

Mesoporous (Cr)MCM-41: A Mild and Efficient Heterogeneous Catalyst for Selective Oxidation of Cyclohexane

A. Sakthivel and P. Selvam¹

Department of Chemistry, Indian Institute of Technology—Bombay, Powai, Mumbai 400 076, India

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Liquid-phase oxidation of cyclohexane was carried out at moderate reaction conditions over mesoporous (Cr)MCM-41 molecular sieves using acetic acid as solvent, hydrogen peroxide as oxidant, and methyl ethyl ketone as initiator. Under these conditions, the catalysts showed high substrate conversion and excellent product selectivity. Although the activity of the catalyst decreased after the first recycle, owing to leaching of nonframework chromium ions, it, however, remained nearly the same thereafter. This observation was further confirmed by washing experiments where the nonframework chromium ions were removed upon ammonium acetate treatment or under reaction conditions. Further, the washed catalyst also showed a activity similar to that of the recycled catalyst. The recycled or washed (Cr)MCM-41, therefore, behaves truly as a heterogeneous catalyst, and thus it forms the first example of a nonleaching chromium-based catalyst reported so far. The use of a stronger oxidizing agent, e.g., tertiary butyl hydroperoxide, resulted in the formation of cyclohexanone as the major product. On the other hand, the use of solvents like methanol, dioxan, and acetone showed lower conversion. Likewise, the use of initiators such as acetone, cyclohexanone, and acetaldehyde also resulted in lower activity. © 2002 Elsevier Science (USA)

Key Words: cyclohexane; cyclohexanol; cyclohexanone; (Cr)MCM-41; oxidation; mesoporous molecular sieves.

INTRODUCTION

Selective oxidation reactions using heterogeneous catalysts are of growing importance for the modern chemical industry. The oxidation products of cyclohexane, viz., cyclohexanol and cyclohexanone, are important intermediates in the production of adipic acid and caprolactam, which are used in the manufacture of nylon-6 and nylon-66 polymers (1–4). In addition, they are also used as solvents for lacquers, shellacs, and varnishes as well as stabilizers and homogenizers for soaps and synthetic detergent emulsions. Furthermore, cyclohexanol ester, viz., cyclohexyl phthalate, is widely used as a plasticizer as well as in the surface-coating industry. Other uses of cyclohexanone are as starting material in the synthesis of insecticides, herbicides, and pharmaceuticals. In general, both cyclohexanol and cyclohexanone

are produced on an industrial scale by the oxidation of cyclohexane or hydrogenation of phenol (1–5). In the early 1940s, Du Pont developed a process in which cyclohexane was oxidized in the presence of air to cyclohexanol and cyclohexanone using cobalt naphthenate or cobalt acetate as catalyst (1, 4). In this process, several by-products, viz., mono- and dicarboxylic acids, esters, aldehydes, ketones, and other oxygenated materials, were generated. Later, in the 1950s, Scientific Design (now Halcon International) developed a new process where anhydrous meta-boric acid was added as a slurry in the oxidation vessel. This led to the formation of borate ester of cyclohexanol (3, 5), which prevents over oxidation (ring-opening products). The resulting cyclohexyl ester is subsequently hydrolyzed to cyclohexanol. In comparison to the former, the latter process showed good yield of cyclohexanol, which, however, requires high investment and a high operating cost to recover and recycle the boric acid.

On the other hand, for the laboratory-scale reaction extensive literature is available on the selective oxidation of cyclohexane using a variety of transition metal compounds in stoichiometric amounts or as homogeneous catalysts (6–15). In the cases of the latter, the use of initiators, e.g., cyclohexanone (3), cyclohexylperoxide (3), methyl ethyl ketone (10), and acetaldehyde (16), shortens the induction period as well as enhances the catalytic activity. However, owing to the limitations of these soluble (homogeneous) catalysts, viz., catalyst separation from the product and the disposal of solid/liquid wastes, which pose serious problems to the environment, in recent years attention has been focused on the development of transition metal-based heterogeneous catalysts with oxygen or peroxides as nonpolluting oxidants (6, 7, 17–25). However, in most cases, extreme reaction conditions such as high pressure (2 MPa) and high temperature (450 K) in conjunction with low activity make the process less attractive. In addition, leaching of active metal ions has often been observed under the reaction conditions (20, 25, 26). Hence, the oxidation of cyclohexane over heterogeneous catalysts under mild/moderate conditions is a topic of great interest. In this regard, chromium-containing mesoporous MCM-41 molecular sieves show promise for certain oxidation reactions (21, 27–30). In

¹ To whom correspondence should be addressed. Fax: +91-22-576-7152/572-3480. E-mail: selvam@iitb.ac.in.

particular, unlike many other systems based on microporous molecular sieves (26, 31, 32) and pillared clays (33, 34), the mesoporous molecular sieves stabilize chromium ions in the matrix, designated (Cr)MCM-41 (29, 30); thus they can act as true heterogeneous catalysts. Therefore, in this investigation, an attempt was made to explore the catalytic activity of mesoporous (Cr)MCM-41 molecular sieves for the titled reaction.

