

Mesoporous Cr-MCM-41: An efficient catalyst for selective oxidation of cycloalkanes

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Abstract

Highly ordered mesoporous Cr-MCM-41 materials with different Si:Cr mole ratios have been synthesized by using the hydrothermal method and avoiding co-precipitation of chromium oxides during synthesis. Detailed characterizations of these two-dimensional hexagonal mesoporous Cr-MCM-41 materials were carried out using powder XRD, TEM, SEM-EDS, N₂ sorption, FT-IR and UV–vis diffuse reflectance measurements. Cr-MCM-41 materials showed excellent catalytic activity and high selectivity in the direct oxidation of cycloalkanes viz. cyclohexane and cyclooctane to cyclohexanone and cyclooctanone, respectively, using dilute aqueous H₂O₂ or *tert*-butyl hydroperoxide (TBHP) as oxidant under mild liquid phase reaction conditions.

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1. Introduction

Open framework microporous and mesoporous metallo-silicates [1–4] have received considerable attention over the last few decades. These materials have found many potential applications in catalysis, separations, coatings and chemical sensing. Mesoporous silica-based materials containing different transition elements could be used as catalyst, exchanger and adsorbent of bulky molecules because of their tunable nanoscale pore opening and exceptionally high internal surface area suitable for the diffusion of bulky organic molecules from the catalytically active sites located inside the pores. Thus, increasing attention has been paid to mesoporous materials with high surface area and narrow pore size distribution because of their diverse applications (e.g., adsorbents, catalysts and host materials). Highly dispersed transition metal cations incorporated within the framework of zeolites and mesoporous molecular sieves have unique properties for catalytic reactions [4]. They are also useful for magnetic

and electrochemical applications [5,6]. To date, a wide-range of transition as well as non-transition elements have been incorporated in these silica-based mesostructures [4]. The incorporation of a trivalent heteroelement in the SiO₂ framework could generate a cation exchange or Brønsted acid site. The adsorptive and catalytic properties of the other trivalent metal analogs of these microporous and mesoporous metallo-silicates are usually different from their aluminum counterparts. Besides the modification of acidity, the presence of multivalent transition metal cations in the framework could also create isolated redox centers, which could be suitable for their application as heterogeneous oxidation catalyst in the presence of mild oxidants [7–14]. Crystalline microporous chromium-silicates [7,8] as well as amorphous mesoporous chromium-silicates [9–12] have been found to act as efficient catalysts for oxidation and isomerization reactions. Successful incorporation of Cr in the tetrahedral lattice site of mesoporous silica could be achieved through careful preparation of the synthesis gel and its subsequent hydrothermal treatment followed by careful calcinations to remove the structure directing surfactants. Here, we have shown that 4.6 wt% Cr could be incorporated successfully preserving the highly

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ordered mesoporous MCM-41 framework by using a simple hydrothermal method and avoiding the co-precipitation of chromium oxides during synthesis. Detailed characterizations of these two-dimensional (2D) hexagonal mesoporous Cr-MCM-41 materials were carried out using powder XRD, TEM, SEM-EDS, N₂ sorption, FT-IR and UV–vis diffuse reflectance measurements. These mesoporous materials have shown excellent catalytic activity in the liquid phase oxidation of cyclohexane and cyclooctane using peroxide oxidants.

2. Experimental

Tetraethyl ortho silicate (TEOS, E-Merck) was used as the silica source in all the syntheses. Cationic surfactant cetyltrimethylammonium bromide (CTAB, Loba Chemie) was used as the structure directing agent and chromium sulfate (Loba Chemie) was used as the chromium source. TMAOH (25% aqueous, Demi Chem) was used to maintain the pH of the medium. For the synthesis of mesoporous Cr-MCM-41 samples, initially TEOS was allowed to mix with an aqueous solution of CTAB and the mixture was stirred for 15 min. Then, the desired amount of Cr₂(SO₄)₃ dissolved in water was added onto this aged silica sol in different mole ratios corresponding to the loading of chromium. TEOS was then allowed to hydrolyze in mild acidic pH slowly. After 1 h, aqueous TMAOH solution was added into it until pH rose to ca. 11.0. 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

$$\text{SiO}_2 : \text{CTAB} : \text{TMAOH} : \text{Cr(III)} : \text{H}_2\text{O} \\ = 1 : 0.25 : (0.2\text{--}0.5) : (0.1\text{--}0.0125) : 90.$$

