

# Mesoporous VMCM-41: highly efficient and remarkable catalyst for selective oxidation of cyclohexane to cyclohexanol

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## Abstract

Liquid phase oxidation of cyclohexane was carried out under milder reaction conditions over mesoporous VMCM-41 molecular sieve catalysts using aqueous hydrogen peroxide as oxidant, acetic acid as solvent, and methyl ethyl ketone as initiator. The catalysts showed high substrate conversion and excellent product (cyclohexanol) selectivity. Although the activity of the catalyst slightly decreased after first recycle, owing to leaching of small amount of non-framework vanadium ions, it, however, remained nearly same thereafter. This observation was further confirmed by washing experiments where the non-framework vanadium ions were removed upon ammonium acetate treatment. Further, the washed catalyst also showed an activity similar to that of the recycled catalyst. Thus, the recycled or washed VMCM-41 behaves truly as heterogeneous catalyst. This observation was complemented and confirmed by both filtrate and quenching studies. The effects of reaction time, temperature, Si/V molar ratio, and catalyst concentration on the catalyst performance were examined in order to optimize the conversion of cyclohexane and selectivity of cyclohexanol. However, the use of strong oxidizing agent, e.g., tertiary butyl hydroperoxide, resulted in the formation of cyclohexanone as the major product. In addition, the use of solvents like methanol, dioxan and acetone showed lower activity. © 2004 Elsevier B.V. All rights reserved.

**Keywords:** Mesoporous; VMCM-41; Selective oxidation; Cyclohexane; Cyclohexanol; Cyclohexanone; Cyclohexyl acetate

## 1. Introduction

Selective oxidation reactions using heterogeneous catalysts are of growing importance for modern chemical industry. Among the numerous reactions, 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]. They are, in general, produced on an industrial scale by the oxidation of cyclohexane or hydrogenation of phenol. On the other hand, there are several expensive and polluting processes have been employed using homogenous catalysts [5]. Hence, in recent years, attention has been focused on the development

of transition metal containing molecular sieves based heterogeneous catalysts with oxygen or peroxides as non-polluting oxidants [6]. 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 [6]. Thus, the oxidation of cyclohexane over environmental friendly heterogeneous catalysts under mild/moderate reaction conditions is a topic of great interest. In this regard, it is noteworthy here that vanadium-containing mesoporous MCM-41 molecular sieves, viz., VMCM-41, show promises for several oxidation reactions [7,8]. Therefore, in this investigation, an attempt has been made to explore the catalytic properties of mesoporous VMCM-41 materials under moderate reaction condition for the oxidation of cyclohexane. The present study on VMCM-41 is also in

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continuation of our work on various metal ions incorporated mesoporous silicate and aluminophosphate molecular sieves, viz., TiMCM-41 [9], AlMCM-41 [10], FeMCM-41 [11], CrMCM-41 [12], FeHMA [13], CoHMA [14], and TiHMA [15].

## 2. Experimental

### 2.1. Starting materials

The following chemicals were employed for the preparation of VMCM-41 and for the oxidation of cyclohexane. Fumed silica ( $\text{SiO}_2$ ; 99.8%; Aldrich), tetramethylammonium hydroxide (TMAOH; 25 wt.%; Aldrich), cetyltrimethylammonium bromide (CTAB; 99%; Aldrich), vanadyl sulfate hydrate ( $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$ ; 99%; Aldrich), sulfuric acid ( $\text{H}_2\text{SO}_4$ ; 98%; BDH), 2-propanol (99.7%; Merck), cyclohexane (99.5%; Merck), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ; 30%; Qualigens), tertiary butylhydroperoxide (TBHP; 70%; Lancaster), acetic acid (99.5%; Fischer), methyl ethyl ketone (MEK; 99%; SD), acetone (99.5%; SD), acetaldehyde (30%; SD). Authentic samples of cyclohexanol (98%; SD) and cyclohexanone (99%; Merck) were used for comparative analysis of the reaction products. All the reagents used in this study were in as-received form.

