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N-doped graphitic carbon-improved Co–MoO_3 catalysts on ordered mesoporous SBA-15 for chemoselective reduction of nitroarenes

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ABSTRACT

Metallic Co–MoO_3 catalysts supported on ordered mesoporous SBA-15 were first prepared through in situ reaction of SBA-15-supported Co–Mo oxides with 1,10-phenanthroline. The resulting Co–MoO_3/NC@SBA-15 catalysts with N-doped carbon (NC) exhibited high catalytic activity and chemoselectivity for selective reduction of various functionalized nitroarenes to the corresponding arylamines in ethanol with hydrazine hydrate at near room temperature (30 °C). For reduction of all tested substrates (28 examples), the catalyst could afford a conversion of > 99% and arylamine selectivity of > 99%. The excellent catalytic performance of the Co–MoO_3/NC@SBA-15 was attributed to the Co–N_x(C)–Mo active sites generated through the interaction between the surface Co–N_x(C) and MoO_3 species, promoting the dissociation of hydrazine molecule into the active H* species for the reduction of nitro groups. After the seventh cycle for reduction of 4-methoxylnitrobenzene, the 2%Co–MoO_3/NC@SBA-15 showed little change in catalytic performance, textural properties, size and dispersion of metal species and valence states of elements, indicating high stability and recyclability.

1. Introduction

The selective reduction of nitro aromatics is one fundamental transformation for the production of functional anilines, which are important intermediates in the production of pharmaceuticals, agrochemicals, dyes, and pigments [1–3]. Traditional reduction routes using reducing agents such as Fe and Zn, generate large amounts of waste acids and residues, causing serious environmental problems [4]. The catalytic reduction of nitro aromatics has been studied for the production of anilines over transition metal-based catalysts using various reducing agents like sodium borohydride [5,6], hydrosilanes [7], pinacol [8], formic acid [9–11], hydrazine or hydrazine derivatives [12,13], and molecular hydrogen [14,15]. From the standpoint of atom-economical and environmentally-friendly chemistry, heterogeneous catalytic reduction with metal catalysts is accepted as a sustainable and efficient process because of easy separation and catalyst recycling. The noble metal catalysts based on Pt [16,17], Pd [18,19], Ru [20,21], and Rh [22,23] are reported to be active for this transformation, however, in most cases the chemoselective reduction of nitro group is poor when other reducible groups such as alkene, nitrile, carbonyl, and halides exist in the benzene ring. Other noble metals like Au [24,25] and Ag [26,27] are selective for the reduction of nitro groups, but are not active. Besides, the high cost and limited availability also prevent noble metal catalysts for industrial applications.

Non-noble transition metal materials including Co nanoparticles [28–30], Co–Ni nanowires [31], mono-metallic or bimetallic oxides of Co, Fe and Mo [32–34], Mo carbides [35], Mo sulfides [36,37], and Fe-complexes [38,39] have been shown to be effective for the selective reduction of nitro aromatics as catalysts or supports. However, the reductions on these catalysts frequently require strict reaction conditions (≥100 °C) and the aid of additives (acid, base and metal salts) [40,41]. The investigation results revealed that the activity and selectivity of non-noble metal catalysts for the reduction of nitro groups depended strongly on the catalyst preparation procedure, properties of metal and supports, nature of reducing agent, etc.

Hydrazine hydrate ($N_2H_4{\cdot}H_2O$) has been widely used as a hydrogen donor for a variety of catalytic reductions because it is abundant and only produces N_2 and water as by-products [42,43]. It is demonstrated that transition metal oxides can facilitate the dissociation of H—N bond of hydrazine into active hydrogen species (H*) for the reduction of nitro groups [44–46]. Herein we have first developed ordered mesoporous silica SBA-15-supported bimetallic Co–MoO_3 catalyst (Co − MoO_3/NC@SBA-15) with N-doped graphite-like carbon (NC) by heat-treating SBA-15-supported Co–Mo oxides (Co_3O_4 − MoO_3/SBA-15) with 1,10-

