



Allylic oxidation of cyclohexene over chromium containing mesoporous molecular sieves

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Abstract

Allylic oxidation of cyclohexene was carried out over mesoporous (Cr)MCM-41 and (Cr)MCM-48 molecular sieve catalysts. In both the cases, 2-cyclohexen-1-one was obtained as the major product with small amounts of cyclohexene oxide and 1,2-cyclohexandiol. (Cr)MCM-48 showed higher activity than (Cr)MCM-41 owing to the high chromium content in the former. The use of polar solvents such as acetonitrile and methanol decrease the 2-cyclohexen-1-one selectivity; however, such a procedure produces double bond oxidized product, viz. cyclohexene oxide. Furthermore, unlike many other chromium-based solid catalysts, the activity over recycled as well as washed (Cr)MCM-41 and (Cr)MCM-48 remains nearly the same, indicating that the mesoporous chromosilicate materials behave truly as heterogeneous catalysts. In other words, after the initial loss of non-framework chromium ions for the first time, no leaching was noticed for the chromium-based systems.

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1. Introduction

The allylic oxidation of olefin into α,β -unsaturated ketones is an important transformation in natural product synthesis [1]. In particular, the oxidation products of cyclohexene and their derivatives, viz. 2-cyclohexen-1-one, 1-methylcyclohex-1-en-3-one, etc., are important in organic synthesis owing to the presence of a highly reactive carbonyl group, which is utilized in cycloaddition reactions [2–4]. Several inorganic oxidants, e.g. lead acetate, selenium dioxide,

cobalt naphthenite, and certain chromium compounds [1–8], were employed for the oxidation of cyclohexene. Although several chromium compounds have shown higher activity, the use of such catalysts in homogeneous medium has several disadvantages owing to the typical problem of separation of products from the catalyst as well as disposal of toxic solid and liquid wastes. Thus considerable attention has been focussed towards the development of chromium-based (heterogeneous) molecular sieve catalysts [9–25] and several oxidation reactions were carried out [13–28]. Among the various catalysts, the chromium containing microporous molecular sieves such as APO-5 [18] and zeolite-Y [28] were found to be active and selective for the oxidation of olefins into corresponding α,β -unsaturated ketones. However, one of the major problems with these catalysts is the leaching of active chromium ions from the matrix under the

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reaction conditions [19,20]. On the other hand, it is interesting to note that certain chromium-incorporated mesoporous molecular sieves, e.g. (Cr)MCM-41 and (Cr)MCM-48, were found to stabilize the active species, and that it does not leach out under the reaction conditions [22–24]. Therefore, in the present investigation, we performed the allylic oxidation of cyclohexene over (Cr)MCM-41 and (Cr)MCM-48 catalysts; the results are reported herein.

2. Experimental

2.1. Catalyst preparation and characterization

The (Cr)MCM-41 and (Cr)MCM-48 molecular sieves were synthesized as per the procedure described earlier [22] with a typical molar gel composition of $1\text{SiO}_2:0.25(\text{TDTMA})_2\text{O}:0.25\text{Na}_2\text{O}:45\text{H}_2\text{O}:0.01\text{Cr}_2\text{O}_3$, and $1\text{SiO}_2:0.25\text{Na}_2\text{O}:0.60\text{CTAB}:60\text{H}_2\text{O}:0.01\text{Cr}_2\text{O}_3$, respectively. The details about the synthesis conditions, calcination procedures and washing studies (ammonium acetate) can be seen elsewhere [22]. All the samples were systematically characterized by various analytical and spectroscopic techniques, viz. X-ray diffraction (XRD; Miniflex, Rigaku), simultaneous thermogravimetry–differential thermal analysis (TG–DTA; Shimadzu), inductively coupled plasma–atomic emission spectroscopy (ICP–AES; Labtam Plasma), diffuse reflectance ultraviolet–visible spectroscopy (DRUV–Vis; Shimadzu) and electron paramagnetic resonance (EPR; Varian) spectroscopy.

2.2. Cyclohexene reaction

The oxidation of cyclohexene (8 mmol) was carried out using 70% TBHP (16 mmol) oxidant in the presence of chlorobenzene (5 ml) solvent using both calcined and washed (Cr)MCM-41 and (Cr)MCM-48 catalysts (50 mg) at 393 K for 12 h. Prior to the reaction, cyclohexene was purified, as per the literature procedure [29], by washing with successive portions of dilute acidified ferrous sulphate solution followed by distilled water. It was then dried with CaCl_2 and distilled under nitrogen atmosphere. The reaction products were analyzed by gas chromatography (GC, NUCON) employing a SE-30 column. They were further confirmed using a combined gas

chromatography–mass spectrometry (GC–MS, HEWLETT) with HP-5 capillary column. Several recycling, washing and quenching experiments were performed, as per the procedure described previously [22], over both calcined and washed catalysts in order to check the leaching of active chromium ions from the matrix. Further, the effect of cyclohexene conversion and product selectivity was studied under different reaction times, temperatures, solvents and catalyst amounts.

