

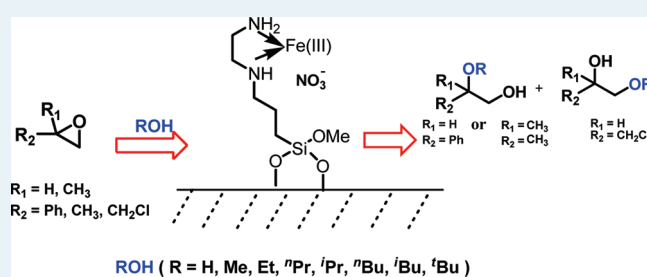
Epoxide Ring-Opening Reactions with Mesoporous Silica-Supported Fe(III) Catalysts

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S Supporting Information

ABSTRACT: A mesoporous silica-supported iron(III) catalyst was successfully synthesized by tethering ethylenediamine ligands onto the mesopore channel walls of mesoporous silica and then using the diamine groups to support Fe(III) ions. The resulting material is shown to be an efficient catalyst for the ring-opening of various epoxides by a series of alcohols as well as water under mild reaction conditions giving good-to-high yields of the corresponding ring-opened products. Among the alcohols tested with styrene oxide substrate giving 2-alkoxy-2-phenylethanol products, MeOH was the most reactive. It gave the highest percent conversion and yield (~100%) within a relatively short reaction time of 6 h, whereas the longer alkyl alcohols gave a relatively lower yield of 93 to ~100% with longer reaction times of 9–56 h. When the alkyl groups of the linear alkyl alcohols were longer, the rates of the catalytic reaction were slower. For instance, EtOH gave ~100% yield in 9 h, but *n*-PrOH produced 93% product in 45 h. Substituted alkyl alcohols produced only 9–62% product in even longer reaction times of 72–144 h, with the more substituted alcohols giving the slower reaction rates. The catalyst was also shown to ring-open other epoxides, such as chloropropylene oxide and 2-methyl-1,2-epoxypropane. The chloropropylene oxide was found to react much more slowly than the 2-methyl-1,2-epoxypropane, whereas the 2-methyl-1,2-epoxypropane underwent catalytic reaction slightly more slowly than styrene oxide in the presence of the catalyst under the same reaction conditions. The catalyst was shown to be reusable multiple times without leaching of the Fe(III) ions.

KEYWORDS: mesoporous catalysts, nanoporous catalysts, ring-opening reactions, supported iron catalyst, epoxides



1. INTRODUCTION

Epoxides are often encountered in nature, both as intermediates in key biosynthetic pathways and as secondary metabolites.^{1–8} In organic synthesis, epoxides are invaluable building blocks for introduction of diverse functionalities into a hydrocarbon backbone in a 1,2-fashion.^{9–11} For instance, ring-opening of epoxides with nucleophiles is an important route to achieve compounds with versatile 1,2-type functional groups, including β -alkoxyalcohols.^{12–14} β -Alkoxyalcohols, in turn, are an important class of organic compounds¹⁵ and precursors for a broad range of pharmaceuticals.^{16–23} The general procedure for β -alkoxyalcohols synthesis is via alcoholysis¹³ involving ring-opening of epoxides with alcohols, which usually requires acid or base catalysts. For instance, the ring-opening of styrene oxide with water or alkyl alcohols in the presence of acidic catalyst produces 1-phenyl-1,2-ethanediol and 2-alkoxy-2-phenylethanol, respectively.^{24–26} These compounds, in turn, are useful precursors for pharmaceuticals such as mandelic acids, which are antibacterial agents and oral antibiotics and also useful intermediates for the synthesis of β -lactam antibiotics.^{19–22} To obtain high regioselectivity of the epoxide ring-opening reaction

toward the desired product, mild conditions and effective catalysts have to be used.^{12–14}

Ring-opening of epoxides can be achieved with various nucleophiles in the presence of many metal complexes composed of transition and rare earth metals, such as Er(III),²⁷ Cu(II),^{28,29,32} In(III),^{30,31} Sn(II),^{28,29} Sn(IV),³² Cr(II) and Cr(III),³³ Al(III),^{34,35} and Co(III);^{36–40} however, many of these metals have high toxicity, are less abundant, or both. In contrast, iron is one of the most inexpensive, most abundant, and more environmentally friendly transition metals.⁴¹ Moreover, many iron salts and complexes are commercially available⁴² or reported in the literature.⁴³ Furthermore, iron has also been used as a catalyst for a broad range of reactions.⁴⁴ The past few years have witnessed a rapid increase in the number of reports on the use of iron in organic synthesis and even in asymmetric catalysis.^{45–52}

The high cost and the toxicity associated with many of the previously reported metal complex catalysts for epoxide ring-opening reactions^{27–40} have also necessitated an increased

Received: December 24, 2010

Revised: March 13, 2011

Published: March 15, 2011

interest in immobilizing the metal complexes onto solid support materials to generate their heterogeneous forms. The area of heterogeneous catalysis is growing to minimize environmental pollution, eliminate some work up procedures, and help easy separation of the catalyst from the reaction mixture at the end of catalytic reactions. To successfully achieve this, a rational choice of the support materials as well as a good strategy for placing the active catalysts on the support materials are required. Many heterogeneous catalysts are often prepared by immobilizing well prepared homogeneous catalysts onto an insoluble solid support such as polymers,^{53–57} zeolite,^{58–64} or silica.⁶⁵ Although there are some examples of iron-containing heterogeneous catalysts based on silica gel,⁶⁵ polymeric support,^{66,67} and metal organic framework (Fe-MOF)⁶⁸ for epoxide ring-opening reactions, these have randomly ordered pores in the case of silica gel, less robust structure in the case of polymer support, or small pore sizes in the case of Fe-MOF. Mesoporous silica possesses robust structure, higher surface area and tunable monodisperse nanometer pores compared to these materials.^{69–71} Thus, the development of synthetic strategies to iron-based heterogeneous catalysts with the use of high surface area mesoporous silica support material is more appealing because it combines the advantages of the robust catalyst support with one of the most abundant and inexpensive metals. However, only recently, a publication has appeared on the use of high-surface-area MCM-41 type mesoporous silica support material for making iron-based heterogeneous catalyst.⁷⁰ The activity of the catalyst was demonstrated in the ammonolysis reaction of epoxides with amines.