EXPERIMENTAL

Starting Materials

The following chemicals were employed for the preparation of (Cr)MCM-41: tetraethyl orthosilicate (TEOS; Aldrich, 98%), chromium nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; Alfa, 98.5%), tetradecyltrimethylammonium bromide (TDTMAB; SISCO, 99%), and sodium hydroxide (NaOH; Loba, 98%) as sources for silicon, chromium, surfactant, and alkali, respectively. Cyclohexane (Merck, 99.5%), hydrogen peroxide (H_2O_2 ; Qualigens, 30%), tertiary butylhydroperoxide (TBHP; Lancaster, 70%), acetic acid (Fischer, 99.5%), methyl ethyl ketone (MEK; SD Fine Chemicals, 99%), cyclohexanone (Merck, 99%), acetone (SD Fine Chemicals, 99.5%), and acetaldehyde (SD Fine Chemicals, 30%) were used for (liquid phase) cyclohexane oxidation reactions. Authentic samples of cyclohexanol (SD Fine Chemicals, 98%) and cyclohexanone (Merck, 99%) were used for comparative analysis of the reaction products.

Synthesis

The (Cr)MCM-41 molecular sieves were hydrothermally synthesized in a Teflon-lined stainless-steel autoclave at 373 K for 24 h with a typical molar gel composition of $1 \text{ SiO}_2 : 0.25 (\text{TDTMA})_2\text{O} : 0.25 \text{ Na}_2\text{O} : 45 \text{ H}_2\text{O} : x \text{ Cr}_2\text{O}_3$ (where $x = 0.0025\text{--}0.02$ with a Si/Cr ratio of 25–200) according to a procedure outlined previously (30). The as-synthesized (Cr)MCM-41 was calcined at 823 K and 6 h in oxygen atmosphere, referred to as calcined (Cr)MCM-41. Since the calcined samples contain a certain amount of nonframework chromium ions (29, 30), they were further treated with ammonium acetate solution (1 M). The resulting sample was designated washed (Cr)MCM-41. For a comparison chromium-grafted MCM-41 (Si/Cr = 50), designated (Cr)MCM-41_(grafted), and (siliceous) MCM-41 were also synthesized and calcined as per the procedure described earlier (35, 36). Further, the microporous analogues, such as (Cr)silicalite-1, (Cr)APO-5, and (Cr)zeolite- β , were also prepared for comparison as per the literature procedure (26, 32).

Characterization

The as-synthesized, calcined, and washed (Cr)MCM-41 as well as the MCM-41 samples were characterized sys-

tematically by powder X-ray diffraction (XRD; Miniflex–Rigaku), Brunauer, Emmett, and Teller (BET) surface area (Smartsorp 90), simultaneous thermogravimetry–differential thermal analysis (TG–DTA; Shimadzu DT-30), electron paramagnetic resonance (EPR; Varian E-112), and diffuse reflectance ultraviolet–visible (DRUV–vis; UV-260 Shimadzu) spectroscopic techniques. The chromium content in the samples was determined by inductively coupled plasma–atomic emission spectroscopy (ICP–AES) on Labtam Plasma Lab 8440 equipment after the sample was dissolved in HF/HNO_3 .

Reaction Procedure

The oxidation of cyclohexane (18 mmol) was carried out in the presence of an initiator (5 mmol) under atmospheric pressure at 373 K for 12 h using 50 mg of calcined or washed (Cr)MCM-41 catalyst with 18 mmol of oxidant and 10 ml of solvent. After the reaction, the catalyst was separated and the products were extracted with ether and analyzed by gas chromatography (Nucon 5700) with carbowax column. The filtered catalysts were reactivated in oxygen atmosphere at 773 K for 6 h for recycling experiments. The reaction was also carried out using solvents such as methanol, 1,4-dioxan, and acetone under the same reaction conditions. Furthermore, the influence of different initiators, e.g., cyclohexanone, acetaldehyde, and acetone, as well as the effect of various oxidants, viz., air, oxygen, H_2O_2 , and TBHP, on the reaction was also investigated.