### 2.2. Synthesis of VMCM-41

Mesoporous VMCM-41 molecular sieves with different Si/V (molar) ratios of 25–200 were synthesized hydrothermally as per the procedure outlined elsewhere [7,16] with typical (molar) gel compositions of:  $\text{SiO}_2:0.135(\text{CTA})_2\text{O}:0.13\text{Na}_2\text{O}:0.075(\text{TMA})_2\text{O}:68\text{H}_2\text{O}:(0.01\text{--}0.08)\text{V}_2\text{O}_5$ . Accordingly, dilute TMAOH was first added to fumed silica slowly and a homogeneous 'Solution-X' was obtained. Simultaneously, 'Solution-Y' was prepared by mixing dilute CTAB and NaOH and stirred for about 30 min. Then, both the 'Solution-X' and 'Solution-Y' were then mixed together to get a clear gel. Finally, the vanadium precursor, viz., vanadyl sulfate hydrate, was added to the above gel and stirred for an hour. The pH of final gel was adjusted to 11.5 by addition of dilute  $\text{H}_2\text{SO}_4$  and the resulting gel was transferred into Teflon-lined stainless steel autoclaves and kept in an air oven at 373 K for 3 days for crystallization. The final solid product, designated as as-synthesized VMCM-41, obtained was filtrated and dried for overnight. The as-synthesized samples were then calcined at 823 K for 2 h in  $\text{N}_2$  with a flow rate of  $50 \text{ ml min}^{-1}$  and heating rate of  $1 \text{ K min}^{-1}$  followed by 6 h in air. Unless otherwise stated, the catalyst used in the present study was VMCM-41 with Si/V = 50. For a comparison, siliceous MCM-41 was prepared according to the procedure described earlier [17]. Likewise, microporous vanadium silicalite-1 (VS-1) was also prepared as per literature procedure [18] with a typical molar gel composition of:  $\text{SiO}_2:0.165(\text{TPA})_2\text{O}:22\text{H}_2\text{O}:0.01\text{V}_2\text{O}_5$ .

### 2.3. Characterization

All the samples were systematically characterized by various analytical and spectroscopic techniques, viz., low angle powder X-ray diffraction (XRD; Rigaku), thermogravimetry-differentially thermal analysis (TG/DTA; Dupont 9900/2100), transmission electron microscopy (TEM; Philips CM 200 operated at 160 kV), nitrogen sorption (Sorptomatic 1990),  $^{51}\text{V}$  and  $^{29}\text{Si}$  magic angle spinning nuclear magnetic resonance ( $^{51}\text{V}$  and  $^{29}\text{Si}$  MAS-NMR; Varian 300X), Fourier transform-infrared (FT-IR; Nicolet Impact-400), diffuse reflectance ultraviolet-visible spectroscopy (DRUV-VIS; JASCO-V-570), electron paramagnetic resonance spectroscopy (EPR; Varian E-112), and inductively coupled plasma-atomic emission spectroscopy (ICP-AES; Labtam Plasma Lab 8440).

### 2.4. Reaction procedure

The oxidation of cyclohexane (18 mmol) was carried out using 50 mg of the catalysts with 30%  $\text{H}_2\text{O}_2$  (18 mmol) as oxidant and acetic acid as solvent medium (10 ml). The reaction was performed using methyl ethyl ketone (MEK; 5 mmol) as initiator at 373 K for 12 h. Further, for the comparison, the reaction was also followed without MEK. After the reaction, the catalyst was separated and the solvent was neutralized with  $\text{NaHCO}_3$ . Then, the products were extracted with diethyl ether and analyzed by gas chromatography (GC; Nucon 5700) using carbowax column. Further, the reaction products were confirmed by GC-MS (HEWLETT G1800A) with HP-5 capillary column. The reaction was also carried out employing various solvents such as methanol, 1,4-dioxan and acetone under the same reaction conditions. Furthermore, the effect of various oxidants, viz., air, oxygen, and TBHP, on the reaction was also investigated.