Herein, we report on the synthesis of iron-containing SBA-15 type mesoporous silica catalysts, in which Fe(III) is coordinated to organoamine groups grafted onto the surface of the mesoporous silica (SBA-15) and its catalytic activity in the alcoholysis or hydrolysis of various epoxides. The catalyst, labeled as Ext-SBA-15-en-Fe(III), was synthesized by simple postgrafting of diaminoorganosilane onto the surface of mesoporous silica, SBA-15, and then by chelating Fe(III) via the diamine ligands. The mesoporous silica-supported Fe(III) catalyst was shown to catalyze the ring-opening of styrene oxide with water and various primary, secondary, and tertiary alcohols, producing 1-phenyl-1,2-ethanediol and 2-alkoxy-2-phenyl ethanol, respectively, in good to excellent yields as well as with high regioselectivity.

The catalyst was also shown to ring-open other epoxides, such as chloropropylene oxide and 2-methyl-1,2-epoxypropane. The chloropropylene oxide was found to react much more slowly than the 2-methyl-1,2-epoxypropane, while the 2-methyl-1,2-epoxypropane underwent catalytic reaction slightly slowly than styrene oxide in the presence of the catalyst under the same reaction conditions. The catalyst showed no leaching of the iron(III) and was shown to be recyclable many times. We have employed supported iron(III) catalyst rather than the commercially available unsupported iron salts simply to produce a conventional heterogeneous catalyst that can easily be separated at the end of the catalytic reaction. The superiority of supported Ext-SBA-15-en-Fe(III) catalyst over iron salts is that it makes the work up procedure at the end of the reaction much simpler and cost-effective. Although the benefits with respect to cost of catalysts and toxicity for iron catalysts may not be as much due to iron's relative more abundance, less cost and more environmental friendliness, the ease of its separation from the reaction products that are potentially useful precursors for pharmaceutical and synthetic materials would still justify the advantage of our approaches and the supported iron catalysts.

2. EXPERIMENTAL SECTION

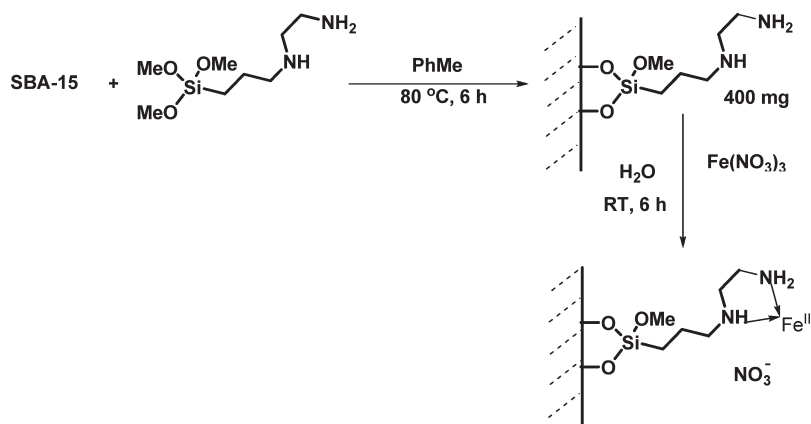
Materials and Reagents. Poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) block copolymer (Pluronic 123, average molecular mass ~5800) was obtained from BASF. Tetraethyl orthosilicate (TEOS), iron(III) nitrate nonahydrate, styrene oxide, chloropropylene oxide, acetone, hexane, and toluene were obtained from Sigma-Aldrich. Hydrochloric acid (36.5%) was obtained from Fischer Scientific. Anhydrous methanol, ethanol, propyl alcohol, isopropyl alcohol, butyl alcohol, isobutyl alcohol, *tert*-butyl alcohol, and 2-methyl-1,2-epoxypropane were obtained from Alfa Aesar. *N*-(2-Aminoethyl)-3-aminopropyltrimethoxysilane was obtained from Gelest, Inc.

Synthesis of Mesoporous Silica, SBA-15. SBA-15 was synthesized as reported previously⁷² by using Pluronic 123 as a templating agent in acidic solution.⁶⁹ Typically, a solution of Pluronic 123/HCl/TEOS/H₂O = 2:12:4.3:26 (mass ratio in g) was stirred at 40 °C for 24 h and then aged at 65 °C for another 24 h. The resulting solution was filtered, and the solid was washed with copious amounts of water, resulting in “as synthesized” SBA-15. Then 4 g of “as synthesized” SBA-15 was dispersed in a solution of ethanol (400 mL) and diethyl ether (400 mL) and stirred at 50 °C for 5 h to remove the template. The solid material was separated by filtration and was dried in an oven at 40 °C for 2 h. This produced surfactant-extracted mesoporous silica, labeled as Ext-SBA-15.

