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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 $\text{FeO}_x/\text{HCMK-3}$) for this reaction with excellent activity and recyclability. $\text{FeO}_x/\text{HCMK-3}$ was prepared by impregnating HNO_3 -treated mesoporous carbon (CMK-3) with iron nitrate solution. The highly dispersed FeO_x species give $\text{FeO}_x/\text{HCMK-3}$ high reducibility and are responsible for the high catalytic performance. Imine synthesis over $\text{FeO}_x/\text{HCMK-3}$ follows a redox mechanism. The oxygen species in $\text{FeO}_x/\text{HCMK-3}$ participate in the reaction and are then regenerated by oxidation with molecular O_2 . 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, CeO_2 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 °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

vials were sealed and shaken for 24 h, and the contents were filtered. A known quantity of HCl was added to each filtrate. The excess acid left in the solution was titrated with NaOH using an automatic potentiometer titrator (LeiCi ZDT-4A). The amounts of acidic sites were calculated based on the assumption that NaOH neutralizes carboxylic, phenolic, and lactonic groups, NaHCO_3 neutralizes carboxylic groups, and Na_2CO_3 neutralizes carboxylic and lactonic groups.

2.4. Catalytic tests

The aerobic oxidative coupling of an alcohol and amine was performed in a 50-mL two-necked flask at atmospheric pressure. A quantity of catalyst (0.3 g) was added to the reactor containing alcohol (1.0 mmol), amine (2.0 mmol), and toluene (10 mL). The mixture was in contact with air, and the reaction temperature was kept at 80 °C. The reaction mixture was extracted via a sampling pipe with a filtrator and then transferred to a vial. The products were analyzed using a gas chromatograph equipped with an HP-5 column and a flame ionization detector. The conversion and yield of the imine product were calculated based on the alcohol to imine ratio. The products were identified using standard compounds and gas chromatography-mass spectrometry. The turnover frequencies (TOFs) were calculated based on benzyl alcohol conversion in the initial stage (60 min) and the amount of FeO_x in the catalyst.

An oxygen-free experiment was performed in a Schlenk tube. First, the $\text{FeO}_x/\text{HCMK-3}$ catalyst was put in a Schlenk tube, and degassed at 80 °C for 1.5 h under vacuum to remove adsorbed O_2 . High-purity N_2 (99.99%) was injected into the Schlenk tube until the pressure was 1 atm. The degassed toluene, benzyl alcohol, and aniline were added to the Schlenk tube. The system was further degassed and balanced with high purity N_2 . The Schlenk tube was then put in an oil bath (80 °C) to start the reaction. After each sample extraction, the system was degassed and balanced with high purity N_2 . All these treatments were to ensure the removal of molecular O_2 from the system. In the recycling experiments, the solid catalyst was separated by filtration and treated at 400 °C for 1 h before the next cycle.

3. Results and discussion

3.1. Catalyst structure and surface properties

Fig. 1 shows the preparation of the carbon-supported FeO_x (5 wt%, calculated based on Fe_2O_3) catalyst. The catalyst support was ordered mesoporous carbon CMK-3 prepared via a hard-template method. The CMK-3 was treated with 4 mol/L HNO_3 at 60 °C for 6 h before use as the catalyst support. The resultant carbon was denoted by HCMK-3. This was a key step in preparing a catalyst with highly dispersed FeO_x species. A large amount of oxygen-containing functional groups formed on the HCMK-3 surface. Table 1 shows that the amounts of functional groups on HCMK-3, including carboxylic, lactonic, and phenolic groups, were all higher than those on CMK-3. The total amount of functional groups was about 1.47 mmol/g. The

Fig. 1. Schematic illustration of synthetic route for $\text{FeO}_x/\text{HCMK-3}$ preparation.

abundant functional groups endow the HCMK-3 support with a hydrophilic surface. This facilitates introduction of iron nitrate solution into the mesopores of the carbon support. The dried solid was calcined at 400 °C for 4 h in an Ar flow to give the $\text{FeO}_x/\text{HCMK-3}$ catalyst.

