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Catalytic olefin epoxidation over cobalt(II) containing mesoporous silica by molecular oxygen in dimethylformamide medium†

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Abstract

Cobalt(II) Schiff base complex has been immobilized onto the surface of Si-MCM-41 to prepare a new catalyst. The amine group containing organic moiety 3-aminopropyl-triethoxysilane has been first anchored on the surface of Si-MCM-41 *via* silicon alkoxide route. The amine group upon condensation with salicylaldehyde affords a bidentate Schiff-base moiety in the mesoporous matrix which is subsequently used for anchoring of cobalt(II) centers. The prepared catalyst has been characterized by UV-vis, infrared (IR), EPR spectroscopic, and small angle X-ray diffraction (XRD) analysis, and N_2 sorption study. The catalytic activity was tested in epoxidation reaction of olefinic compounds including styrene and allyl alcohol with molecular oxygen at atmospheric pressure in dimethylformamide medium in the absence of additional sacrificial reductant. Reactions seem proceeded through radical formation mechanism. The immobilized catalyst showed good activity and epoxide selectivity in the alkene epoxidation. Notably catalyst can be recovered and reused without any loss of activity.

Department of Chemistry, Jadavpur University, Kolkata 700 032, India. E. Mail: snkoner@chemistry.jdvu.ac.in; Tel.: +91 33 24572778; Fax: +91 33 24146414. [†]Electronic supplementary information (ESI) available: EPR spectrum of Co-MCM-41 and pore size distribution plots of Si-MCM-41 and Co-MCM-41.

1. Introduction

The catalytic epoxidation of alkenes is a reaction of great industrial interest given the numerous applications of epoxides as precursors in the production of specialty and agrochemicals.[1] Conventional procedure for epoxidation of alkene is oxidation by stoichiometric amount of peracids.[2] However, peracids are very expensive, hazardous to handle, and they are non-selective for the epoxide formation and also lead to formation of undesirable products, creating a lot of wastes.[3] Besides, commercial manufacturing method of epoxides involving chlorohydrin causes serious environmental problem. Therefore, many alternative oxidizing agents such as $NaIO_4$, $NaOCl$, $PhIO$, $ROOH$, and H_2O_2 have been used for the epoxidation of alkenes. Alkyl hydroperoxides are used on a large scale in industrial epoxidation, for example, in Halcon-Arco and Sumitomo processes.[4] Recycling of co-product, that is, *tert*-BuOH, has been realized in the Sumitomo process. In this context, selective oxidation of hydrocarbons with molecular oxygen is an elegant reaction because of its low cost and environmentally friendly nature.[5] Avoidance of formation of any co-products from oxidant can be achieved by using molecular oxygen. Many efforts have been made to seek methods of epoxidation with molecular oxygen.[6-10] Amongst them, Mukaiyama epoxidation system,[9, 11, 12] which uses metal complex as the homogeneous catalyst, with aldehydes or alcohols as the co-reductant is very effective. However, possibility of recovering and reusing of catalyst is

only remote in the homogeneous catalytic process. Hence, in view of environmental and economic considerations use of molecular oxygen as an oxidant for the heterogeneous epoxidation reaction of alkenes is of interest.[13] Cobalt ions and its coordination complexes catalyze selective oxidation of alkanes and alkylbenzenes with O_2.[14] Cobalt complexes are also used in epoxidation of alkenes with *tert*-butyl hydroperoxide (TBHP) and iodosylbenzene.[15] The catalytic oxidation of terminal olefins, including styrene, by O_2 to the corresponding 2-ketones and 2-alcohols using a cobalt(II) complex has been reported.[16,17] Cobalt-salen complexes were reported to show catalytic activity for epoxidation of styrene with O_2 in presence of a co-reductant, isobutyraldehyde.[18] Recently, Mallat *et al.* has described influence of organic solvents as a "sacrificial" solvent in oxidation reactions.[19] They proposed an alternative explanation of the epoxidation on the basis of a solvent co-oxidation mechanism. Oxidation of mono-terpenes by oxygen employing $CoCl_2$ catalyst has been investigated, and in this case allylic oxidation takes place predominantly.[20] Cobalt-based heterogeneous catalysts have been employed for the selective oxidation of alkanes, especially cyclohexane and alkenes.[21–30] Aerial oxidation of styrene catalyzed by cobalt complex immobilized HMS catalyst has been reported by Pruß *et al.*[31] Though conversion of styrene was 98% yield of styrene oxide was 44%. Tang *et al.* used Co^{II}-exchanged zeolite as catalyst for epoxidation of styrene by molecular oxygen.[32] Jasra *et al.* also carried out catalytic epoxidation of styrene[33a] and cycloalkenes[33b] to their corresponding epoxides using molecular oxygen in presence of Co^{2+}-exchanged zeolite X. It has been proposed that a $DMF–Co^{3+}OO^{\bullet}$ superoxo complex plays the key role in the oxygen transfer to the $C = C$ bond.[33] DMF being used as solvent it has definite roles in this mechanism. It coordinates

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with cobalt sites to form the active oxygen species during the reaction. However, examples of epoxidation of alkenes by molecular oxygen without using a co-reductant are scarce.[34] Recently, Beier *et al.* has used metal–organic framework catalyst STA-12(Co) which shows high activity in the aerobic epoxidation of *E*-stilbene in DMF.[35]

In the course of our continuing investigation on different organic reactions using ordered mesoporous silica materials as heterogeneous catalytic support we have found that the hybrid material demonstrates desirable catalytic efficacy.[36-41] Herein, we report the anchoring of cobalt(II) Schiff-base moiety on the surface of mesoporous silica, Si-MCM-41. 3-aminopropyl-triethoxysilane has been first anchored on the surface of Si-MCM-41 *via* silicon alkoxide route. The amine group upon condensation with salicylaldehyde affords Schiff-base in the mesoporous matrix for anchoring cobalt(II) ions. The catalyst exhibits excellent activity towards catalytic epoxidation reaction of olefins with molecular oxygen in DMF medium.

