

Co(III)-containing mesoporous silica as an efficient catalyst in selective dihydroxylation of cyclohexene

S. Samanta^a, S.C. Laha^b, N.K. Mal^c, A. Bhaumik^{a,*}

^a Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India

^b Department of Chemistry, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Republic of Korea

^c Dynamic Materials Research Group, National Institute of Advance Industrial Science and Technology, Ikeda, Osaka 563-8577, Japan

Received 26 March 2004; received in revised form 10 August 2004; accepted 12 August 2004

Abstract

Cobalt-containing mesoporous silica have been synthesized hydrothermally using different Co content (Si/Co mole ratios 5–30) in the synthesis gel using the self-assembled molecular array of cationic surfactant cetyltrimethylammonium bromide as a supramolecular template under very mild acidic conditions. Powder XRD, N₂ adsorption, TEM, SEM/EDS, UV–visible and FT-IR tools have been employed to characterize these materials. Characterization data suggested that the Co(III) species have been anchored strongly in the 2D-hexagonal mesoporous silica framework. These Co(III)-containing mesoporous materials showed excellent catalytic activity and high *trans*-selectivity in the liquid phase dihydroxylation of cyclohexene under mild liquid phase reaction conditions using hydrogen peroxide, *tert*-butyl hydroperoxide (TBHP) or molecular O₂, as oxidants and acetonitrile solvent.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Catalysis; Cobalt; Cyclohexene dihydroxylation; Mesoporous materials; Peroxides

1. Introduction

The selective oxidation of alkanes, alkenes and aromatic hydrocarbons is one of the most attractive processes for the conversion of petroleum products to value added fine chemicals [1,2]. Many of these processes utilized metal complex and related catalysts to promote both the rate of reaction and product selectivity [3–5]. More energy efficient reaction involving dioxygen, hydrogen peroxide or other easily accessible and environmentally friendly oxidants have gained considerable interest over the years [6]. These catalytic oxidation reactions over transition metal incorporated zeolites or related microporous and mesoporous materials are of current research interest because of their easy and eco-friendly work-up [7,8]. Many Co-complexes [9] have been used in the presence of dioxygen for selective C–H oxidation. How-

ever, the practical application of these catalysts is severely limited due to the poor thermal stability of the complexes under oxidative conditions. Among these oxidation reactions cyclohexane/ene oxidation continues to be a challenge [10].

Although there are many reports on the incorporation of cobalt in microporous and mesoporous aluminumphosphates [11–14] and their catalytic activity in selective oxidation reactions using molecular oxygen or peroxides, there are only few reports on the loading of Co into the mesoporous silica [15,16] based materials and their catalytic application. In general, the quality of mesoporous materials, hexagonal or disordered ones, can vary largely by the addition of hetero-elements in the silica containing synthesis gel. Jentys et al. [17] have reported the preparation of highly dispersed and stable Co clusters in MCM-41 using a direct synthesis method. A route for the preparation of mesoporous metallosilicates via post-synthesis metal incorporation into frameworks of siliceous mesoporous materials has been suggested by Ryoo

* Corresponding author. Tel.: +91 3324734971; fax: +91 3324732805.
E-mail address: msab@mahendra.iacs.res.in (A. Bhaumik).

et al. [18] to overcome the deposition of metal oxide on the surfaces of silica mesostructure during hydrothermal synthesis. The coordination of cobalt ions in $\text{MeAPO}_4\text{-n}$ molecular sieve frameworks is related to the structural features of the $\text{AlPO}_4\text{-n}$ system, the amount of metal loading and the preparation procedure. Different characterization techniques have been utilized to obtain information about the isomorphous substitution of Co in the framework atoms of $\text{MeAPO}_4\text{-n}$ and their chemical environment [19,20]. It was found that only part of the framework cobalt(II) ions could be oxidized to cobalt(III) ion and consequently, can be catalytically active [19]. In the dihydroxylation of cyclohexene usually the reaction can proceed via epoxidation followed by its hydrolysis in the presence of metal hydroperoxides under liquid phase condition. OsO_4 , KMnO_4 , peracids, etc. are conventionally used for the dihydroxylation reaction, which are toxic, expensive and involving difficult work-up process, or presence of co-oxidant [21] and the products are often contaminated with undesired over oxidized products. OsO_4 is particularly useful for the synthesis of *cis*-1,2-cyclohexanediol [22] from cyclohexene.