RESULTS AND DISCUSSION

The XRD patterns of as-synthesized, calcined, washed, and recycled (Cr)MCM-41 (Fig. 1) showed the reflections, viz., 100, 110, 200, and 200, which are typical characteristics of mesoporous (hexagonal) MCM-41 structure (37, 38). Table 1 summarizes the average unit cell parameter, a_0 , of (Cr)MCM-41 with different Si/Cr ratios. In general, the incorporation of a larger cation, such as Cr(III) (0.76 Å),

TABLE 1
XRD and ICP–AES Data of (Cr)MCM-41 with Different Chromium Content

Sample ^a	XRD ^b a_0 (Å)	ICP–AES ^c	
		Si/Cr (molar ratio)	Chromium content (wt%)
(Cr)MCM-41(200)	41.93	392	0.27
(Cr)MCM-41(100)	43.59	194	0.57
(Cr)MCM-41(50)	44.42	112	1.23
(Cr)MCM-41(25)	45.51	46	1.98

^a Numbers in parentheses indicate the nominal Si/Cr ratios.

^b As-synthesized samples.

^c Calcined samples.

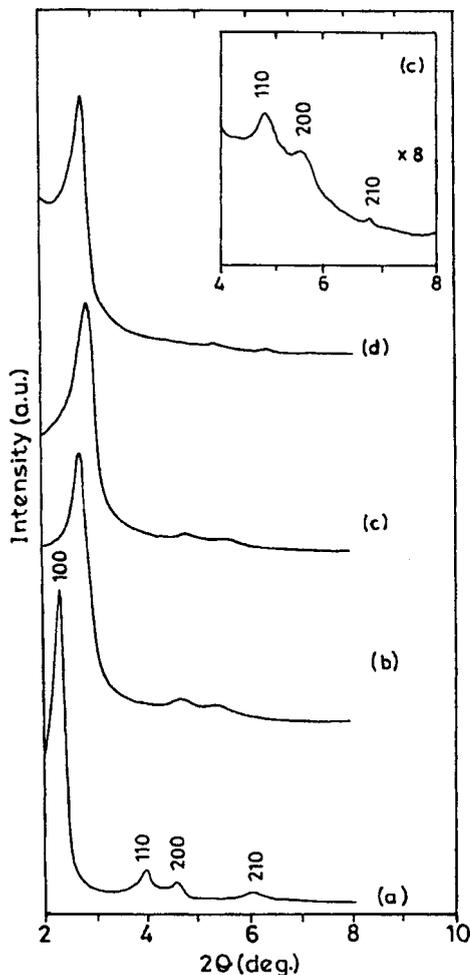


FIG. 1. XRD patterns of (Cr)MCM-41: (a) as-synthesized, (b) calcined, (c) washed, and (d) recycled.

in tetrahedral geometry for Si(IV) (0.40 Å) is expected to increase to a significant extent the lattice parameter. However, as can be seen from Table 1, only a small increase in the lattice constant is noticed. This indicates, that there is no appreciable incorporation of chromium into the mesoporous matrix. However, the observed slight expansion in a_0 values and shifting of the reflections to the lower 2θ values (higher d values) can be explained by filling the pores with chromium species, which slightly deform in the matrix. This effect has also been observed for a mesoporous matrix filled with InP (39) and CdS (40) particles. Unless otherwise stated, the catalyst used in the present study was (Cr)MCM-41 with Si/Cr = 50. Table 2 lists a_0 values of various forms of a (Cr)MCM-41 sample synthesized with a Si/Cr (molar) ratio of 50. The decrease in a_0 values for the calcined samples compared to the as-synthesized samples could be attributed to the shrinkage of the lattice as a consequence of the removal of template molecules. However, a slight decrease of the a_0 values for the washed and recycled samples could be due to reversal of the deformed matrix as

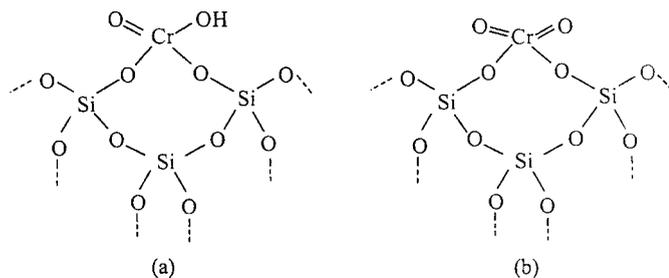
TABLE 2

XRD and ICP-AES Data of Various (Cr)MCM-41

Sample	XRD a_0 (Å)	ICP-AES	
		Si/Cr (molar ratio)	Chromium content (wt%)
Calcined (Cr)MCM-41	37.22	112	1.23
Recycled (Cr)MCM-41	36.70	161	0.76
Washed (Cr)MCM-41	36.04	157	0.77

a consequence of the removal of nonframework chromium ions from the mesopores (39, 40). However, the diffraction patterns (Fig. 1) remain nearly the same even after the recycling experiment or washing treatment, indicating the intactness of the structure.

