Novel mesoporous (Cr)MCM-48 molecular sieves: Promising heterogeneous catalysts for selective oxidation reactions

Sudhir E. Dapurkar,[a] Ayyamperumal Sakthivel[a] and Parasuraman Selvam*[ab]

[a] *Department of Chemistry, Indian Institute of Technology–Bombay, Powai, Mumbai 400 076, India. E-mail: selvam@iitb.ac.in*
[b] *New Industry Creation Hatchery Center, Tohoku University, Aoba-yama 04, Sendai 980 8579, Japan. E-mail: selvam@aki.che.tohoku.ac.jp*

Received (in Montpellier, France) 17th February 2003, Accepted 18th March 2003
First published as an Advance Article on the web 19th June 2003

A series of chromium-containing mesoporous MCM-48 molecular sieves, (Cr)MCM-48, with varying Si/Cr ($25-\infty$) ratios were synthesized hydrothermally, and characterized systematically by various analytical and spectroscopic techniques. The catalytic performance of the materials was evaluated for the oxidation reactions of certain industrially important organics such as ethylbenzene, cyclohexene and cyclohexane. For all the chosen reactions, the catalyst with a Si/Cr ratio of 50 showed very good conversion and excellent selectivity of the products. Furthermore, (Cr)MCM-48 exhibits much higher activity than the one-dimensional mesoporous (Cr)MCM-41 due to the incorporation of chromium ions in large concentrations as well as to the three-dimensional pore system of the former. Unlike many other chromium-based heterogeneous catalysts, the (Cr)MCM-48 showed only a slight decrease in catalytic activity during first recycling (or second run) experiments, and thereafter it remains nearly the same. Further, the quenching experiments as well as washing studies clearly support the above conclusion. In addition, it can also be deduced from several recycling, washing, filtrate and quenching studies that the leaching of the active chromium ions from the mesoporous matrix is minimal compared to almost all the chromium-based heterogeneous catalysts reported so far. The catalytic activity of (Cr)MCM-48 was also compared with various chromium-containing microporous silicalite-1 and beta, *i.e.*, (Cr)S-1 and (Cr)β, molecular sieves.

1. Introduction

Oxidation is a fundamental transformation in organic synthesis, and numerous methods are reported in the literature.[1–3] The selective oxidation of hydrocarbons is one of the main processes since the reaction products are either vital themselves or as intermediates in numerous industrial organic chemicals.[4–7] On the other hand, the oxidation products of cyclohexane, *viz.*, cyclohexanol and cyclohexanone, are key intermediates in the production of caprolactam (a monomer in the manufacture of nylon-6) and adipic acid (a building block for a number of polyamide fibers, *e.g.*, nylon-66, and polyurethane resins). While the oxidation of olefin into α,β-unsaturated ketone has been utilized in the synthesis and transformations of several natural products, the oxidation products of ethylbenzene and cyclohexene are widely employed as intermediates in organic, steroid, and resin syntheses. However, the selective oxidation of hydrocarbons is still a challenge to scientific community as they are currently oxidized by environmentally detrimental chromates and permanganates in stoichiometric amounts.[2,3] Hence, the development of catalytic methods involving clean oxidants for the selective oxidation of hydrocarbons is of great practical interest, besides the intrinsic importance of C–H activation chemistry. In the past, several attempts have been made on the selective oxidation of alkylaromatics and cycloalkanes as well as allylic oxidation using a variety of transition metal compounds either in stoichiometric amounts or in catalytic quantities (homogeneous) in combination with eco-friendly oxidants.[2,3,8–10] However, such established traditional processes generate solid/liquid wastes in alarming levels, the disposal of which poses a serious threat to the environment. Moreover, the use of such catalysts often causes inconvenience during reaction and work-up. Furthermore, these processes also lead to several other problems like difficulty in separation, recovery and recycling of the catalysts after reaction as well as the disposal of wastes, deactivation complications, *etc.*, which makes them highly unattractive.