The XRD patterns show that $\text{FeO}_x/\text{HCMK-3}$ retains the ordered arrangement of the parent HCMK-3 support (Fig. 2a). The three diffraction peaks in the range $2\theta = 0.75^\circ\text{--}3^\circ$ can be indexed to the (100), (110), and (200) reflections of the HCMK-3 hexagonal space group. Wide-angle XRD patterns show that both samples have two broad diffraction peaks, centered at 24.5° and 44° (Fig. 2b), which are assigned to diffractions from the (002) and (100) graphite planes of the carbon supports [37]. No crystalline phase related to iron oxides was observed, indicating that the iron oxide particles are small or the degree of crystallization is low. The Raman spectra of $\text{FeO}_x/\text{HCMK-3}$ and HCMK-3 show two peaks, at 1358 and 1598 cm^{-1} , which are assigned to the D and G bands of the carbon support (Fig. 2c) [38,39]. No peak below 1000 cm^{-1} attributable to crystalline iron oxides can be observed [40,41]; this also indicates that the iron oxide particles in $\text{FeO}_x/\text{HCMK-3}$ are small. The N_2 adsorption-desorption isotherms show that $\text{FeO}_x/\text{HCMK-3}$ gives isotherms typical of an ordered mesostructure (type IV) with a well-defined step in the adsorption curve near $p/p_0 = 0.5$ (Fig. 2d). The surface area, pore volume, and pore size of $\text{FeO}_x/\text{HCMK-3}$ are similar to those of HCMK-3, indicating that the iron oxides do not block the mesopores of the CMK-3 support.

TEM images confirm that $\text{FeO}_x/\text{HCMK-3}$ retains the ordered structure of the CMK-3 support (Fig. 3a). No Fe particles were observed in the region examined, even at high resolution (Fig.

Table 1

Boehm titration results for CMK-3 and HCMK-3.

Sample	Content of functional groups (mmol/g)			
	Carboxylic	Lactonic	Phenolic	Acidic
CMK-3	0.01	0.11	0.12	0.24
HCMK-3	0.24	0.34	0.89	1.47

Fig. 2. Low-angle (a) and wide-angle (b) XRD patterns for HCMK-3 and FeO_x/HCMK-3; (c) Raman spectra of HCMK-3 and FeO_x/HCMK-3; (d) N₂ adsorption-desorption isotherms of FeO_x/HCMK-3 (inset shows pore size distribution).

3b and c). STEM and energy-dispersive X-ray mapping were performed to investigate iron oxide dispersion (Fig. 3d and e). The results show that Fe species are nearly homogeneously dispersed on the HCMK-3 surface, but the particle size still cannot be ascertained based on these measurements. A sample with a low FeO_x loading (0.25 wt%) was prepared to clarify the FeO_x dispersed state on the HCMK-3 surface. FeO_x particles still cannot be observed in the HRTEM image (not shown), but some light spots (about 2–3 nm) can be distinguished in the HAADF-STEM image (Fig. 3f). These results suggest that FeO_x species are present as two-dimensional or even sub-nano clusters. These clusters could be the constituent units of the highly dispersed FeO_x on the carbon support. The HRTEM and HAADF-STEM images together confirm that the FeO_x species are highly dispersed on the HCMK-3 support surface.

XPS shows that there are no obvious differences between the Fe 2*p* binding energies of FeO_x/HCMK-3 and bulk Fe₂O₃ (Fig. 4a). The Fe 2*p*_{1/2} and Fe 2*p*_{3/2} peaks appear at 724.2 and 710.9 eV, respectively. This indicates that most of the Fe species are present in the iron oxides in the +3 valence state [42,43]. Clear differences can be observed in the O 1*s* spectra. The binding energies in the deconvoluted O 1*s* XPS spectrum are in accordance with those reported in the literature [44,45]. The O 1*s* spectrum of bulk Fe₂O₃ can be deconvoluted into two peaks (Fig. 4b). Peak I, in the range 529.5–530.5 eV, is assigned to O²⁻ ions in the iron oxide lattice. Peak II, centered at about 532 eV, is related to oxygen in surface OH groups or oxygen vacancies in Fe₂O₃. The peak II/peak I area ratio is 0.21 for bulk Fe₂O₃. The FeO_x/HCMK-3 O 1*s* spectrum can be deconvoluted into three peaks. The new peak (peak III) at 534 eV is attrib-

uted to oxygen functional groups remaining on the catalyst surface. The peak II/peak I area ratio is 3.54 for FeO_x/HCMK-3, which is much higher than that for bulk Fe₂O₃. This is caused by the small size of the iron oxide particles and interactions between iron oxides and the carbon support.

