

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

Cite this: *Catal. Sci. Technol.*, 2014, 4, 1820

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A 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 had first been anchored on the surface of Si-MCM-41 via a silicon alkoxide route. Upon condensation with salicylaldehyde, the amine group 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) analyses, and N<sub>2</sub> sorption studies. The catalytic activity was tested in epoxidation reactions of olefinic compounds, including styrene and allyl alcohol, with molecular oxygen at atmospheric pressure in dimethylformamide medium in the absence of additional sacrificial reductant. The reactions seemed to proceed through a radical formation mechanism. The immobilized catalyst showed good activity and epoxide selectivity in the alkene epoxidation. Notably, the catalyst can be recovered and reused without any loss of activity.

Received 20th January 2014,  
Accepted 25th February 2014

DOI: 10.1039/c4cy00084f

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## 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 speciality chemicals and agrochemicals.<sup>1</sup> The conventional procedure for epoxidation of alkenes is oxidation by stoichiometric amounts of peracids.<sup>2</sup> However, peracids are very expensive, hazardous to handle, and non-selective for epoxide formation, and also lead to the formation of undesirable products, creating a lot of waste.<sup>3</sup> Besides, the commercial manufacturing method for epoxides involving chlorohydrin causes serious environmental problems. Therefore, many alternative oxidizing agents, such as NaIO<sub>4</sub>, NaOCl, PhIO, ROOH, and H<sub>2</sub>O<sub>2</sub>, have been used for the epoxidation of alkenes. Alkyl hydroperoxides are used on a large scale in industrial epoxidation, for example, in the Halcon-Arco and Sumitomo processes.<sup>4</sup> Recycling of the 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.<sup>5</sup> Avoidance of the formation of any co-products from

the oxidant can be achieved by using molecular oxygen. Many efforts have been made to find epoxidation methods using molecular oxygen.<sup>6–10</sup> Amongst them, the Mukaiyama epoxidation system,<sup>9,11,12</sup> which uses a metal complex as the homogeneous catalyst with aldehydes or alcohols as the co-reductant, is very effective. However, there is only a remote possibility of recovering and reusing the catalyst in homogeneous catalytic processes. Hence, in view of the environmental and economic considerations, use of molecular oxygen as an oxidant in heterogeneous epoxidation reaction of alkenes is of interest.<sup>13</sup> Cobalt ions and their coordination complexes catalyze the selective oxidation of alkanes and alkylbenzenes with O<sub>2</sub>.<sup>14</sup> Cobalt complexes are also used in the epoxidation of alkenes with *tert*-butyl hydroperoxide (TBHP) and iodosylbenzene.<sup>15</sup> The catalytic oxidation of terminal olefins, including styrene, by O<sub>2</sub> to the corresponding 2-ketones and 2-alcohols using a cobalt(II) complex has been reported.<sup>16,17</sup> Cobalt-salen complexes were reported to show catalytic activity for the epoxidation of styrene with O<sub>2</sub> in the presence of a co-reductant, isobutyraldehyde.<sup>18</sup> Recently, Mallat *et al.* described the influence of organic solvents as “sacrificial” solvents in oxidation reactions.<sup>19</sup> They proposed an alternative explanation of epoxidation on the basis of a solvent co-oxidation mechanism. Oxidation of mono-terpenes by oxygen employing a CoCl<sub>2</sub> catalyst has been investigated, and in this case allylic oxidation takes place predominantly.<sup>20</sup> Cobalt-based heterogeneous catalysts have been employed for the selective oxidation of alkanes, especially cyclohexane, and

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† Electronic supplementary information (ESI) available: EPR spectrum of Co-MCM-41 and pore size distribution plots of Si-MCM-41 and Co-MCM-41.