Owing to the limitations of stoichiometric reagents/homogeneous catalysts, and in the wake of increasingly stringent environmental legislation, attention is being focused towards the design and development of greener processes such as heterogeneous catalytic oxidation. The inherent advantages of heterogeneous catalysis, which affords interesting opportunities for environmentally benign production of fine chemicals and pharmaceuticals, as well as the ever-increasing demand for some of these products has been the driving force for the change to environmental benign processes and technologies in chemical industry.[2,3,11–13] In particular, zeolite and clay materials have contributed significantly to the development of new methodologies in organic transformations to replace the conventional, waste-generating processes. In this regard, several chromium-based heterogeneous catalysts, *e.g.*, molecular sieves, pillared clays, supported systems and silica gels,[14–28] are found to be promising. Of the numerous available options, chromium-containing molecular sieve-based catalysts such as (Cr)Silicalite-1,[17,21] (Cr)APO-5,[21] (Cr)APO-11,[21] (Cr)SAPO-37,[26] (Cr)β,[20,24] (Cr)HMS,[18] (Cr)MCM-41,[18,19,22,23,27,28] *etc.* have shown potential for the selective oxidation reactions. However, in most cases, extreme reaction conditions in conjunction with low activity make the process highly undesirable. Moreover, the catalysts are often susceptible to solvolysis by polar molecules such as water, diols and acids present in oxidation mixtures resulting in extensive leaching of active species metal ions under the reaction conditions.[21,29,30] In addition, the catalysts are persistently deactivated by strong interaction of such polar solvents thereby preventing diffusion of the reactants to the active sites. It is, however, noteworthy here that we, recently, reported mesoporous (Cr)MCM-41 molecular sieves,[27,31–33] which show promise for a variety of industrially relevant transformations. Although (Cr)MCM-41 exhibits high activity under mild conditions, the catalyst, however, showed a considerable initial loss in activity due to leaching of non-framework chromium ions. Therefore, the development of highly efficient processes/catalysts that generates low amounts of residues/byproducts with good activity is one of the main challenges to the scientific community. Thus, realizing the importance of catalytic oxidation and the urgent need to develop stable chromium-based heterogeneous catalysts, in this investigation, an attempt was made to synthesize, characterize and explore the catalytic properties of mesoporous (Cr)MCM-48 molecular sieves. The catalytic activity was tested for the oxidation of cyclohexane, ethylbenzene and allylic oxidation of cyclohexene reactions. Further, performance as well as the resistance against leaching under various reaction conditions of (Cr)MCM-48 catalysts were evaluated in comparison with frequently reported mesoporous (Cr)MCM-41 as well as microporous (Cr)Silicalite-1, designated as (Cr)S-1, and (Cr)Beta, designated as (Cr)β catalysts.

2. Experimental

2.1 Starting materials

The following starting materials were used for the synthesis of (Cr)MCM-48. Cetyltrimethylammonium bromide (CTAB; Aldrich; 99%), tetraethyl orthosilicate (TEOS; Aldrich; 98%), chromium nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$; Alfa; 98.5%), sodium hydroxide (NaOH; Loba; 98%) were used as sources for template, silicon, chromium and alkali, respectively. In addition, Tetradecyltrimethyl ammonium (TDTMA; SISCO, 99%) bromide, tetrapropyl ammonium bromide (TPAB; Merck, 99%) and tetraethyl ammonium hydroxide (TEAOH; Aldrich, 35 wt%) were used as the templates for the synthesis of (Cr)MCM-41 and (Cr)S-1, and (Cr)β, respectively. Further, fumed silica (SiO_2; Aldrich, 99.8%) and sodium aluminate ($NaAlO_2$; EM Science, 39.9%) were used as the silica and aluminium sources for the synthesis of (Cr)MCM-41 and (Cr)β, respectively.

2.2 Synthesis

The mesoporous (Cr)MCM-48 materials were hydrothermally synthesized in Teflon-lined stainless steel autoclaves, as per the following procedure, with a typical molar gel composition of: SiO_2:0.25 (Na_2O):0.30 $(CTA)_2O$:62 H_2O:(0.0025–0.02) Cr_2O_3. Initially, an aqueous solution of CTAB (25 wt%) was added in NaOH and stirred for 30 min. A solution of chromium nitrate in water was added to TEOS and stirred for 20 min. The latter was added to the first mixture and stirred for another 30 min for homogenization. The resulting gel was subjected for hydrothermal treatment at 373 K for 8 days. The solid product obtained was washed, filtered and dried at 373 K for 12 h. The as-synthesized samples were calcined using a tubular furnace in an oxygen atmosphere at 823 K for 6 h. For a comparison, mesoporous (Cr)MCM-41[27,31] and microporous, (Cr)S-1,[17,21] and (Cr)β[20,24] catalysts were also synthesized hydrothermally as per the reported procedures with the following typical gel composition: (Cr)MCM-41–SiO_2:0.25 $(TDTMA)_2O$:0.25 Na_2O:45 H_2O:0.01 Cr_2O_3; (Cr)S-1–SiO_2:0.5 Na_2O:0.5 $(TPA)_2O$:100 H_2O:0.01 Cr_2O_3; and (Cr)β–SiO_2:0.037 Al_2O_3:0.435 $(TEA)_2O$:0.037 Na_2O:17.2 H_2O:0.012 Cr_2O_3. In addition, chromium-free siliceous MCM-41 and MCM-48 samples were also prepared and characterized as per the procedure outlined previously,[34] with typical gel (molar) compositions of: SiO_2:0.135 $(CTA)_2O$:0.075 $(TMA)_2O$:0.13 Na_2O:68 H_2O for the former, and SiO_2:0.3 $(CTA)_2$:0.25 Na_2O:60 H_2O for the latter. Unless otherwise stated, the catalysts used in the present investigation were with a silicon-to-chromium (molar) ratio of 50.