2. Experimental

2.1. Materials

All solvents used were of AR grade and they were distilled and dried before use. Fumed SiO$_2$, the cationic surfactant cetyltrimethylammonium bromide (CTAB, 98%), 3-aminopropyl-triethoxysilane (3-APTES), hexahydrate cobalt nitrate, salicylaldehyde, styrene, cyclooctene, cyclohexene, 1-hexene, 1-octene, allyl alcohol, *tert*-butyl-hydroperoxide (70% aqueous) were purchased from Sigma-Aldrich/Fluka or Merck (India) and were used as received.

2.2. Synthesis of Si-MCM-41

Mesoporous Si-MCM-41 was prepared according to the literature method[42] with slight modification as mentioned in our earlier publication,[36] using $C_{16}H_{33}N(CH_3)_3Br$ (CTMABr) as the template and tetra-butylammonium bromide (TBABr) with a molar composition of the reactants: 1.0 SiO_2 : 0.48 $CTMA^+$: 0.96 TBA^+ : 0.39 Na_2O : 0.29 H_2SO_4 : 110 H_2O. The gel mixture was stirred for 24 h at room temperature and transferred into a Teflon-lined autoclave and heated statically at 100°C for 4 days. The solid product was obtained by filtration, washed with distilled water, dried in air at room temperature and calcined at 550°C for 6 h first in nitrogen and then next 6 h in air in order to remove the templates. The mesoporous material thus obtained is designated as Si-MCM-41.

2.3. Functionalization of Si-MCM-41 with organosilanes

Organic modification of Si-MCM-41 with 3-aminopropyltriethoxysilane (3-APTES) has been performed by stirring 0.2 g of Si-MCM-41 with 0.016 mL 3-APTES (0.068 mmol) in dry chloroform at room temperature for 12 h under N_2 atmosphere. The white solid MCM-41-$(SiCH_2CH_2CH_2NH_2)_x$ thus produced was filtered and washed with chloroform and dichloromethane. This solid was then refluxed with 0.008 g of salicylaldehyde (0.068 mmol) in methanol (10 cm^3) for 3 h at 60°C to generate the desired Schiff-base moiety. The resulting yellowish solid was then collected by filtration and dried in a desiccator (Scheme 1). The elemental analysis for MCM-41-$(SiCH_2CH_2CH_2NH_2)_x$ found: C, 4.99; H, 4.3; N, 1.89%.

2.4. Anchoring of cobalt(II) in functionalized MCM-41

Cobalt anchored mesoporous material was prepared by dissolving 0.01 g of $Co(NO_3)_2 \cdot 6H_2O$ (0.034 mmol) in 10 mL dry methanol and stirring the functionalized Si-

MCM-41 (0.2 g) in suspension at room temperature for 12 h. The greenish yellow solid thus formed was filtered, washed with methanol using soxhlet and dried under vacuum at 50°C for 24 h (Scheme 1). The catalyst thus obtained is designated as Co-MCM-41. Atomic absorption spectrometric result showed cobalt content of the catalyst is *ca.* 0.8 % (wt). The elemental analysis for Co-MCM-41 found: C, 3.26; N, 0.40%. Hence, the molar ratio for N:Co ≈ 2.1 and for C:Co ≈ 20, which indicates that the cobalt(II) ions have N_2O_2 ligand environment as shown in Scheme 1.

2.5. Catalytic epoxidation reactions

The catalytic epoxidation reactions were carried out under oxygen atmosphere in liquid phase in a batch reactor at desired temperature. Typically, a 50 mL three-neck round-bottomed flask equipped with a water condenser containing 1 g alkene in 8 mL dry N, N-dimethylformamide (DMF) solvent and 50 mg of Co-MCM-41 catalyst is kept in a preheated oil bath. Oxygen gas is bubbled through the reaction mixture at atmospheric pressure at a flow rate of *ca.* 3.0 cm^3min^{-1}. The reaction mixture was magnetically stirred continuously for 24 h. The products of the epoxidation reactions were collected at different time intervals and were identified and quantified by gas chromatography.

2.6. The reusability of the catalyst

After reaction the catalyst was recovered from the reaction mixture by filtration and washed thoroughly with DMF and dichloromethane then dried over vacuum at room temperature. The used catalyst was reused for the epoxidation of styrene in DMF maintaining same reaction condition.

2.7. Catalyst characterization

Infrared spectra were measured on Shimadzu S-8400 Fourier transform infrared (FTIR) spectrometer. EPR spectrum was measured on JEOL JES-FA 200 EPR spectrometer. To quantify the catalytic reaction Varian CP3800 gas chromatograph equipped with a flame ionization detector and CP-Sil 8 CB capillary column was used. The cobalt content of the sample was measured by atomic absorption spectrometric analysis on a Perkin-Elmer Aanalyst spectrometer. Carbon and nitrogen were estimated on a Perkin Elmer 240C elemental analyzer. The powder X-ray diffraction (XRD) patterns of the samples were recorded with a Scintag XDS-2000 diffractometer using CuK_α radiation. N_2 sorption studies were undertaken using Quantachrome Autosorb (iQ) automated gas sorption system. Prior to sorption experiments, samples were outgassed at 250 ºC for *ca.* 8-9 h under vacuum (10^{-3} Torr). Diffuse reflectance (DR) UV-vis-NIR spectra were recorded on a Perkin-Elmer Lambda 19 UV-vis-NIR spectrometer equipped with a diffuse reflectance integrating sphere coated with $BaSO_4$, which also served as a standard. All spectra were recorded at room temperature under ambient atmosphere. GC-MS analysis of the reaction products was performed on a Perkin Elmer CLarus SQ8 GC-MS analyzer as well as Waters Xebo G2-S QTof high resolution mass analyzer. Other instruments used in this study were the same as reported earlier.[36]