In recent times more environment friendly process for the transformation of organics have gained considerable momentum [23]. The main area of concern is the large volume of effluents produced by variety of chemical processes. Improvement can be made in several ways, such as using alternative reagents and catalysts, increasing efficiency of the process, easier separation of products from reactants and recycling of reagents or catalysts. These eliminate the requirement for laborious and inefficient extraction processes. One of the major contributors to waste in a chemical process is the separation of product or catalyst from the reaction mixture. This stage often generates large volumes of waste effluent. At the same time during the solvent extraction, the catalyst often gets destroyed. Thus, elimination of these steps is highly desirable and this is one of the major goals of green chemistry [24]. Here, we report the selective, one pot and eco-friendly catalytic oxidation of cyclohexene over Co-containing mesoporous silica using different oxidants like aqueous H_2O_2 , *tert*-butylhydroperoxide (TBHP, 70% aqueous) and molecular O_2 to *cis*- and *trans*-1,2-cyclohexanediol without any other undesired over oxidized products.

2. Experimental

Usually mesoporous silica based materials are synthesized in either acidic or basic condition [25–27]. Cobalt-containing mesoporous silica samples were synthesized under modified mild acidic condition employing acid hydrolysis of organosilica source followed by the addition of base for precipitation and condensation. $\text{CoCl}_3 \cdot 5\text{H}_2\text{O}$ (Loba Chemie), was used as a Co(III) source in this study. Tetraethyl orthosilicate (TEOS, E-Merck) was used as a silica source and cationic surfactant cetyltrimethylammonium bromide (CTAB, Loba Chemie)

was used for structure direction under acidic synthesis condition. Tetramethylammonium hydroxide (TMA-OH, 25% aqueous, Demi Chem) was used to maintain the pH (4.5–6.5) of the synthesis gel. In a typical synthesis TEOS was first allowed to mix with an aqueous solution of CTAB prepared by dissolving its required amount in deionized water. Then the required amount of Co(III) salt was dissolved in water and added onto this aged silica sol in different mole ratios corresponding to the desired loading of Co. TEOS was then allowed to hydrolyze slowly in acidic pH. After 1 h aqueous TMA-OH solution was added onto it until pH rose to 4.5–6.5 and a thick bluish homogeneous gel formed. The final mixture was vigorously stirred for 1 h and then autoclaved at 353 K for 2–3 days. The molar ratio of various constituents of the hydrothermal gels were $\text{SiO}_2 : \text{Co(III)} : \text{CTAB} : \text{TMA-OH} : \text{H}_2\text{O} = 1 : (0.2 - 0.05) : 0.25 : (0.1 - 0.15) : 120$.

After the hydrothermal treatment, the bluish gray solid products were filtered, washed repeatedly with deionized water and dried in air. As-synthesized samples were calcined slowly in the flow of air at 773 K for 8 h to remove the template molecules. Calcined samples were gray in color. All the samples were identified by powder XRD using a Seifert XRD 3000P diffractometer on which the small and wide-angle goniometers are mounted. The X-ray source was Cu $\text{K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) with a voltage and current of 40 kV and 20 mA, respectively. Mesophases of different samples were analyzed using a JEOL, JEM 2010 transmission electron microscope (TEM). The accelerating voltage was 200 kV. Prior to the TEM measurements, a small amount of sample was sonicated in methanol/ethanol for 10 min, and then a drop of the dispersed liquid was dropped onto the holey carbon coated copper grid, followed by drying at room temperature. N_2 adsorption measurements were carried out using an Autosorb-1 (Quantachrome) at 77 K. Pre-treatment of the sample was done at 473 K for 3 h under high vacuum. A Bruker AM-300 NMR was used for MAS NMR measurement with a 7 mm zirconia rotor and 2.5–3.5 kHz speed for more than 5 h, scanning around 5000 scans. The ^{29}Si NMR was referenced with respect to external TMS. Morphology and particle size of different samples were analyzed using a Philips XI-30/FEG, XL-serial Scanning Electron Microscope with an EDS (New XL-30) attachment. UV–visible diffuse reflectance spectra were recorded on a Shimadzu UV 2401PC with an integrating sphere attachment. BaSO_4 was used as background standard. For the Fourier transform infrared (FT-IR) measurement a Nicolet Magna IR 750 was used. A Perkin Elmer 2380 AAS (atomic absorption spectrophotometer) was used for wet chemical analysis. EPR spectra were acquired using a Varian EPR spectrophotometer equipped with manual data acquisition. Prior to the chemical analysis solid samples were dissolved in minimum amount of concentrated HF and HCl solutions followed by evaporation for three times before making up the desired volume by distilled water. Liquid phase oxidation reactions were carried out in a two-necked round bottom flask fitted with a water condenser and placed in an