2.3 Characterization

All the samples were systematically characterized by various analytical and spectroscopic techniques. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku-miniflex diffractometer using a nickel filtered Cu–Kα radiation ($\lambda = 1.5418$ Å) and a step size of 0.02°. Transmission electron micrograph (TEM) was recorded on a Philips CM 200 microscope operated at 160 kV. Thermogravimetry/differential thermal analysis (TG/DTA) was performed using a Dupont 9900/2100 thermal analysis system under nitrogen atmosphere (50 ml min^{-1}) with a heating rate of 10 °C min^{-1}. Surface area analysis was performed on a Sorptomatic-1990 instrument. Before the measurement, the calcined sample was evacuated at 523 K for 12 h under vacuum (10^{-3} torr). The surface area and pore size were estimated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. The pore volume was determined from the amount of N_2 adsorbed at $P/P_o = 0.5$. Diffuse reflectance ultraviolet and visible (DRUV-VIS) spectra were recorded on UV-260 Shimadzu spectrophotometer with Whatman-40 filter paper as standard. Electron spin resonance (ESR; Varian E-112) spectra were recorded both at room temperature and liquid N_2 temperature. Inductively coupled plasma-atomic emission (ICP-AES; Labtam Plasma Lab 8440) analysis was used to detect the chromium concentration in the catalysts.

2.4 Reaction procedure

Ethylbenzene oxidation. The oxidation of ethylbenzene (8 mmol) was carried out using 70% TBHP (16 mmol) as oxidant in the presence of chlorobenzene (5 ml) as solvent using (Cr)MCM-48 as catalyst (50 mg) at 393 K for 12 h.

Cyclohexene oxidation. The oxidation of cyclohexene (8 mmol) was carried out using 70% TBHP (16 mmol) oxidant in the presence of chlorobenzene (5 ml) as solvent using catalysts (50 mg) at 393 K for 12 h. Prior to the reaction, cyclohexene was purified by washing with successive portions of dilute acidified ferrous sulfate solution followed by distilled water. It was then dried with $CaCl_2$ and distilled under nitrogen atmosphere.

Cyclohexane oxidation. The oxidation of cyclohexane (18 mmol) was carried out in the presence of methyl ethyl ketone (5 mmol) as initiator at 373 K for 12 h using 50 mg of the catalyst with H_2O_2 (18 mmol) as oxidant and acetic acid (10 ml) as solvent. After the reaction, the catalyst was separated and the products were extracted with ether. The separated catalysts were reactivated at 773 K for 6 h in oxygen atmosphere for recycling experiments.

2.5 Product analysis

After the reaction, the catalyst was separated and the reaction products were analyzed by gas chromatography (Nucon 5700) with SE-30 and carbowax column. This was further confirmed by combined gas chromatography-mass spectrometry (GC-MS, HEWLETT G1800A) with an HP-5 capillary column.

2.6 Washing studies

In order to remove the non-framework chromium ions present in the mesoporous matrix, the calcined samples were treated

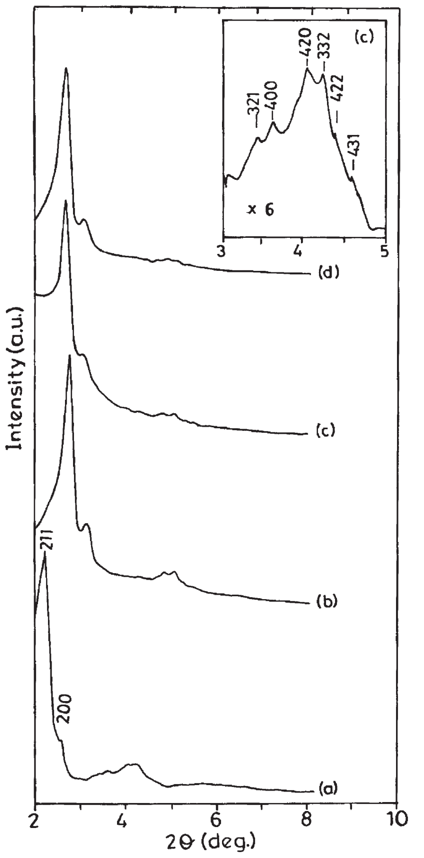

Fig. 1 XRD patterns of (Cr)MCM-48(50): (a) as-synthesized, (b) calcined, (c) washed and (d) recycled. Inset: XRD pattern of washed (Cr)MCM-48.

with ammonium acetate solution (1 M) as per the following procedure. About 100 mg of the catalyst was stirred with 30 ml of the solvent for 12 h at room temperature and filtered. This procedure was repeated a couple of times so as to ensure all the non-framework chromium ions were removed from the catalyst. In the final step, the catalyst was filtered, washed, dried at 373 K and recalcined at 773 K for 6 h in an oxygen atmosphere. The resulting sample is designated as (ammonium acetate) washed catalyst.