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phenanthroline, which exhibited excellent activity and chemoselectivity for the catalytic reduction of various substituted nitroarenes to arylamines without any additive with $N_2H_4{\cdot}H_2O$. The influences of Co contents, supports, organic carbon sources, reducing agents and reaction conditions on the catalytic properties of the Co–MoO_3/NC@SBA-15 were systematically investigated for the reduction of 4-methoxylnitrobenzene as a model reaction. Furthermore, the reduction of various substituted nitroarenes was examined and possible reduction mechanism was proposed over bimetallic Co–Mo catalyst.

2. Experimental

2.1. Chemicals

Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, M_{av} = 5800) was purchased from Aldrich. Other various chemicals of reagent grade such as Co $(NO_3)_2{\cdot}6H_2O$, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, 1,10-phenanthroline monohydrate ($C_{12}H_8N_2{\cdot}H_2O$), and $(NH_4)_6Mo_7O_{24}{\cdot}_4H_2O$ and $N_2H_4{\cdot}H_2O$ aqueous solution (80 wt%) and so on, and commercial activated carbon (AC), CeO_2, ZrO_2 and TiO_2 as supports were from Sinopharm Chemical Reagent Co., Ltd. SBA-15, MCM-41, mesoporous γ-Al_2O_3 (γ-MA) and C_3N_4 supports were synthesized through the procedures reported in the document [47–51]. Before use, all supports were treated in air or N_2 atmosphere at 550 °C for 6 h to remove water and impurities.

2.2. Catalyst preparation

The Co–MoO_3/NC@SBA-15 catalysts were prepared by a facile two-step impregnation method with water-ethanol solutions of metal nitrates and 1,10-phenanthroline, respectively, followed by pyrolysis and reduction in N_2 atmosphere (Scheme 1). Typically, the required amounts of $Co(NO_3)_2{\cdot}6H_2O$ and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ were dissolved in a mixed solution of water and ethanol (v/v = 1:3) (40 mL) at room temperature. The SBA-15 powder (1.0 g) was added into the above solutions under vigorous stirring, and then the suspension was continuously stirred to remove the solvent at 40 °C. The solids were dried at 100 °C overnight, and calcined in air at 400 °C for 6 h to produce the $x$$Co_3O_4$–$MoO_3$/SBA-15 materials with various Co mass percentages (x = 0, 1.0%, 2.0%, 3.0%, 4.0%, 5.0%), where the nominal Mo mass percentage was set at 6.0%, which was proved to present the optimal catalytic performance for the selective reduction of nitroarenes in the preliminary experiments. The 2.0%Co_3O_4/SBA-15 material was also prepared by the same way except use of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$.

The prepared $x$$Co_3O_4$ − MoO_3/SBA-15 (1.0 g) or 2.0%Co_3O_4/SBA-15 powders (1.0 g) were suspended into a solution of water–ethanol (v/v = 1:3) (40 mL) containing 1,10-phenanthroline monohydrate (1.2 g) and sonicated for 30 min, and then the solvent was evaporated under stirring at 40 °C. The obtained solid was dried at 100 °C overnight, and finally was treated in a flow of high-purity N_2 (50 ml min^{-1}) at 700 °C for 2 h with a heating rate of 5 °C min^{-1} to form xCo − MoO_3/NC@SBA-15 or 2.0%Co/NC@SBA-15 catalysts.

2.0%Ni − MoO_3/NC@SBA-15 and 2.0%Fe − MoO_3/NC@SBA-15 catalysts were prepared by the same route, except that $Ni(NO_3)_2{\cdot}6H_2O$ and iron(III) acetylacetonate ($Fe(C_5H_7O_2)_3$) were used as Ni and Fe sources, respectively.