Synthesis of Ethylenediamine-Functionalized Mesoporous Silica and Its Immobilization with Iron(III). A 500 mg portion of the dried Ext-SBA-15 sample was stirred with excess *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (3.68 mmol) in 250 mL toluene at 80 °C for 6 h. The solution was filtered, and the residue was quickly washed with toluene (3 × 20 mL), and then with ethanol (3 × 20 mL) and air-dried. The resulting dried sample was denoted as Ext-SBA-15-en. Then the dried Ext-SBA-15-en (200 mg) was dispersed in an aqueous solution containing iron(III) nitrate nonahydrate (400 mg, 1 mmol) and distilled water (100 mL) and stirred at room temperature for 6 h. This amount of iron salt for the 200 mg of dried Ext-SBA-15-en was chosen to guarantee a slight excess of Fe(III) in the solution as compared with the number of organodiamine groups in the Ext-SBA-15-en material, but to be close enough to a 1:1 molar ratio of the Fe(III) and diamine groups. The moles of organodiamine per gram of sample was determined beforehand by elemental analysis. The resulting solution from a mixture of Ext-SBA-15-en and Fe(III) was deep orange in color. The solid was filtered after 6 h, and the residue was washed with 500 mL of distilled water. After washing, the filtrate was checked for free iron(III) by potassium thiocyanate test. The resulting pale beige solid was air-dried and labeled as Ext-SBA-15-en-Fe(III).

A control sample was also prepared by stirring Ext-SBA-15 (200 mg), which contained no ethylenediamine in it, with Fe(III) nitrate nonahydrate (400 mg) and distilled water (100 mL) at room temperature for 6 h. The resulting sample, denoted as Ext-SBA-15-Fe(III), looked white, indicating that it barely adsorbed the Fe(III) ions from the solution. An additional control sample was prepared by drying Ext-SBA-15-en-Fe(III) under vacuum at 130 °C to remove as much physisorbed water from its surface as possible. This sample, labeled as Ext-SBA-15-en-Fe(III)-Very-Dried, was used as a reference material to test the possibility of ring-opening of styrene oxide by any traces of water that

Scheme 1. Synthesis of Ext-SBA-15-en-Fe(III)



mesoporous catalysts, including our Ext-SBA-15-en-Fe(III), could have.

A calcined SBA-15 material was also used to make a catalyst labeled as Cal-SBA-15-en-Fe(III) for comparison purposes. The mesostructured SBA-15 was kept in a furnace and heated at 600 °C for 5 h to remove the polymer templates and prepare calcined SBA-15 (Cal-SBA-15). Then *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane was grafted onto Cal-SBA-15, and the material was filtered, washed, and dried in the same way as above. The resulting sample was treated with aqueous Fe(III) solution in the same way as above, producing Cal-SBA-15-en-Fe(III) catalyst.

Ring-Opening of Epoxides with Alcohols. In a typical epoxide ring-opening reaction, the catalyst, Ext-SBA-15-en-Fe(III) (20 mg), was added into a solution of styrene oxide (0.9 mmol) and 5 mL of anhydrous alcohol (MeOH, ethanol, propyl alcohol, isopropyl alcohol, butyl alcohol, isobutyl alcohol, or *tert*-butyl alcohol). Please note that the anhydrous alcohol was an excess reagent. The solution was stirred at room temperature or at elevated temperature to get the corresponding β -alkoxyalcohols. The progress of the reaction was monitored with TLC in a 20:80 ratio of ethyl acetate/hexane solution and by gas chromatography (GC). The product was also characterized by ^1H NMR in CDCl_3 and mass spectrometry. The ring-opening reactions for the other epoxide substrates, that is, chloropropylene oxide and 2-methyl-1,2-epoxypropane, and characterization of their products were also conducted in the same way.

Ring-Opening of Epoxides with Water as a Nucleophile. The catalyst (20 mg) was added into a solution containing styrene oxide (0.9 mmol) and a 1:1 mixture of distilled water and acetone (5 mL). The solution was stirred at room temperature to get the corresponding 1-phenyl-1,2-ethanediol. The progress of the reaction was monitored with TLC in a 20:80 ratio of ethyl acetate/hexane solution and by gas chromatography (GC). The product was also characterized by ^1H NMR in CDCl_3 and mass spectrometry.

Instrumentation. Analytical thin layer chromatography was performed on EM Reagent, 0.25 mm silica gel 60 F_{254} plates obtained from VWR. Visualization was accomplished with UV light. Infrared spectra were recorded on an ATI Mattson Genesis Series FT-Infrared spectrophotometer. Proton nuclear magnetic resonance spectra (^1H NMR) were recorded on a Varian VNMRs 400 MHz instrument using CDCl_3 solvent as an internal standard (CDCl_3 at 7.26 ppm). Mass spectra were obtained on a Finnigan LCQ-DUO mass spectrometer. The nitrogen gas adsorption–desorption

measurements were carried out on Micromeritics Tristar 3000 volumetric adsorption analyzer after degassing the samples at 160 °C for 12 h. The powder X-ray diffraction of the material was measured by a Histar diffractometer at 295 K using monochromatized Cu $K\alpha$ ($\lambda = 1.54 \text{ \AA}$) radiation. Thermogravimetric analysis (TGA) or decomposition profiles were acquired for the mesoporous materials and the catalyst with a TGA Q 50 thermogravimetric analyzer. The TGA data were collected under a nitrogen atmosphere (60 cm^3/min) in the temperature range of 25–700 °C at a rate of 10 °C/min. Transmission electron microscopy (TEM) images were taken with a TOPCON-002B electron microscope. The catalytic reaction mixtures were analyzed by GC (HP 6850) equipped with an FID detector and an HP-1, 30 m long \times 0.25 mm i.d. column. Elemental analyses of the catalyst were carried out at Robertson Microtit Laboratories, NJ. The metal (Fe) loading in the fresh catalyst as well as the recycled catalysts and possible leached Fe in the reaction solutions was determined by ICP–AES analysis, also at Robertson Microtit Laboratories, NJ.

3. RESULTS AND DISCUSSION

3.1. Synthesis of Ethylenediamine-Functionalized Mesoporous Silica and Its Immobilization with Iron(III). The synthesis of SBA-15 functionalized with organoamine groups was achieved by stirring surfactant-extracted Ext-SBA-15 with an excess amount of *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane in toluene at 80 °C for 6 h. This produced an ethylenediamine-functionalized mesoporous silica sample or Ext-SBA-15-en. Then the Ext-SBA-15-en was stirred with iron(III) nitrate nonahydrate to obtain the desired iron catalyst, which was denoted as Ext-SBA-15-en-Fe(III) (Scheme 1). The immobilized ethylenediamine on the surface of the mesoporous silica served as a bidentate ligand to coordinate to Fe(III).