All the as-synthesized (Cr)MCM-41 samples were green in color and changed to yellow upon calcination. The former is due to the presence of trivalent chromium ions in octahedral geometry and the latter is due to higher valent chromium ions, viz., chromate and/or polychromate ions, in the tetrahedral environment. The BET surface area ($1066 \text{ m}^2 \text{ g}^{-1}$) of the calcined sample and TG (45 wt% loss) of the as-synthesized sample further support the mesoporous nature of (Cr)MCM-41. TG of calcined (Cr)MCM-41 (41) showed a relatively small weight loss (10 wt%) compared to siliceous MCM-41 (18 wt%), which suggests that part of the silanol groups in the siliceous matrix may possibly be consumed for stabilization of chromium ions (Scheme 1) in a manner similar to that reported for chromium oxide supported on a silica matrix (42). Further ^{29}Si MAS-NMR studies showed distinct signals at -111 and -100 ppm (43), which are assigned to Q_4 and Q_3 (silicon) sites, respectively (44). However, the Q_3 site ($\equiv\text{Si}-\text{OH}$) is considerably reduced for (Cr)MCM-41 compared to siliceous MCM-41, which clearly supports the stabilization of chromium ions *via* silanol groups (defect sites). The estimated (ICP-AES) chromium content in various (Cr)MCM-41 samples is shown in Table 1. It is clear from this table that the samples show a considerable decrease in chromium content compared to that of the initial gel composition. The loss in chromium could however be



SCHEME 1

accounted for by the presence of soluble chromium hydroxide in the mother liquor of the as-synthesized samples. On the other hand, the washed sample (see Table 2) shows a further loss of chromium owing to the removal of nonframework chromium ions from the matrix. Interestingly, unlike many other chromium-based microporous molecular sieves (26, 31, 32), the chromium content in the (Cr)MCM-41 remains nearly the same even after recycling experiments (cf., Table 2), which suggests that there is no further leaching of chromium under the reaction conditions.

The DRUV-vis spectra of as-synthesized (Cr)MCM-41 showed typical absorption bands (29, 41) at ~ 642 , 445, and 290 nm, corresponding to ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$, and ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ transitions, respectively, typical of trivalent chromium in octahedral coordination (45, 46). On the other hand, the calcined, washed, and recycled samples (Fig. 2) show strong charge-transfer (oxygen to chromium) bands at 375 nm ($1t_1 \rightarrow 2e$ symmetry allowed) along with a weak shoulder at 445 nm ($1t_1 \rightarrow 2e$ symmetry forbidden) and a very weak shoulder at 322 nm ($1t_1 \rightarrow 2e$ symmetry forbidden) (see Fig. 2 inset) assigned to chromate, polychromate, and dichromate species, respectively (45, 46). The EPR spectra of as-synthesized (Cr)MCM-41 showed a broad spectrum with $g_{\text{eff}} \sim 1.98$ (41), indicating the presence of trivalent chromium in octahedral coordination, while for the calcined samples a sharp signal at $g_{\text{eff}} = 1.97$ was observed (Fig. 3), which is characteristic of pentavalent chromium in tetrahedral coordination (see also Scheme 1). The results are in good agreement with literature, where chromium is present as both Cr(V) and Cr(VI) species (45, 46). On the other hand, the EPR signal for washed and recycled catalysts samples is about two to two and a half times higher than the calcined samples owing to change in coordination of chromium species upon various treatments (47).

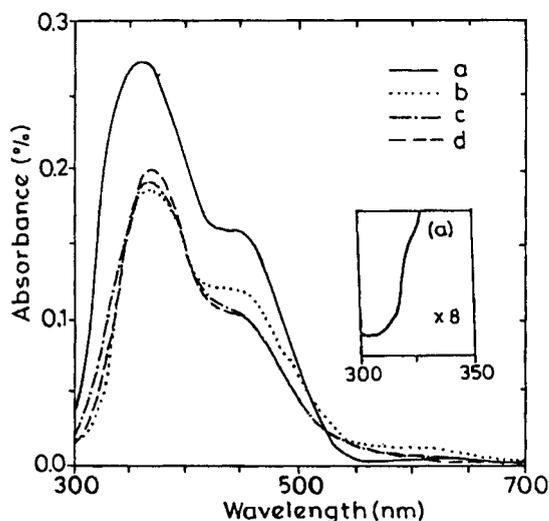


FIG. 2. DRUV-vis spectra of (Cr)MCM-41: (a) calcined, (b) recycled, (c) washed, and (d) washed and recycled.

