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Article

Aerobic oxidative coupling of alcohols and amines to imines over iron catalysts supported on mesoporous carbon



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ABSTRACT

Direct oxidative coupling of an alcohol and amine, with air or molecular oxygen as the oxygen source, is an environmentally friendly method for imine synthesis. We developed an Fe catalyst supported on mesoporous carbon (denoted by FeO_x/HCMK-3) for this reaction with excellent activity and recyclability. FeO_x/HCMK-3 was prepared by impregnating HNO₃-treated mesoporous carbon (CMK-3) with iron nitrate solution. The highly dispersed FeO_x species give FeO_x/HCMK-3 high reducibility and are responsible for the high catalytic performance. Imine synthesis over FeO_x/HCMK-3 follows a redox mechanism. The oxygen species in FeO_x/HCMK-3 participate in the reaction and are then regenerated by oxidation with molecular O₂. The reaction involves two consecutive steps: oxidative dehydrogenation of an alcohol to an aldehyde and coupling of the aldehyde with an amine to give an imine. Oxidative dehydrogenation of the alcohol is the rate-determining step in the reaction.

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1. Introduction

Imines are important nitrogen compounds; they contain a reactive C=N moiety [1,2]. Imines are nitrogen sources and can undergo various transformations. They are widely used in biological, agricultural, and pharmaceutical synthetic processes [3–6]. The condensation of aldehydes or ketones with amines is the traditional method for imine synthesis, and is usually performed in the presence of an acidic catalyst [7–9]. Recently, the direct oxidative coupling of an alcohol and amine to give an imine has attracted increasing attention because of its environmentally friendly properties [10–16]. Air or molecular oxygen can be used as the oxygen source for the production of various types of desirable imines from appropriate alcohols and amines as starting reagents, with water as the only by-product. Effective noble-metal-based homogeneous and

heterogeneous catalysts such as supported Au, Ru, Pd, and Pt have been reported [17–24]. However, the high price of these noble metals and the need to use inorganic or organic bases as additives in the reaction system limit their large-scale application in imine synthesis.

Recently, a few metal oxide catalysts that can catalyze this imine synthesis have been reported [25–27]; for example, CeO₂ is an effective catalyst for imine formation from benzyl alcohol and aniline at low temperature (60 °C), with a high yield of 96% after 24 h [25]. Manganese oxides supported on hydroxyapatite (MnO_x/HAP) also show high activity in the oxidative coupling of alcohols and amines [26]. When benzyl alcohol and aniline were used, a 92% yield of the imine was obtained after reaction for 24 h at 80 °C. The catalytic activity, especially the capacity to activate molecular oxygen, is highly dependent on the redox properties of the metal oxides. They determine the

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catalytic behavior of the metal oxide in the oxidative dehydrogenation step. Tuning the redox properties of metal oxide catalysts should therefore be an efficient method for developing high-performance catalysts for imine synthesis via oxidative coupling.

Among various metal oxides, iron oxides have the advantages of ready availability, low cost, and low toxicity [28–32]. However, iron oxides show low activities in the oxidative coupling of alcohols and amines to imines [25]. This could be related to the intrinsic inert properties of a bulk material, such as a low surface-to-bulk atomic ratio and low surface energy. We recently reported that the redox properties of iron oxides can be tuned by forming highly dispersed iron oxide species on carbon supports [33,34]. The catalysts show high redox activities in O_2 activation. This property of these iron oxide species might enable them to catalyze oxidative coupling of alcohols and amines to imines.

In this work, carbon-supported FeO_x ($FeO_x/HCMK-3$) was used as a catalyst for oxidative coupling of alcohols and amines to imines. A 98.8% yield of imine was obtained in the oxidative coupling of benzyl alcohol and aniline after reaction for 6 h at 80 °C. The $FeO_x/HCMK-3$ catalyst was efficient in the synthesis of a series of imine compounds. The correlations between the activity and physicochemical properties of the catalyst were investigated based on a series of characterization results. The reaction mechanism of imine synthesis over $FeO_x/HCMK-3$ was also explored.

2. Experimental

2.1. Materials

All chemicals were analytical grade and used without further purification. Double-distilled water was used in all experiments.