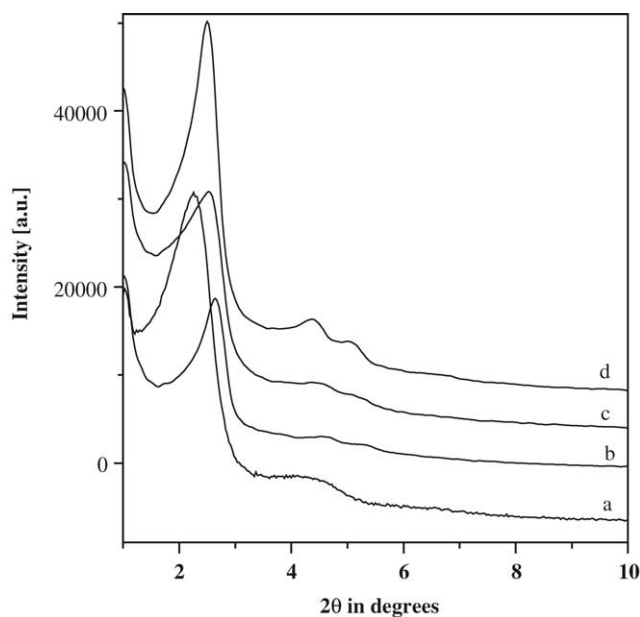


Fig. 1. XRD pattern of as-synthesized (sample 1, a) and calcined Co(III)-containing mesoporous silica samples 2 (b), 3 (c) and 1 (d).

oil bath at 333–353 K with vigorous stirring. All samples used as catalyst were dried for 4 h at 373 K before use. H_2O_2 or TBHP oxidants were added immediately before the start of the reactions. Air bubbles were constantly passed at a very slow rate through the reaction mixture when molecular oxygen was used as oxidant. At different time intervals products were removed and were analyzed by capillary GC (Agilent 4890D, FID). By comparing the retention times with the known standards identification of the product was performed.

3. Results and discussion

3.1. Synthesis

Three Co-containing mesoporous silica samples and a Co-free pure silica MCM-41 sample have been synthesized with different Si/Co mole ratios 8, 15, 30 and ∞ , respectively, in the synthesis gel. These samples have been designated as samples 1, 2, 3 and 4, respectively. The Si/Co mole ratios in the final products after the removal of template were 6.5, 13.7 and 27.2 (as measured by AAS) for samples 1, 2 and 3, respectively.

3.2. Characterizations

Fig. 1 shows the XRD patterns of the as-synthesized (a, sample 1) and calcined cobalt-containing mesoporous samples 3 (b), 2 (c) and 1 (d). These materials showed low angle reflections only, with no noticeable high angle reflections. Co-rich samples showed a little broader diffraction pattern. The d_{100} for the low angle reflections of the as-synthesized and calcined sample 3 were 3.62 and 3.43 nm, respectively. Crystalline cobalt oxide usually has several reflections [28] between 10° and 50° of 2θ . The absence of any noticeable high angle reflections indicated that the material is amorphous and free from cobalt oxide impurity phases. Fig. 2 shows a TEM image of a representative mesoporous cobalt silicate (sample 3). Hexagonal arrangement of the pores was quite clear. The Fourier-transformed pattern with sixfold rotation axis (Fig. 2b) suggests the hexagonal structure with a lattice constant of (001) of 3.4 nm, which is in very close agreement with the powder XRD data. The electron diffraction pattern of a portion (inset, Fig. 2a) also supports this 2D-hexagonal mesostructure.