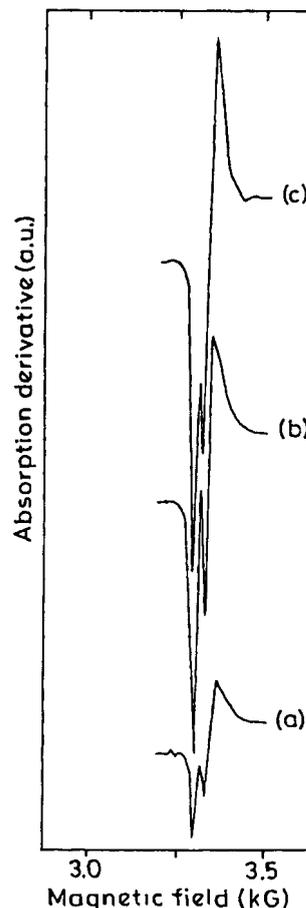


FIG. 3. EPR spectra of (Cr)MCM-41: (a) calcined, (b) first recycled, and (c) washed.

Figure 4 depicts the effect of reaction time over calcined (Cr)MCM-41. It can be seen from the figure that the (cyclohexane) conversion increases with time, while the (cyclohexanol) selectivity decreases. At the initial stages, a small amount of cyclohexyl acetate was observed along with cyclohexanol. However, as the time proceeds a slight decrease in cyclohexanol selectivity is noticed, with a corresponding increase in both cyclohexyl acetate and cyclohexanone selectivity. The formation of the latter, however, could be attributed to secondary oxidation of cyclohexanol. The formation of cyclohexyl acetate at a higher reaction time could be due to a possible termination reaction between unreacted cyclohexyl and acetoxy radicals. Figure 5 shows the influence of reaction temperature, and it is clear from the figure that both the substrate conversion and the product selectivity increase with reaction temperature. At higher reaction temperature (383 K), the activity decreases, owing to a possible decomposition of H_2O_2 (6) as well as to the formation of cyclohexyl acetate by interaction of a cyclohexyl radical and an acetoxy radical. At lower temperature, the cyclohexanol selectivity decreases due to incomplete hydrolysis of cyclohexyl acetate. Figure 6 shows the effect of chromium content on the reaction. It can be seen from

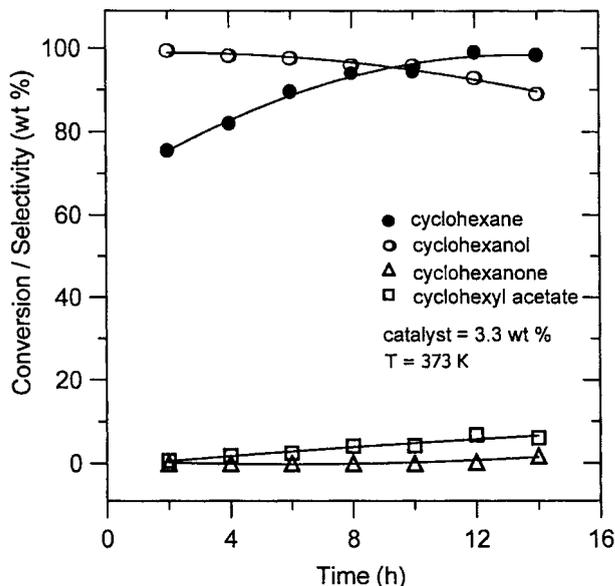


FIG. 4. Effect of reaction time on the conversion and selectivity over (Cr)MCM-41.

the figure that cyclohexane conversion increases with an increase in chromium content and remains constant at a Si/Cr of 50. However, the cyclohexanol selectivity decreases for Si/Cr = 25 due to the presence of more chromium, which favors the formation of ring oxidized products such as hexanoic acid and heptanal. This is further supported by reaction over a homogeneous catalyst (CrO_3) where the increase in catalyst amount (from 3 to 5 wt%) leads to considerable amount of ring-oxidized products (from 0.7 to 4.4 wt%).

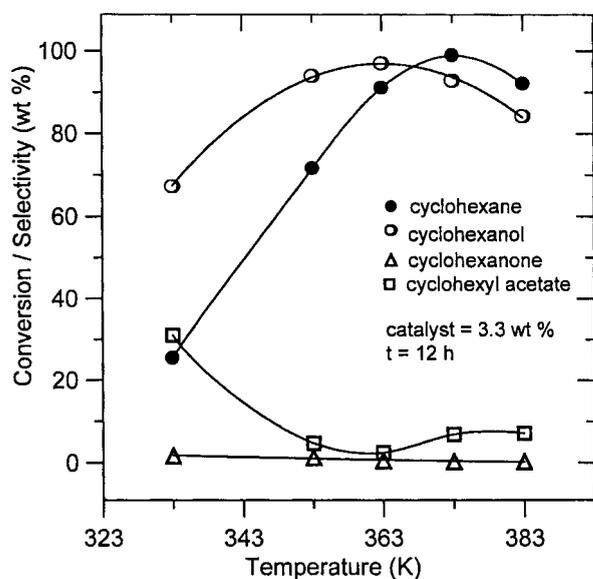


FIG. 5. Effect of reaction temperature on the conversion and selectivity over (Cr)MCM-41.