### 2.5. Washing studies

In order to remove non-framework vanadium ions, if any, present in the mesoporous matrix, the calcined samples were treated with ammonium acetate solution (1 M) as per the following procedure: about 100 mg of the calcined catalyst was stirred with 30 ml of ammonium acetate solution for 12 h at room temperature. It was then filtered, washed, dried at 373 K. The treated catalyst was recalcined at 723 K for 6 h, and the resulting samples are designated as washed catalyst.

### 2.6. Recycling studies

To check the stability and recycling ability as well as leaching of vanadium ions from the VMCM-41 under reaction conditions, several recycling experiments were carried out for all the catalysts. The typical recycling procedure was as follows: after the initial reaction, the catalyst was separated from the reaction mixture and washed with acetone and dried at 353 K

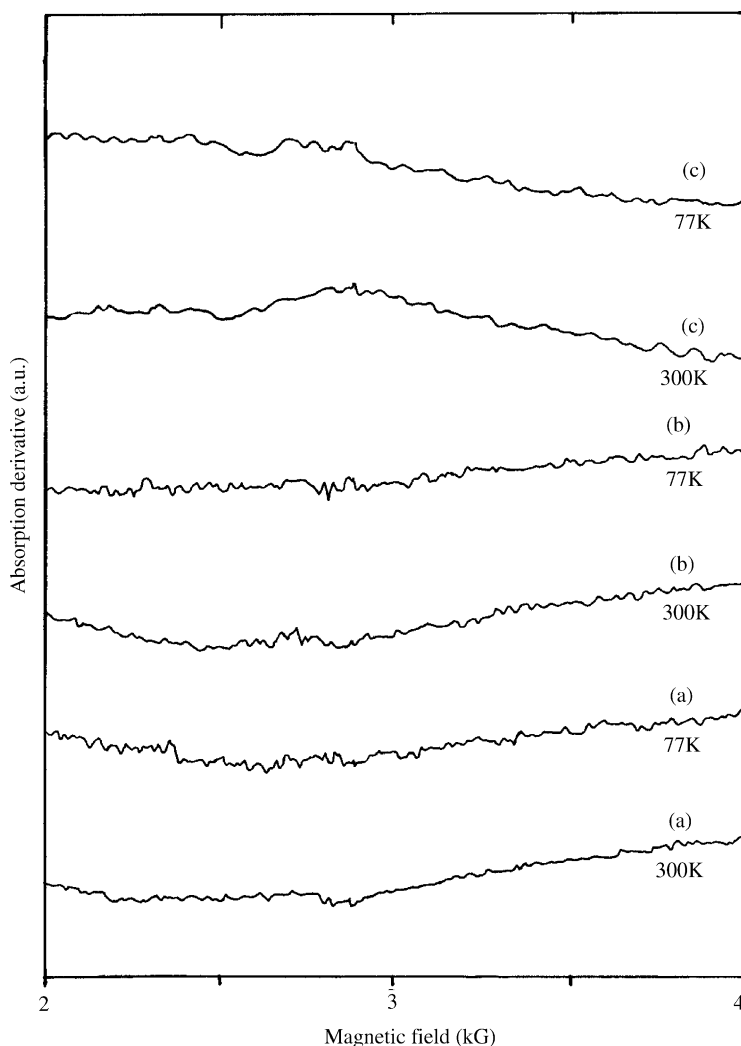


Fig. 1. EPR spectra at 300 and 77 K of VMCM-41(50): (a) as-synthesized, (b) calcined, and (c) washed.

followed by the activation at 823 K for 6 h in air. The reaction was then carried out on the recycled activated catalyst.

### 2.7. Filtrate/quenching studies

The heterogeneous nature of the catalysts was tested by carrying out filtrate and quenching experiments. In the case of the former, the filtration was done by separating the catalyst from the reaction mixture at room temperature. The reaction was then followed on both filtrates as well as on the filtered catalyst. While in the case of the latter, the quenching experiments were performed by separating catalyst from the reaction mixture under the reaction conditions, the reaction was followed on the filtrate solution.