The catalyst (Ext-SBA-15-en-Fe(III)) and the parent materials (Ext-SBA-15 and Ext-SBA-15-en) were characterized by N_2 gas adsorption measurement (Figure 1). The N_2 gas adsorption measurements showed a type IV isotherm that is characteristic of mesoporous materials for all the three samples (Figure 1A). Their BJH pore size distributions showed that the materials had monodisperse pore sizes (Figure 1B). Furthermore, the BET surface areas of Ext-SBA-15, Ext-SBA-15-en, and Ext-SBA-15-en-Fe(III) were 470, 204, and 194 m^2/g , respectively. These results indicated that the surface area of the SBA-15 material

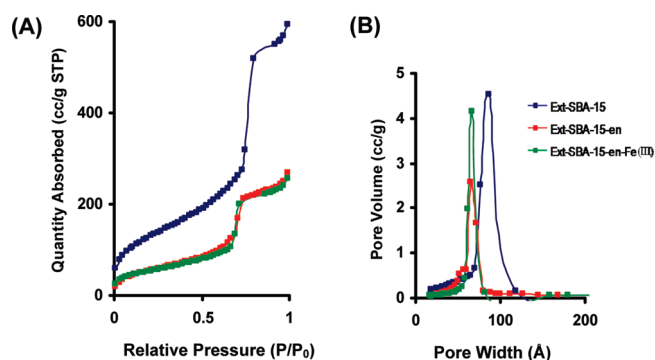


Figure 1. Nitrogen gas adsorption isotherms and pore size distributions of parent mesoporous materials and Ext-SBA-15-en-Fe(III) catalyst.

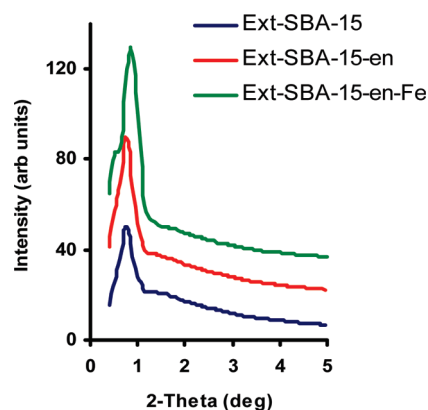


Figure 2. XRD patterns of Ext-SBA-15, Ext-SBA-15-en, and Ext-SBA-15-en-Fe(III) catalyst.

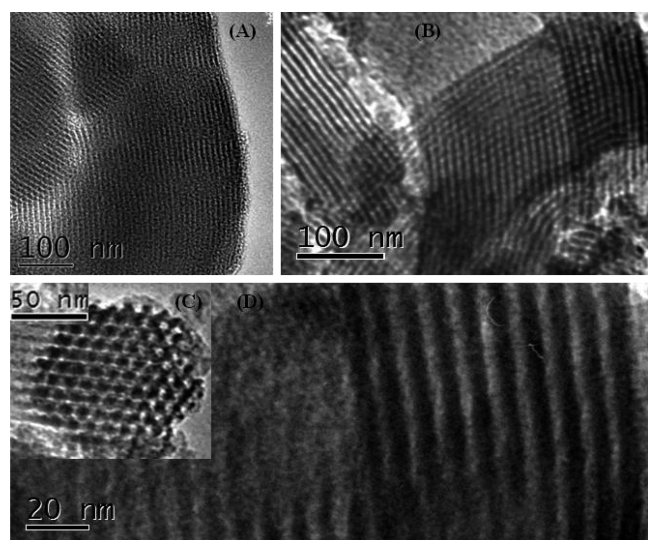


Figure 3. (A) TEM image of Ext-SBA-15 and (B–D) TEM image of Ext-SBA-15-en-Fe(III) catalyst.

decreased when diaminoorganosilane was grafted and iron(III) ions were introduced into its mesopores. The significant decrease in the surface area of the materials in going from the native (or parent) to the functionalized material is because of the

Table 1. Structural Properties of Mesoporous Materials and Ext-SBA-15-en-Fe(III) Catalyst

sample	surface area (m ² /g)	pore size (Å)	<i>d</i> ₁₀₀ (Å)
Ext-SBA-15	470	72	116
Ext-SBA-15-en	204	67	118
Ext-SBA-15-en-Fe	194	67	104

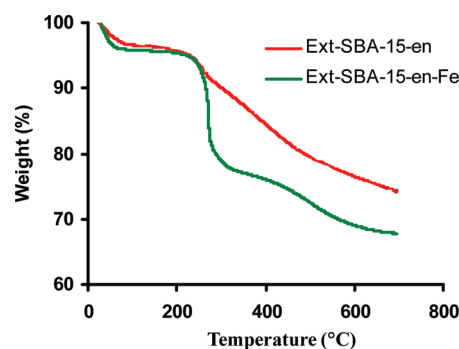


Figure 4. Thermogravimetric traces of Ext-SBA-15-en material and Ext-SBA-15-en-Fe(III) catalyst.

presence of organic groups in the mesopores of the material. *N*-(2-Aminoethyl)-3-aminopropyl groups are rather bulkier and thus take up a significant portion of the void space of the mesopores. Similar results on the reduction of the surface area of mesoporous materials upon grafting by organic groups have been published previously.^{72–74}

The materials, both before and after postgrafting, were also characterized by powder X-ray diffraction (XRD) (Figure 2) and TEM (Figure 3). The XRD patterns of all the samples showed sharp peaks corresponding to the (100) Bragg reflection, indicating that the materials possessed hexagonally ordered mesostructures. Furthermore, the result suggested that the ordered SBA-15 mesostructure remained intact, even after postgrafting it with the organoamines or organoamine–iron(III) complexes. The (100) peaks were indexed and gave unit cell sizes of ~12–13 nm. These and other physical properties of the material are listed in Table 1. The TEM images of the samples before and after postgrafting also revealed the presence of ordered mesostructures in the materials (Figure 3). Thus, except for the pore size reduction, the monodispersity and mesoporosity of the pores remained unchanged after immobilization of organoamine and organoamine–iron(III) complexes within the pores of the materials. The structure of the material also remained intact even after the material was used as catalyst in catalytic reactions multiple times, as confirmed by powder X-ray diffraction patterns and TEM images (Figures S1–S3 in Supporting Information).