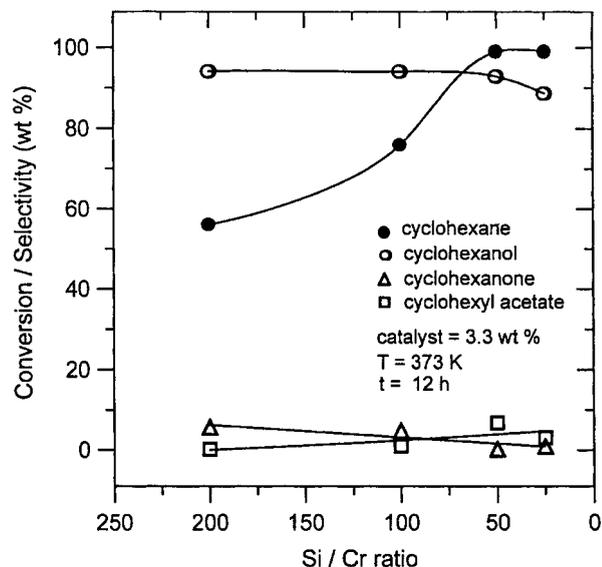


FIG. 6. Effect of Si/Cr ratio on the conversion and selectivity over (Cr)MCM-41.

Table 3 presents the result of oxidation of cyclohexane over various (Cr)MCM-41 catalysts under optimized experimental conditions. In all cases, cyclohexanol was obtained as the major product, and only a small amount of other products, viz., cyclohexanone and cyclohexyl acetate, were identified. It can also be seen from this table that the calcined catalyst showed high activity while a considerable decrease in activity was noticed, the first time, for the recycled samples, owing to leaching of active (nonframework) chromium ions under the reaction conditions. On the other hand, the activity remained nearly the same in the subsequent cycles. The lower conversion during recycling experiments could, however, be attributed to lower chromium content (0.76 wt%) as well as to the presence of more pentavalent chromium ions in the matrix (see Fig. 3). It is interesting that the washed catalyst (0.77 wt%) also showed a result similar to that of the recycled (Cr)MCM-41. Further, recycling of both cycled and washed catalysts does not affect the reaction any further; thus the catalyst behaves truly as heterogeneous. This observation of the loss of chromium content upon recycling/washing treatments is well supported by DRUV-vis studies, where the initial decrease in the absorption band intensity was noted for the calcined (Cr)MCM-41 (Fig. 2a). However, spectra remain nearly the same for the washed and recycled samples (Figs. 2b–2d). Further, the results are corroborated by the filtrate as well as by the quenching studies carried out on washed catalysts (see Table 3). In addition, the ICP-AES data (see Table 2) are in line with the above findings. The cyclohexane reaction was also carried out on catalyst containing Si/Cr = 25 (1.98 wt% chromium), which showed very high conversion (Table 3). The activity remained high even after the cycling and/or washing treatments (1.07 wt%).

TABLE 3
Oxidation of Cyclohexane over (Cr)MCM-41^a

Catalyst	Conversion (wt%)	Selectivity (%)			
		Cyclohexanone	Cyclohexanol	Cyclohexyl acetate	Others ^b
Calcined (Cr)MCM-41	98.9	0.3	92.9	6.8	—
First recycle	72.1	0.6	95.3	4.1	—
Second recycle	74.5	0.8	95.3	3.9	—
Washed (Cr)MCM-41	72.2	1.4	90.7	7.9	—
First recycle	74.6	—	93.3	6.7	—
Second recycle	71.1	0.5	98.5	1.0	—
Filtrate solution	5.4	—	80.1	19.9	—
Quenched solution	6.3	—	83.3	16.7	—
Calcined (Cr)MCM-41 ^c	99.0	1.0	88.7	3.1	7.2
First recycle ^c	90.1	1.7	91.7	3.7	2.9
Washed (Cr)MCM-41 ^c	89.7	1.3	91.9	4.3	2.5
Calcined (Cr)MCM-41 ^d	11.3	0.7	85.6	10.9	2.8
MCM-41	11.6	—	96.4	3.6	—
No catalyst	9.0	—	78.1	21.9	—

^a Reaction conditions: substrate:oxidant (H₂O₂) = 1:1; catalyst = 3.3 wt%; temperature = 373 K; and time = 12 h.

^b Hexanoic acid, cyclohexene, and heptanal.

^c Catalyst with Si/Cr = 25.

^d Without initiator.