3. Results and discussion

All the as-synthesized samples were initially green and changed to yellow upon calcination. The former is due to the presence of trivalent chromium ions and the latter is due to the presence of higher valent chromium ions, viz. chromate and/or polychromate ions. Figs. 1 and 2 depict the XRD patterns of (Cr)MCM-41 and (Cr)MCM-48, respectively. The diffraction patterns are typical of mesoporous MCM-41 and MCM-48 structures [30,31] even after various treatments. TG studies of the calcined samples [32] showed a relatively small weight loss (10% for (Cr)MCM-41 and 5% for (Cr)MCM-48) as compared to their siliceous analogues (18% for MCM-41 and 22% for MCM-48), suggesting that part of the silanol groups are consumed for the stabilization of chromium ions in the mesoporous matrix [22] in a similar manner to that reported for chromium oxide supported on silica matrix [9,10,33]. This is well supported by ^{29}Si MAS–NMR studies [23], where the calcined samples show a weak signal at -100 ppm (Q_3 site; $\equiv\text{Si}-\text{OH}$), suggesting a reduction in the silanol groups. Table 1 presents ICP–AES results of the estimated chromium content

Table 1
ICP–AES data of (Cr)MCM-41 and (Cr)MCM-48

Sample	Si/Cr (molar ratio)	Cr content (wt.%)
(Cr)MCM-41		
Synthesis gel	50	1.96
Calcined catalyst	112	1.23
Washed catalyst	157	0.77
Recycled catalyst	161	0.76
(Cr)MCM-48		
Synthesis gel	50	1.96
Calcined catalyst	87	1.58
Washed catalyst	121	0.98

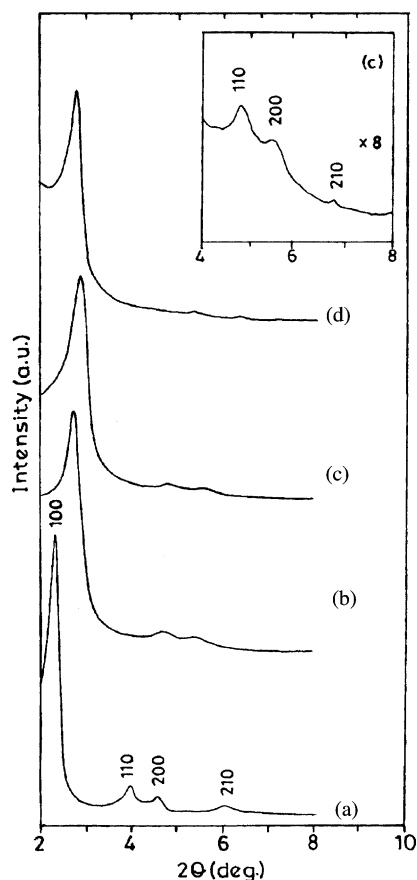


Fig. 1. XRD pattern of (Cr)MCM-41: (a) as-synthesized, (b) calcined, (c) washed, and (d) recycled.

of calcined, washed and recycled (Cr)MCM-41 and (Cr)MCM-48 samples. It is clear from this table that, after the initial loss of (non-framework) chromium ions, no further leaching was noticed after various treatments.

DRUV–VIS studies of as-synthesized samples (Figs. 3a and 4a) showed bands around 620, 440 and 270 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 [11]. On the other hand, the calcined (Figs. 3b and 4b) and washed (Figs. 3c and 4c) samples show strong charge transfer (oxygen to chromium) bands around 375 nm ($1t_1 \rightarrow 2e$ symmetry allowed) along with very weak shoulder at 322 nm ($1t_1 \rightarrow 2e$ symmetry forbidden; see inset)

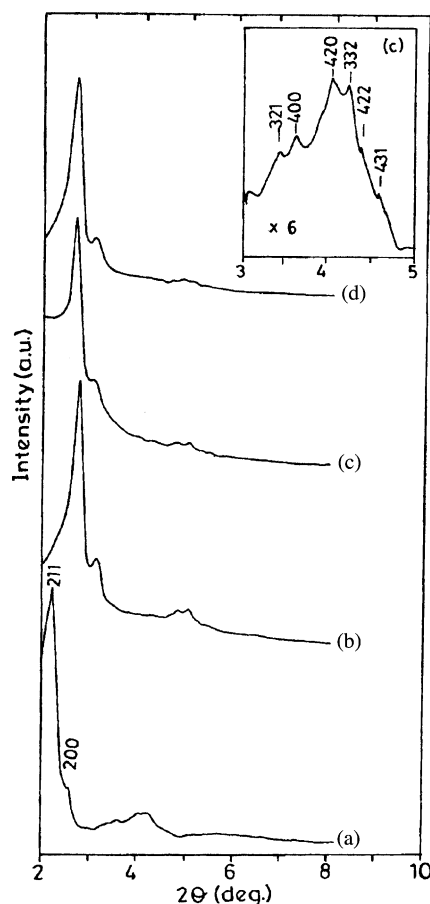


Fig. 2. XRD pattern of (Cr)MCM-48: (a) as-synthesized, (b) calcined, (c) washed, and (d) recycled.

and a weak band at 445 nm ($1t_1 \rightarrow 2e$ symmetry forbidden), assigned to chromate, dichromate and polychromate species, respectively [11,34–36]. EPR spectra (not reproduced here) of as-synthesized samples [32] showed an intense and broad signal around $g_{\text{eff}} = 1.97$, indicative of the presence of octahedral Cr(III) ions [34–36]. However, the calcined samples [32] showed sharp signals at $g_{\text{eff}} = 1.98$, characteristic of Cr(V) in a tetrahedral coordination [34–36]. The latter could; however, be produced by the partial oxidation of trivalent chromium during calcination. Further, (Cr)MCM-41 shows a more intense signal compared to (Cr)MCM-48 indicates the presence of relatively more hexavalent chromium in the latter.