Diffuse reflectance infrared Fourier transform (DRIFT) spectra show that some oxygen-containing groups remain on the FeO_x/HCMK-3 surface (Fig. 5a). Further FT-IR spectra were obtained to clarify whether the Fe species were located in iron oxides or present as Fe³⁺ ions coordinated with these functional groups. A sample consisting of Fe³⁺ ions supported on HCMK-3 (denoted by Fe-HCMK-3) was prepared via the same impregnation method as was used to prepare FeO_x/HCMK-3, with HNO₃-treated CMK-3 as a support. The Fe species loading was the same as that for FeO_x/HCMK-3. The difference is that after impregnation, the sample was dried in an oven at 80 °C for 12 h to obtain Fe-HCMK-3, whereas further thermal treatment at 400 °C in an Ar flow for 4 h is needed to obtain FeO_x/HCMK-3. The peak at 469 cm⁻¹ in the FT-IR spectrum of FeO_x/HCMK-3 (Fig. 5b) can be attributed to the stretching vibration of Fe–O, similar to that of Fe₂O₃. However, this signal is different in the Fe-HCMK-3 spectrum. A combination of the FT-IR and XPS results confirms that Fe is mainly located in iron oxide species (i.e., FeO_x). The formation of FeO_x species in FeO_x/HCMK-3 is a result of the high treatment temperature. The oxygen-containing functional groups in HCMK-3 can interact with these two-dimensional FeO_x species.

The H₂-TPR profiles (Fig. 6) show that the iron oxide species in FeO_x/HCMK-3 are more reducible than those in bulk Fe₂O₃. There are three reduction peaks present in the profile of bulk

Fig. 3. TEM (a), HRTEM (b, c), HAADF-STEM (d), and energy-dispersive X-ray mapping images (e) of FeO_x/HCMK-3; (f) HAADF-STEM image of 0.25 wt% FeO_x/HCMK-3 catalyst.

Fe₂O₃. The narrow peak (centered at 430 °C) can be ascribed to the reduction of Fe₂O₃ to Fe₃O₄. The two overlapping peaks in the range 450–800 °C can be ascribed to further reduction to FeO/Fe species [46,47]. For FeO_x/HCMK-3, only one broad peak is present in the range 200–600 °C. The start and center of this peak are clearly at lower temperatures than those for bulk Fe₂O₃, confirming the high reducibility of FeO_x/HCMK-3. The amounts of H₂ consumed by FeO_x/HCMK-3 and Fe₂O₃ during

Fig. 4. Fe 2p (a) and O 1s (b) XPS spectra of FeO_x/HCMK-3 and bulk Fe₂O₃.

TPR were 2.13 and 18.10 mmol/g, respectively. The FeO_x content in FeO_x/HCMK-3 was 5 wt%, therefore the stoichiometric consumption of H₂ by FeO_x should be 0.93 mmol/g, which is lower than the actual amount of H₂ consumed (2.13 mmol/g). A combination of the H₂-TPR, XPS, and DRIFT results shows that additional H₂ is consumed (1.2 mmol/g) because of the presence of oxygen-containing functional groups in FeO_x/HCMK-3. The quantity of reduced functional groups in FeO_x/HCMK-3 was determined based on H₂-TPR of HCMK-3. The results show that H₂ consumption by HCMK-3 was about 1.08 mmol/g, which is consistent with H₂ consumption by the carbon support in FeO_x/HCMK-3 (1.2 mmol/g).