3. Results and discussion

3.1. Spectroscopic measurements

The FTIR spectra (Fig. 1) of mesoporous silica showed bands at around 1090, 800, and 470 cm^{-1} assigned to characteristic vibrations of the mesoporous framework (Si–O–Si) and a broad band around 3450 cm^{-1} mainly for the adsorbed H_2O molecules. These

absorption peaks were not much affected after organic modification and cobalt complex immobilization. Comparison of IR spectra of Si-MCM-41 (a) and MCM-41-$(SiCH_2CH_2CH_2NH_2)_x$ (b) showed the presence of N-H and C-H vibration bands in the 3100-2800 cm^{-1} and 1550-1250 cm^{-1} region in the IR spectra of MCM-41-$(SiCH_2CH_2CH_2NH_2)_x$. In the spectrum of MCM-41-$(SiCH_2CH_2CH_2NH_2)_x$, the IR bands at 1546 cm^{-1} could be assigned to bending vibrations of amine group. Appearance of N-H and C-H vibration bands in the 3100-2800 cm^{-1} and 1550-1250 cm^{-1} region upon grafting of 3-APTES onto Si-MCM-41 confirm the attachment of aminopropyl groups on the surface of the support. These bands were absent in the case of Si-MCM-41. The characteristic band for azomethine group (C=N) of cobalt(II) complex moiety appears at *ca.* 1632 cm^{-1} in the IR spectra of Co-MCM-41 (c). The IR band of azomethine group for Schiff-base moiety appears at 1643 cm^{-1} which upon complex formation with Co^{II} shifted to a lower frequency in Co-MCM-41 indicating coordination of Schiff-base with cobalt.

The UV-vis spectra in the 300-600 nm range of the supported Schiff-base and Co-MCM-41 are shown in Fig. 2. Electronic spectra of the supported Schiff base showed mainly two bands. Band within the 285-370 nm range is assigned to the π→π* transitions of the C=N chromophore, while the longer wavelength band at 370-470 nm is due to an intramolecular charge transfer (CT transition) involving the whole molecule.[43] On complex formation these bands were shifted to the higher wavelength, suggested the coordination of azomethine nitrogen with Co(II). The red shift of absorption band in the UV–vis spectra upon immobilization of metal complex in zeolite cages has been observed in several studies reported previously.[44-46]

The powder EPR spectrum of Co-MCM-41 measured at 300 K consists of several nuclear hyperfine lines (see ESI; Figure S1). The signals are weak as the metal content in the sample is very low. Co-MCM-41 clearly shows an axial spectrum with $g_{\parallel}$ and $g_{\perp}$ values of the catalyst are calculated to be 2.19 and 2.01, respectively. Zeolite encaged Co-salen complex also demonstrates a similar kind of EPR spectrum.[47] Spectroscopic studies of Co-MCM-41, therefore, indicate that cobalt(II) complex formed in MCM-41 matrix may be depicted as shown in Scheme 1.

3.2. Small angle X-ray diffraction studies

The X-ray diffraction pattern of Si-MCM-41 shows a typical three-peak pattern[48, 49] with a very strong d_{100} = 40.44 Å reflection at $2\theta \approx 2.18°$ and two other weaker reflections at $2\theta \approx 3.75°$ and $2\theta \approx 4.32°$ for d_{110} and d_{200}, respectively, from the quasi-regular arrangement of mesopores with hexagonal symmetry (Fig. 3). Si-MCM-41 shows an additional peak at $2\theta \approx 5.71°$ which can be assigned to d_{210} reflection. All the peaks are well-resolved indicative of good quality material. Co-MCM-41 exhibits a strong d_{100} reflection with the spacing of *ca.* 35.64 Å reflection at $2\theta \approx 2.48°$ with almost same intensity and two other weaker reflections at $2\theta \approx 4.31°$ and $2\theta \approx 5.00°$ for d_{110} and d_{200}, respectively, while the weakest reflection for d_{210} has been buried in the background noise. Comparison of X-ray powder diffraction patterns of Co-MCM-41 and Si-MCM-41 shows that the typical three-peak pattern of MCM-41 has been retained after the anchoring of cobalt(II) complex in Si-MCM-41. However, all the diffraction lines shifted to the higher angles. A similar type of behavior was observed by Brukett *et al.* in phenyl-modified mesoporous sieves[50] and by Lim and Stein for directly synthesized thiol-MCM-41.[51] Upon post-synthesis grafting cobalt Schiff-base complex into Si-MCM-41, an

overall decrease in the intensity of the diffraction lines was noticed. This result could be attributed to the lowering of local order, such as variations in the wall thickness, or might be due to the reduction of scattering contrast between the channel wall of silicate framework and Schiff base ligand present in Co-MCM-41, as it was previously mentioned by Lim and Stein.[51] Marler *et al.* have reported that the intensity of the diffraction lines decreases systematically on increase in concentration of organic sorbates in boron-containing MCM-41.[52] Therefore, shift of the diffraction lines to the higher angle and decrease in the intensity of the peaks upon organic modification of Si-MCM-41 and subsequent complex formation with cobalt(II) are not inconsistent.