Fig. 5 shows the effect of reaction time on the catalytic activity over calcined and washed (Cr)MCM-41

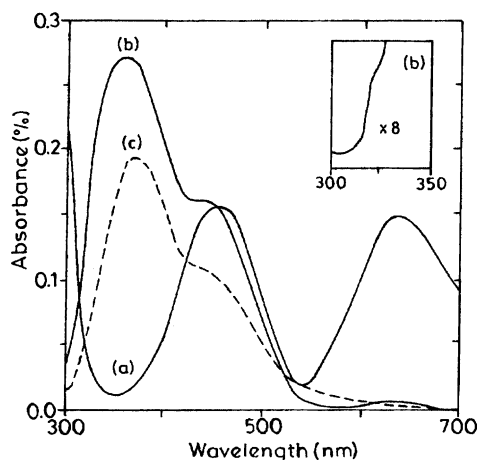


Fig. 3. DRUV-Vis spectra of (Cr)MCM-41: (a) as-synthesized, (b) calcined, and (c) washed.

catalysts. It can be seen from the figure that the cyclohexene conversion increases with increase in reaction time. The observed higher selectivity of 2-cyclohexen-1-one may be explained based on the reaction mechanism (Scheme 1) [1–3,7,8]. Accordingly, TBHP **1a** interacts with chromate species **1b** to produce chromium peroxospecies **1c**. The latter further reacts with cyclohexene, by abstraction of hydrogen from the allylic position, leading to allylic free-radical **1d**. The resulting species is then oxidized to 2-cyclohexen-1-one **1e**; i.e. via the formation of

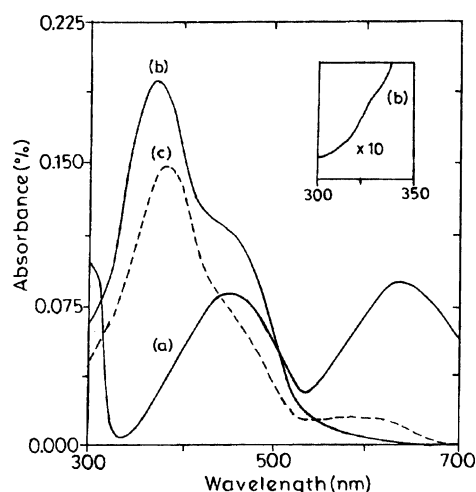


Fig. 4. DRUV-Vis spectra of (Cr)MCM-48: (a) as-synthesized, (b) calcined, and (c) washed.