## 3. Results and discussion

All the as-synthesized and calcined VMCM-41 samples were white in colour. Fig. 1 shows the EPR spectra of var-

ious vanadium samples. It can be seen from this figure that the absence of EPR signal for the as-synthesized, calcined and washed samples, both at room as well as liquid nitrogen temperatures, confirms the presence of  $V^{5+}$  in the VMCM-41 [16]. Although vanadyl sulfate was used for the preparation, the absence of  $V^{4+}$  in the VMCM-41 indicates that during the synthesis procedure  $V^{4+}$  may have been oxidized to  $V^{5+}$  as aerial oxidation of  $V^{4+}$  to  $V^{5+}$  is known to occur rapidly in alkaline medium [19]. Fig. 2 depicts representative XRD patterns of the calcined, washed, recycled and washed recycled VMCM-41(50). As can be seen from this figure that the diffraction patterns are typical of mesoporous hexagonal MCM-41 structure [20,21]. Further, the diffraction profiles remain same even after the recycling and/or washing experiments suggesting the intactness of the structure.

Table 1 summarizes the average unit cell parameter, vanadium contents, and  $N_2$  sorption data of various VMCM-41 samples. As expected, in all the cases, an increase in the  $d$  spacing (or  $a_0$ -values) compared to its siliceous analogue was noted. The observed expansion could, however, be attributed

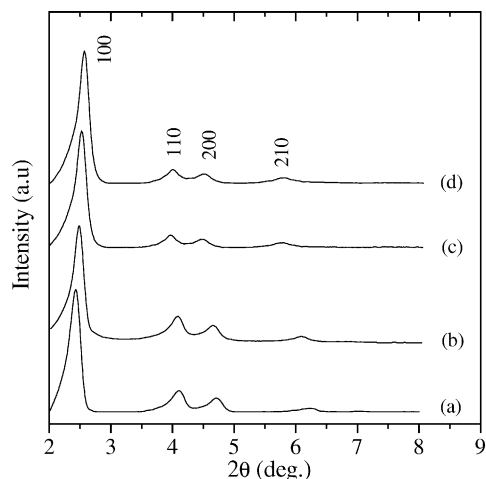


Fig. 2. XRD spectra of VMCM-41(50): (a) calcined, (b) washed, (c) recycled, and (d) washed and recycled.

to the larger (crystal) radius of  $V^{5+}$  (0.495 Å) than that of  $Si^{4+}$  (0.40 Å) [22], and/or to the longer V–O (1.8 Å) bond distance as compared to Si–O (1.6 Å) [7]. On the other hand, the loss in vanadium for the washed sample shows a removal of non-framework vanadium ions from the matrix. Interestingly, the vanadium content in the VMCM-41 remains nearly the same even after recycling experiments suggesting that there is no further leaching of vanadium under reaction conditions.

TG of as-synthesized VMCM-41 samples (not reproduced here) showed ~40 wt.% weight loss attributed to the removal of adsorbed water and surfactant molecules. On the other hand, the calcined sample shows a weight loss around 20 wt.% (not reproduced here) due to the adsorbed water molecules. DTA gave the corresponding endothermic/exothermic transitions (also not reproduced here) characteristic of mesoporous MCM-41 materials [23]. Further, the  $N_2$  sorption data (see Table 1) on various vanadium samples supports the mesoporous nature of catalyst [20,21]. Fig. 3 presents the TEM of VMCM-41, which shows a regular hexagonal array of uniform channels typical of MCM-41 [21,24], along with an ED pattern which confirms the pe-