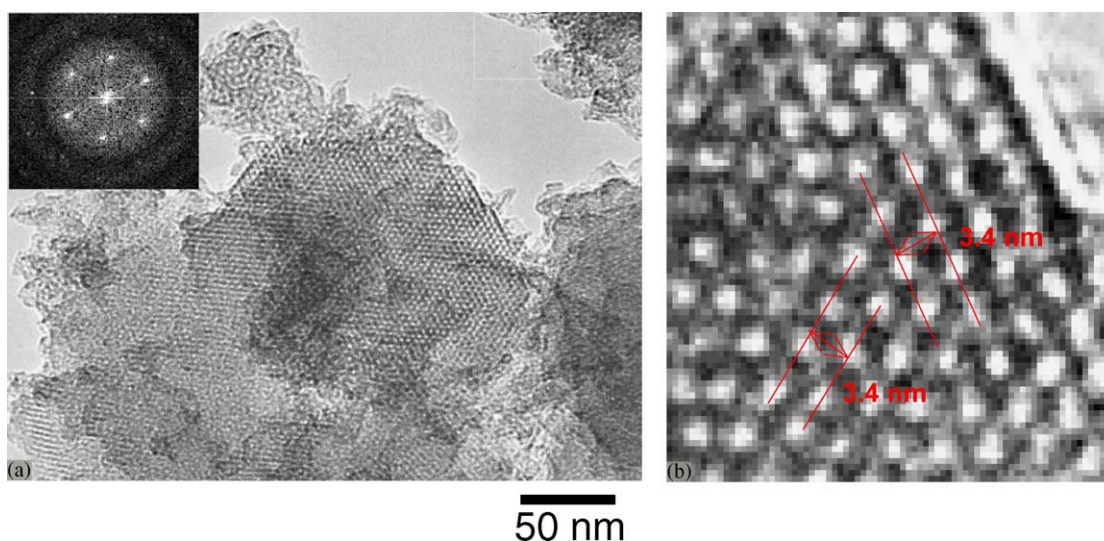


Fig. 2. TEM image of the Co(III)-containing mesoporous silica sample 3.

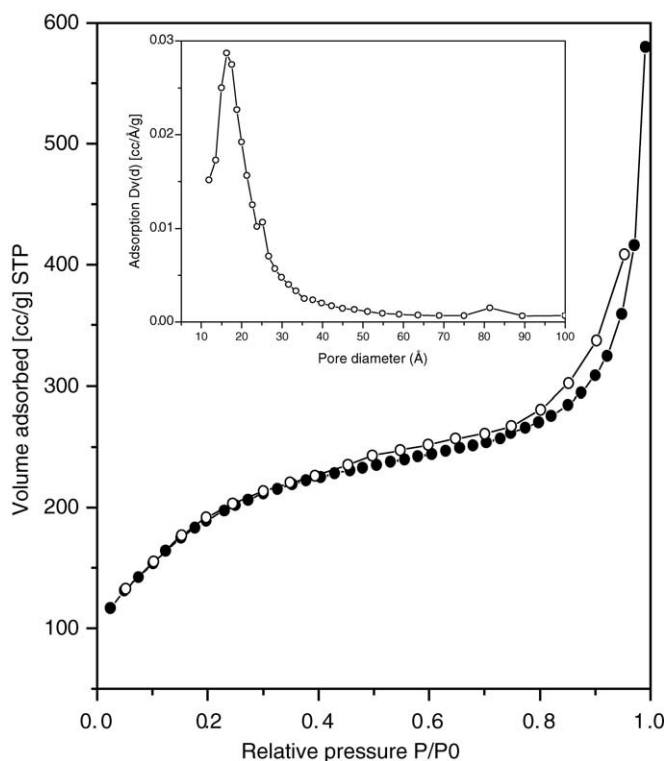


Fig. 3. N_2 adsorption/desorption isotherms of sample 1. Adsorption points are marked by filled circles, and that for desorption ones are by open circles. Pore size distribution has been shown in the inset.

Fig. 3 illustrates the N_2 adsorption/desorption isotherms of calcined sample 1 (taken as a representative). These isotherms resembled the type IV isotherm, typical for mesoporous materials [25,29]. BET surface areas measured from these isotherms were 556, 638 and $1020 \text{ m}^2 \text{ g}^{-1}$, for samples 1, 2 and 4, respectively. Surface areas of these cobalt-containing mesoporous silica samples were moderately large. Pore size distribution employing the BJH model is shown in the inset of Fig. 3. Quite broad distribution of pores with maximum at ca. 17 \AA was observed. The pore size estimated from the TEM image analysis agrees well with that from N_2 adsorption isotherm.

The ^{29}Si MAS NMR spectral pattern for calcined sample 2 is shown in Fig. 4. This pattern is quite broad like amorphous mesoporous silica. Three major peaks in this sample at -95.5 , -103.8 and -111.0 ppm were observed. These peaks have been assigned to tetrahedral Q^2 , Q^3 and Q^4 silica species, respectively. High Q^4 percentage indicated highly condensed network. Such a high Q^4 concentration is of paramount importance for the catalytic activity of silica based catalyst in liquid phase partial oxidation reactions in the presence of aqueous H_2O_2 as oxidant, since reduction of surface silanols introduces high hydrophobicity (and thus more affinity towards organic substrates) [30,31].