2.7 Recycling studies

The leaching of chromium ions (under reaction conditions) from the mesoporous matrix was also verified by carrying out several recycling experiments on both calcined and washed catalysts. The recycling experiments were carried out as follows. After the first reaction, the catalyst was recovered from the reaction mixture by filtration and washed with acetone. It was then dried and calcined at 823 K for 6 h in an oxygen atmosphere. The regenerated catalyst was used for further studies.

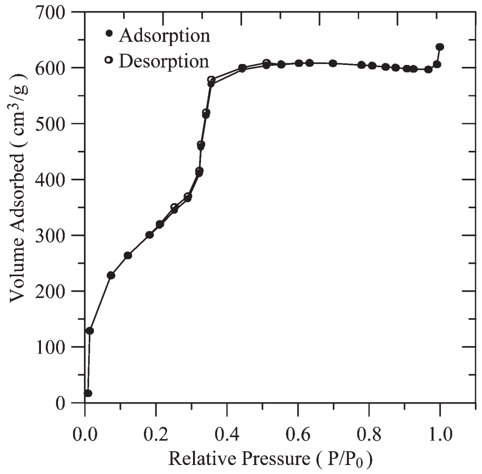

Fig. 2 N_2 adsorption–desorption isotherm of calcined (Cr)MCM-48.

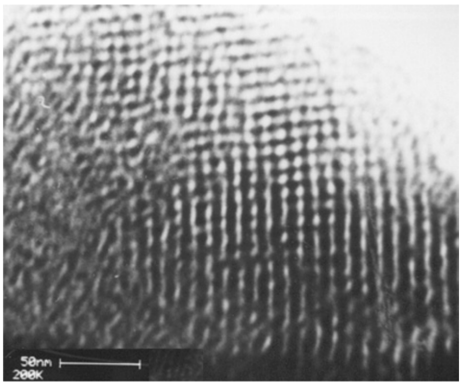

Fig. 3 TEM image of calcined (Cr)MCM-48.

2.8 Filtrate studies

The leaching behaviour of chromium ion can also be confirmed by the filtrate experiments, *i.e.*, by carrying out the reaction with the "filtrate solution" obtained from treating the calcined/washed catalyst with oxidant and solvent at room temperature (300 K). The ethylbenzene reaction was performed using this filtrate solution at 393 K for 12 h without any further addition of the oxidant.

2.9 Quenching studies

Since, it is well known from the work of Lempers and Sheldon[21] that there is a possibility of re-adsorption of leached (chromium) species onto the catalyst, and in order to avoid this problem, the reaction was followed using "quenched solution", which was obtained by separating the reactant mixture containing the catalyst, substrate, solvent and oxidant under the reaction temperature, 393 K for both ethylbenzene and cyclohexene, and 373 K for cyclohexane, after 2 h by filtration. The reaction was then continued as per the standard procedure on the quenched solution, and without any further addition of the oxidant.

3. Results and discussion

Fig. 1 shows the XRD patterns of various (Cr)MCM-48 samples, which are typical of mesoporous MCM-48 structure; all

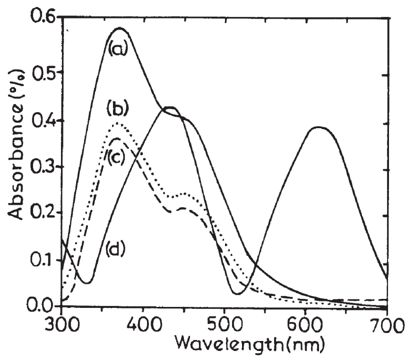

Fig. 4 DRUV-VIS spectra of spectra of (Cr)MCM-48: (a) calcined, (b) 1st recycled, (c) 2nd recycled, (d) as-synthesized.

Table 1 Oxidation of various organics over (Cr)MCM-48 molecular sieves

	Ethylbenzene[a]		Cyclohexene[a]		Cyclohexane[b]	
Catalyst	Conversion (wt%)	Acetophenone selectivity (wt%)	Conversion (wt%)	2-cyclohexen-1-one selectivity (wt%)	Conversion (wt%)	Cyclohexanol selectivity (wt%)
Calcined (Cr)MCM-48	76.3	85.9	67.4	82.9	97.1	98.8
• After 2 h	40.7	66.7	28.1	96.0	80.4	90.9
• Filtrate solution	(23.1)	89.4	—	—	—	—
• Quenched solution[c]	50.9 (10.2)	68.0	42.0 (13.9)	91.4	92.0 (11.6)	94.4
• 1st recycled catalyst	54.5	69.8	46.8	76.1	92.1	95.0
• 2nd recycled catalyst	47.4	67.5	35.9	75.5	91.9	93.9
Washed (Cr)MCM-48	47.1	73.6	33.2	73.7	90.2	95.9
• After 2 h	22.2	56.0	17.9	90.6	52.6	96.8
• Filtrate solution	(4.9)	49.7	(1.4)	74.1	(5.0)	94.3
• Quenched solution[c]	27.3 (5.1)	46.0	19.7 (1.8)	87.4	57.4 (4.8)	97.4
• 1st recycled catalyst	46.0	71.0	33.9	75.5	91.5	95.6
• 2nd recycled catalyst	45.2	68.9	36.1	79.9	89.8	92.8
MCM-48	4.3	61.0	3.7	51.1	10.9	95.1
No catalyst	4.7	60.0	2.7	41.6	9.0	78.1