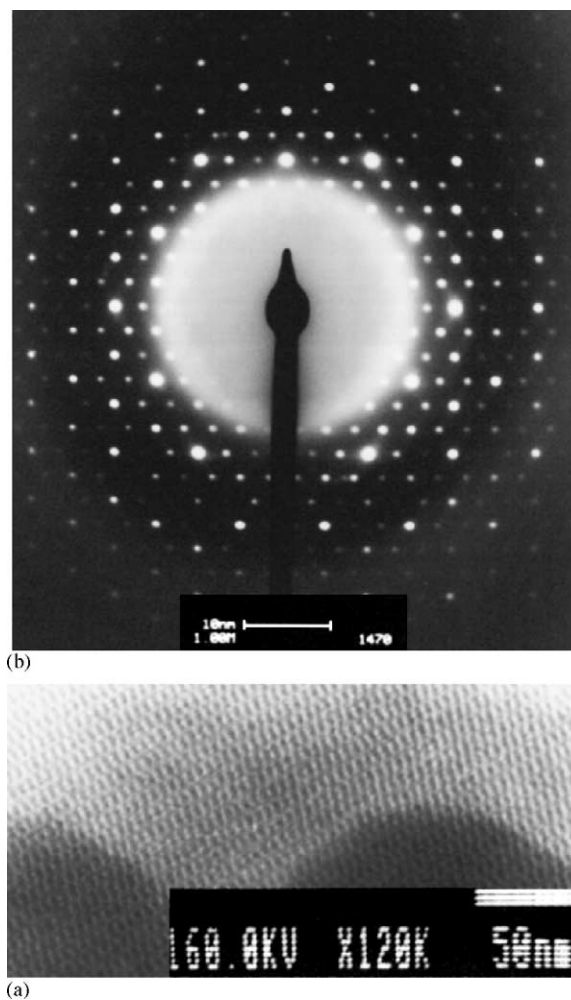


Fig. 3. (a) TEM and (b) ED of VMCM-41.

riodicity and high crystallinity of VMCM-41. This is highly consistent with XRD results.

Fig. 4 shows  $^{29}Si$  MAS-NMR spectra of as-synthesized MCM-41 and VMCM-41. The spectra consist of two distinct signals, viz., –110.0 ppm ( $Q_4$ ), –100.0 ppm ( $Q_3$ ) along with a very weak signal at –90.1 ppm ( $Q_2$ ) corresponding

Table 1  
XRD, ICP-AES, and  $N_2$  sorption data of various VMCM-41 samples

Sample <sup>a</sup>	$a_0$ (Å) (XRD)	V-content <sup>b</sup> (wt.%)	Pore volume (ml g <sup>-1</sup> )	$N_2$ sorption pore diameter (Å)	Surface area (m <sup>2</sup> g <sup>-1</sup> )
SiMCM-41	40.84	–	0.91	27	1040
VMCM-41(200)	41.30	0.21	0.86	26	1012
VMCM-41(100)	43.62	0.32	0.81	27	980
VMCM-41(50) <sup>c</sup>	46.08	0.76	0.85	29	919
VMCM-41(50) <sup>d</sup>	46.02	0.65	–	–	–
VMCM-41(50) <sup>e</sup>	45.95	0.63	0.71	27	846
VMCM-41(50) <sup>f</sup>	46.01	0.64	–	–	–
VMCM-41(25)	48.02	1.23	0.69	24	892

<sup>a</sup> Numbers in parentheses indicate the nominal Si/V ratios.

<sup>b</sup> ICP-AES.

<sup>c</sup> Calcined sample.

<sup>d</sup> Washed sample.

<sup>e</sup> Recycled sample.

<sup>f</sup> Washed and recycled.

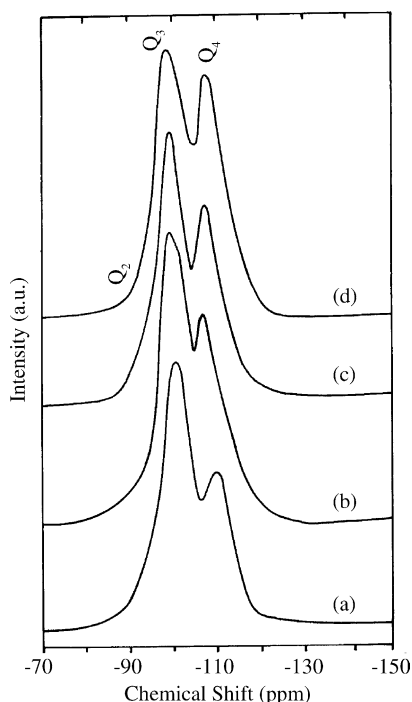
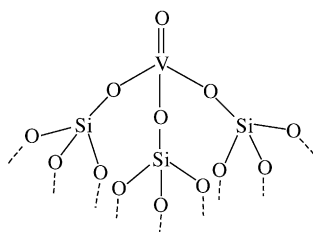