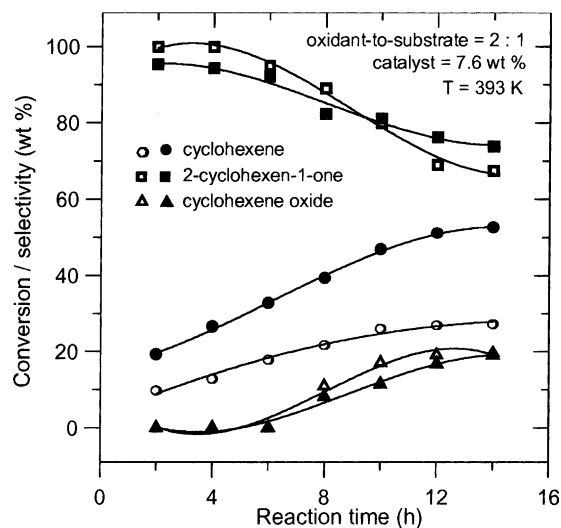
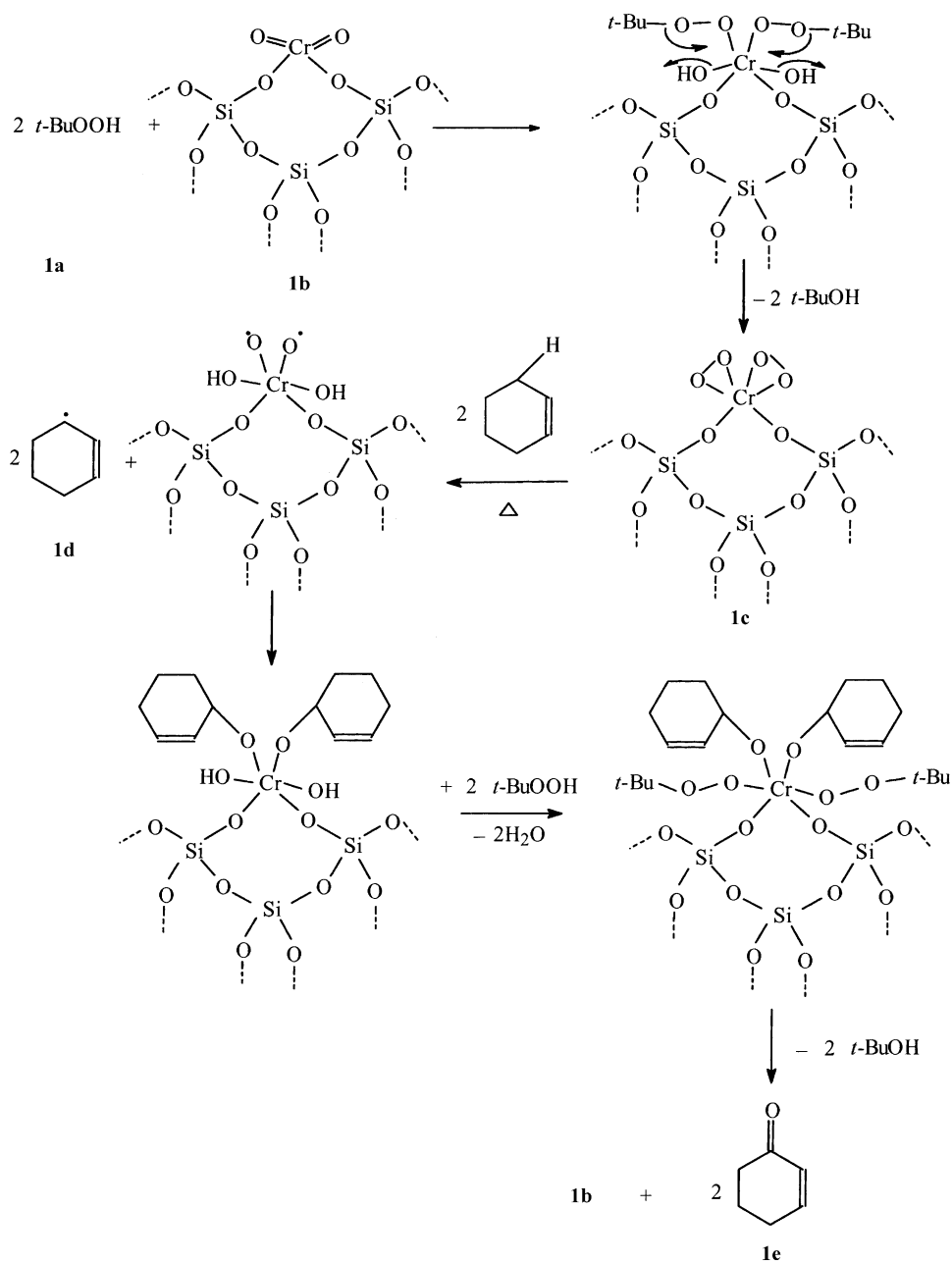


Fig. 5. Effect of reaction time on conversion and selectivity over calcined (Cr)MCM-41 (filled symbols), and washed (Cr)MCM-41 (opened symbols).

cyclohexenyl chromate ester. However, the selectivity of 2-cyclohexen-1-one decreases with time due to the formation of side products, viz. cyclohexene oxide and 1,2-cyclohexandiol. Further, no appreciable change in conversion is observed after 12 h. It is important to note that the calcined (Cr)MCM-41 showed higher (cyclohexene) conversion and (2-cyclohexen-1-one) selectivity compared to washed catalyst. This could be due to the presence of higher chromium content in the former. In general, the allylic oxidation of cyclohexene requires 2:1 stoichiometric molar ratio of oxidant:substrate. However, under the reaction condition employed in this study, all the TBHP cannot be used for this reaction owing to a possible partial decomposition and/or remaining unreacted TBHP. Hence, the reaction may require higher amount of the oxidant for a complete conversion [37]. Therefore, we have carried out the reaction over both calcined and washed (Cr)MCM-41 catalysts by varying the oxidant:substrate ratio, the results are presented in Fig. 6.

It is clear from Fig. 6 that the cyclohexene conversion and 2-cyclohexen-1-one selectivity increases with increase in oxidant amount. However, no appreciable increase in selectivity was observed above 3:1 oxidant:substrate ratio. It should also be noted here that the TBHP efficiency is found to be higher for the 2:1 ratio. At higher ratios, a competitive



Scheme 1.

reaction of double bond oxidation favors the formation of 1,2-cyclohexandiol and, hence, a decrease in 2-cyclohexen-1-one selectivity. Likewise, at lower oxidant:substrate ratio (1:1), a considerable amount of cyclohexene oxide is formed, but it decreases con-

tinuously with increase in oxidant amount, which may be accounted for additional oxidation of cyclohexene oxide into 1,2-cyclohexandiol. This may be explained by considering the second pathway of the reaction mechanism (Scheme 2). Accordingly, TBHP