The UV–visible spectra of mesoporous silica with different cobalt loadings as well as Co_2O_3 are shown in Fig. 5. Co-containing mesoporous silicas showed a very-broad absorption band in the $360\text{--}625 \text{ nm}$ wavelength region (Fig. 5,

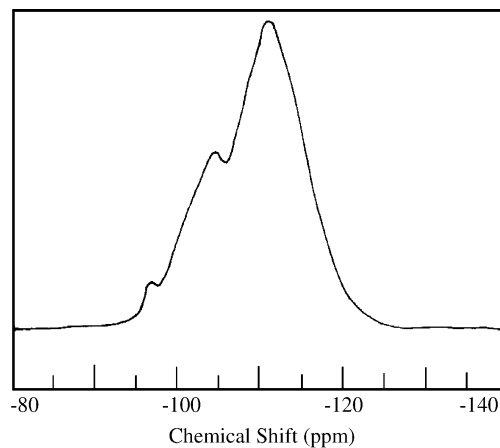


Fig. 4. Solid state MAS NMR of sample 1.

curves b–d). This could be attributed to the d–d transition. Corresponding pure silica Si-MCM-41 (Fig. 5e) showed almost no absorption in the region $200\text{--}800 \text{ nm}$. Usually, a high-energy absorption edge due to tetrahedral coordination of other 3d transition elements has been observed for other metallosilicate molecular sieves [19,32]. On the other hand, crystalline Co_2O_3 showed distinct sharp peaks (Fig. 5a) at 357, 324 and 307 nm. Absence of any band at ca. 357 nm or below ruled out any possibility of isolated or extra-framework cobalt species in these mesoporous cobalt silicate samples. For the calcined samples 1–3, EPR spectra (not shown) corresponding to the high spin patterns for Co^{3+} were observed, suggesting the presence of Co(III) in these mesoporous materials. EPR spectra remained unchanged after the catalytic reactions, indicating that the oxidation state and chemical environment remain unchanged after reaction and that the

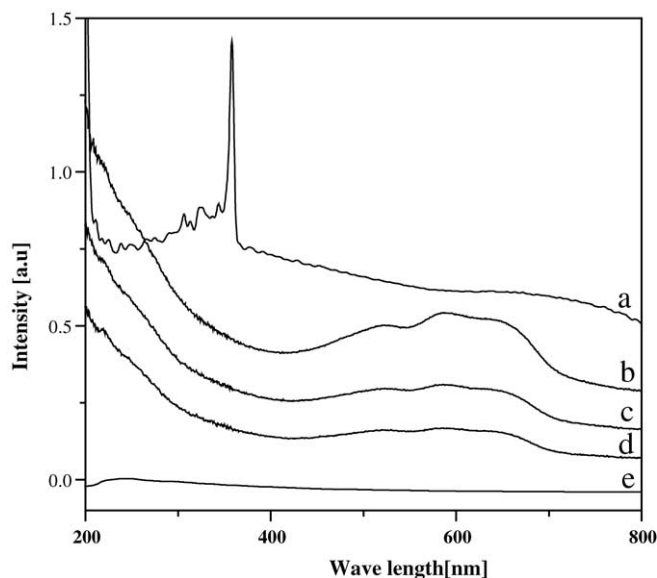


Fig. 5. UV–visible diffuse reflectance spectra of Co_2O_3 (a), calcined Co(III)-containing mesoporous silica samples 1 (b), 2 (c), 3 (d) and Si-MCM-41 (e).

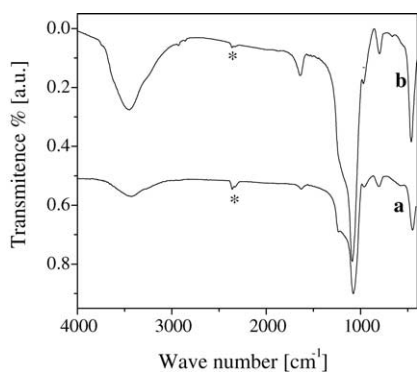


Fig. 6. FT-IR spectra of calcined pure silica MCM-41 (a) and Co(III)-containing mesoporous silica sample 2 (b). Peaks for CO₂ contamination have been marked by an asterisk.

cobalt species are anchored strongly in the mesoporous silica framework.