[a] Reaction conditions: Substrate:Oxidant = 1:2; 5 ml chlorobenzene (solvent); Catalyst = 6 wt%; Temperature = 393 K; Time = 12 h. [b] Reaction conditions: Substrate:Oxidant = 1:1; 10 ml Acetic acid (solvent); Catalyst = 3.3 wt%; Temperature = 373 K; Time = 12 h. [c] Values in parenthesis indicate the conversion due to leached chromium.

the reflections were indexed on the basis of cubic symmetry.[34–36] Fig. 2 depicts the N_2 sorption isotherms of calcined (Cr)MCM-48, which follow type IV isotherm, characteristic of mesoporous materials. Further, they also exhibit high pore volume (0.88 $cm^3\ g^{-1}$), huge specific surface area (1140 $m^2\ g^{-1}$) and large pore diameter (30 Å). Fig. 3 illustrates the TEM image of calcined (Cr)MCM-48, which clearly indicates the good quality of the sample.[37] The TG of the calcined samples show a relatively small weight loss (5% for (Cr)MCM-48) as compared to its siliceous analogues (22% for MCM-48) suggesting that part of the silanol groups are consumed for stabilization of chromium ions in the matrix in a similar manner as reported for chromium oxide supported on silica matrix[38] as well as for (Cr)MCM-41.[31] The DTA shows the corresponding exothermic/endothermic transitions in accordance with the TG results.

The DRUV-VIS spectrum of as-synthesized sample (Fig. 4d) show absorption bands centering at 620 and 440 corresponding to trivalent chromium in octahedral coordination.[27,31,39–42] On the other hand, the calcined samples display a new prominent band (Fig. 4a) centering at 367 nm with a shoulder around 440 nm. They are assigned to charge transfer bands associated with chromate and/or polychromate type species.[27,31–33,39–42] As expected, the recycled catalysts (Fig. 4b and 4c) showed a decrease in absorption band intensities due to the removal of non-framework chromium ions under reaction conditions. The EPR spectra of as-synthesized samples (not reproduced here) depict a broad spectra ($g_{\text{eff}} = 1.98$) indicating the presence of trivalent chromium in octahedral coordination, while for the calcined samples a sharp signal at $g_{\text{eff}} = 1.97$ (not reproduced here) is noticed, which is characteristic of pentavalent chromium in tetrahedral coordination.[31,32,40–42]

Table 1 summarizes the oxidation results of ethylbenzene, cyclohexene, and cyclohexane over (Cr)MCM-48. It is clear from this table that the catalyst shows very good conversion for the substrates and excellent selectivity of the products. More importantly, the activity is much higher than (Cr)MCM-41 (Table 2) as well as many other chromium-based catalysts reported so far. However, as expected, a decrease in catalytic activity was observed in all cases upon recycling

Table 2 Oxidation of various organics over (Cr)MCM-41 molecular sieves

	Ethylbenzene[a]		Cyclohexene[a]		Cyclohexane[b]	
Catalyst	Conversion (wt%)	Acetophenone selectivity (wt%)	Conversion (wt%)	2-cyclohexen-1-one selectivity (wt%)	Conversion (wt%)	Cyclohexanol Selectivity(wt%)
Calcined (Cr)MCM-41	70.0	92.0	51.1	76.3	98.9	92.9
• After 2 h	26.9	93.0	17.9	89.4	71.3	91.6
• Filtrate solution	(20.9)	(92.0)	—	—	—	—
• Quenched solution[b]	55.0 (28.1)	87.0	29.5 (11.6)	74.5	85.5 (14.2)	94.6
• 1st recycled catalyst	43.0	94.0	41.8	68.5	75.1	95.3
• 2nd recycled catalyst	30.2	75.0	33.3	69.7	74.5	95.3
Washed (Cr)MCM-41	32.0	72.3	27.0	67.7	72.2	90.7
• After 2 h	15.0	71.0	12.1	90.6	42.1	89.4
• Filtrate solution	(5.1)	73.3	(1.5)	68.4	(4.7)	87.1
• Quenched solution[c]	17.3 (2.3)	79.0	13.4 (1.3)	79.1	48.6 (6.3)	83.3
• 1st recycled catalyst	30.3	75.5	25.7	69.0	73.6	93.3
• 2nd recycled catalyst	31.2	68.9	25.0	69.0	71.1	98.5
MCM-41	4.1	67.1	3.1	47.1	11.6	96.4
No catalyst	4.7	60.0	2.7	41.6	9.0	78.1