3.3. Nitrogen sorption study

The nitrogen sorption experiments showed that the Si-MCM-41 has the BET surface area (A_{sBET}) of 1136 m^2g^{-1} and the primary mesopore volume (V_p) of 0.61 cm^3g^{-1} (Fig. 4). The average pore diameter is calculated to be 22.6 Å for Si-MCM-41 using the BJH method. All the calculated values are in agreement with those reported for good quality mesoporous MCM-41.[53a] The N_2 adsorption isotherm as well as pore size distribution of the Co-MCM-41 was different from that of Si-MCM-41. Co-MCM-41 displays a considerably lower N_2 uptake (BET surface area 365 m^2g^{-1}) in comparison to the Si-MCM-41. These isotherms are of type IV with well-defined sharp inflections observed in p/p_0 ranges 0.1–0.3 for Si-MCM-41 and 0.2–0.4 for Co-MCM-41, which represent spontaneous filling of the mesopores due to capillary condensation. This indicates that the overall mesoporous structure of the parent support was retained in the immobilized catalyst. While the pore size distribution curve shows a remarkably narrow peak with average pore size of w_{BJH} = 22.6 Å for Si-MCM-41 indicating uniformity in pore

distribution, Co-MCM-41 shows a wide variety of pores with a highest peak at ~ 23 Å (see ESI; Figures S2 and S3). However, this is not inconsistent with the fact that anchoring of cobalt complex might not be uniform through out the mesoporous silica matrix. The decrease in BET surface area and loss of uniformity of pore size of Co-MCM-41 in comparison to the corresponding values for Si-MCM-41 clearly demonstrate that anchoring of cobalt Schiff-base moiety into the mesoporous silica has significant effects on pore structure of the catalyst. One of the possible reasons for this remarkable difference in the BET surface area between Si-MCM-41 and Co-MCM-41 might be the anchoring of considerable amount of cobalt Schiff-base moiety into the nanosized pores of the mesoporous material. However, considering the amount of cobalt present in Co-MCM-41 decrease in surface area is significantly high. This can be caused by partial amorphization[53b] of the layered phase of mesoporous material during anchoring of Co complex.

3.4. Epoxidation reactions

Catalytic efficacies of the prepared catalyst were tested in the epoxidation of both aromatic and aliphatic alkenes including straight chain and cyclic alkenes with molecular oxygen. The performance of the catalyst in terms of conversions, selectivities and turnover numbers (TON) are given in Table 1. The epoxidation of styrene with molecular oxygen gives styrene oxide in 45% yield (selectivity ~90%) (Table 1) under the heterogeneous condition; along with this, a small (5%) amount of benzaldehyde is also detected. Turnover number of ~707 has been attained in the catalytic epoxide production in this particular reaction. Epoxidation of styrene with molecular oxygen over a variety of cobalt catalysts under heterogeneous condition has been studied in the recent past (Table

2). Cobalt-salen catalyst immobilized in silica was applied in molecular oxygen epoxidation of styrene in the presence of butyraldehyde.[54] A CoO_x−MCM-41 prepared by ultrasonic deposition–precipitation of cobalt tricarbonyl nitrosyl in decalin was reported to catalyze the epoxidation of alkenes by O_2 in the presence of excess isobutyraldehyde, which functioned as the co-reductant.[27]

The linear aliphatic olefins, such as 1-hexene, 1-octene, can be directly oxidized by molecular oxygen to afford the corresponding 1, 2-epoxy alkanes. As shown in Table 1 the yield of 1, 2-epoxy alkane is about 47% for 1-hexene and 30% for 1-octene. It shows that the catalytic activity decreases along with length of olefin. This may due to the larger hexyl group of 1-octene connected to double bond sterically hinders it in approaching to the catalyst metal center with respect to 1-hexene which its double bond carries a smaller butyl group. Again there may be some electronic effect i.e. higher electron density of the double bond is expected to show more epoxidation reactivity. Therefore, cyclooctene and cyclohexene with double bonds driven from secondary carbons exhibit more activities in comparison with 1-hexene and 1-octene, which contain double bonds between secondary and primary carbons. Cyclohexene shows 54% conversion to form cyclohexene oxide as the major product with 74% selectivity; along with this, 2-cyclohexen-1-ol was also generated owing to allylic C-H oxidation. Kameyama et al.[55] studied epoxidation of cyclohexene with molecular oxygen with co-reductant isobutyraldehyde catalyzed by cobalt porphyrin complexes immobilized on montmorillonite which shows ~66% conversion with 1, 2-epoxycyclohexane yield ~56%. Bulkier cycloalkene, cyclooctene have also been effectively converted to selectively cyclooctene oxide (conversion 78%, selectivity 100%). Jinka et al. has performed epoxidation of cycloalkenes using

molecular oxygen with NaCoX96 catalyst and observed only 26% conversion of cyclohexene and 47% conversion of cyclooctene.[33] Tang *et al.* introduced the cobalt metal into the MCM-41 by template ion exchange (TIE) method to study styrene epoxidation reaction.[56] However, they did not investigate the possibility of leaching of cobalt metal from the surface of MCM-41, which is common amongst the ion-exchanged catalyst. Notably, cobalt metal is not leaching out during catalytic reaction in case of Co-MCM-41 (vide infra). In our case metal ions are covalently attached into the organic modified Si-MCM-41.