The thermogravimetric traces (Figure 4) indicated a weight loss below 100 °C for all the samples due to loss of water adsorbed on the materials. The weight loss in Ext-SBA-15-en in the range 100–450 °C could be due mainly to the loss of organoamine groups.

The amount of amine or organodiamine groups in the fresh catalyst was obtained by CHN elemental analysis, which gave C (10.72%), H (1.75%), and N (6.17%) (Table S1). This gave 4.41 mmol of N or 2.21 mmol of organodiamine per gram of sample, which is a reasonable quantity and very consistent with those in

Scheme 2. Ring-Opening of Epoxides with Alcohols Using Iron Catalyst, Ext-SBA-15-en-Fe(III)

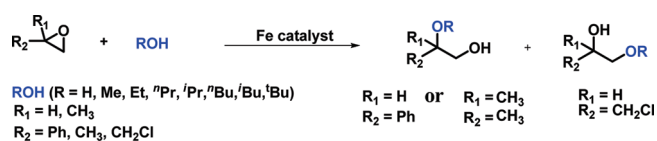


Table 2. Ring-Opening of Epoxides Using Ext-SBA-15-en-Fe(III) as Catalyst^a

entry	alcohol	temp (°C)	time (h)	% yield ^b	TOF (h ⁻¹) ^c
1	H ₂ O	RT	2	~100	157 343
2	MeOH	RT	6	~100	52 448
3	EtOH	RT	9	~100	34 965
4	<i>n</i> -PrOH	80	45	93	6503
5	<i>i</i> -PrOH	80	72	50	2185
6	<i>n</i> -BuOH	80	56	96	5395
7	<i>i</i> -BuOH	80	144 (6 days)	62	1355
8	<i>t</i> -BuOH	80	144 (6 days)	9	197

^a Attempted reaction between styrene oxide and MeOH without the Ext-SBA-15-en-Fe(III) catalyst gave no product in 5 and 48 h and only 11% after 96 h. ^b Yield is calculated by GC. ^c Calculated using the 0.143 mmol/g Fe(III) that was obtained by ICP–AES for the Ext-SBA-15-en-Fe(III) sample.

other previously reported amine-functionalized mesoporous materials.⁷³ Furthermore, when combined with the percent of C of 10.72%, a C/N ratio of 2.02 was obtained for the material. This value is very close to the theoretical C/N ratio for *N*-(2-aminoethyl)-3-aminopropyl ligand, which is ~2.14. ICP–AES analysis gave 3876 ppm (or 0.39%) for Fe, which was calculated to be 70 μmol Fe/g sample. Assuming a maximum of three NO₃⁻ counterions for each Fe(III), we have accounted 3 × 70 μmol (or 0.21 mmol) of the total 4.41 mmol N in a gram of sample to NO₃⁻ groups. This leaves the diamine/Fe(III) ratio to be 30 and above 1.0. Thus, the high diamine/Fe(III) ratio might be simply because each Fe(III) might have been coordinated to more than one diamine group forming tris(diamine)–Fe(III) type complexes, many of diamines might be sterically hindered to coordinate with Fe(III) ions, or both.

Catalytic Activity of the Catalyst in Ring-Opening of Epoxide. The catalytic properties of Ext-SBA-15-en-Fe(III) in epoxide ring-opening reactions were studied using the reaction between styrene oxide and water or different alcohols including primary, secondary, and tertiary alcohols (Scheme 2) at room temperature or at an elevated temperature of 80 °C. The corresponding hydrolysis or alcoholysis products, 1-phenyl-1,2-ethanediol or β-alkoxyalcohols, were obtained in good to excellent yields (Table 2). In the latter case, 2-alkoxy-2-phenylethanol products were regioselectively formed as characterized by TLC in a 20:80 ratio of ethyl acetate/hexane solution and by ¹H NMR.

The rate of the reaction varied depending on the type of reactant used. Water was found to ring open styrene oxide the fastest, giving ~100% 1-phenyl-1,2-ethanediol in 2 h. The rates of the reactions with alcohols varied significantly depending on their structures.

For instance, methanol gave a yield of 100% 2-methoxy-2-phenylethanol in 6 h at room temperature. Styrene oxide also reacted with ethanol at room temperature, but took a slightly

Table 3. Control Experiments of Attempted Ring-Opening Reactions of Styrene Oxide Using Ext-SBA-15 Containing No Fe(III) or Ext-SBA-15-Fe(III) Containing No Ethylenediamine, but Stirred with Fe(III) Solution (made by stirring Ext-SBA-15 with Fe(III) nitrate)^a

entry	catalyst	reactant	time (h)	% yield ^b
1	Ext-SBA-15	MeOH	48	NR
2	Ext-SBA-15-Fe	MeOH	48	NR
3	Ext-SBA-15-Fe	MeOH	96	11.31

^a Ext-SBA-15 = surfactant extracted SBA-15 with no ethylenediamine and no Fe(III) in it; Ext-SBA-15-Fe(III) = Ext-SBA-15-Fe(III) containing no ethylenediamine but stirred in aqueous Fe(III) nitrate solution. The reaction was performed at room temperature. ^b NR = no reaction; yield was calculated by GC.