[a] Reaction conditions: Substrate:Oxidant = 1:2; 5 ml chlorobenzene (solvent); Catalyst = 6 wt%; Temperature = 393 K; Time = 12 h. [b] Reaction conditions: Substrate:Oxidant = 1:1; 10 ml Acetic acid (solvent); Catalyst = 3.3 wt%; Temperature = 373 K; Time = 12 h. [c] Values in parenthesis indicate the conversion due to leached chromium.

Table 3 Catalytic performance of various chromosilicate molecular sieves for the cyclohexane oxidation reaction[a]

	Conversion (wt%)			
Catalyst	1st run	2nd run	3rd run	4th run
(Cr)MCM-48	97.1	92.1	91.7	91.9
(Cr)MCM-41	98.9	72.1	72.2	72.8
(Cr)β	56.1	30.7	21.4	19.5
(Cr)S-1	44.8	28.5	22.1	20.6

[a] Reaction conditions: Substrate:Oxidant = 1:1; 10 ml Acetic acid (solvent); Catalyst = 3.3 wt%; Temperature = 373 K; Time = 12 h.

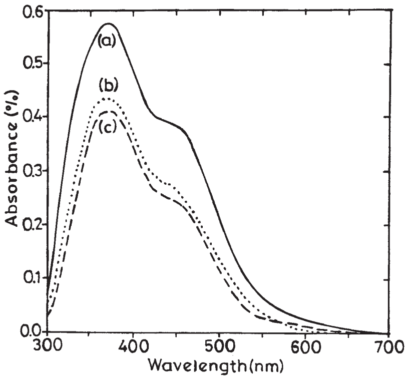

Fig. 5 DRUV-VIS spectra of (Cr)MCM-48: (a) calcined, (b) ammonium acetate washed, (c) recycled.

experiments, owing to the leaching of non-framework chromium ions from the matrix under the reaction conditions. This observation is in accordance with the DRUV-VIS studies where a change in the absorption intensities is noticed for the recycled samples (*see* Fig. 4). This is further confirmed by filtrate and quenching studies where the latter give typical conversion close to or slightly higher than that obtained from the former. The substantial activity of the filtrate solution is accounted for the leached chromium (homogeneous medium) while for the quenched solution, a combined effect of both heterogenous and homogeneous medium is responsible.

It is, however, important to note that unlike many other chromium-based microporous molecular sieve catalysts, *e.g.*, (Cr)S-1 and (Cr) β, which exhibit a significant loss in activity owing to a continuous leaching of active chromium ions from the matrix, the mesoporous materials losses the activity only in the 1st recycling (2nd run) experiments (Table 3). The observed leaching pattern of microporous materials is in good agreement with Sheldon and co-workers.[21,29,30] Furthermore, ICP-AES results unambiguously support the above observation where the absence and presence of chromium is noticed in the quenched solutions obtained from the recycled mesoporous and microporous catalysts, respectively. It is also to be noted here that DRUV-VIS studies of (Cr)MCM-48 show only a marginal change in the absorption band intensity for the 2nd recycled or 3rd run (see Fig. 4c). The results are further verified with (ammonium acetate) washed samples where the activity of the mesoporous catalysts remains nearly constant even after several recycling experiments (see Tables 1 and 2). This is in accordance with DRUV-VIS studies where the washed catalyst (Fig. 5b) shows nearly similar absorption intensities as that of the recycled catalyst (Fig. 5c), which markedly supports the above conjecture. In addition, ICP-AES results of filtrate and quenched solutions (washed catalyst) give no indication of the presence of chromium. Moreover, the reactions carried out over the quenched and filtrate solutions of the washed catalysts corroborate the above conclusion in that they show very low conversion, which is nearly the same as that obtained without the use of catalyst or in blank reactions (see Tables 1 and 2). Thus, the nearly unaltered (or marginally affected) catalytic activity after the first cycle or after washing experiments suggest that the leaching of the active chromium ions from the mesoporous matrix is minimal.

At this juncture, it is also worth noting that irrespective of the substrate molecules, the catalytic activity of (Cr)MCM-48 is always higher than (Cr)MCM-41. Furthermore, it is also interesting to note that even after various treatments, the (Cr)MCM-48 catalysts possess much higher chromium content than the corresponding (Cr)MCM-41 catalysts (*cf.* Tables 4 and 5). Thus, the superior performance of the former could be attributed to the three-dimensional pore system as well as to the stabilization of the larger amount of chromium in the former (0.98%) than in the latter (0.77%). It is also worth mentioning here that the (Cr)MCM-48 catalyst showed good structural stability (see Fig. 1d) even after (several runs) cycling experiments. Thus, the catalyst can very well be reused without affecting either the activity or the catalyst characteristics.