See DOI: 10.1039/c4cy00084f

alkenes.<sup>21–30</sup> Aerial oxidation of styrene catalyzed by an immobilized cobalt–HMS (Hexagonal Mesoporous Silica) catalyst has been reported by Pruß *et al.*<sup>31</sup> Though styrene conversion was 98%, the yield of styrene oxide was 44%. Tang *et al.* used Co<sup>II</sup>-exchanged zeolite as a catalyst for the epoxidation of styrene by molecular oxygen.<sup>32</sup> Jasra *et al.* also carried out the catalytic epoxidation of styrene<sup>33a</sup> and cycloalkenes<sup>33b</sup> to their corresponding epoxides using molecular oxygen in the presence of Co<sup>2+</sup>-exchanged zeolite X. It has been proposed that a DMF–Co<sup>3+</sup>OO<sup>•</sup> superoxo complex plays the key role in the oxygen transfer to the C=C bond.<sup>33</sup> The DMF solvent has a definite role in this mechanism. It coordinates with cobalt sites to form the active oxygen species during the reaction. However, examples of epoxidation of alkenes by molecular oxygen without a co-reductant are scarce.<sup>34</sup> Recently, Beier *et al.* used the metal–organic framework catalyst STA-12(Co) which shows high activity in the aerobic epoxidation of *E*-stilbene in DMF.<sup>35</sup>

In the course of our continuing investigation of different organic reactions using ordered mesoporous silica materials as heterogeneous catalytic supports, we have found that hybrid materials demonstrate desirable catalytic efficacy.<sup>36–41</sup> Herein, we report the anchoring of a cobalt(II) Schiff-base moiety on the surface of mesoporous silica, Si–MCM-41. 3-Aminopropyl-triethoxysilane was first anchored on the surface of Si–MCM-41 *via* a silicon alkoxide route. Upon condensation with salicylaldehyde, the amine group affords a Schiff-base in the mesoporous matrix for anchoring cobalt(II) ions. The catalyst exhibits excellent activity in the 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<sub>2</sub>, 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 and *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,<sup>42</sup> with a slight modification as mentioned in our earlier publication,<sup>36</sup> using C<sub>16</sub>H<sub>33</sub>N(CH<sub>3</sub>)<sub>3</sub>Br (CTMABr) as the template and tetrabutylammonium bromide (TBABr), with the molar composition of the reactants: 1.0 SiO<sub>2</sub>:0.48 CTMA<sup>+</sup>:0.96 TBA<sup>+</sup>:0.39 Na<sub>2</sub>O:0.29 H<sub>2</sub>SO<sub>4</sub>:110 H<sub>2</sub>O. The gel mixture was stirred for 24 h at room temperature, 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 in nitrogen and then for 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) was 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<sub>2</sub> atmosphere. The white solid MCM-41–(SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>x</sub> 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<sup>3</sup>) 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<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>x</sub> found: C, 4.99; H, 4.3; N, 1.89%.

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

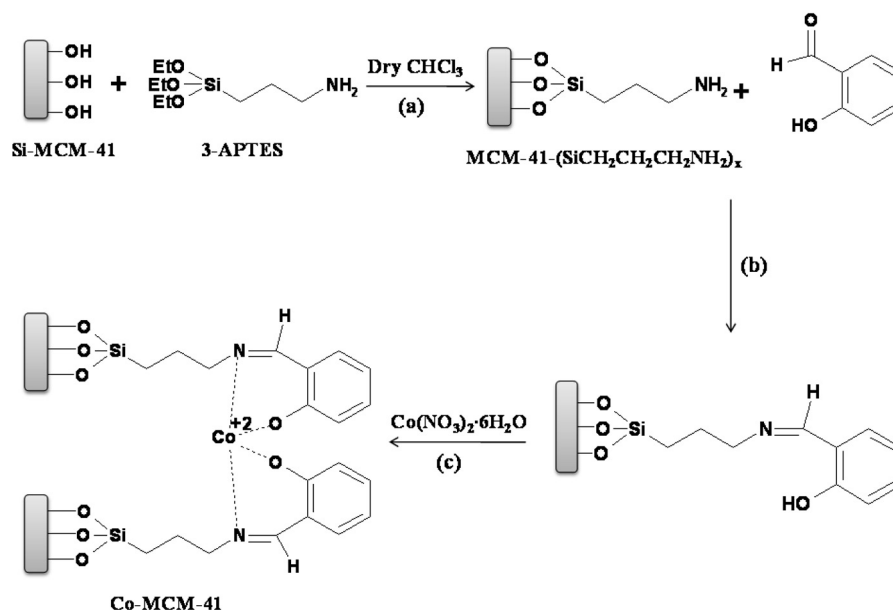
The cobalt-anchored mesoporous material was prepared by dissolving 0.01 g of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.034 mmol) in 10 mL dry methanol and stirring with the functionalized Si–MCM-41 (0.2 g) in suspension at room temperature for 12 h. The greenish yellow solid thus formed was filtered, washed with methanol using a Soxhlet extractor 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 results showed that the 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 N:Co molar ratio ≈ 2.1 and the C:Co molar ratio ≈ 20, which indicates that the cobalt(II) ions have an N<sub>2</sub>O<sub>2</sub> ligand environment as shown in Scheme 1.