Solvent plays a crucial role in the epoxidation reactions. We have also performed the epoxidation reaction of styrene in different solvents like acetonitrile, chloroform, hexane, ethyl acetate even in high boiling alcohols like *n*-decyl alcohol; however, no conversion of styrene to its oxide was detected. Only acylamide such as DMF is particularly efficient in providing both high conversion and high epoxide selectivity in this case. Notably, Beier *et al.* had suggested radical reaction pathway operating in DMF promoted epoxidations.[35] In the reaction medium the oxygen species with a radical nature is generated by the activation of molecular oxygen over the DMF-coordinated Co(II) site. To clarify this point, the influence of the addition of a radical scavenger, hydroquinone, on catalytic performance has been investigated. The results revealed that styrene conversion decreased to almost zero after addition of a small amount of hydroquinone (Fig. 5), confirming the radical nature of the active oxygen species formed by molecular oxygen with cobalt(II) in presence of DMF. However Opre *et al.* suggested another pathway in which DMF first interacts with molecular oxygen leading to its autoxidation to form *N*-(hydroperoxymethyl)-*N*-methylformamide, which subsequently acts as an

oxygen transfer agent in the epoxidation of styrene, thereby producing *N*-formyl-*N*-methylformamide in considerable amounts.[34] We have analyzed the reaction solution by GC-MS analyzer as well as high resolution mass spectrometer, however, we could not detect the formation of N-formyl-N-methylformamide like moiety in the reaction products.

3.5. Separation, heterogeneity test and catalyst reuse

The major advantages of the use of heterogeneous catalysts are its recovery from the reaction mixtures and possible reuse. To test if metal is leached out from the solid catalyst during reaction, we have carried out hot filtration test. After the reaction the solid catalyst was filtered out in hot condition. Then the filtrate was treated with aqua-regia several times and the mixture was evaporated to dryness in a hot plate to remove the organic part. After preparing the aqueous solution of the filtrate it was subjected to atomic absorption spectroscopic analysis. The analysis show cobalt was absent in the solution. Besides, the liquid phase of the reaction mixture is collected by filtration after ~30% of the epoxidation reaction is completed and the residual activity of the supernatant solution after separation of the catalysts was studied. The supernatant solution kept at the catalytic reaction condition as stated above and the composition of the solution was determined by GC. No progress of reaction was observed during this period, which excludes the presence of active species in solution.

The Co-MCM-41 catalyst has been recovered from reaction mixture and has been reused successively three times under the same reaction conditions. The solid catalyst has been recovered by filtration after each reaction and has been washed thoroughly with

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DMF. The recovered catalyst is found to exhibit almost the same catalytic activity for styrene epoxidation reaction by molecular oxygen in every run as shown in Fig. 6.

Conclusion

In summary, we were succeeded to prepare a new example of cobalt-based heterogeneous catalyst by anchoring cobalt(II) centers into mesoporous silica matrix via silicon-alkoxide chemistry. Importantly, the cobalt-based catalyst Co-MCM-41 is active in aerobic epoxidation reactions in DMF. Co-MCM-41 catalyzes epoxidation reaction of a variety of olefinic substrates including allyl-alcohol in heterogeneous medium. Notably catalyst can be recovered and reused without any loss of activity.

Acknowledgment

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Legends to the figures

Fig. 1 IR spectra of: (a) Si-MCM-41; (b) MCM-41-(SiCH$_2$CH$_2$CH$_2$NH$_2$)$_x$; (c) Co-MCM-41 catalyst.

Fig. 2 UV-vis spectra of supported Schiff-base and Co-MCM-41.

Fig. 3 Small angle XRD pattern of: (a) Si-MCM-41; (b) Co-MCM-41.

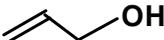Fig. 4 N$_2$ adsorption/desorption isotherms of (a) Si-MCM-41 and (b) Co-MCM-41.

Fig. 5 Percentage conversion *versus* time plot for comparison between reactions with a radical scavenger and a control reaction without adding radical scavenger.

Fig. 6 Reuse of Co-MCM-41 for the epoxidation of styrene with O_2: (■) styrene conversion, (○) epoxide selectivity.
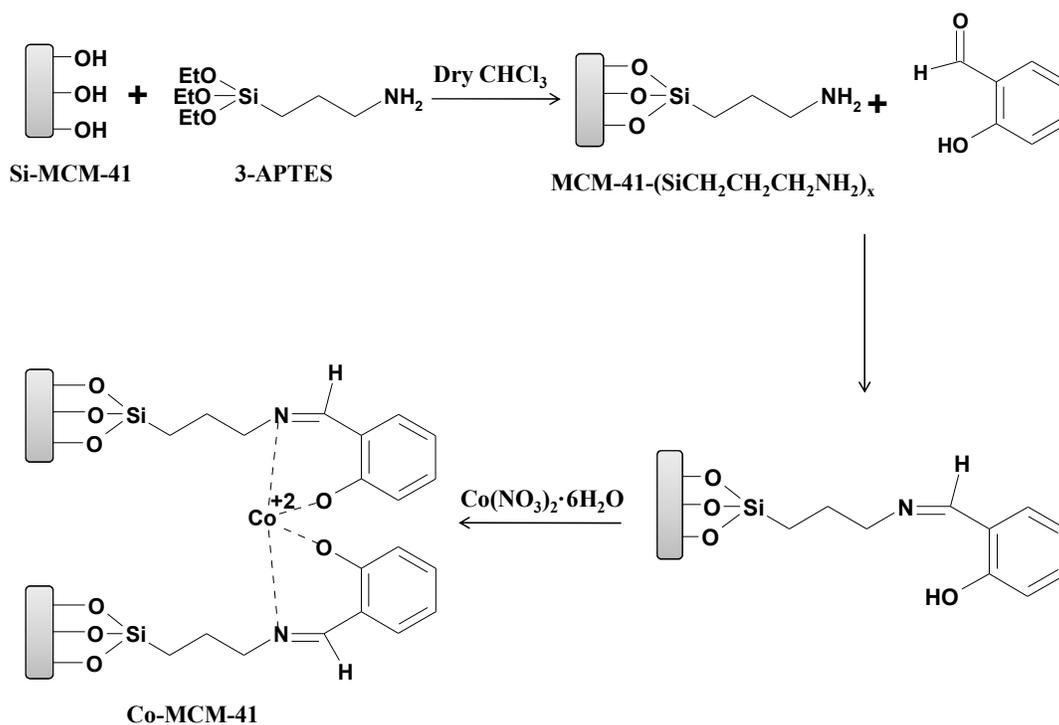
Scheme 1 (a) Modification of Si-MCM-41 channel wall: APTES/CHCl$_3$; (b) condensation with salicylaldehyde in methanol; (c) metal complex formation: Co(NO$_3$)$_2$·6H$_2$O/MeOH.