Further, the reaction was carried out in the absence of catalyst or initiator or with chromium-free MCM-41. In all cases, a low conversion (see Table 2) was noted. Thus, it is clear from all these studies that the amount of chromium ions present in the mesoporous matrix plays an important role in the reaction.

The reaction was also carried out (48) over (Cr)MCM-41_(grafted), (Cr)zeolite- β , (Cr)silicalite-1, and (Cr)APO-5,

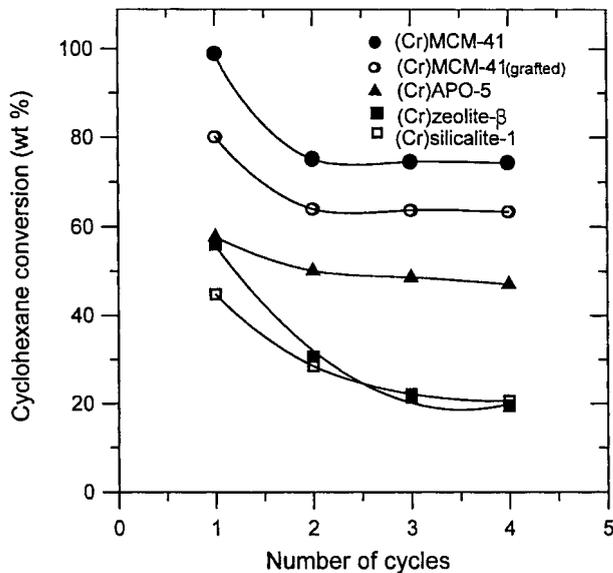


FIG. 7. Oxidation of cyclohexane over various chromium-containing molecular sieves.

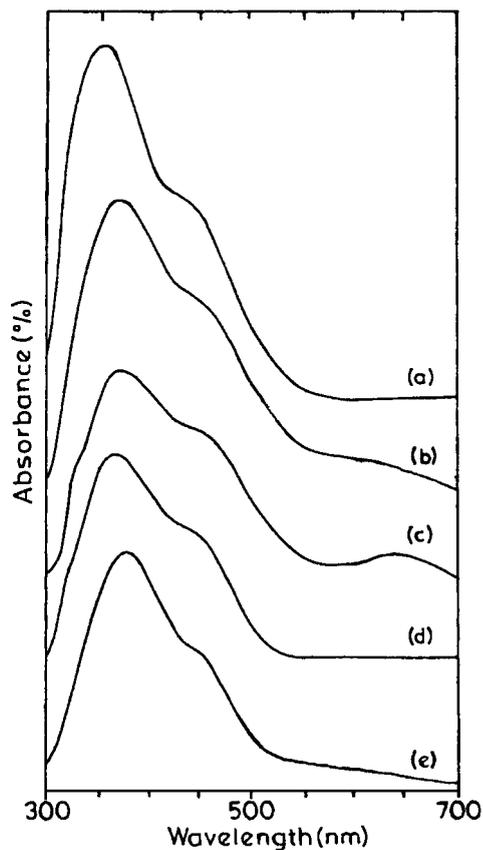


FIG. 8. DRUV-vis spectra of (a) (Cr)MCM-41, (b) (Cr)MCM-41_(grafted), (c) (Cr)APO-5, (d) (Cr)zeolite- β , and (e) (Cr)silicalite-1.

TABLE 4
Influence of Initiators on the Oxidation of Cyclohexane^a

Initiator	Conversion (wt%)	Selectivity (%)			
		Cyclohexanone	Cyclohexanol	Cyclohexyl acetate	Others ^b
MEK	98.9	0.3	92.9	6.8	—
Cyclohexanone	67.0	31.3	62.5	1.5	4.7
Acetone	64.6	32.1	64.1	2.8	1.0
Acetaldehyde	45.9	9.7	88.5	1.4	0.4

^a Reaction conditions: substrate : oxidant (H₂O₂) = 1 : 1; catalyst = 3.3 wt%; temperature = 373 K; and time = 12 h.