After the hydrothermal treatment, the solid products were filtered, washed with water and dried in air. The surfactant was removed from the as-synthesized mesoporous chromium-silicate through calcinations (heating rate 2 K min⁻¹) for 8 h at 773 K. As-synthesized samples (pale green in color) turned pale yellow after calcinations. The mesophases of the as-synthesized as well as template free samples were identified by small-angle powder XRD using a Seifert XRD 3000P diffractometer on which the small and wide-angle goniometers are mounted. X-ray source was Cu K α radiation ($\alpha = 0.15406$ nm) with a voltage and current of 40 kV and 20 mA, respectively, were used. For the trans-

mission electron microscopy measurement, Jeol JEM 2010 microscope operated at an accelerated voltage 200 kV was used. N₂ adsorption measurements were carried out using a Belsorp 28SA at 77 K. Prior to N₂ adsorption, samples were degassed for 2 h at 373 K. For the Fourier transform infrared (FT-IR) measurement, a Nicolet Magna IR 750 was used. The liquid phase reactions were performed in a magnetically stirred round-bottomed flask fitted with a condenser and placed in a temperature controlled oil bath. Typically, 0.01 mol of the substrate was dissolved in 10.0 ml acetonitrile (solvent), and to this was added the required amount of catalyst (20 wt% with respect to the substrate) and then the mixture was preheated to 353 K. The reaction started when the peroxide (H₂O₂ or *tert*-butyl hydroperoxide, TBHP) was added to the reaction mixture. The substrate:TBHP mole ratio was kept at 1.0 and 2.0 for different set of reactions. Samples of the reaction aliquots were taken at regular intervals and after cooling the filtrate the progress of the reaction was monitored by an Agilent 4890D gas chromatography (FID detector) fitted with a capillary column. 0.5 ml *n*-heptane was introduced to each of the reaction mixtures as internal standard before analysis.

3. Results and discussion

We have prepared mesoporous Cr-MCM-41 samples with Si:Cr mole ratios of 40:1, 20:1 and 10:1 in the synthesis gels. These samples have been designated as samples 1–3, respectively. Physico-chemical properties of various chromium-silicate samples synthesized in the present study are given in Table 1. Sample 4, pure silica MCM-41, was synthesized under otherwise identical synthesis conditions except the addition of Cr(III) precursor in the gel. Chemical analysis of these chromium-silicate samples after calcination revealed the absence of any organic SDA. AAS data showed that the Si:Cr mole ratios for samples 1–3 were 37.5, 17.7 and 15.2, respectively. An optimum incorporation of Cr for the ordered chromium-silicate mesophase was observed for sample 2 (4.6 wt% Cr). Increasing the chromium loading further in the gel resulted in (broadening of the XRD peak) poorly ordered mesoporous structure (sample 3).

XRD pattern of the different mesoporous samples 1–4 are shown in Fig. 1a–d. As seen in Fig. 1b–d, all four small-angle peaks of 1 0 0, 1 1 0, 2 0 0 and 2 1 0 planes, respectively, corresponding to the 2D hexagonal mesophase of MCM-41 [15]

Table 1
Physico-chemical properties of different samples^a

Sample number	Si:Cr mole ratio		Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)
	Gel	Product		
1	40	37.5	667	0.62
2	20	17.7	584	0.54
3	10	15.2	460	0.47
4	∞	–	970	0.76

^a Chemical analysis data obtained through a AAS analyzer and surface area and pore size distribution was obtained through N₂ adsorption measurements.