**Table 1** Heterogeneous Alkenes Epoxidation Catalyzed by Co-MCM-41[e]

Alkenes	Reaction Temp. (°C)	Conversion (wt %)	% Yield of products		TON[d]
			Epoxide	Other	
	80	50	45	5[a]	707
	75	54	40	14[b]	970
	80	78	78	-	1044
	80	47	47	-	824
	80	35	30	5	460
	50	12	12[c]	-	304
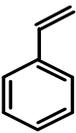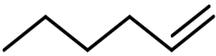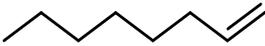
[a] Benzaldehyde. [b] 2-Cyclohexen-1-ol was formed. [c] R-(+)-glycidol. [d] Turn Over Number = moles converted / moles of active site. The products of the epoxidation reactions were collected at different time intervals and were identified and quantified by Varian CP3800 gas chromatograph equipped with an FID detector and a CP-Sil 8 CB capillary column. [e] Reaction conditions: alkenes (1 g); catalyst (50 mg); flow rate of O_2, 3.0 $cm^3 min^{-1}$; DMF (8 mL).

Table 2 Epoxidation of Styrene with Molecular Oxygen Catalyzed by a Variety of Cobalt Catalysts

Catalyst	Conversion (wt%)	% Yield of Products		TON[a]	References
		Epoxide	Other		
Co-MCM-41	50	45	5	707	This Study
Co-MCM-41	45	28	17	169	56
Co^{2+}-X	44.2	26.5	17.7	13.2	32
Co^{2+}-Y	45.3	28.2	17.1	13.5	32
Immobilized Co-salen complex in Silica	58	37	21	10	54
Cobalt-hydroxyapatite (CoHAp)	91	49	42	94	34
NaCoX96	100	67	33	16.4	33a
CoALPO-36	46	16	30	54	30

[a] Turn Over Number = moles converted / moles of active site.
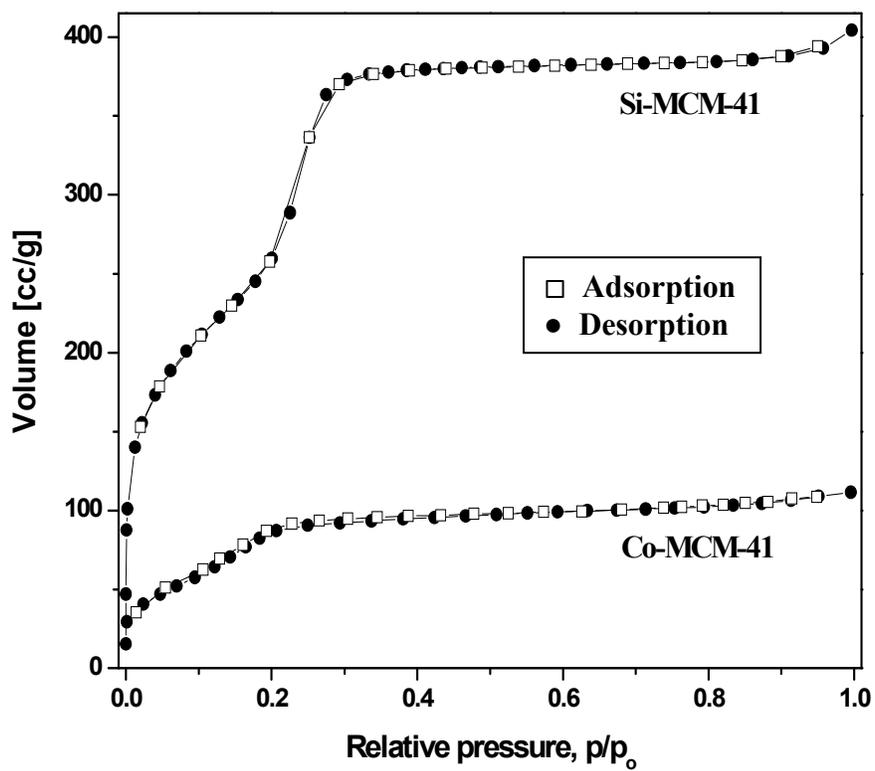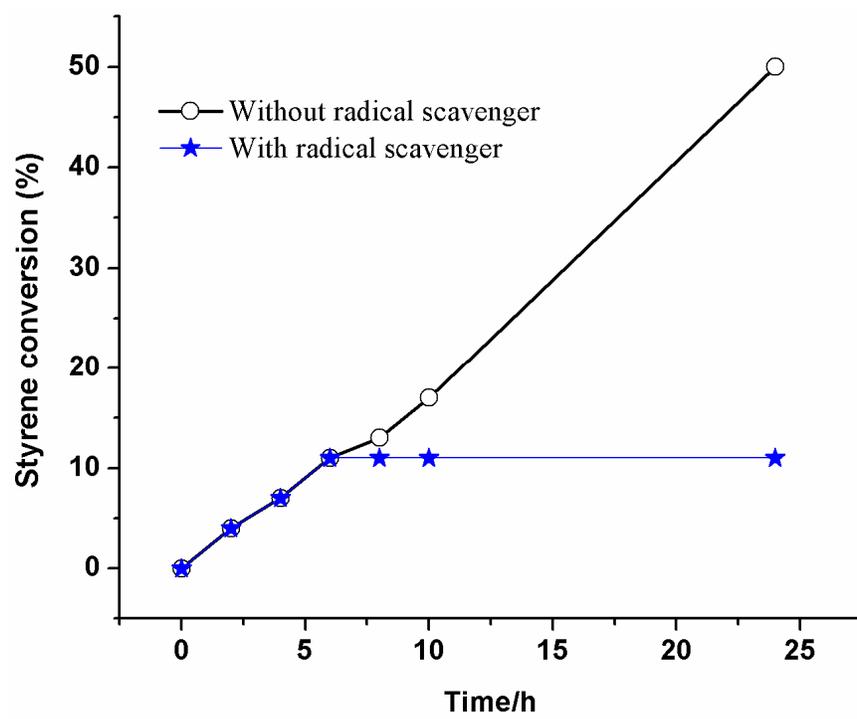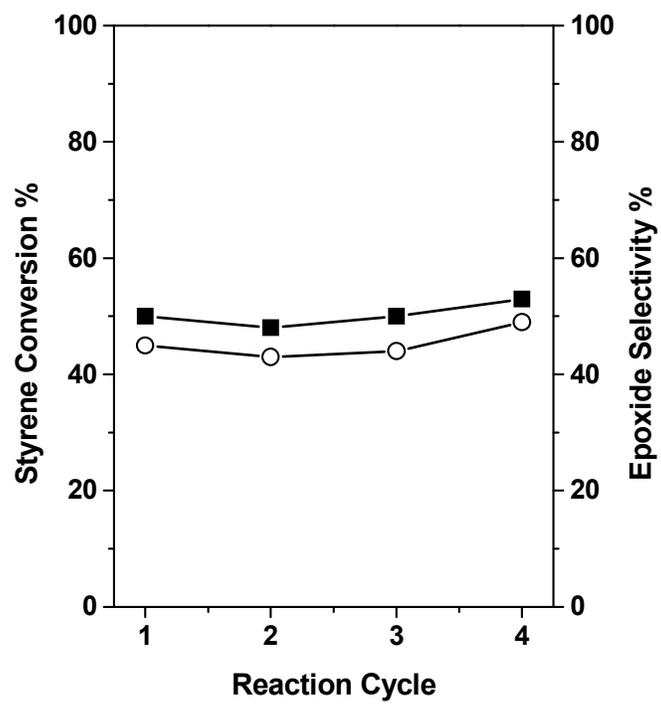
Fig. 1