FT-IR spectra of the calcined samples 1 and 4 are shown in Fig. 6. Sharp peaks in the FT-IR spectra of these as-synthesized mesoporous samples at 3334, 2915 and 2845 cm⁻¹ were observed. These could be attributed to SiO–H and C–H stretching vibrations for the template CTAB. Disappearance of the C–H peaks in the calcined products indicated complete removal of the template CTAB. Major peaks at 3450, 1220–1070 and 972 cm⁻¹ were observed for the calcined samples. A broad peak at 3450 cm⁻¹ could be attributed to O–H stretching of the defect Si–OH groups and residual water. A broad band observed at 1220–1070 corresponds to Si–O–Si vibration for all the samples. A relatively strong band observed at ca. 972 cm⁻¹ for samples 1–3 could be attributed to the framework Co–O–Si vibrations as observed for other metallosilicates [32]. Pure silicalites also often show a very moderate band in this region as was observed in Fig. 6a. Presence of such a relatively strong band is an indication of incorporation of isolated tetrahedral Co³⁺ species in the mesoporous silica. In Fig. 7 the SEM image of the as-synthesized mesoporous cobalt silicate (sample 1)

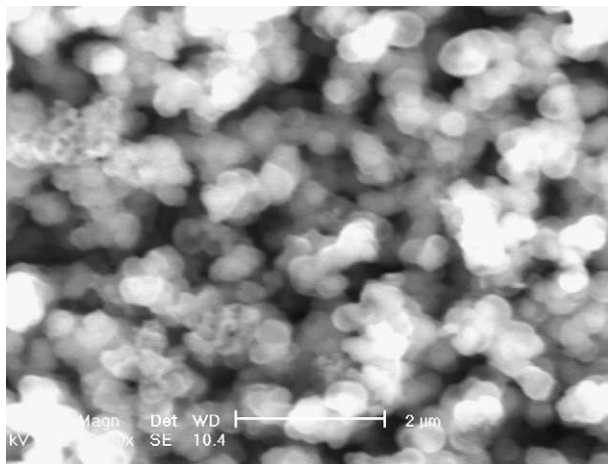


Fig. 7. SEM image of sample 2.

is shown. Spherical to plate-like morphology of the uniform tiny particles with particle sizes in the range 50–80 nm were observed.

3.3. Catalysis

Cobalt-containing molecular sieves have been reported in various catalytic reactions [33–35] under gas or liquid phase condition. Table 1 gives conversion and product selectivity for the oxidation of cyclohexene in the presence of dilute H₂O₂, TBHP and molecular O₂ as oxidant over mesoporous cobalt silicate samples using acetonitrile solvent. It is pertinent to mention that H₂O₂ conversion in all the cases is above 90% using acetonitrile as solvent. In solvents methanol and chloroform, the reaction rates were slow and it took 18–20 h to reach only 15–26% conversion with almost equal molar concentrations of *cis*- and *trans*-1,2-cyclohexanediols as the main products. Neither pure silica MCM-41 nor Co₂O₃ showed any catalytic activity using these oxidants under identical reaction conditions. As seen from Table 1, with increase in reaction temperature TON for different set of reaction increases. Low Co loaded samples (2 and 3) showed better catalytic efficiency (Table 1, entries 4, 5 and 7). Mainly *cis*- and *trans*-1,2-diol products along with minor amount of epoxide were found in the reaction mixture. High *trans* selectivity between the diastereomers of cyclohexanediol was observed when TBHP or O₂ was used as oxidant (Table 1, entries 6–9). This may be due to the higher stability of transition state involving the *trans*-adduct. The reaction was repeated for each of the oxidants and in all the cases almost equal (*vis-a-vis* first run) conversion was observed. Interestingly, no cobalt was found to leach from the solid catalysts after the reactions.

Almost no or negligible amount of intermediate epoxide was detected even at the early stages of different reaction mixtures, indicating that Co-containing mesoporous silica catalyzed the present dihydroxylation reaction at a very fast rate and the C–OH bond formation occurred possibly inside the mesopore. If the reaction could proceed through epoxidation, the oxirane ring opening would have occurred via attack of external H₂O molecules of the medium resulting in dihydroxylation. This suggested that unlike other dihydroxylation reactions [36], where the reaction proceeds via epoxidation followed by its hydrolysis, the present dihydroxylation reaction possibly proceeds via C=C bond breaking and simultaneous C–OH bond formation through a radical pathway. Since the diols were formed as the predominant product for all the oxidants, H₂O₂, TBHP and O₂, at 353 K in acetonitrile, the intermediate oxygenated species is more hydrophilic than cyclohexene. In our earlier results [36], we had shown that more hydrophobic epoxide undergoes rapid hydrolysis over the TS-1/aqueous H₂O₂/organic triphase system. This is because of the fact that compared to the intermediate the hydroxylated products are highly water soluble. Thus, the presence of water facilitates the removal of the product from the catalyst surface. Water coming from dilute H₂O₂/TBHP