### 2.5. Catalytic epoxidation reactions

The catalytic epoxidation reactions were carried out under an oxygen atmosphere in the liquid phase in a batch reactor at the 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 was kept in a pre-heated oil bath. Oxygen gas was bubbled through the reaction mixture at atmospheric pressure at a flow rate of *ca.* 3.0 cm<sup>3</sup> min<sup>−1</sup>. 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 the reaction, the catalyst was recovered from the reaction mixture by filtration, washed thoroughly with DMF and dichloromethane, and then dried under vacuum at room temperature. The used catalyst was reused for the epoxidation of styrene in DMF, maintaining the same reaction conditions.



**Scheme 1** (a) Modification of Si-MCM-41 channel wall: APTES/ $\text{CHCl}_3$ ; (b) condensation with salicylaldehyde in methanol; (c) metal complex formation:  $\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ /MeOH.

## 2.7. Catalyst characterization

Infrared spectra were recorded on a Shimadzu S-8400 Fourier transform infrared (FTIR) spectrometer. EPR spectra were recorded on a JEOL JES-FA 200 EPR spectrometer. To quantify the catalytic reactions, a Varian CP3800 gas chromatograph equipped with a flame ionization detector and a 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 Analyst spectrometer. The amounts of carbon and nitrogen were estimated using 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  $\text{CuK}_\alpha$  radiation.  $\text{N}_2$  sorption studies were undertaken using a Quantachrome Autosorb (iQ) automated gas sorption system. Prior to sorption experiments, samples were outgassed at  $250^\circ\text{C}$  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  $\text{BaSO}_4$ , 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 a Waters Xevo G2-S QT high resolution mass analyzer. Other instruments used in this study were the same as those reported earlier.<sup>36</sup>

## 3. Results and discussion

### 3.1. Spectroscopic measurements

The FTIR spectra (Fig. 1) of mesoporous silica showed bands at approximately  $1090$ ,  $800$ , and  $470\text{ cm}^{-1}$ , assigned to

characteristic vibrations of the mesoporous framework (Si–O–Si), and a broad band at approximately  $3450\text{ cm}^{-1}$ , mainly due to the adsorbed  $\text{H}_2\text{O}$  molecules. These absorption peaks were not significantly affected by organic modification and cobalt complex immobilization. A comparison of the IR spectra of Si-MCM-41 (a) and  $\text{MCM-41-(SiCH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_x$  (b) showed the presence of N–H and C–H vibration bands in the  $3100\text{--}2800\text{ cm}^{-1}$  and  $1550\text{--}1250\text{ cm}^{-1}$  regions in the IR spectrum of  $\text{MCM-41-(SiCH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_x$ . In the spectrum of  $\text{MCM-41-(SiCH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_x$ , the IR band at  $1546\text{ cm}^{-1}$  could be assigned to bending vibrations of the amine group. The appearance of N–H and C–H vibration bands in the  $3100\text{--}2800\text{ cm}^{-1}$  and  $1550\text{--}1250\text{ cm}^{-1}$  regions upon grafting of 3-APTES onto Si-MCM-41 confirmed 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 the azomethine group ( $\text{C=N}$ ) of the cobalt(II) complex moiety appeared at *ca.*  $1632\text{ cm}^{-1}$  in the IR spectrum of Co-MCM-41 (c). The IR band for the azomethine group of the Schiff-base moiety appeared at  $1643\text{ cm}^{-1}$ , and shifted to a lower frequency upon complex formation with  $\text{Co}^{\text{II}}$  in Co-MCM-41, indicating coordination of the Schiff-base with cobalt.