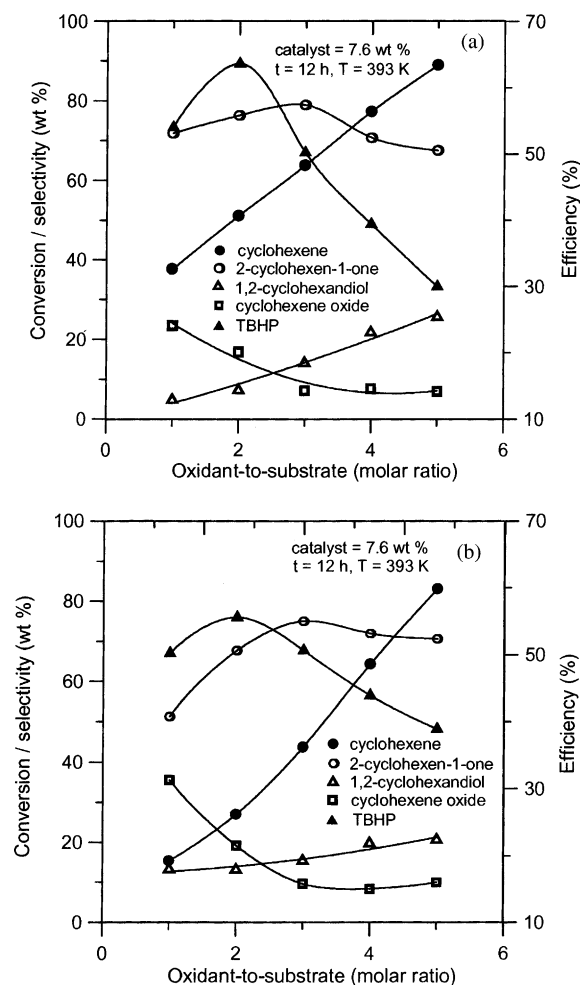


Fig. 6. Effect of oxidant:substrate ratio on conversion and selectivity over (Cr)MCM-41: (a) calcined, and (b) washed.

1a interacts with chromate species **1b**, leading to tertiary butyl peroxy radical **2a**. The interaction of **2a** with the double bond of cyclohexene results in the formation of epoxide **2b**, which can be further oxidized into diols (1,2-cyclohexandiol, **2c**). This is in good agreement with earlier observations under homogeneous reaction conditions [8]. Further, the abstraction of hydrogen from the allylic carbon leads to allylic radical, which requires a lower activation energy than the attack of peroxy radical at double bond [2,3]. On the other hand, it is interesting to note that the calcined samples display a more pronounced increase in 1,2-cyclohexandiol (Fig. 6a) than

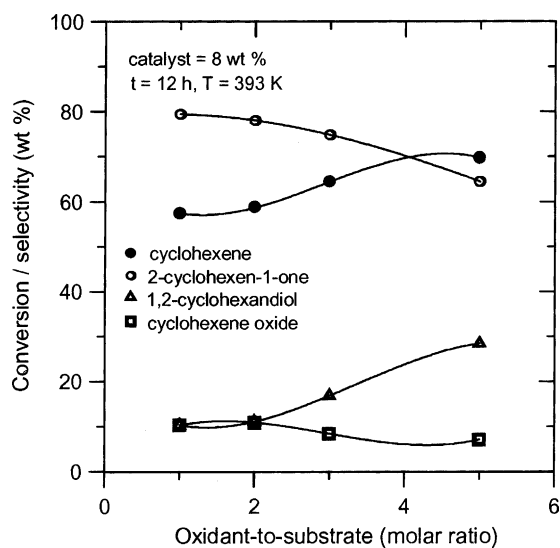
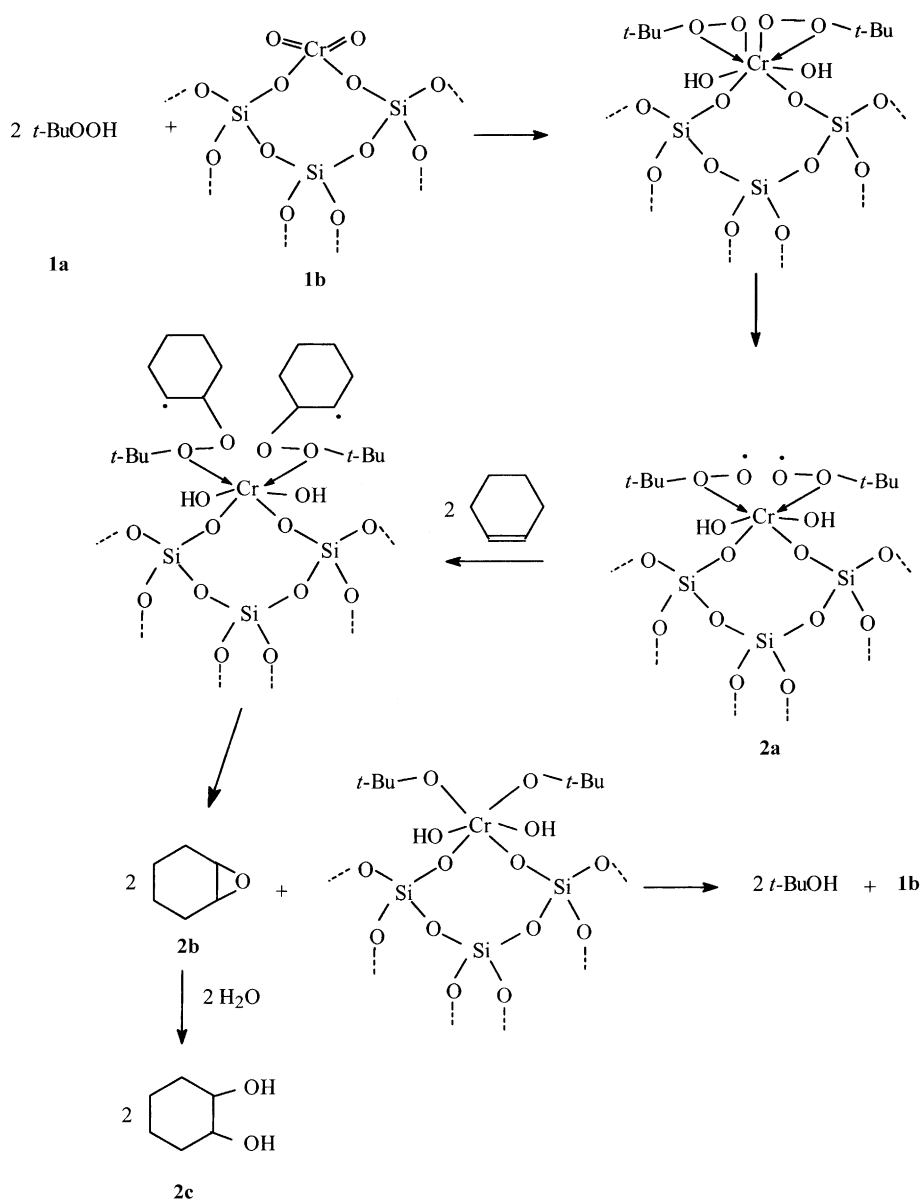