Table 1
Oxidation of cyclohexene catalysed by Co-containing mesoporous silica^a

Oxidant	Temperature (K)	% Conversion	Product selectivity (%)			TON ^b (mol/mol-Co)
			Epoxide	<i>Cis</i> -diol	<i>Trans</i> -diol	
H ₂ O ₂	333	47.2	3.2	45.1	51.7	13.4
H ₂ O ₂	343	60.0	–	31.7	68.3	17.1
H ₂ O ₂	353	80.6	–	35.6	64.4	23.0
H ₂ O ₂ ^c	353	78.0	1.2	34.3	64.5	42.5
H ₂ O ₂ ^d	353	70.2	1.8	40.4	57.8	69.4
TBHP	353	85.6	1.7	7.3	91.0	24.6
TBHP ^c	353	83.6	1.3	10.0	88.7	45.8
O ₂	333	67.5	3.7	15.5	80.8	19.3
O ₂	353	80.2	2.4	19.2	78.4	22.9

^a Solvent 5 g acetonitrile for 0.82 g cyclohexene, catalyst = 20 wt.% with respect to the substrate, sample 1 used as catalyst unless otherwise mentioned. Reaction time = 12 h for all the reactions.

^b Turn over number = moles of substrate converted per mole of Co.

^c Sample 2 was used as catalyst.

^d Sample 3 was used as catalyst.

and their decomposition products helped in the formation of considerable dihydroxylated product. When molecular O₂ was used as oxidant, the reaction mixture was devoid of any residual water. However, in this case also predominantly diol products (high *trans*-1,2-cyclohexanediol selectivity) were obtained.

4. Conclusions

Cobalt could be incorporated in the 2D-hexagonal mesoporous silica materials hydrothermally under mild acidic conditions using the self-assembly of cationic surfactant CTAB. XRD pattern showed only low angle reflections corresponding to the 2D-hexagonal mesophase. BET surface areas of samples with different cobalt loadings were moderately high and pore diameters estimated using the BJH model showed broad pore size distribution. TEM images showed hexagonal arrangement of the pores. Solid-state MAS NMR data suggested moderately good cross-linking with less number of defect sites in this material. A strong UV–visible band in the 425–625 nm region and an FT-IR peak at 972 cm⁻¹ could be attributed to the incorporation of isolated cobalt(III) species in the silica matrix. The template molecules were successfully removed through calcination at 773 K without structural collapse. These cobalt-containing mesoporous cobalt silicate samples showed excellent catalytic activity in liquid phase oxidation of cyclohexene to *cis*- and *trans*-1,2-cyclohexanediol isomers (high *trans* selectivity) using H₂O₂, TBHP and molecular oxygen as oxidants.

Acknowledgement

This work was partly supported by Department of Science and Technology (grant number SR/FTP/CS-24/2001 and Nanoscience and Nanotechnology initiative) and Council for Scientific and Industrial Research (grant number

01(1800)/02/EMR-II), New Delhi. Authors wish to thank Dr. A. Manna for his help in SEM/EDS analysis.