The UV-vis spectra of the supported Schiff-base and Co-MCM-41 in the  $300\text{--}600\text{ nm}$  range are shown in Fig. 2. The electronic spectrum of the supported Schiff base showed two main bands. The band within the  $285\text{--}370\text{ nm}$  range is assigned to the  $\pi \rightarrow \pi^*$  transitions of the  $\text{C=N}$  chromophore, while the longer wavelength band at  $370\text{--}470\text{ nm}$  is due to an intramolecular charge transfer (CT transition) involving the whole molecule.<sup>43</sup> On complex formation, these bands were shifted to higher wavelength, suggesting coordination of the

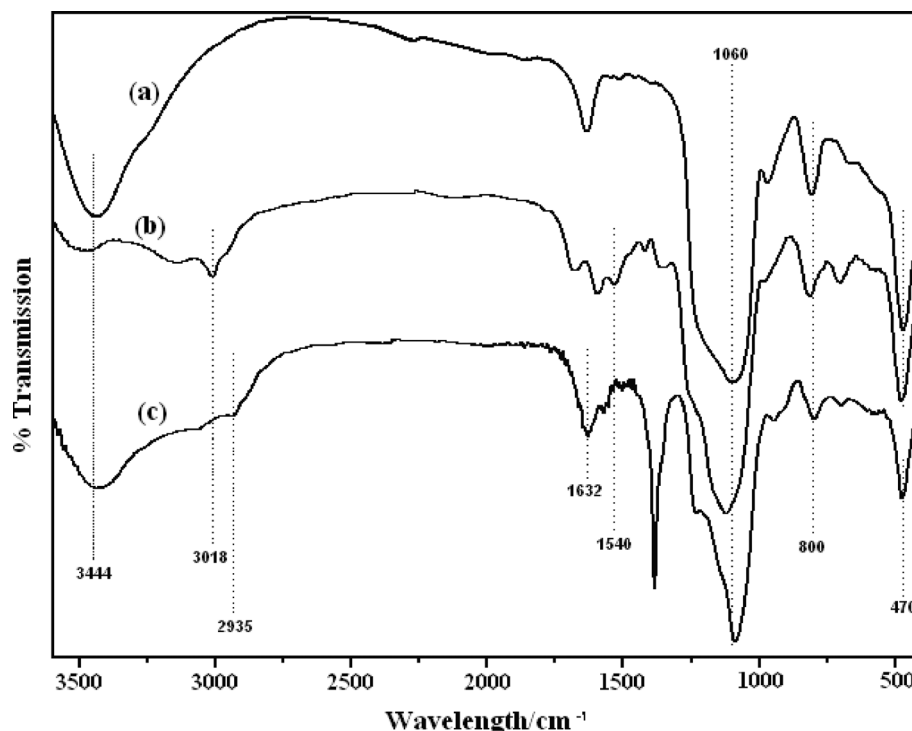


Fig. 1 IR spectra of: (a) Si-MCM-41; (b) MCM-41-(SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>x</sub>; (c) Co-MCM-41 catalyst.

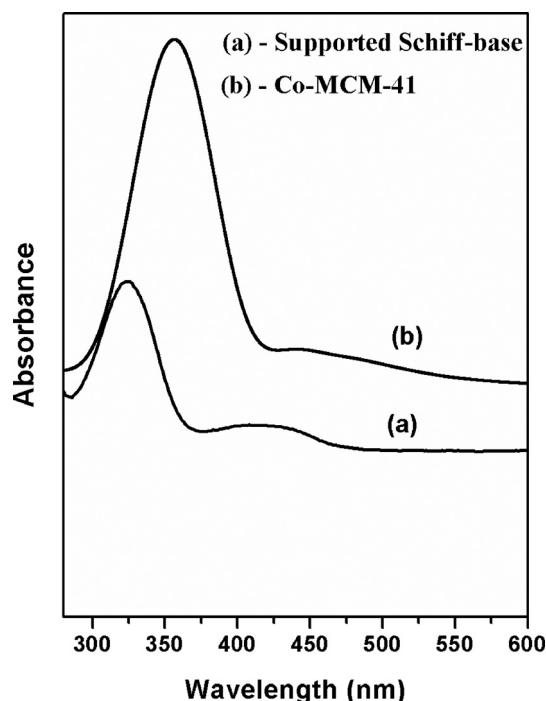


Fig. 2 UV-vis spectra of the supported Schiff-base and Co-MCM-41.

azomethine nitrogen with Co(II). The red shift of the absorption band in the UV-vis spectrum upon immobilization of a metal complex in a zeolite cage has been observed in several previously reported studies.<sup>44–46</sup>

