reported to be active for the one-pot reductive amination under mild conditions. For example, the PdAg bimetallic nanocatalyst can promote the one-pot reductive amination at room temperature and atmospheric hydrogen pressure with high yields [13]. Nowadays, great effort has been developed to the search of non-noble metal catalysts to replace noble metal catalysts for the chemical transformations. To this context, heterogeneous carbon-supported iron oxide and cobalt oxide catalysts were studied for this type reaction [14,15]. For example, the one-pot reductive amination over the carbon-supported iron oxide catalyst produced 45~91% yields of secondary amines within 30 h at 170 °C and 70 bar H₂ [15]. Obviously, these processes have potential safety issues regarding the handling of explosive H₂ at harsh conditions.

So far, organic synthesis by transfer hydrogenation has attracted great interest with CO/H₂O as the hydrogen donor via water–gas shift reaction [16]. Apart from being well known as a very useful C1 building block in the chemical industry, CO has also been considered to be a useful reductant in organic synthesis [17,18]. Compared with H₂ and other hydrogen donors, CO is produced in multiton quantities as a by-product of the steel

* Corresponding author.

E-mail address: zhangzehui@mail.scuec.edu.cn (Z. Zhang).

1) Previous work:



Scheme 1. Methods for the synthesis of secondary amines via reductive amination.

industry [19]. H_2 is a potential clean energy, and thus the use of CO instead of H_2 will also provide much more clean energy to our society. Therefore, the use of CO not only resolves the concerns of environment, but also makes the chemical process more economic and more sustainable [20]. In addition, there is no explosive risk on the use of CO for the chemical reactions. To the best of our knowledge, there have been only two examples on the reductive amination over either homogeneous or heterogeneous noble rhodium catalysts (Scheme 1, Method B) [21,22]. For example, Chusov and List reported the reductive amination of carbonyl compounds with amines to generate the corresponding secondary amines with yields of 70~98% over homogeneous $\text{Rh}_2(\text{OAc})_4$ catalyst at 120~140 °C and 20~100 bar CO pressure in tetrahydrofuran [21]. In this work, CO was the real reducing reagent, and this catalytic system was obviously not suitable for the reductive amination of carbonyl compounds with nitro compounds. Thus, it is highly desirable to perform the one-pot reductive amination over heterogeneous non-noble metal catalysts with a high activity and a high selectivity.

Currently, nitrogen-doped carbon-supported metal catalysts have gained considerable attention for advanced catalysis [23,24]. The incorporation of nitrogen in the carbon architecture played multiple roles in the improvement of the catalytic activity such as the stabilization of metal nanoparticles and the enhancement of the electron transfer ability [25]. ZIF-67 (ZIF: zeolitic imidazolate framework), which is composed of cobalt cation and 2-methylimidazole ligand, is a promising precursor for the preparation of nitrogen-doped carbon supported cobalt catalysts [26]. Herein, nitrogen-doped carbon-supported cobalt catalysts by the pyrolysis of ZIF-67 were prepared and studied for the one-pot reductive amination of carbonyl compounds with nitro compounds (Scheme 1). To the best of our knowledge, this process is unprecedented.

2. Experimental section

2.1. Synthesis of ZIF-67

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99%, 0.45 g) in 3 mL of water was added to a solution of 2-methylimidazole (99%, 5.5 g) in 20 mL of water. Then the mixture was stirred at 25 °C for 6 h. The resulting purple precipitates were obtained via centrifugation and washed with water and methanol for twice, respectively, and finally dried in a vacuum oven.

2.2. Catalyst preparation

ZIF-67 (2.0 g) was pyrolyzed at three representative temperatures (600, 800 and 900 °C) for 8 h in a nitrogen atmosphere at a

heating rate of 3 °C/min from room temperature. The as-prepared materials were denoted as the Co/N-C-T catalysts, where T indicates the pyrolysis temperature. On the meanwhile, the Co/N-C-600 catalyst was heated in the air at 250 °C for 4 h to get the Co/N-C-600-Air catalyst, in which metallic Co nanoparticles were oxidized to its oxidation state.

2.3. Catalyst characterization

Transmission electron microscope (TEM) images of the samples were obtained on an FEI Tecnai G^2-20 instrument. The samples were firstly dispersed in ethanol with an assist of ultrasonication and dropped onto copper grids for observation. Micropore and mesopore surface area and pore size measurements were performed with N_2 adsorption/desorption isotherms at 77 K on a V-Sorb 2800P instrument. Before measurements, the samples were degassed at 100 °C for 12 h. X-ray powder diffraction (XRD) patterns of samples were determined with a Bruker advanced D8 powder diffractometer ($\text{Cu K}\alpha$). All XRD patterns were collected with a scanning rate of 0.016°/s. X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo VG scientific ESCA MultiLab-2000 spectrometer with a monochromatized Al $\text{K}\alpha$ source (1486.6 eV) at constant analyzer pass energy of 25 eV. The binding energy was estimated to be accurate within 0.2 eV. All binding energies were corrected referencing to the C1s (284.6 eV) peak of the contamination carbon as an internal standard. The cobalt content in the catalysts was quantitatively determined by inductively coupled atomic emission spectrometer (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation). Raman spectra were measured on a confocal laser micro-Raman spectrometer (Thermo Fisher DXR) equipped with a diode laser of excitation of 532 nm (laser serial number: AJC1200566). Spectra were obtained at a laser output power of 1 mW (532 nm), and a 0.2 s acquisition time with 900 lines/mm grating (Grating serial number: AJG1200531) in the wavenumber range of 50–3500 cm^{-1} . Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker EMX spectrometer. The EPR experiments were conducted with a center field of 3507.815 G and a frequency of 9.83 GHz using an Elexsys probe head with 15 mg of sample placed in a 4 mm tube.

2.4. Catalytic transfer hydrogenation of nitrobenzene

In a typical run, the Co/N-C-600 catalyst (20 mg), nitrobenzene (1 mmol) and water (10 mL) were charged in a 50 mL autoclave, which was equipped with a magnetic stirring bar and a temperature controller. After the removal of air with CO, the autoclave was charged with 20 bar CO at room temperature. Then the autoclave was heated at 110 °C for 10 h with a magnetic stirring at 1000 rpm. After cooling to room temperature, the organic products in the reaction mixture were extracted by ethyl acetate, and the chemicals in the reaction mixture were quantified by gas chromatography (GC) with toluene as the internal standard.

2.5. General procedure for the one-pot reductive amination

The reaction procedure for the one-pot reductive amination was almost the same as described above with some modifications. Firstly, apart from the addition of nitrobenzene (1 mmol), the Co/N-C-600 catalyst (20 mg) and water (10 mL) into the autoclave, benzaldehyde (2 mmol) was also added. In addition, reactions were performed at 170 °C and 40 bar CO. Toluene and phenyl ether were used as double internal standards, in which phenyl ether was used to quantify the imines and secondary amines. The products in the reaction mixture were identified by comparison of their retain times with the authentic chemicals, and further confirmed by GC-MS (Agilent 7890A GC/5973 MS, HP-5 column).

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