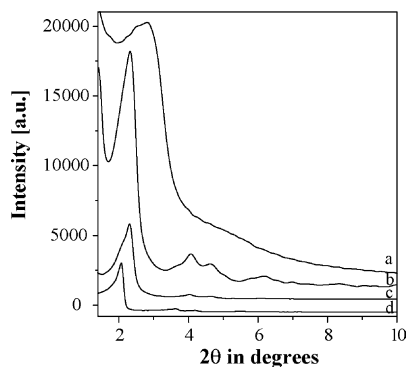


Fig. 1. XRD pattern of calcined sample 3 (a), sample 2 (b), sample 1 (c), and sample 4 (d).

was observed in samples 1, 2 and 4. No distinctive higher order peaks were observed in either of the samples. However, for sample 3, a single broad peak was observed. TEM images of these mesoporous chromium-silicate samples showed the existence of hexagonal arrangement of uniform mesopores (Fig. 2). These results suggested that this chromium-silicate material has highly ordered two-dimensional hexagonal mesophase. The peak positions remained almost unchanged after removal of the surfactant, although little change in the intensity was observed. Since there were no noticeable high angle reflections in the XRD patterns of these mesoporous chromium-silicate, the pore walls are amorphous in nature. No diffraction line corresponding to chromium oxide crystallites was observed in either of the samples synthesized using this method. This result suggested that the occluded chromium oxide species were not formed.

In Fig. 3, N_2 adsorption/desorption isotherms for Cr-containing mesoporous silica (sample 2, taken as representative) are shown. Pore size distribution for this sample is shown in the inset. Isotherms, as shown in Fig. 3, were type IV [15–17] in nature. Pore size distribution was very narrow and of relatively lower range vis-à-vis mesoporous materials synthesized using CTAB surfactant [15]. Average pore diameter for this mesoporous chromium-silicate sample based on the

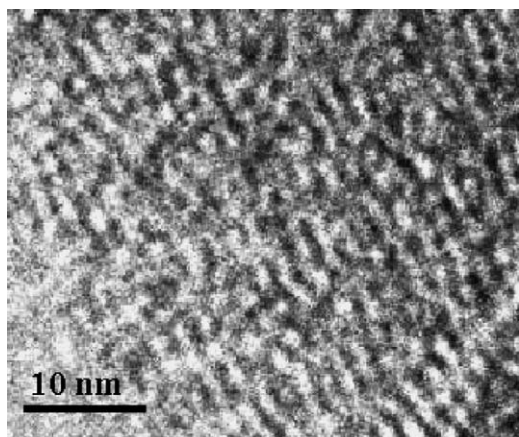


Fig. 2. TEM image of sample 2.

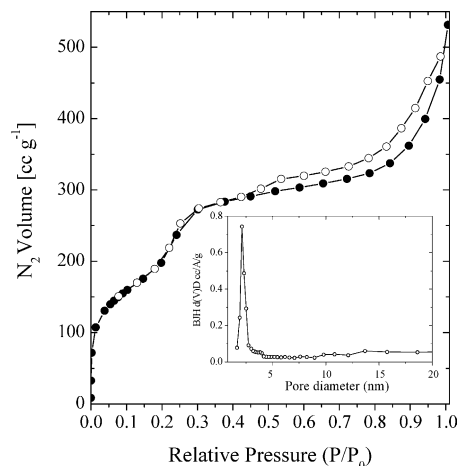


Fig. 3. N_2 adsorption/desorption isotherms of sample 2. Adsorption points are marked by filled circles, and that for desorption ones are by open circles. Pore size distribution has been shown in the inset.

BJH model was 2.1 nm. The adsorption/desorption isotherms and corresponding pore size distributions for other samples followed the same pattern. The BET surface areas of these mesoporous chromium-silicate were medium to high, considering moderately high concentration of chromium (667, 584 and $460 \text{ m}^2 \text{ g}^{-1}$, respectively, for samples 1–3). Pore diameters and d -spacings measured from TEM image analysis agreed well with these experimental data obtained from XRD and N_2 sorption.