The powder EPR spectrum of Co-MCM-41 measured at 300 K consists of several nuclear hyperfine lines (see ESI;†

Fig. S1). The signals are weak as the metal content in the sample is very low. Co-MCM-41 clearly shows an axial spectrum, in which the  $g_{||}$  and  $g_{\perp}$  values of the catalyst are calculated to be 2.19 and 2.01, respectively. A zeolite-encaged Co-salen complex also demonstrates a similar type of EPR spectrum.<sup>47</sup> Spectroscopic studies of Co-MCM-41, therefore, indicate that the cobalt(II) complex formed in the 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,<sup>48,49</sup> with a very strong  $d_{100} = 40.44$  Å reflection at  $2\theta \approx 2.18^\circ$  and two other weaker reflections at  $2\theta \approx 3.75^\circ$  and  $2\theta \approx 4.32^\circ$  for  $d_{110}$  and  $d_{200}$ , respectively, due to the quasi-regular arrangement of mesopores with hexagonal symmetry (Fig. 3). Si-MCM-41 shows an additional peak at  $2\theta \approx 5.71^\circ$  which can be assigned to the  $d_{210}$  reflection. All the peaks are well-resolved, indicative of a good quality material. Co-MCM-41 exhibits a strong  $d_{100}$  reflection with a spacing of ca. 35.64 Å at  $2\theta \approx 2.48^\circ$  with almost the same intensity as that of Si-MCM-41, and two other weaker reflections at  $2\theta \approx 4.31^\circ$  and  $2\theta \approx 5.00^\circ$  for  $d_{110}$  and  $d_{200}$ , respectively, while the weakest reflection for  $d_{210}$  has been buried in the background noise. A comparison of the 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 the cobalt(II) complex in Si-MCM-41. However, all the diffraction lines shifted to higher angles. A similar type of behavior was observed by Burkett *et al.* in phenyl-modified mesoporous sieves,<sup>50</sup> and

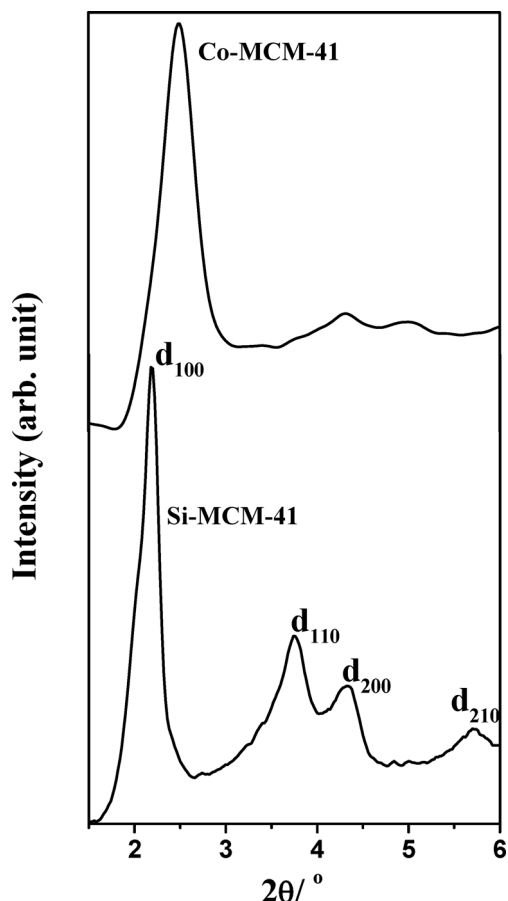


Fig. 3 Small angle XRD patterns of: Si-MCM-41; Co-MCM-41.

by Lim and Stein in directly synthesized thiol-MCM-41.<sup>51</sup> Upon post-synthesis grafting of the 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 lowering of the local order, such as variations in the wall thickness, or might be due to reduction of the scattering contrast between the channel wall of the silicate framework and the Schiff base ligand present in Co-MCM-41, as previously mentioned by Lim and Stein.<sup>51</sup> Marler *et al.* reported that the intensity of the diffraction lines decreases systematically on increasing the concentration of organic sorbates in boron-containing MCM-41.<sup>52</sup> Therefore, the shift of the diffraction lines to higher angle and the 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 Si-MCM-41 has a BET surface area ( $A_{\text{SBET}}$ ) of  $1136 \text{ m}^2 \text{ g}^{-1}$  and a primary mesopore volume ( $V_p$ ) of  $0.61 \text{ cm}^3 \text{ g}^{-1}$  (Fig. 4). The average pore diameter of Si-MCM-41 is calculated to be  $22.6 \text{ Å}$  using the Barrett-Joyner-Halenda (BJH) method. All the calculated values are in agreement with those reported for good quality