longer time of 9 h compared with methanol to give ~100% yield of 2-ethoxy-2-phenylethanol. Similarly propyl alcohol reacted with styrene oxide to give a 93% yield of the corresponding product, but only after a longer reaction time of 45 h. Isopropyl alcohol gave even a much lower yield after longer reaction times in comparison with methanol, ethanol, and propyl alcohol (Table 2). The latter may be due to the steric hindrance of the two methyl groups of isopropyl alcohol compared to propyl alcohol, ethanol, or methanol. The decrease in the rates of the reactions became even more pronounced when butyl alcohol, isobutyl alcohol, and *tert*-butyl alcohol were used as nucleophiles. Butyl alcohol gave a yield of 96% in 56 h at 80 °C, whereas isobutyl alcohol and *tert*-butyl alcohol gave a yield of 62% and 9%, respectively, when the reaction was run for 144 h at 80 °C. Generally, it was observed that the reaction of styrene oxide with primary alcohols was faster than those of secondary and tertiary alcohols. Of all the alcohols studied, methanol was found to be the most reactive for ring-opening of styrene oxide in terms of percentage conversion and reactivity. The difference in reactivity may be explained as resulting from the steric bulk of alcohols when going from primary to secondary to tertiary alcohols. Similar results of higher catalytic activity for methanol compared with other alcohols in epoxide ring-opening reactions were also reported for other catalysts.⁶⁵

A control reaction between styrene oxide and MeOH at room temperature with no catalyst or mesoporous material in the reaction solution gave no reaction product in 48 h. Similarly, the control experiment of attempted ring-opening reactions of styrene oxide using Ext-SBA-15 containing no Fe(III) also gave no product (Table 3). Even the material, Ext-SBA-15-Fe, which contained no ethylenediamine but was stirred with Fe(III) solution, gave no reaction product in the reaction mixture of styrene oxide and MeOH at room temperature in 48 h-reaction time. Furthermore, it gave 11% yield of 2-methoxy-2-phenylethanol product only after 96 h-reaction time. This clearly showed that the reaction was catalyzed by Fe(III). Furthermore, it indicated the importance of a ligand such as organoamine in the material to anchor Fe(III) better and to produce an efficient catalyst.

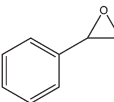
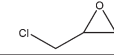
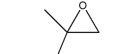
In addition to the solvent extracted SBA-15 mesoporous silica, a calcined SBA-15, whose P123 polymer templates were removed by calcination, was used for the preparation of the Fe(III) catalyst, Cal-SBA-15-en-Fe(III). The latter showed less catalytic efficiency than the corresponding catalyst made from the solvent-extracted Ext-SBA-15 (or Ext-SBA-15-en-Fe(III) catalyst) (Table S2). This is most likely due to the presence of less silanol for

Table 4. Temperature Dependence Study of Ring-Opening of Styrene Oxide with Propyl Alcohol Using Ext-SBA-15-en-Fe(III) Catalyst

entry	temp (°C)	time (h)	% yield ^a
1	RT	24	0
2	40	24	3.2
3	60	24	43.9
4	80	24	97.6

^a Yield is calculated by GC.

Table 5. Scope of Catalytic Activity of the Ext-SBA-15-en-Fe(III) Catalyst in the Ring-Opening of Different Substituted Epoxide with MeOH^a

Entry	Epoxide	Alcohol	Temperature (°C)	Time (h)	% Yield
1.		MeOH	50	5	~100 ^b
2.		MeOH	50	6	30 ^c
3.		MeOH	50	6	85 ^d

^a Reaction between 0.9 mmol of epoxide and 5 mL of anhydrous MeOH in the presence of 20 mg of Ext-SBA-15-en-Fe(III) catalyst. ^b The more-substituted alcohol regioisomer 2-methoxy-2-phenylethanol was obtained. ^c The less-substituted alcohol regioisomer 1-chloro-3-methoxy-2-propanol was obtained. ^d The more-substituted alcohol regioisomer 2-methoxy-2-methyl-1-propanol was obtained.

grafting aminoorganosilane and subsequently Fe(III) on the calcined SBA-15 material (Figure S5). Thus, most of our studies have focused on Ext-SBA-15-en-Fe(III) catalyst.

From our results above, water was found to react faster than alcohols in the epoxide ring-opening reactions catalyzed by the Ext-SBA-15-Fe(III) catalyst. On the other hand, mesoporous silicas in general as well as our Ext-SBA-15-en-Fe(III) mesoporous catalyst contain trace amount of physisorbed water, as also shown in our TGA results above. Thus, further control experiments were necessary to determine if this trace amount of water in the catalysts was capable of ring-opening of the epoxides in the reaction mixtures containing epoxides and alcohols, and generating the corresponding 2-alkoxy-2-phenylethanol byproduct.

Two catalysts were prepared to allow us investigate this: (1) Ext-SBA-15-en-Fe(III), dried under ambient conditions, and (2) Ext-SBA-15-en-Fe(III), dried under vacuum at 130 °C for 2 h to remove as much trace water as possible. When the catalyst that was dried under ambient conditions was mixed with neat styrene oxide but with no other reactant or solvent, no reaction or ring-opened product was obtained in 24 h of reaction time at room temperature. This suggested that the possible trace water in the catalyst did not participate in the epoxide ring-opening reaction. We performed another reaction with the same catalyst but by using anhydrous toluene—a solvent not capable of ring-opening of epoxides. This also gave no ring-opened product. These results further corroborated that the trace amount of water in the Ext-SBA-15-en-Fe(III) did not participate in the epoxide ring-opening reactions.