These results show that oxygen functional groups play im-

Fig. 5. (a) DRIFT spectra of CMK-3, HCMK-3, and FeO_x/HCMK-3; (b) FT-IR spectra of FeO_x/HCMK-3, Fe-HCMK-3, and Fe₂O₃.

Fig. 6. H₂-TPR profiles of FeO_x/HCMK-3 and bulk Fe₂O₃.

portant roles in the formation of highly dispersed iron oxide species. They render the HCMK-3 support surface negatively charged. Zeta-potential measurements show that HCMK-3 is negatively charged at pH 1.0–8.0 (Fig. 7). Untreated CMK-3 is positively charged at pH less than 5.1. FeO_x/HCMK-3 was prepared by impregnation with Fe(NO₃)₃ aqueous solution. The pH of the Fe³⁺-containing solution was 1.65 (Fig. 7). Under these preparation conditions, there is an electrostatic force between the positively charged metal ions and negatively charged carbon surface (Fig. 1). This could be the main reason for the homogeneous dispersion of Fe ions on the carbon surface. In the subsequent thermal treatment, these surface oxygen functional groups provide strongly active sites for anchoring FeO_x species, and suppress iron oxide aggregation.

3.2. Catalytic performance

Fig. 8 shows the catalytic activity of FeO_x/HCMK-3 in the oxidative coupling of benzyl alcohol and aniline to an imine at 80 °C. The imine was identified using gas chromatography-mass spectrometry. For comparison, the reaction was also performed using bulk Fe₂O₃ and HCMK-3. The activity of bulk Fe₂O₃ was low. Only a 13.2% yield of imine was obtained after reaction for 8 h at 80 °C. The HCMK-3 support was almost inactive under the test conditions. For FeO_x/HCMK-3, the yield

Fig. 7. Zeta-potential profiles for CMK-3 and HCMK-3; pH is the value for impregnation process, i.e., iron nitrate solution containing HCMK-3.

Fig. 8. Time dependences of imine formation from aerobic oxidative coupling of benzyl alcohol and aniline over FeO_x/HCMK-3, bulk Fe₂O₃, and HCMK-3. Reaction conditions: benzyl alcohol 1 mmol, aniline 2 mmol, catalyst 0.3 g, toluene 10 mL, 80 °C, air 1 bar.

of imine after reaction for 6 h was 98.8%. The TOF for FeO_x/HCMK-3 in the initial stage was 2.9 h⁻¹. The catalytic performance of FeO_x/HCMK-3 at 60 °C was also investigated for comparison with those of other reported catalytic systems. The TOF was 0.6 h⁻¹. Comparisons with results reported in the literature [19,25,26] show that this TOF is higher than those for non-noble-metal oxide catalysts (e.g., CeO₂ and MnO_x/HAP), but a little lower than those of supported Au catalysts under similar reaction conditions. The reaction was also performed using equimolar amounts of the alcohol and amine. A 78.4% yield of the imine was obtained after reaction for 8 h. All these results indicate that FeO_x/HCMK-3 is an effective catalyst for imine formation.

Multiple aerobic oxidation cycles were performed to examine the recoverability of FeO_x/HCMK-3 (Fig. 9). The catalyst retained high activity after five cycles, with only 3% and 5% decreases in the third and fifth cycles compared with the first one. Loss of Fe from the catalyst to the reaction mixture was determined using ICP-AES. Trace amounts of Fe (0.02 ppm, 0.02‰ of total Fe) were detected, indicating that Fe active sites

Fig. 9. Reusability of FeO_x/HCMK-3 in imine synthesis by aerobic oxidative coupling of benzyl alcohol and aniline. Reaction conditions: benzyl alcohol 1 mmol, aniline 2 mmol, catalyst 0.3 g, toluene 10 mL, 80 °C, air 1 bar, 3 h. Recovered catalysts were treated under Ar at 400 °C for 1 h.

were not lost. The XRD patterns show that there was no aggregation of iron oxide species in the used FeO_x/HCMK-3. All these results suggest that iron oxide active sites are stable in the FeO_x/HCMK-3 catalyst. The decrease in the imine yield was mainly caused by loss of catalyst in the recycling process. The catalyst was recycled by filtration and then thermally treated at 400 °C for 1 h under Ar to remove adsorbed reagents. Catalyst loss (about 7%) is inevitable during this process.