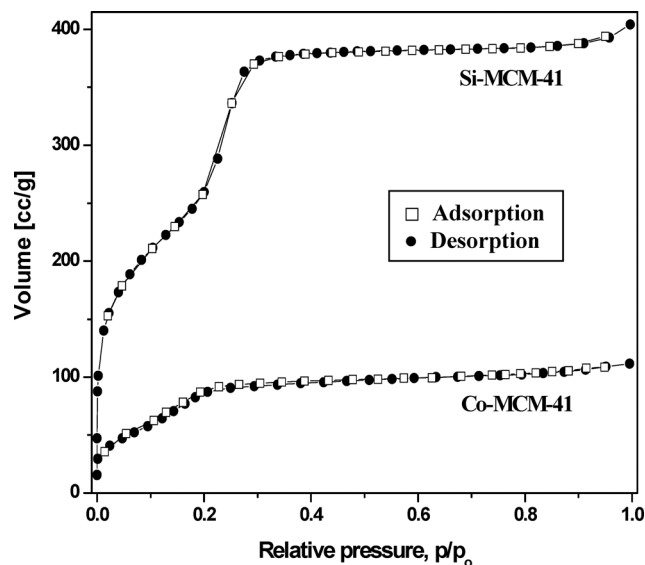


Fig. 4  $\text{N}_2$  adsorption-desorption isotherms of Si-MCM-41 and Co-MCM-41.

mesoporous MCM-41.<sup>53a</sup> The  $\text{N}_2$  adsorption isotherm and the pore size distribution of Co-MCM-41 were different to those of Si-MCM-41. Co-MCM-41 displays a considerably lower  $\text{N}_2$  uptake (BET surface area  $365 \text{ m}^2 \text{ g}^{-1}$ ) in comparison to Si-MCM-41. These isotherms are type IV, with well-defined sharp inflections observed in the  $p/p_0$  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 for Si-MCM-41 shows a remarkably narrow peak with an average pore size of  $w_{\text{BJH}} = 22.6 \text{ Å}$ , indicating uniformity of the pore distribution, Co-MCM-41 shows a wide variety of pore sizes, with a highest peak at  $\sim 23 \text{ Å}$  (see ESI†; Fig. S2 and S3). However, this is not inconsistent with the fact that anchoring of the cobalt complex might not be uniform throughout the mesoporous silica matrix. The decrease in BET surface area and the loss of uniformity of pore size for Co-MCM-41 in comparison with Si-MCM-41 clearly demonstrate that anchoring of the cobalt Schiff-base moiety into the mesoporous silica has significant effects on the pore structure of the catalyst. One possible reason for this remarkable difference in the BET surface areas of Si-MCM-41 and Co-MCM-41 might be anchoring of a considerable amount of the cobalt Schiff-base moiety into the nanosized pores of the mesoporous material. However, considering the amount of cobalt present in Co-MCM-41, the decrease in surface area is significantly large. This could be caused by partial amorphization<sup>53b</sup> of the layered phase of the mesoporous material during anchoring of the Co complex.

### 3.4. Epoxidation reactions

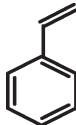





The catalytic efficacy of the prepared catalyst was tested in the epoxidation of both aromatic and aliphatic alkenes,



including straight chain and cyclic alkenes, with molecular oxygen. The performance of the catalyst in terms of conversion, selectivity and turnover number (TON) is given in Table 1. The epoxidation of styrene with molecular oxygen gives styrene oxide in 45% yield (selectivity ~90%) (Table 1) under heterogeneous conditions; in addition to this, a small amount (5%) of benzaldehyde is detected. A turnover number of ~707 for catalytic epoxide production is attained in this particular reaction. Epoxidation of styrene with molecular oxygen over a variety of cobalt catalysts under heterogeneous conditions has been studied in the recent past (Table 2). A cobalt–salen catalyst immobilized in silica was applied in the epoxidation of styrene with molecular oxygen in the presence of butyraldehyde.<sup>54</sup> CoO<sub>x</sub>–MCM-41, prepared by ultrasonic deposition–precipitation of cobalt tricarbonyl nitrosyl in decalin, was reported to catalyze the epoxidation of alkenes by O<sub>2</sub> in the presence of excess isobutyraldehyde, which functioned as the co-reductant.<sup>27</sup>