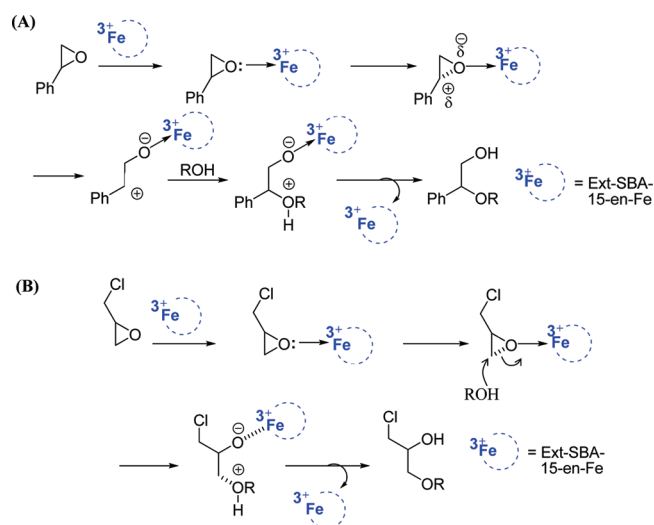


Figure 5. The proposed mechanism of ring-opening reaction of epoxides with alcohols catalyzed by Ext-SBA-15-en-Fe(III) catalyst (A) showing the S_N1 mechanism, which applies for ring-opening of styrene oxide and 2-methyl-1,2-epoxypropane, and (B) showing the S_N2 mechanism which applies for ring-opening chloropropylene oxide.

In another control experiment, involving the Ext-SBA-15-en-Fe(III) that was dried at 130 °C under vacuum (Ext-SBA-15-en-Fe(III)-VeryDried) as a catalyst in the reaction between styrene oxide and MeOH, only the MeOH ring-opened product resulted. Most importantly, the latter gave ~100% conversion in the same reaction time as its Ext-SBA-15-en-Fe(III) counterpart that was dried under ambient conditions. All the samples gave the ring-opened products only from the added reactant (or solvent) and none from the trace water in the catalysts, as proved by GC, mass spectrometry, and ¹H NMR. Hence, the percent conversions of the reactions obtained from GC could also be safely interpreted as percent yields, giving ~100% yield in some cases.

The effect of temperature on the epoxide ring-opening catalytic reaction was studied by using the reaction between styrene oxide and propyl alcohol. The reaction was done at RT and 40, 60, and 80 °C, and the reaction yield after 24 h was monitored by GC. These results are summarized in Table 4. It was observed that the rate of the reaction increased with increasing temperature. For example, at room temperature there was no formation of product after 24 h. When the temperature was slightly increased to 40 °C, the yield was 3.2% after 24 h. But, when the reaction temperatures were increased to 60 and 80 °C, a moderate yield of 43.9% and a good yield of 97.6%, respectively, were obtained after 24 h. Thus, with bulkier alcohols, the reaction was and should be performed only at 80 °C to get reasonable yields. On the other hand, the ring opening of styrene oxide with water was faster, even when performed at room temperature, or took much less time to get to completion compared to the reactions with alcohols.

The Ext-SBA-15-en-Fe(III) catalyst was also proven to ring-open other epoxides, such as chloropropylene oxide and 2-methyl-1,2-epoxypropane (Table 5). The chloropropylene oxide was found to react much more slowly than the 2-methyl-1,2-epoxypropane, whereas the 2-methyl-1,2-epoxypropane underwent catalytic reaction more slowly than styrene oxide under the same reaction conditions. Furthermore, the regioselectivity of the

Table 6. Test of Recyclability of the Catalyst Using Ring-Opening of Styrene Oxide by MeOH Using Ext-SBA-15-en-Fe(III) Catalyst

entry	time (h)	temp (°C)	% yield
1st run	5	50	~100
2nd run	5	50	~100
3rd run	5	50	~100
4th run	5	50	~100
5th run	5	50	~100

products was found to vary depending on the type of the reactant. While the ring-opening reaction between styrene oxide or 2-methyl-1,2-epoxypropane and MeOH with Ext-SBA-15-en-Fe(III) catalyst gave the corresponding less-substituted alcohol regioisomers, the reaction between chloropropylene oxide and MeOH resulted in the more-substituted alcohol regioisomer product. These differences in reactivity as well as regioselectivity can be attributed to the relative steric and electronic differences among the reactants, which affect the reaction mechanisms as shown in Figure 5.

In epoxide ring-opening reactions, the iron in Ext-SBA-15-en-Fe(III) catalyst can act as a Lewis acid center. Further, acid-catalyzed ring-opening reactions are known to go through either a S_N1 or S_N2 reaction mechanisms (Figure 5).^{31,68} Thus, the plausible mechanism could be the coordination of iron(III) of the catalyst with the oxygen atom in the epoxide ring through an acid–base interaction, which in turn increases the electrophilicity of the carbon atoms in the epoxide (Figure 5). The nucleophiles (water or the alcohols) then attack one of the two carbon atoms in the epoxide ring either through S_N1 or S_N2 mechanism to give the ring-opened product. The high regioselectivity to the less substituted alcohol regioisomers under acid-catalyzed ring-opening for styrene oxide and 2-methyl-1,2-epoxypropane is due mainly to the polarization of the C–O bond,⁷⁵ which leads to a more substituted, stable carbocation or a favorable S_N1 reaction mechanism. In this case, the nucleophile attacks the more substituted or more stable carbocation formed from the epoxide. However, chloropropylene oxide undergoes acid-catalyzed ring-opening through a S_N2 reaction mechanism, favoring the more substituted alcohol. In this case, the nucleophile attacks the less substituted carbon in the epoxide ring for steric reasons. We have confirmed the regioisomer products formed from our reaction with ^1H and ^{13}C NMR spectra (Figure S6). Our results are also consistent with those reported for ring opening reactions of similar reactants catalyzed by homogeneous or metal organic framework catalysts.^{31,68}

The Ext-SBA-15-en-Fe(III) mesoporous silica catalyst was shown to be easily recyclable at least five times (Table 6). Upon completion of the reaction, the catalyst was recovered from the reaction mixture by simple filtration, washed with the corresponding alcohol and was then used in the next reaction run. The fresh catalyst as well as the recycled catalysts (after recycling one, two, three, four, and five times) gave ~100% conversion for the reaction between styrene oxide and MeOH in 5 h at 50 °C (Table 6).