The oxidation of cyclohexane was also studied over both calcined and washed (Cr)MCM-48 with different silicon-to-chromium ratios and the results are presented in Table 4. It is clear from this table that the catalytic conversion increases with increase in chromium content, *i.e.*, from a Si/Cr ratio of 200 to 50. However, as expected, in all cases, a decrease in conversion was observed on washed catalysts due to leaching of non-framework chromium from the matrix. A similar observation was also made for (Cr)MCM-41 (see Table 5). Hence, all further experiments were carried out over washed catalysts. In order to check the influence of the various parameters on the reaction as well as for a detailed study, we have chosen cyclohexane as the substrate, and the reaction was performed with various catalyst amounts over (Cr)MCM-48(100). The results are shown in Fig. 6. It is clear from the figure that the conversion increases with increase in catalyst amount. However, at higher catalyst concentration there is a considerable decrease

Table 4 Oxidation of cyclohexane over various (Cr)MCM-48 molecular sieves[a]

	Calcined catalysts				Washed catalyst			
	Chromium content	Cyclohexane conversion	Selectivity (wt%)		Chromium content	Cyclohexane conversion	Selectivity (wt%)	
Catalyst[b]	(wt%)	(wt%)	Cyclohexanol	Cyclohexanone	(wt%)	(wt%)	Cyclohexanol	Cyclohexanone
(Cr)MCM-48 (25)	2.39	90.3	95.1	1.2	1.65	84.8	93.0	6.0
(Cr)MCM-48 (50)	1.58	97.1	98.8	1.0	0.98	90.2	95.9	3.7
(Cr)MCM-48 (100)	0.92	87.8	98.9	1.1	0.56	68.9	98.5	1.5
(Cr)MCM-48 (200)	0.45	64.4	98.7	1.3	0.28	47.1	99.0	1.0

[a] Reaction conditions: Substrate:Oxidant = 1:1; 10 ml Acetic acid (solvent); Catalyst = 3.3 wt%; Temperature = 373 K; Time = 12 h. [b] Number in parenthesis indicate the nominal Si/Cr molar ratio in synthesis gel.

Table 5 Oxidation of cyclohexane over (Cr)MCM-41 molecular sieve with different Si/Cr ratios[a]

	Calcined catalyst				Washed catalyst			
	Chromium content	Cyclohexane Conversion	Selectivity (%)		Chromium content	Cyclohexane Conversion	Selectivity (%)	
Catalyst[b]	(wt%)	(wt%)	Cyclohexanol	Cyclohexanone	(wt%)	(wt%)	Cyclohexanol	Cyclohexanone
(Cr)MCM-41 (25)	1.98	99.0	88.7	1.0	1.01	89.7	91.9	1.3
(Cr)MCM-41 (50)	1.23	98.9	92.9	0.3	0.77	72.2	90.7	1.4
(Cr)MCM-41 (100)	0.57	75.9	94.1	4.9	0.43	59.7	90.8	1.1
(Cr)MCM-41 (200)	0.27	62.2	94.1	5.7	0.21	47.3	90.5	0.8

[a] Reaction conditions: Substrate:Oxidant = 1:1; 10 ml Acetic acid (solvent); Catalyst = 3.3 wt%; Temperature = 373 K; Time = 12 h. [b] Number in parenthesis indicate the nominal Si/Cr molar ratio in synthesis gel.

in cyclohexanol selectivity owing to formation of cyclohexanone and a trace amount of ring oxidized product.

Fig. 7 presents the results of the oxidation of cyclohexene over (Cr)MCM-48 washed catalysts using chlorobenzene and methanol as solvents and different catalyst amounts. As described earlier,[9] the reaction is highly dependent on solvents, the use of polar solvents favours oxidation at the double bond, whereas the non-polar solvents leads to allylic oxidation. It can be seen from the figure that cyclohexene conversion as well as 2-cyclohexen-1-one selectivity is high with non-polar solvent, *viz.*, chlorobenzene. However, the use of polar solvents such as methanol, the conversion (cyclohexene) as well as 2-cyclohexen-1-one selectivity decreases and that cyclohexene oxide is obtained as the major product. Further, it can also be seen from this figure that, irrespective of the solvents used, the cyclohexene conversion increases as the catalyst amount is increased. However, the selectivity of the products displays a different pattern. That is, in the case of chlorobenzene, 2-cyclohexen-1-one was obtained as main product along with small amounts of cyclohexene oxide. Furthermore, 2-cyclohexen-1-one selectivity increases with increase in catalyst amount while the corresponding cyclohexene oxide selectivity decreases. This is in line with the earlier observation using homogeneous catalysts, *e.g.*, pyridinium chlorochromate.[3] On the other hand, at lower catalyst concentration and in presence of methanol; cyclohexene oxide was obtained as major product while at higher catalyst amount selectivity decreases at the cost of 2-cyclohexen-1-one. The formation of the latter could, however, be accounted for by the increase in catalyst amount, *vis-à-vis* higher chromium content in the sample.