Linear aliphatic olefins, such as 1-hexene and 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. This shows that the catalytic activity decreases with increasing olefin chain length. This may be due to the fact that the larger hexyl group connected to the double bond of 1-octene sterically hinders its approach to the catalyst metal center, compared with 1-hexene, in which the 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 result in higher epoxidation reactivity. Therefore, cyclooctene and cyclohexene with double bonds between two secondary carbons exhibit higher 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; in addition, 2-cyclohexen-1-ol was generated,

**Table 1** Heterogeneous alkene epoxidation catalyzed by Co–MCM-41<sup>c</sup>

Alkenes	Reaction temp. (°C)	Conversion (wt%)	% Yield of products		TON <sup>d</sup>
			Epoxide	Other	
	80	50	45	5 <sup>a</sup>	707
	75	54	40	14 <sup>b</sup>	970
	80	78	78	—	1044
	80	47	47	—	824
	80	35	30	5	460
	50	12	12 <sup>c</sup>	—	304

<sup>a</sup> Benzaldehyde. <sup>b</sup> 2-Cyclohexen-1-ol was formed. <sup>c</sup> R-(+)-glycidol. <sup>d</sup> Turnover number = moles converted/moles of active site. The products of the epoxidation reactions were collected at different time intervals and were identified and quantified using a Varian CP3800 gas chromatograph equipped with an FID detector and a CP-Sil 8 CB capillary column. <sup>e</sup> Reaction conditions: alkenes (1 g); catalyst (50 mg); flow rate of O<sub>2</sub>: 3.0 cm<sup>3</sup> min<sup>-1</sup>; 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 <sup>a</sup>	References
		Epoxide	Other		
Co–MCM-41	50	45	5	707	This study
Co–MCM-41	45	28	17	169	56
Co <sup>2+</sup> –X	44.2	26.5	17.7	13.2	32
Co <sup>2+</sup> –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

<sup>a</sup> Turnover number = moles converted/moles of active site.

owing to allylic C–H oxidation. Kameyama *et al.*<sup>55</sup> studied the epoxidation of cyclohexene with molecular oxygen with the co-reductant isobutyraldehyde catalyzed by cobalt porphyrin complexes immobilized on montmorillonite, which showed ~66% conversion to 1,2-epoxycyclohexane (yield ~56%). The bulkier cycloalkene, cyclooctene, has also been effectively and selectively converted to cyclooctene oxide (conversion 78%, selectivity 100%). Jinka *et al.* performed epoxidation of cycloalkenes using molecular oxygen with the NaCoX96 catalyst, and observed only 26% conversion of cyclohexene and 47% conversion of cyclooctene.<sup>33</sup> Tang *et al.* introduced cobalt metal into MCM-41 by a template ion exchange (TIE) method to study the styrene epoxidation reaction.<sup>56</sup> However, they did not investigate the possibility of leaching of cobalt metal from the surface of MCM-41, which is common amongst ion-exchanged catalysts. Notably, cobalt metal does not leach out during the catalytic reaction in the case of Co-MCM-41 (*vide infra*). In our case, the metal ions are covalently attached to organically modified Si-MCM-41.

Solvent plays a crucial role in epoxidation reactions. We have also performed the epoxidation reaction of styrene in different solvents, such as acetonitrile, chloroform, hexane, and ethyl acetate, and even in high boiling alcohols like *n*-decyl alcohol; however, no conversion of styrene to its oxide was detected. Only acylamides, such as DMF, are particularly efficient in providing both high conversion and high epoxide selectivity in this case. Notably, Beier *et al.* suggested that a radical reaction pathway operates in DMF-promoted epoxidations.<sup>35</sup> In the reaction medium, a radical oxygen species 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 the 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),