In Fig. 4a–c, UV–vis diffuse reflectance spectra of mesoporous chromium-silicates (samples 1–3, respectively) are shown. The spectrum for bulk Cr_2O_3 is given in Fig. 4d for comparison. The UV–vis spectra of the chromium-silicate materials showed strong absorption band in the 200–620 nm wavelength with maxima at ca. 280, 370, 440, and 600 nm. A similar absorption band associated with $\text{O} \rightarrow \text{Cr}$ charge transfer has been observed for Cr-MCM-41 materials [18,19]. Bulk Cr_2O_3 showed a broad adsorption band in 220–400 nm and mild absorption maxima at 440 and 600 nm (Fig. 4d). Sample 3 with poorly ordered mesostructure also showed a weak shoulder around 440 and 600 nm different from that observed in the cases of highly ordered mesoporous

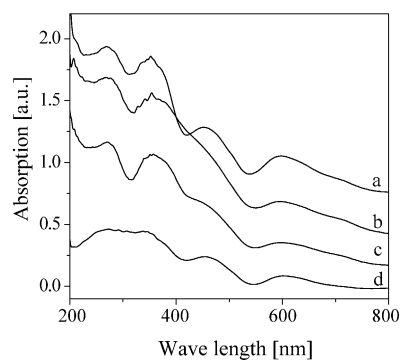


Fig. 4. UV–vis diffuse reflectance spectra of calcined mesoporous sample 3 (a), sample 2 (b), sample 1 (c) and Cr_2O_3 (d).

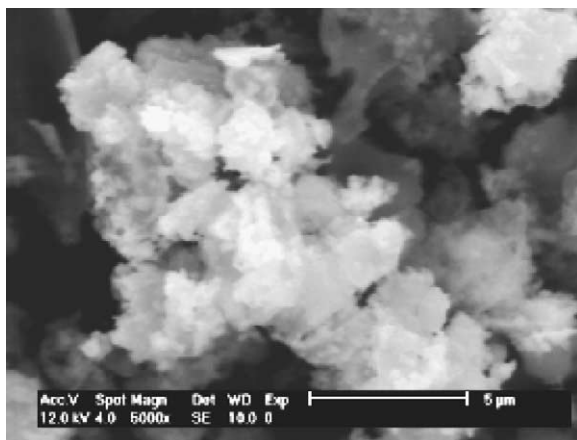


Fig. 5. SEM image of sample 2.

chromium-silicate samples 1 and 2. This result suggested that beyond 4.6 wt% loading of chromium some extra framework chromium oxide species start growing. Impregnation of the mesoporous silica samples with chromium species through template ion exchange also offered similar observations [19].

FT-IR spectra of the as-synthesized and surfactant free mesoporous chromium-silicate samples showed a broad band in the hydroxyl region between 3700 and 3000 cm^{-1} with maximum in the range 3400 – 3450 cm^{-1} . This band can be assigned due to the framework Si–O–H as well as Si(OH)Cr groups in interaction with the defect sites and adsorbed water molecules. Various C–H stretching vibrations due to the presence of the organic surfactant molecules, which appeared in the as-synthesized sample at 2925 and 2840 cm^{-1} disappeared after the removal of the surfactant. Si–O–Si and Si–O–Cr framework vibrations, which appear in the region 860 – 1400 cm^{-1} , became much narrower in the region of 900 – 1360 cm^{-1} after surfactant removal. In Fig. 5, SEM image of a representative mesoporous chromium-silicate sample is shown. Particle size was quite small (60 – 80 nm) and

uniform in nature. Uniform nanosize crystallites of transition metal-containing mesoporous materials are of special importance for their catalytic activity in liquid phase reactions.

Liquid crystal templating pathway for cationic surfactant micelles in aqueous solution are commonly employed for the synthesis of silica-based mesoporous materials. pH in such synthesis process can be varied widely, mild to strong alkaline (8.5 – 12.0) or strong acid (0.5 – 2.0) conditions. In the present case, silicon alkoxide was first hydrolyzed by very mild acidic chromium sulfate solution. This was followed by the condensation of silica and chromium species as the pH rose with the addition of aqueous TMAOH solution. The final pHs for the hydrothermal gels were kept between 10.8 and 11.0 , which helps the condensation of chromium-silicate nuclei rather than that between individual silicate and chromate moieties. The self-assembly of the surfactant-silicate mesostructure is largely dependent on the strong ionic interaction between surfactant micelles and inorganic metallo-silicate species. Beyond $4.6\text{ wt}\%$ loading of Cr in the metallo-silicate precursor gel, more local strain seemed to be created in the mesostructure leading to a poorly ordered mesophase (sample 3).