Fig. 7. Effect of oxidant:substrate ratio on conversion and selectivity over CrO₃.

the corresponding washed samples (Fig. 6b), indicating that the non-framework chromium in the former may have an influence on the product formation. That is, the leached non-framework chromium—the higher the TBHP content, the higher the leaching—may in turn (homogeneously) catalyze cyclohexene oxide into 1,2-cyclohexandiol. In order to check this, we performed the reaction over chromium trioxide (under homogeneous conditions) with different oxidant:substrate ratios; the results are presented in Fig. 7. The figure shows a continuous increase in the formation of 1,2-cyclohexandiol, with the increase of TBHP content, thus clearly supporting the observation of the increased 1,2-cyclohexandiol selectivity with higher oxidant:substrate ratio over calcined catalysts.

Tables 2 and 3 summarize the results of cyclohexene oxidation under optimized experimental conditions, along with several recycling experiments over calcined as well as washed (Cr)MCM-41 and (Cr)MCM-48 catalysts. As expected, the calcined samples (first run) of both (Cr)MCM-41 and (Cr)MCM-48 show higher conversion; however, a considerable decrease in conversion was noticed during recycle (second run) experiments owing to the dissolution of (non-framework) chromium ions from the matrix. In order to clarify whether or not homogeneous catalytic reactions can take place after removing



Scheme 2.

the used catalyst, quenching experiments were carried out over both calcined and washed catalysts. That is, under the reaction conditions, the catalyst from the reaction mixture was separated by filtration, and the reaction was continued on the filtrate (quenched solution). It is worthy noting here that the quenched solution obtained from the calcined catalyst showed a

considerable activity (~12–15%), thus indicating that the homogeneous catalytic reactions could take place even after removing the catalyst owing to the presence of a significant amount of chromium (~0.3–0.4 wt.%) in solution as observed by ICP–AES. On the other hand, the quenched solution obtained from the washed catalyst showed no or very little activity (<2%)

Table 2

Oxidation of cyclohexene to cyclohexen-1-one over (Cr)MCM-41^a

Condition	Conversion (wt.%)	Selectivity (%) ^b		
		2-Cyclohexen-1-one	Cyclohexene oxide	1,2-Cyclohexandiol
Calcined (Cr)MCM-41				
First run	51.1	76.3	15.3	7.2
Quenched solution ^c	11.6	74.5	13.8	11.7
Second run	41.8	68.5	18.7	12.8
Third run	33.3	69.7	19.9	10.4
Fourth run	29.6	72.3	19.6	8.1
Fifth run	27.5	73.2	19.2	7.6
Washed (Cr)MCM-41				
First run	27.0	67.7	17.8	13.1
Quenched solution ^d	1.3	79.1	17.2	3.7
Second run	25.7	69.0	17.7	12.3
Third run	25.0	69.9	18.4	11.7
Siliceous MCM-41				
First run	3.1	47.1	45.8	7.1
No catalyst				
First run	2.7	41.6	52.0	6.4

^a Experimental conditions: catalyst = 7.6 wt.%; oxidant:substrate = 2:1; temperature = 393 K; time = 12 h.^b Trace amount of 2-cyclohexen-1-ol was detected by GC–MS.^c Contains 0.33 wt.% chromium.^d No detectable chromium by ICP–AES.