Experiments were performed to identify the active sites in FeO_x/HCMK-3 (Table 2). When Fe(NO₃)₃ was used as the catalyst, the yield of imine after reaction for 8 h was 1.8%. Even in the co-presence of Fe(NO₃)₃ and HCMK-3, the imine yield was only 5.0%. These results differ from those reported by Zhang et al. [48], mainly because different reaction conditions were used. Under their reaction conditions, Fe(NO₃)₃ shows moderate activity in imine synthesis and the activity can be greatly enhanced by addition of 2,2,6,6-tetramethyl-1-piperidinyloxy [48]. We also investigated the catalytic performance of Fe-HCMK-3. An imine yield of 24.6% was obtained over Fe-HCMK-3 after reaction for 8 h; this is much lower than the yield achieved using FeO_x/HCMK-3. Loss of Fe into the reaction mixture was detected using ICP-AES; the amount was about 33.65 ppm, which is 3.2% of the total amount of Fe loaded on Fe-HCMK-3. All these results suggest that Fe³⁺ ions or coordinated Fe species were not active in the imine synthesis reaction. Supported FeO_x species were the effective and stable active sites. The highly dispersed FeO_x species on the HCMK-3 surface could affect the redox properties of the FeO_x/HCMK-3 catalyst. The reducibility of these iron oxide species could be responsible for the high activity in this reaction.

The general applicability of the FeO_x/HCMK-3 catalyst was also investigated. Eleven imines were obtained by oxidative coupling of amines with various alcohols. Table 3 (entries 1–7) shows that the FeO_x/HCMK-3 catalyst is active in reactions using benzyl alcohol derivatives with either electron-rich or electron-poor substituents, especially 4-methylbenzyl alcohol, 4-methoxybenzyl alcohol, and 4-isopropylbenzyl alcohol (the imine yields were 93.2%, 90.7%, and 84.2%, respectively, after reaction for 8 h). FeO_x/HCMK-3 also catalyzed the reaction of phenethyl alcohol and allylic alcohols (e.g., *trans*-2-hexenol) with aniline to give the corresponding imines when the reaction temperature and time were increased (Table 3, entries 8 and 9). Table 3 shows that FeO_x/HCMK-3 is active in the aerobic oxidative coupling of aliphatic amines (e.g., cyclohexylamine

Table 2

Imine synthesis by oxidative coupling of benzyl alcohol and aniline over various catalysts.

Entry	Catalyst	Time (h)	Yield (%)
1	FeO _x /HCMK-3	6	98.6
2	None	8	0.9
3*	Fe(NO ₃) ₃	8	1.8
4*	Fe(NO ₃) ₃ + HCMK-3	8	5.0
5	Fe-HCMK-3	8	24.6
6	Fe ₂ O ₃	8	13.2
7	HCMK-3	8	5.1

Reaction conditions: benzyl alcohol 1 mmol, aniline 2 mmol, catalyst 0.3 g, toluene 10 mL, 80 °C, air 1 bar. *The amount of Fe(NO₃)₃ was calculated based on the Fe content in FeO_x/HCMK-3.

Table 3

Aerobic oxidative coupling of various alcohols and anilines over FeO_x/HCMK-3 catalyst.

$R^1-CH_2OH + R^2-NH_2 \xrightarrow[80\text{ }^\circ\text{C Air}]{FeO_x/HCMK-3\text{ catalyst}} R^1-CH=CH-R^2 + H_2O$			
Entry	Product	Time (h)	Yield (%)
1		6	98.0
2		8	93.2
3		8	90.7
4		8	84.2
5		8	80.7
6		10	75.1
7		10	64.2
8*		12	55.9
9*		12	36.4
10		8	85.8
11		8	80.6

Reaction conditions: alcohol 1 mmol, amine 2 mmol, catalyst 0.3 g, toluene 10 mL, 80 °C, air 1 bar. *Temperature: 100 °C.

and *n*-butylamine) with benzyl alcohol (Table 3, entries 10 and 11). These results clearly show that FeO_x/HCMK-3 is an efficient catalyst in oxidative coupling reactions.