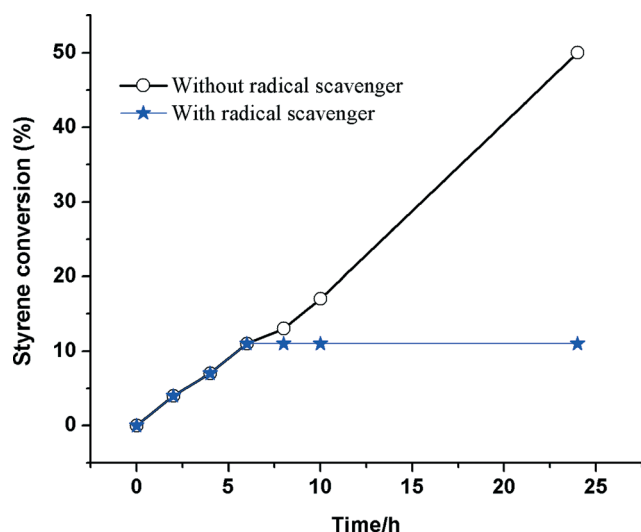


Fig. 5 Percentage conversion versus time plots for comparison between reactions with a radical scavenger and a control reaction without a radical scavenger.

confirming the radical nature of the active oxygen species formed by molecular oxygen with cobalt(II) in the 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.<sup>34</sup> We have analyzed the reaction solution using a GC-MS analyzer, as well as a high resolution mass spectrometer, however, we could not detect the formation of an *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 recovery from the reaction mixture and possible reuse. To test whether metal is leached out from the solid catalyst during the reaction, we carried out a hot filtration test. After the reaction, the solid catalyst was filtered out under hot conditions. Then, the filtrate was treated with *aqua regia* several times and the mixture was evaporated to dryness on 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 showed that cobalt was absent from the solution. In addition, the liquid phase of the reaction mixture was collected by filtration after ~30% of the epoxidation reaction was completed, and the residual activity of the supernatant solution after separation of the catalyst was studied. The supernatant solution was kept under the catalytic reaction conditions, as stated above, and the composition of the solution was determined by GC. No reaction progress was observed during this period, which precludes the presence of active species in solution.

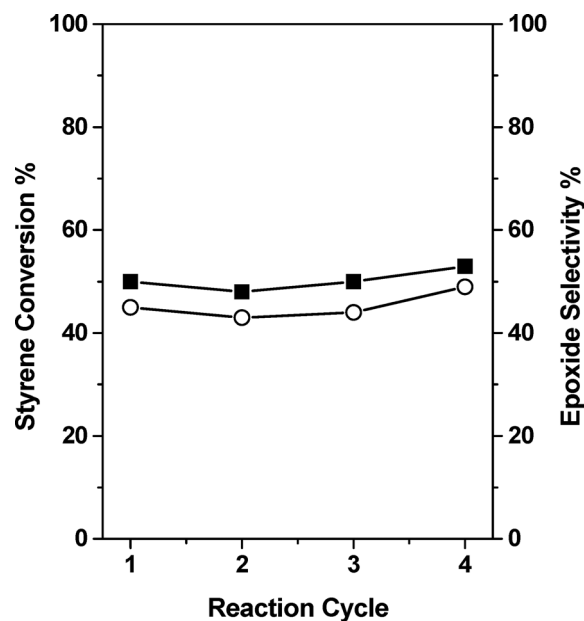


Fig. 6 Reuse of Co-MCM-41 for the epoxidation of styrene with O<sub>2</sub>: (■) styrene conversion, (○) epoxide selectivity.

The Co-MCM-41 catalyst was recovered from the reaction mixture and reused three times under the same reaction conditions. The solid catalyst was recovered by filtration after each reaction and was washed thoroughly with DMF. The recovered catalyst was found to exhibit almost the same catalytic activity for the epoxidation of styrene by molecular oxygen in every run, as shown in Fig. 6.

## Conclusion

In summary, we succeeded in preparing a new example of a cobalt-based heterogeneous catalyst by anchoring cobalt(II) centers into a 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 the epoxidation reactions of a variety of olefinic substrates, including allyl alcohol, in a heterogeneous medium. Notably, the catalyst can be recovered and reused without any loss of activity.

## Acknowledgements

Financial support from a grant from CSIR, New Delhi (grant no. 01(2542)/11/EMR-II) (to S.K.) is gratefully acknowledged. S.B. thanks CSIR, New Delhi, India (no. 09/096(0671)2k11-EMR-I) for a Senior Research Fellowship.

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