Table 3

Oxidation of cyclohexene to cyclohexen-1-one over (Cr)MCM-48^a

Condition	Conversion (wt.%)	Selectivity ^b		
		2-Cyclohexen-1-one	Cyclohexene oxide	1,2-Cyclohexandiol
Calcined (Cr)MCM-48				
First run	67.4	82.9	4.0	12.4
Quenched solution ^c	13.9	91.4	6.3	2.3
Second run	46.8	76.1	14.3	9.6
Third run	37.6	75.5	16.0	8.4
Fourth run	35.9	76.9	16.6	6.5
Washed (Cr)MCM-48				
First run	33.2	73.7	17.3	9.0
Quenched solution ^d	1.8	87.4	10.0	2.6
Second run	33.9	75.5	15.1	9.4
Third run	36.1	79.9	11.6	8.5
Siliceous MCM-48				
First run	3.7	51.1	39.6	9.3

^a Experimental conditions: catalyst = 7.6 wt.%; oxidant:substrate = 2:1; temperature = 393 K; time 12 h.^b Trace amount of 2-cyclohexen-1-ol was detected by GC–MS.^c Contains 0.39 wt.% chromium.^d No detectable chromium by ICP–AES.

Table 4
Effect of solvent on oxidation of cyclohexene over calcined catalysts^a

Solvent	Conversion (wt.%)	Selectivity (%) ^b		
		2-Cyclohexen-1-one	Cyclohexene oxide	1,2-Cyclohexandiol
Calcined (Cr)MCM-41				
Chlorobenzene	51.1	76.3	15.3	7.2
Acetonitrile	45.7	36.3	19.5	44.2
Methanol	35.5	–	93.3	6.7
Calcined (Cr)MCM-48				
Chlorobenzene	67.4	82.9	3.1	12.4
Acetonitrile	48.6	53.9	15.2	30.9
Methanol	48.1	26.0	73.2	0.8

^a Reaction conditions: catalyst = 7.6 wt.%; temperature = 393 K; time = 12 h; oxidant:substrate = 2:1.

^b Trace amount of 2-cyclohexen-1-ol was detected by GC–MS.

conversion), suggesting a complete absence of homogeneous catalytic reaction. This is further confirmed by ICP–AES results, where no chromium was detected for the quenched solution of the washed catalyst. It is also interesting to note that, after the second recycle (or third run), the activity of the calcined catalysts remains nearly the same, indicating no further leaching of chromium ions from the matrix. A similar observation was also made earlier for ethyl benzene oxidation reaction [22]. On the other hand, the washed catalysts show low conversion (first run) due to a lower chromium content (cf. Table 1), as compared to the calcined catalysts; their catalytic activity is; however, nearly unaltered even for the first recycle (or second run) experiments, suggestive of the absence of non-framework chromium ions in the matrix. At this juncture, it is quite remarkable to note that the

(Cr)MCM-48 catalyst showed much higher activity than (Cr)MCM-41. The observed high activity in the former case could be attributed to higher chromium content (as revealed by ICP–AES analysis; as shown in Table 1) as well as the presence of a relatively lower amount of pentavalent chromium (from EPR studies [32]). It is also worth mentioning here that no change in the structure was noticed for both the washed and recycled catalysts of (Cr)MCM-41 and (Cr)MCM-48, indicating that the structure remains intact even after various treatments (as observed from XRD patterns; see Figs. 1 and 2).

Tables 4 and 5 display the results of the influence of various solvents on the reaction over both calcined and washed catalysts of (Cr)MCM-41 and (Cr)MCM-48. It can be seen from these tables that, irrespective of the solvents used, the calcined catalysts

Table 5
Effect of solvent on oxidation of cyclohexene over washed catalysts^a

Solvent	Conversion (wt.%)	Selectivity ^b		
		2-Cyclohexen-1-one	Cyclohexene oxide	1,2-Cyclohexandiol
Washed (Cr)MCM-41				
Chlorobenzene	27.0	67.7	17.8	13.1
Acetonitrile	23.1	24.7	47.7	27.6
Methanol	21.7	–	94.9	5.1
Washed (Cr)MCM-48				
Chlorobenzene	33.2	75.5	15.1	9.4
Acetonitrile	28.7	41.9	25.5	32.6
Methanol	27.4	13.0	76.9	10.1

^a Reaction conditions: catalyst = 7.6 wt.%; temperature = 393 K; time 12 h; oxidant:substrate = 2:1.