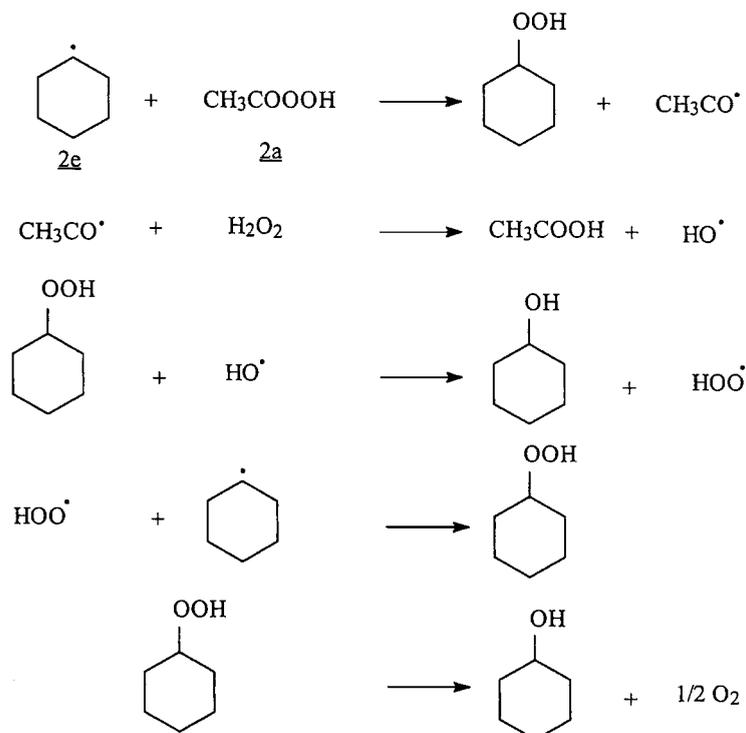
^b Hexanoic acid and cyclohexene.

TABLE 5
Oxidation of Cyclohexane over (Cr)MCM-41 with Different Solvents^a

Solvents	Conversion (wt%)	Selectivity (%)			
		Cyclohexanone	Cyclohexanol	Cyclohexyl acetate	Others ^b
Acetic acid	98.9	0.3	92.9	6.8	—
Methanol	36.7	—	98.3	0.4	1.3
1,4-Dioxan	36.6	2.4	95.9	0.3	1.4
Acetone	27.6	25.3	73.7	0.1	0.9

^a Reaction conditions: substrate : oxidant (H₂O₂) = 1 : 1; catalyst = 3.3 wt%; temperature = 373 K; and time = 12 h.

^b Hexanoic acid and cyclohexene.



SCHEME 3

TABLE 6
Oxidation of Cyclohexane over (Cr)MCM-41 with Different Oxidants^a

Oxidant	Conversion (wt%)	Selectivity (%)			
		Cyclohexanone	Cyclohexanol	Cyclohexyl acetate	Others ^b
H ₂ O ₂	98.9	0.3	92.9	6.8	—
O ₂	86.5	—	97.2	2.8	—
Air	52.4	—	99.0	1.0	—
TBHP	60.5	80.8	—	8.3	10.9

^a Reaction conditions: substrate : oxidant (H₂O₂) = 1 : 1; catalyst = 50 mg (3.3 wt%); temperature = 373 K; and time = 12 h.

^b Hexanoic acid and cyclohexene.

cyclohexane (52). On the other hand, the use of symmetric ketones such as cyclohexanone and acetone may produce a stable chelate complex, which may be difficult to cleavage, and therefore a decrease in conversion. In the case of acetaldehyde, the lower conversion is attributed to a possible oxidation of the aldehyde to the corresponding acids.

Table 5 summarizes the influence of various solvents on the reaction. It can be seen from the table that a relatively lower conversion was obtained in the case of methanol, acetone, and 1,4-dioxan due to possible partial decomposition of H₂O₂ under the reaction conditions. However, in the case of acetic acid, the activity can be attributed to the stabilization of H₂O₂ as peroxy acetic acid species **2a** (6). The reaction was also carried out with different oxidants, e.g., 70% TBHP, molecular O₂, and air, and the results are listed in Table 6. It can be seen from the table that the use of molecular O₂ and air leads to a decrease in substrate conversion due to a milder oxidizing nature as well as to difficulty in activation (6). Although the use of TBHP decreases the conversion, it produces cyclohexanone as the major product with considerable amounts of cyclohexyl acetate and other ring oxidized products. The observed higher cyclohexanone selectivity may possibly be due to stronger oxidation efficiency of TBHP (24), thereby leading to a secondary reaction, viz., oxidation of cyclohexanol to cyclohexanone, and other ring oxidation reactions, e.g., hexanoic acid (24).

CONCLUSIONS

In summary, it can be concluded that a mesoporous (Cr)MCM-41 molecular sieve is an efficient and promising catalyst for cyclohexane oxidation under moderate reaction conditions. Among the various oxidants, H₂O₂ was found to be more suitable for high substrate conversion and selective formation of cyclohexanol. Although the chromium ions leach out in the initial stages, like many other chromium-based catalysts, e.g., microporous molecular sieves, pillared clays, and supported systems, it is only the nonframework

ions which come out from the matrix. However, unlike the other chromium-based systems, the chromium ions in mesoporous material remain intact, i.e., a certain amount is stabilized in the matrix which do not leach out even after several recycling/washing treatments. Hence, (Cr)MCM-41 behaves truly as a heterogeneous catalyst, thus forming the first example of chromium-based non-leaching solid materials.

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