2.2. Catalyst preparation

SBA-15 templates were prepared using a triblock copolymer, $EO_{20}-PO_{70}-EO_{20}$ (P123; EO: ethylene oxide; PO: propylene oxide), as the surfactant and tetraethyl orthosilicate (TEOS) as the silica source, using the procedure reported by Zhao et al. [35]. Typically, TEOS (4.68 mL) was added to 2 mol/L HCl (60 mL) containing P123 (2 g) at 35 °C. After stirring in a water bath (35 °C) for 24 h, the mixture was transferred to Teflon-lined stainless steel autoclaves (100 mL) and heated to 100 °C for 3 d. The resultant solid product was separated by filtration, dried at 100 °C for 12 h, and calcined at 550 °C for 6 h.

CMK-3 was prepared using SBA-15 as a hard template and sucrose as the carbon source [36]. Typically, SBA-15 silica (1.0 g) was added to a solution containing sucrose (1.25 g), sulfuric acid (0.14 g), and distilled water (5.0 g). The mixture was kept in an oven for 6 h at 80 °C. The temperature was then increased to 160 °C and maintained for 6 h. The heating procedure was repeated after addition of the carbon precursor (0.8 g of sucrose, 0.09 g of H_2SO_4 , and 5.0 g of H_2O) to achieve complete infiltration of the internal pores of the SBA-15 silica. The car-

bon-silica composite was obtained by pyrolysis at 900 °C for 6 h under an Ar flow and then washing in 10 wt% HF aqueous solution to remove the silica template.

The carbon-supported iron oxide catalyst was prepared using a wet impregnation method. Typically, an Fe-containing solution was obtained by dissolving $Fe(NO_3)_3 \cdot 9H_2O$ in a certain amount of water. Before added to the iron nitrate solution, the CMK-3 support was treated in 4 mol/L HNO_3 solution at 60 °C for 6 h (denoted by HCMK-3). After stirring for about 3 h at room temperature, the mixture was heated at 80 °C under atmospheric pressure to evaporate the water. The as-synthesized catalyst was thermally treated at 400 °C for 4 h under an Ar flow. The iron oxide loading was 5 wt% (calculated based on Fe_2O_3) and the resultant material was denoted by $FeO_x/HCMK-3$. For comparison, a sample consisting of Fe^{3+} ions supported on HCMK-3 (denoted by Fe-HCMK-3) was also prepared by the same impregnation method and using HNO_3 -treated CMK-3 as a support. The difference was that after impregnation the sample was dried in an oven at 80 °C for 12 h without further thermal treatment at 400 °C in an Ar flow for 4 h. The Fe species loading was the same as that on $FeO_x/HCMK-3$. Bulk Fe_2O_3 was also prepared using a conventional precipitation method with $Fe(NO_3)_3 \cdot 9H_2O$ as the Fe source and ammonia as the precipitating agent (pH 9). The resultant material was calcined at 400 °C for 4 h in air.

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded with a Rigaku X-ray diffractometer using $Cu K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Transmission electron microscopy (TEM) images and high-angle annular dark field scanning TEM (HAADF-STEM) images were obtained using a FEI Tecnai F20 instrument with an accelerating voltage of 200 kV, equipped with an energy-dispersive X-ray spectroscopy analyzer. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo ESCA LAB 250 system with an $Mg K\alpha$ source (1254.6 eV). N_2 adsorption-desorption isotherms were recorded at $-196 \text{ }^\circ\text{C}$ using a Micromeritics ASAP 2010N analyzer. Raman spectra were recorded using a Bruker RFS 100 Raman spectrometer with an Ar laser (532 nm) as the excitation source. Temperature-programmed reduction (TPR) was performed using a Tianjin Xianquan TP-5079 adsorption analyzer. Before examination, the catalysts (30 mg of $FeO_x/HCMK-3$, 10 mg of Fe_2O_3) were treated in an Ar (99.99%) flow at 400 °C for 30 min. The zeta-potential curve was plotted as a function of pH, from 2 to 8 (Zeta PALS analyzer, Brookhaven Instruments Corporation, USA). The sample was suspended in aqueous 0.01 mol/L NaCl solution. The pH was adjusted using 1.0 mol/L NaOH and HCl solutions. The Fe content was estimated using inductively coupled plasma atomic emission spectroscopy (ICP-AES; Perkin-Elmer emission spectrometer). Fourier transform infrared (FT-IR) spectra were recorded using a Thermo Nicolet 6700 FT-IR spectrometer. The Boehm titration method was used to determine the amounts of surface groups. The carbon support (100 mg) was placed in 10 mL of a 0.05 mol/L solution containing NaOH, Na_2CO_3 , and $NaHCO_3$. The

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