^b Trace amount of 2-cyclohexen-1-ol was detected by GC–MS.

constantly show higher activity than the corresponding washed catalysts, indicating the influence of the amount of chromium on the reaction (see also Table 1). In addition, as described earlier [1], the reaction is highly dependent on solvents. The use of polar solvents favors the oxidation at double bond, whereas non-polar solvents lead to allylic oxidation. It can be seen from the table that cyclohexene conversion as well as 2-cyclohexen-1-one selectivity is high with a non-polar solvent such as chlorobenzene. However, as the polarity of the solvent increases, e.g. chlorobenzene < acetonitrile < methanol, the cyclohexene conversion as well as selectivity of 2-cyclohexen-1-one decreases. On the other hand, the use of methanol results in the formation of cyclohexene oxide as the major product. In the case of (Cr)MCM-48, a considerable amount of 2-cyclohexen-1-one is noticed, which may be accounted for the presence of more chromium in the matrix (0.98 wt.%) as compared to (Cr)MCM-41 (0.77 wt.%). In order to check the influence of chromium content on the product selectivity, we performed the reaction over washed (Cr)MCM-41 with different catalyst amounts using chlorobenzene and methanol as solvents; the results are presented in Fig. 8. It can be seen from this figure that the substrate conversion increases, for both chlorobenzene and methanol, with the increase in catalyst amount. In the case of the former, 2-cyclohexen-1-one was obtained as major product along with a small amount of cyclohexene oxide. The 2-cyclohexen-1-one selectivity increases with increase in catalyst amount while the corresponding cyclohexene oxide selectivity decreases. The higher 2-cyclohexen-1-one selectivity at higher catalyst amount could be attributed to higher chromium content, which favors the first reaction pathway (Scheme 1). This is in line with the earlier observation using homogeneous catalysts, e.g. pyridinium chlorochromate [1]. However, with the use of methanol as solvent at lower catalyst amount, cyclohexene oxide was obtained as major product. Upon increase of the catalyst amount, cyclohexene oxide selectivity decreases at the cost of cyclohexen-2-one. The formation of the latter could be due to the fact that an increase in catalyst amount increases the chromium content, thus favoring the first reaction pathway (Scheme 1) [8] and leading to the formation of a considerable amount of 2-cyclohexen-1-one. Finally, the following are the optimized conditions

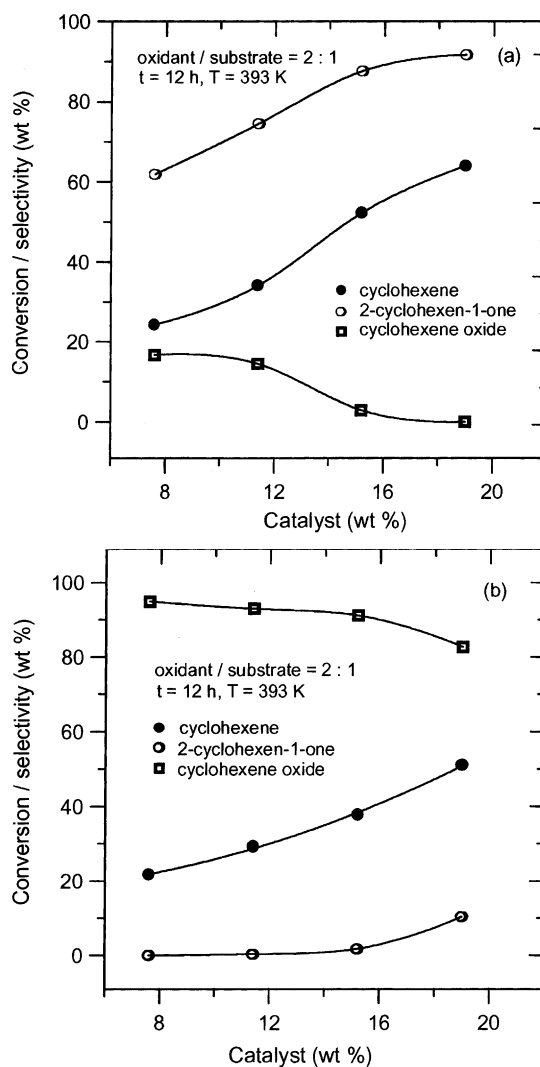


Fig. 8. Effect of catalyst concentration over washed (Cr)MCM-41: (a) chlorobenzene as solvent, and (b) methanol as solvent.

for the chosen reaction: solvent = chlorobenzene; oxidant:substrate = 2:1; reaction temperature, 393 K; reaction time = 12 h; catalyst amount = 7.6 wt.%. Under these conditions, the washed (Cr)MCM-41 and (Cr)MCM-48 catalysts showed good activity. Since the washed catalysts contain lower chromium content (cf. Table 1), an increase in the catalyst amount, for example, 19 wt.% in the case of (Cr)MCM-41, showed much highest activity: viz. 70% conversion; >90% selectivity; 87% TBHP efficiency.

4. Conclusion

In summary, this study proves that both (Cr)MCM-41 and (Cr)MCM-48 catalysts are promising for allylic oxidation reaction. The conversion (cyclohexene) and selectivity (2-cyclohexen-1-one) are highly dependent on various reaction conditions. A maximum substrate conversion with good 2-cyclohexen-1-one selectivity was obtained using chlorobenzene as solvent at 393 K for 12 h. Further, the use of a polar solvent, viz. methanol, favors cyclohexene oxide. The recycling and washing studies demonstrate that both (Cr)MCM-41 and (Cr)MCM-48 behave truly as heterogeneous catalysts.

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