Three additional experiments were performed to clarify the reaction mechanism over FeO_x/HCMK-3; the results are shown in Fig. 10. Fig. 10a shows that the oxygen species in FeO_x/HCMK-3 are active in the aerobic oxidative reaction. Even without the presence of O₂, an 8.7% yield of imine was obtained after reaction for 8 h at 80 °C. This experiment was performed in a Schlenk tube (see the experimental section for details). The FeO_x/HCMK-3 catalyst was first degassed at 80 °C for 1.5 h under vacuum to remove adsorbed O₂. After adding the reactants and solvent, the system was further degassed and then balanced with high-purity N₂. All these treatments were performed to ensure the removal of molecular O₂ from the system. This result shows that the oxygen species in FeO_x/HCMK-3 participate in the reaction. The oxidative coupling of alcohols and amines on FeO_x/HCMK-3 occur via a redox mechanism [25,26]. During imine synthesis over FeO_x/HCMK-3, benzaldehyde was detected in the initial stage and the amount slowly decreased with time (Fig. 10b). This suggests that benzalde-

Fig. 10. (a) Effects of catalytic conditions on performance of FeO_x/HCMK-3 in imine formation by aerobic oxidative coupling of benzyl alcohol and aniline. Reaction conditions: benzyl alcohol 1 mmol, aniline 2 mmol, catalyst 0.3 g, toluene 10 mL, 80 °C, air or N₂ 1 bar. (b) Time dependence of imine formation by oxidative coupling of benzyl alcohol and aniline over FeO_x/HCMK-3. Reaction conditions: benzyl alcohol 1 mmol, aniline 2 mmol, catalyst 0.3 g, toluene 10 mL, 80 °C, air 1 bar. (c) Time dependences of imine formation by coupling of benzaldehyde and aniline with and without FeO_x/HCMK-3 catalyst. Reaction conditions: benzaldehyde 1 mmol, aniline 2 mmol, catalyst 0.3 g, toluene 10 mL, 80 °C, air 1 bar.

hyde might be an intermediate and that the reaction proceeds in two consecutive steps: (1) oxidative dehydrogenation of the alcohol to benzaldehyde and (2) imine formation by reaction of benzaldehyde with aniline.

We recently reported that FeO_x/HCMK-3 catalyzes the oxidation of benzyl alcohol to benzaldehyde with air as the oxygen source [33]. Benzyl alcohol conversion of 72% was observed after reaction for 8 h. In the imine synthesis, benzyl alcohol conversion improved to 98.8% after reaction for 6 h. The second step in imine formation accelerates the conversion of benzyl alcohol. Fig. 10c shows that FeO_x/HCMK-3 efficiently catalyzes imine synthesis from benzaldehyde and aniline. The reaction rate is 372.8 mmol h⁻¹ g⁻¹ (calculated based on iron oxide sites), which is 4.5 times higher than that for imine formation from benzyl alcohol and aniline (82.0 mmol h⁻¹ g⁻¹). This confirms that oxidative dehydrogenation of alcohol is the rate-determining step in the reaction. Based on the above results and related literature reports [49,50], a plausible reaction mechanism for imine formation from an alcohol and aniline on FeO_x/HCMK-3 is proposed (Scheme 1). Oxidative dehydrogena-

tion of benzyl alcohol by oxygen species occurs at the redox sites of FeO_x/HCMK-3. Iron is reduced from valence +3 to +2. The produced benzaldehyde reacts with aniline over FeO_x/HCMK-3 to afford the corresponding imine. FeO_x/HCMK-3 is regenerated by oxidation of the reduced FeO_x/HCMK-3 with O₂.