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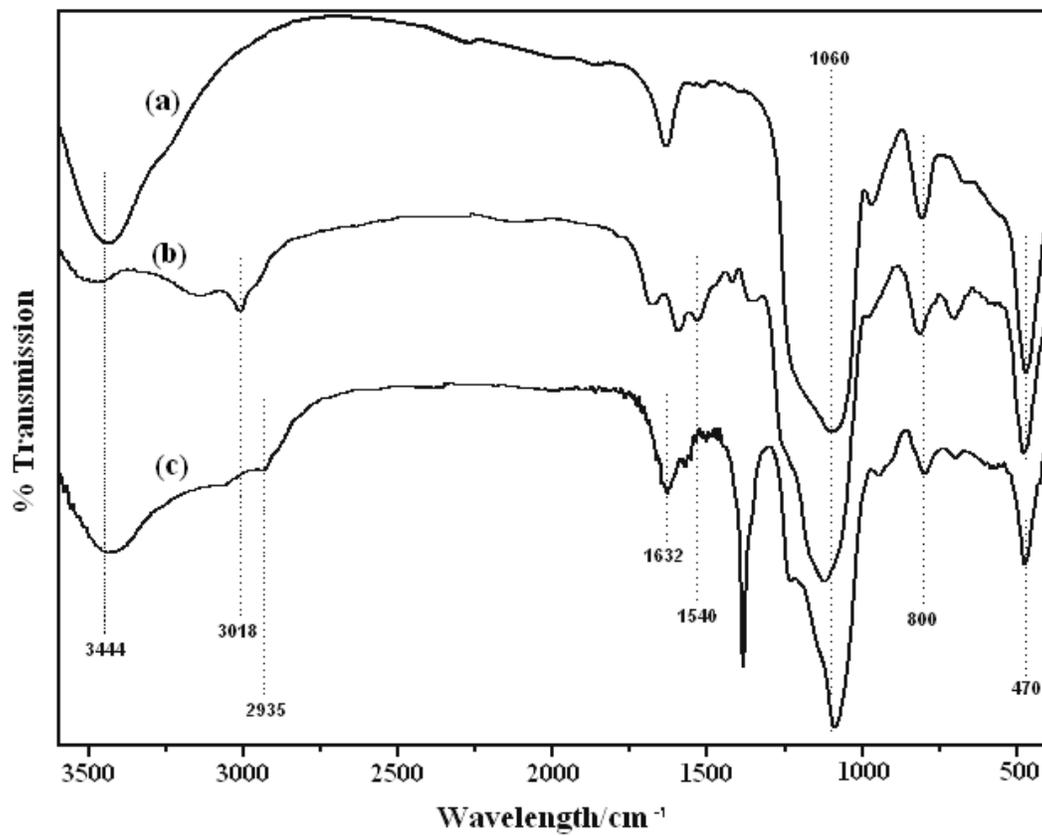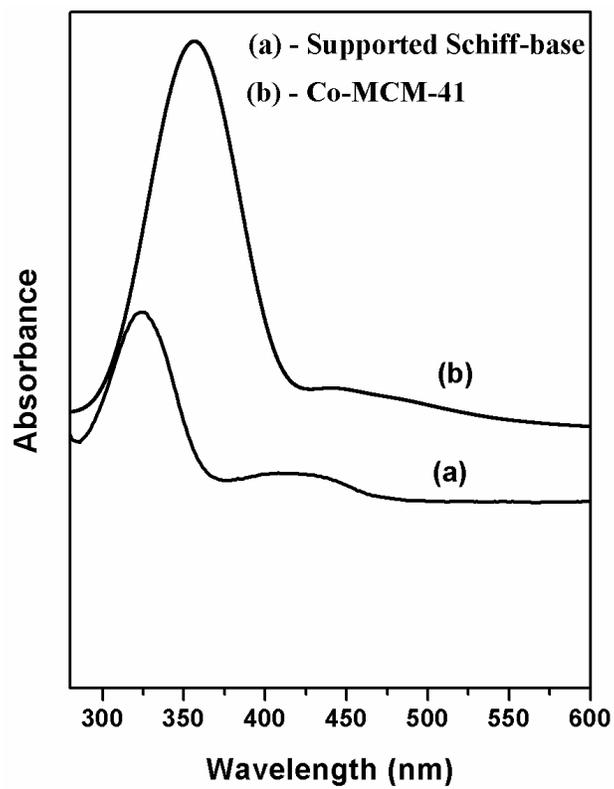
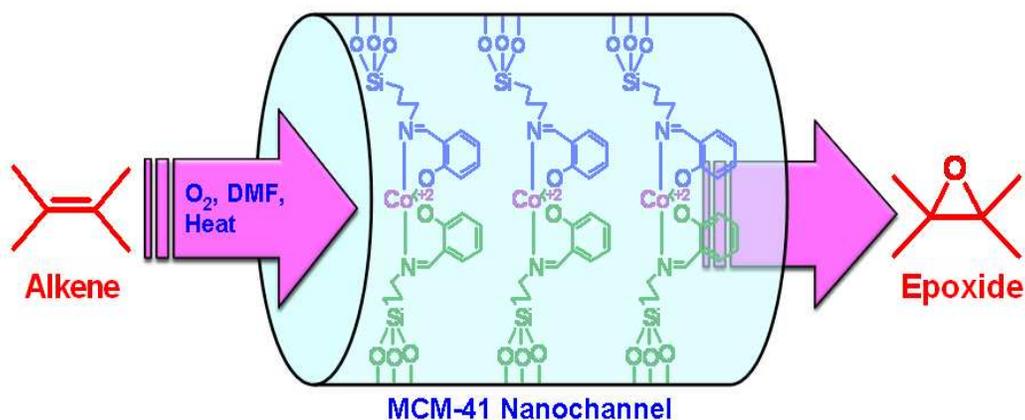Fig. 2
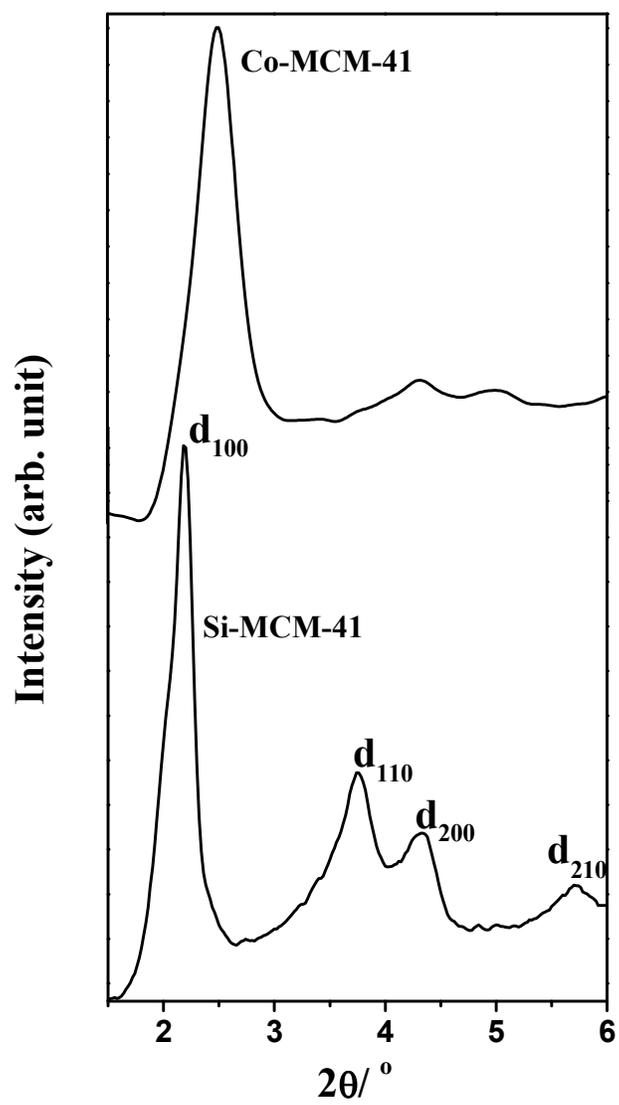
Fig. 3

Fig. 4

Fig. 5

Fig. 6

For Table of Contents Entry

Catalytic olefin epoxidation over cobalt(II) containing mesoporous silica by molecular oxygen in dimethylformamide medium

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Cobalt(II) Schiff base complex has been anchored onto the surface of Si-MCM-41 to prepare a new catalyst. The catalyst is capable to catalyze epoxidation reaction of olefinic compounds including styrene and allyl alcohol by molecular oxygen at atmospheric pressure in DMF medium. Notably, catalyst can be recovered and reused without any loss of activity.