Epoxides can be ring-opened by various nucleophiles under acidic, basic, or neutral conditions.^{37–40} However, in some cases, the ring-opening of epoxides such as styrene oxide with methanol to achieve the alcoholysis products under basic or acidic conditions results in polymerization and low regioselectivity at

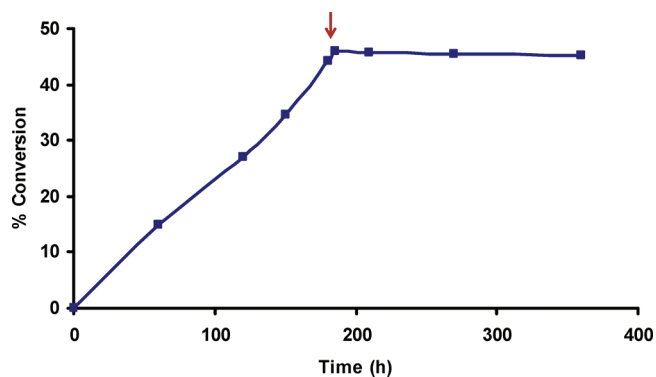


Figure 6. Percent conversion versus reaction time in a leaching experiment. The brown arrow indicates the time the catalyst was filtered and separated from the reaction mixture and the supernatant was then run by itself afterward.

high temperatures.⁷⁶ In our case, mild reaction conditions were used, which gave high regioselectivity.

In addition, epoxide ring-opening reactions can be achieved by many triflates and some perchlorates; for example, $\text{Yb}(\text{OTf})_3$,⁷⁷ $\text{Al}(\text{OTf})_3$,⁷⁸ $\text{TiCl}_3(\text{OTf})_3$,⁷⁹ and $\text{Fe}(\text{ClO}_4)_3$.⁸⁰ The main disadvantages with these are that triflates are expensive and perchlorates are toxic. In other examples, $\text{Fe}(\text{ClO}_4)_3$ ^{66,67} and FeCl_3 ⁸¹ supported on silica gel were reported to act as heterogeneous catalysts for ring-opening of epoxides. However, the “true” heterogeneous nature of these catalysts in the reactions is not clear because the recyclability and leaching studies for these catalysts are not included in the reports. The reaction can just as well be catalyzed by the Fe ions that are possibly leached from the support materials, which is not uncommon for supported metal catalysts.⁸² In contrast, on the basis of our recyclability and leaching tests (see below), our Ext-SBA-15-en-Fe(III) catalyst was shown to be “truly heterogeneous”. Furthermore, the efficiency and catalytic property of our Ext-SBA-15-en-Fe(III) catalyst was comparable to a commercially available iron-based metal–organic framework material [Fe(BTC)] (BTC: 1,3,5-benzenetricarboxylate), which was recently reported to show excellent catalytic activity and reusability for epoxide ring-opening reactions.⁶⁸

Leaching Experiment. Hot-filtration based leaching test was performed to determine if iron(III) leached from the catalyst into the reaction mixture and possibly participated in the catalytic reaction. The catalyst was centrifuged and separated from the reaction mixture, and the supernatant was further run by itself. There was almost no further conversion of styrene oxide, even after 3 h reaction time when the supernatant was stirred by itself after removing the catalyst from it (Figure 6).

The result from the hot-filtration test was further corroborated by elemental analyses of the recyclable catalysts and the reaction mixtures after the third cycle. The percentages of Fe and C, H, and N were analyzed by ICP–AES and CHN analysis, respectively (Table S1). This was done for the fresh catalyst, the catalysts after recycling three and five times, and the reaction mixture after recycling three times (Table S1). The elemental analysis results for the fresh catalyst were already discussed above. The elemental analysis of the recycled materials showed higher percent C and slightly lower percent N. The lower percentage of N relative to C in the recycled catalysts compared with that in the fresh catalyst was merely the result of the presence of some physisorbed styrene

oxide or organics in the former. Most importantly, ICP–AES showed that there was barely any change in the amount of Fe in all the recycled catalysts compared with the fresh catalyst. Furthermore, no detectable iron (<1 ppm) in the reaction solutions was obtained. This result further suggested that the Fe(III) ions from the catalysts did not leach into the solution.

CONCLUSION

We have described the synthesis of an efficient iron-containing mesoporous silica catalyst for ring-opening of various epoxides with water and a variety of alcohols. The material was synthesized by postgrafting of ethylenediamine groups on mesoporous silica and subsequently letting iron(III) attach onto the ethylenediamine groups. This synthetic method has advantages because it involves easily available, less costly, and nontoxic reagents and produces an easily recyclable catalyst that shows no leaching and generates high yields of the products. Furthermore, the availability and nontoxicity of iron as well as the mild synthetic and reaction conditions involved makes the synthetic process appealing from an environmental point of view.

ASSOCIATED CONTENT

S Supporting Information. Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ACKNOWLEDGMENT

We gratefully acknowledge the financial assistance by the US National Science Foundation (NSF), CAREER Grants Nos. CHE-1004218 and NSF DMR-0968937 for this work. T.A. also thanks NSF for naming him as one of its 10 NSF American Competitiveness and Innovation (NSF-ACI) Fellows for 2010 and the accompanying grant for his group's research work. We thank Prof. Jing Li for letting us use the TGA instrument in her lab, Dr. Thomas J. Emge for PXRD analysis, and Mr. Saquib Ahmed for help on TEM imaging.

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