4. Conclusions

FeO_x/HCMK-3 with highly dispersed iron oxide species shows high activity and recyclability in aerobic oxidative coupling of alcohols and amines to imines. The excellent catalytic performance of FeO_x/HCMK-3 is ascribed to its high reducibility. The lattice oxygens in FeO_x/HCMK-3 can participate in imine synthesis, and the reaction follows a redox mechanism over FeO_x/HCMK-3. Two consecutive steps are involved in the reaction: oxidative dehydrogenation of an alcohol to an aldehyde and coupling of the aldehyde with an amine to an imine. Oxidative dehydrogenation of alcohol is the rate-determining step in the reaction.

Scheme 1. Proposed reaction mechanism for imine formation over FeO_x/HCMK-3.

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Graphical Abstract

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

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Mesoporous-carbon-supported iron oxide is a highly efficient and recyclable catalyst for imine synthesis by oxidative coupling of alcohols and amines with air as the oxygen source.

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介孔炭负载铁基催化剂上醇与胺氧化偶合合成亚胺

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摘要: 亚胺是一类重要的含氮有机化合物, 广泛应用于生物医药、精细化工和农业生产中。由于其分子中具有不饱和 C=N 双键, 亚胺化合物可以通过不同化学过程(如氧化还原、加成、偶合等)合成多种衍生物。工业上合成亚胺普遍采用羰基化合物与胺偶合反应获得, 由于该反应需要强酸作为催化剂和脱水剂, 在应用中往往对设备造成不同程度的破坏。选择氧气或空气为氧化剂, 通过醇与胺氧化偶合反应合成亚胺, 其副产物只有水, 是一条较为绿色的合成路线。近期研究表明, 均相和负载型贵金属催化剂(如 Pd, Pt 和 Au 等)在该反应中表现出较好的低温催化性能, 但需要在反应过程中添加大量碱性助剂。一些非贵金属氧化物催化剂如 CeO₂ 和 MnO_x/HAP 等在该过程中表现出一定的催化活性, 但其催化效率普遍较低, 往往需要在 24 h 甚至更长反应时间实现~90% 亚胺收率。因此仍需开发一些更为高效的非贵金属催化剂用于上述反应。

本文以经过硝酸活化处理的有序多孔炭(CMK-3)为载体, 制备了负载型氧化铁催化剂(FeO_x/HCMK-3), 考察了它在苯甲醇与苯胺氧化偶合合成亚胺反应中的催化性能, 同时结合一系列表征手段研究了催化剂物理化学性质与其催化性能之间的关系。X 射线衍射和氮吸附脱附结果显示, 负载后的样品仍然保持了介孔炭原有的孔道结构, 没有出现较大的氧化铁粒子; 透射电镜、高角暗场扫描透射电镜及能量散射谱结果进一步显示, 氧化铁物种相对均匀地分散在载体表面; 程序升温还原结果显示, 与块体氧化铁相比, FeO_x/HCMK-3 上的氧化铁物种(FeO_x)更易被还原, 这可能与氧化铁粒子较小有关。

反应结果显示, 在空气氛围中 FeO_x/HCMK-3 能够高效催化醇与胺的氧化偶合反应, 反应 6 h 亚胺收率即达到 98.8%。催化剂具有较高的稳定性, 可多次循环使用, 没有检测到铁物种流失。此外, FeO_x/HCMK-3 在多种苯甲醇衍生物与苯胺的氧化偶合反应中都表现出较好的催化性能。

结合表征和反应结果可以推测, 催化剂上的氧物种参与了反应过程, FeO_x/HCMK-3 催化剂具有较强的活化氧分子的能力, 反应在该催化剂上可能遵循氧化-还原机理。该催化剂上醇与胺氧化偶合反应主要经历两个连续的反应过程: 首先苯甲醇被 FeO_x/HCMK-3 催化剂上的活泼氧物种氧化生成苯甲醛中间体; 随后, 在反应中生成的醛在催化剂上迅速与胺反应生成亚胺化合物, 同时催化剂通过与空气中氧分子反应恢复到初始状态, 完成整个催化循环。

关键词: 铁基催化剂; 亚胺合成; 氧化偶合; 介孔炭; 分子氧

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