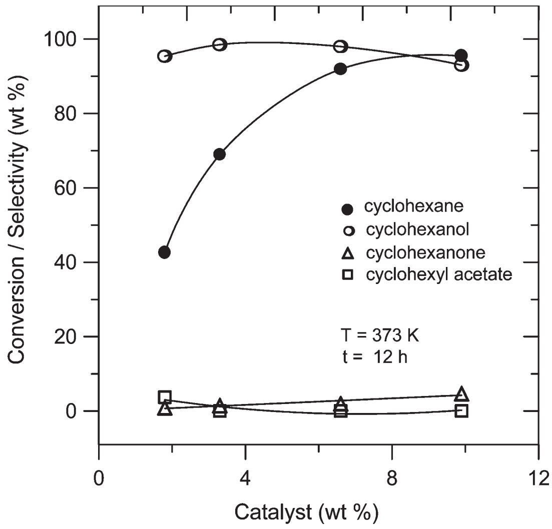

Fig. 6 Effect of catalyst amount on cyclohexane oxidation over washed (Cr)MCM-48 (100).

4. Conclusion

In summary, it is concluded from this investigation that the mesoporous (Cr)MCM-48 material functions as a promising heterogeneous catalyst for selective oxidation of various organics such as ethylbenzene, cyclohexene and cyclohexane with very high activity. Further, it is also demonstrated that large quantities of chromium can be incorporated and stabilized in MCM-48 matrix. Thus, the presence of a high amount of chromium in (Cr)MCM-48, besides the three-dimensional

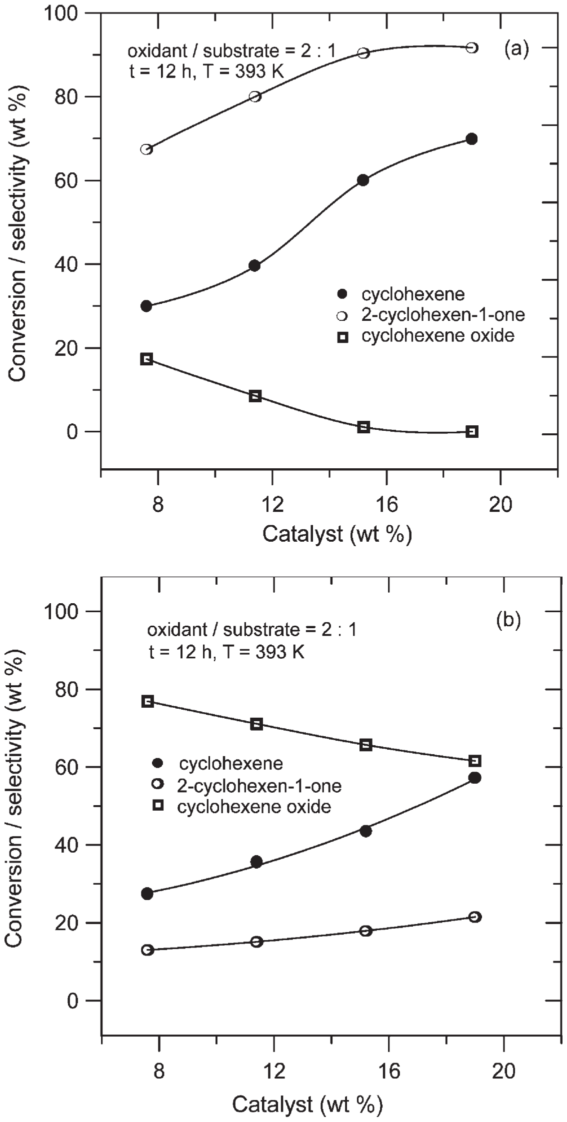

Fig. 7 Effect of catalyst amount as well as solvent on the oxidation of cyclohexene over (Cr)MCM-48: (a) chlorobenzene and (b) methanol.

pore structure characteristics, leads to the superior catalytic activity. Furthermore, it is also deduced from this study that the leaching of chromium is minimized markedly in both (Cr)MCM-48 and (Cr)MCM-41 under the reaction conditions, which is in contrast with many other chromium-based heterogeneous catalysts reported in the literature. Therefore, the mesoporous-based chromosilicate molecular sieves may show promise for oxidation reactions including those of bulkier molecules.

Acknowledgements

The authors thank the referees for valuable suggestions and critical comments, and Professor A. Miyamoto for kind support and encouragement. Thanks are also due to RSIC, IIT-Bombay for TG-DTA, EPR and GC-MS measurements.

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