References

- [1] A.E. Shilov, G.B. Shul'pin, Chem. Rev. 97 (1997) 2897.
- [2] L.I. Simandi, Dioxygen Activation and Homogeneous Catalytic Oxidation, Elsevier, Amsterdam, 1991.
- [3] J.T. Groves, K.V. Shalyaev, J. Lee, in: K.M. Kadish (Ed.), The Porphyrin Handbook, vol. 4, Academic Press, San Diego, CA, 1999, p. 17.
- [4] R.A. Sheldon, J.K. Kochi, Metal-catalyzed Oxidations of Organic Compounds, Academic Press, New York, 1981; G.-J.T. Brink, I.W.C.E. Arends, R.A. Sheldon, Science 287 (2000) 1636.
- [5] S.T. Oyama, J.W. Hightower (Eds.), Catalytic Selective Oxidation, American Chemical Society, Washington, 1993.
- [6] Y. Nishiyama, T. Hayashi, Y. Nakagawa, N. Mizuno, Angew. Chem. Int. Ed. 40 (2001) 3639.
- [7] J.H. Clark, Pure Appl. Chem. 73 (2001) 103.
- [8] H. Nur, S. Ikeda, B. Ohtani, Chem. Comm. (2000) 2235.
- [9] J.Y. Qi, H.-X. Ma, X.-J. Li, Z.Y. Zhou, M.C.K. Choi, A.S.C. Chan, Q.-Y. Yang, Chem. Comm. (2003) 1294.
- [10] U. Schuchardt, D. Cardoso, R. Sercheli, R. Pereira, R.S. da Cruz d, M.C. Guerreiro, D. Mandelli, E.V. Spinacé, E.L. Pires, Appl. Catal. A: General 211 (2001) 1.
- [11] A.A. Verberckmoes, M.G. Uytterhoeven, R.A. Schoonheydt, Zeolites 19 (1997) 180.
- [12] J. Poner, J. Ejka, J. Ddeek, B. Wichterlová, Micropor. Mesopor. Mater. 37 (2000) 117.
- [13] D.S. Kim, S.H. Chang, W.S. Ahn, Appl. Catal. A: General 179 (2002) 175.
- [14] N. Nagaraju, G. Kuriakose, New J. Chem. (2003) 765.
- [15] D.H. Park, S.S. Park, S.J. Choe, Bull. Kor. Chem. Soc. 20 (1999) 715.
- [16] J. Panpranot, J.G. Goodwin Jr., A. Sayari, J. Catal. 211 (2002) 530.
- [17] A. Jentys, N.H. Pham, H. Vinek, M. English, J.A. Lercher, Microporous Mater. 6 (1996) 13.
- [18] R. Ryoo, S. Jun, J.M. Kim, M.J. Kim, Chem. Commun. (1997) 2225.
- [19] M. Hartmann, L. Kevan, Chem. Rev. 99 (1999) 635.
- [20] L. Canesson, Y. Boudeville, A. Tuel, J. Am. Chem. Soc. 119 (1997) 10754.

- [21] T.J. Donohoe, K. Blades, P.R. Moore, M.J. Waring, J.J.G. Winter, M. Helliwell, N.J. Newcombe, G. Stemp, *J. Org. Chem.* 67 (2002) 7946.
- [22] T. Göbel, K.B. Sharpless, *Angew. Chem., Int. Ed. Eng.* 32 (1993) 1329.
- [23] R.S. Drago, *Coord. Chem. Rev.* 117 (1992) 185.
- [24] J.H. Clark, *Supported Reagents in Organic Reactions*, VCH, Weinheim, 1994.
- [25] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, *Nature* 359 (1992) 710.
- [26] Q. Huo, D.L. Margolese, U. Ciesla, P. Feng, T.E. Gier, P. Sieger, R. Leon, P.M. Retroff, F. Schulth, G.D. Stucky, *Nature* 368 (1994) 317.
- [27] X.S. Zhao, G.Q. Lu, G.J. Millar, *Ind. Eng. Chem. Res.* 35 (1996) 2075.
- [28] S. Valeri, A. Borghi, G.C. Gazzadi, A. di Bona, *Surf. Sci.* 423 (1999) 346.
- [29] S.J. Gregg, K.S.W. Sing, *Adsorption Surface Area and Porosity*, Academic Press, London, 1982.
- [30] T. Tatsumi, K.A. Koyano, N. Igarashi, *Chem. Commun.* (1998) 325.
- [31] X.S. Zhao, G.Q. Lu, A.K. Whittaker, G.J. Millar, H.Y. Zhu, *J. Phys. Chem. B* 101 (1997) 6525.
- [32] R. Szostak, *Molecular Sieves: Principles of Synthesis and Identification*, Van Nostrand Reinhold, New York, 1989.
- [33] T. Tsoncheva, R. Dimitrova, C. Minchev, *Appl. Catal. A: General* 171 (1998) 241.
- [34] S. Cabrera, J. El Hakouri, C. Guillem, J. Latorre, A. Beltrán-Porter, D. Beltrán-Porter, M.D. Marcos, P. Amorós, *Solid State Sci.* 2 (2000) 405.
- [35] S.K. Mohapatra, S.U. Sonavane, R.V. Jayaram, P. Selvam, *Tetrahedron Lett.* 47 (2002) 8527.
- [36] A. Bhaumik, T. Tatsumi, *J. Catal.* 176 (1998) 305.