3.1. Catalysis

Chromium-containing mesoporous materials were used as catalysts for the oxidation of cyclohexane and cyclooctane using aqueous peroxides as oxidant. Oxidation of cyclohexane [20,21] and cyclooctane [22–24] has been achieved over different oxidants under critical reaction conditions. The conversion and the selectivity of different oxidized products over Cr-MCM-41 samples are listed in Table 2. As seen from the data, these Cr-MCM-41 materials exhibited good catalytic performance along with very high selectivity towards cycloalkanone product. Cyclohexanone and cyclooctanone was observed as the main product over all the catalysts. Minor amount of cyclohexanol and cyclooctene were ob-

Table 2

Oxidation of cyclooctane catalysed by Cr-MCM-41^a

Sample number	Reaction time (h)	Percent conversion of cycloalkanes ^b	Peroxide	Product selectivity (%)		TOF ^d (h ⁻¹)
				Cycloalkanone	Others ^c	
1	30	57.5	TBHP	93.5	6.5	2.00
2	24	84.0	TBHP	88.9	11.1	1.77
3	20	73.4	TBHP	82.2	17.8	1.61
2 ^e	20	94.4	TBHP	94.8	5.2	2.39
– ^f	30	0.8	TBHP	100.0	–	–
2	24	38.5	H ₂ O ₂	89.4	10.6	0.80
2	20	92.1	TBHP	95.0	5.0	3.05
2	14	37.2	H ₂ O ₂	85.3	14.7	1.75
1	18	34.0	H ₂ O ₂	90.4	9.6	2.60
– ^f	24	3.5	H ₂ O ₂	67.5	32.5	–

^a Solvent acetonitrile; catalyst = 20 wt% with respect to the substrate; substrate:TBHP = 1:1 unless otherwise mentioned.

^b For entries 1–6, substrate is cyclooctane; for entries 7–10, substrate is cyclohexane.

^c Others include mainly cycloalkenes and cycloalkanols.

^d Turn-over frequency is moles of cyclooctane converted per mole of Cr per h.

^e Substrate:TBHP = 2.0, conversion level is normalized to 100.

^f Blank reaction in absence of catalyst.

tained (Table 2). Peroxide selectivity was very high specially when TBHP was used as oxidant. The highest loading of Cr observed in these mesoporous materials has a Si:Cr mole ratio of 15.2 (sample 3) in the product. This sample shows relatively poor catalytic activity than sample 2 (Table 2). It was previously reported [23,24] that the activity of V- and Cr-silicate molecular sieves in liquid phase oxidation reactions was due to minor amounts of metal leaching out of the solid catalyst and being present in the reaction mixture. We have checked for any hypothetically leached Cr species under similar reaction conditions. We found no activity in the liquid phase alone after filtering out the catalyst from the reaction media. It is evident that no Cr species leached out of the catalyst and the reaction was stopped after catalyst removal. Thus, it can be concluded that the activity of the catalyst was due to the Cr active centers in the mesoporous silica framework as observed previously over other Cr-containing molecular sieves [12,25–28]. A blank reaction without any catalyst showed negligible conversion (Table 2, entry 5) indicating that the oxidation of cyclooctane is purely catalytic in nature.

4. Conclusions

Highly ordered mesoporous chromium-silicate Cr-MCM-41 materials have been synthesized using cationic surfactant as structure directing agent under mild hydrothermal condition and at weakly alkaline pH. Loading of chromium has been found to control the ordering of this mesophase, very high loading leading to disordered mesophase. N₂ adsorption measurements indicated medium to high BET-specific surface area, uniform mesopore opening and high pore volume in these samples synthesized by using the present hydrothermal method. UV–vis diffuse reflectance data indicated that the tetrahedral chromium species has been incorporated into the tetrahedral lattice site of silica. These mesoporous Cr-MCM-41 samples showed excellent catalytic activity in the liquid phase one-pot oxidation of cyclohexane and cyclooctane to cyclohexanone and cyclooctanone, respectively using TBHP and H₂O₂ as oxidant.

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