MCM-41, γ-MA, CMK-3, AC, C_3N_4, CeO_2, ZrO_2, TiO_2-supported 2.0%Co − MoO_3/NC were prepared by the similar method, but CMK-3, AC, C_3N_4-supported 2.0%Co_3O_4 − MoO_3 materials were calcined in N_2 atmosphere at 400 °C for 6 h.

2.0%Pd/NC@SBA-15, 2.0%Pt/NC@SBA-15 and 2.0%Au/NC@SBA-15 catalysts containing 2.0 wt% noble metals were prepared by the same way to the 2.0%Co − MoO_3/NC@SBA-15, except that Pd/SBA-15, Pt/SBA-15 and Au/SBA-15 materials were prepared by the impregnation route of SBA-15 with an aqueous solution of $PdCl_2$, H_2PtCl_6, and $HAuCl_4$, respectively.

2.0%Co − MoO_3/NC@SBA-15 − B, M, and C catalysts were also prepared through impregnating 2.0%Co_3O_4 − MoO_3/SBA-15 (1.0 g) with water–ethanol solutions (40 mL) containing 2,2′-bipyridine (1.2 g), 2-methylimidazole (1.2 g) and β-cyclodextrin (1.2 g) as organic carbon precursors, respectively. The procedure was the same as that of the 2.0%Co − MoO_3/NC@SBA-15.

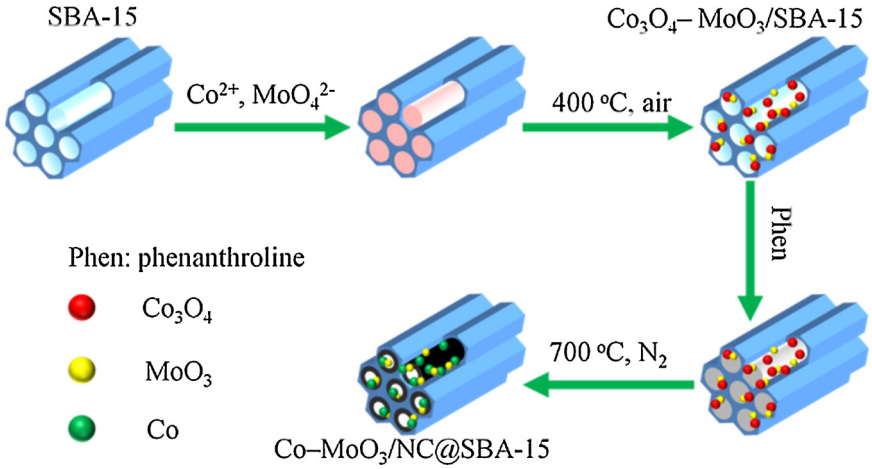
2.3. Catalyst characterization

X-ray diffraction (XRD) patterns were collected with a Rigaku D/MAX-2200 X-ray diffractometer using Cu Kα radiation (λ = 0.1542 nm) operated at a voltage of 40 kV and a current of 40 mA.

N_2 adsorption and desorption measurements were performed on a Micromeritics ASAP 2020 Sorptometer at −196 °C. Before the analysis, the sample was outgassed at 200 °C for 8 h. The specific surface area (S_{BET}) was calculated by the Brunauer–Emmett–Teller (BET) method in the relative pressure (P/P_0) range of 0.05 − 0.25. Pore size distribution was obtained from the adsorption branch by the Barrett–Joyner–Halenda (BJH) method. The pore size (D_p) was read from the maximum of the pore distribution curve. The pore volume (V_p) was calculated from the adsorbed amount at P/P_0 = 0.99.

Transmission electron microscopy (TEM) micrographs were taken with a JEOL JEM-2010F field emission microscope operating at 200 kV. The sample was prepared by drying an ethanolic dispersion of the well-ground catalyst powder on a holey-carbon-coated copper grid.

X-ray photoelectron spectra (XPS) were obtained on an ESCALAB 250Xi spectrometer equipped with monochromatized Al Kα radiation



Scheme 1. General preparation procedure of Co − MoO_3/NC@SBA-15.

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