Fig. 4.  $^{29}\text{Si}$  MAS-NMR spectra of as-synthesized: (a) MCM-41, (b) VMCM-41(100), (c) VMCM-41(50), and (d) VMCM-41(25).

to  $\text{Si}(\text{OSi})_4$ ,  $\text{Si}(\text{SiO})_3(\text{OH})$ , and  $\text{Si}(\text{OSi})_2(\text{OH})_2$ , respectively [23,25]. It can be seen from this figure that the intensity of  $Q_3$  signal decreases as the vanadium concentration increases in the samples. This implies that there is an interaction between vanadium ions and hydroxyl groups in the silicate MCM-41 matrix, and as a consequence, the  $Q_3$  signal intensity decreases [26,27]. A similar observation was also noticed in the case of microporous molecular sieve materials [28,29]. Thus, during the synthesis, vanadyl ions ( $\text{V}=\text{O}$ ) may possibly be bonded to silanol groups ( $\text{Si}-\text{O}$ ) in the MCM-41 matrix so as to form mainly  $(\text{SiO})_3(\text{V}=\text{O})$  units (Scheme 1).  $^{51}\text{V}$  MAS-NMR of VMCM-41(50) shows a signal at  $\sim 533$  ppm (not shown here), relative to  $\text{VOCl}_3$  as a reference, indicating that the presence of pentavalent vanadium in the tetrahedral framework of VMCM-41 [7,8]. However, the absence of signal around  $\sim 300$  ppm indicates that no bulk vanadium oxide phase is present in the sample.

DRUV-VIS spectra of various vanadium samples show two intense absorption maxima around 275 nm ( $(\pi)\text{t}_2$  (d)e) and 340 nm ( $(\pi)\text{t}_1$  (d)e) (Fig. 5). This is attributed to the



Scheme 1.

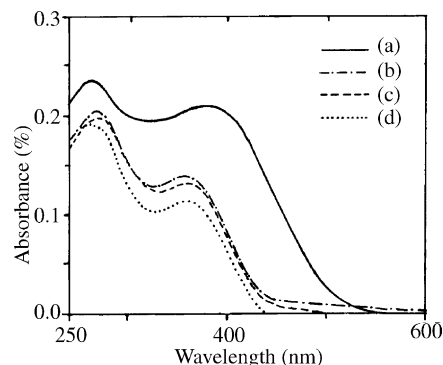


Fig. 5. DRUV-VIS spectra of VMCM-41: (a) calcined, (b) washed, (c) recycled, and (d) washed and recycled.

charge transfer bands associated with  $\text{O}^{2-}$  to  $\text{V}^{5+}$  in tetrahedral environment [16,27,30]. No band in visible region was noticed for the as-synthesized samples. Again, this observation supports the presence of  $\text{V}^{5+}$  in the matrix, which is in accordance with EPR studies. FT-IR spectra of various calcined vanadium sample shows bands at  $\sim 1230$ ,  $\sim 1080$ , and  $\sim 460$   $\text{cm}^{-1}$ , which are assigned to the symmetric stretching and bending of  $\text{Si}-\text{O}-\text{Si}$  vibration, respectively [23]. On the other hand, the diffuse band at  $\sim 960$   $\text{cm}^{-1}$  is attributed to defect sites ( $\text{Si}-\text{O}$ ), which normally appears in siliceous samples. However, the band is sharp in the case of VMCM-41 and increases vanadium content (not shown here) owing to the influence of  $\text{V}=\text{O}$  group in the silicate framework [16].

Fig. 6 depicts the effect of reaction time on the cyclohexane reaction over calcined VMCM-41. It can be seen from this figure that the (cyclohexane) conversion increases with time, while (cyclohexanol) selectivity decreases, and that the optimum conversion and selectivity could be achieved at about 12 h. It can also be noticed from this figure that, at the initial stages, a small amount of cyclohexyl acetate was observed along with cyclohexanol. The former increases slightly with time, which could possibly due to termination reaction be-

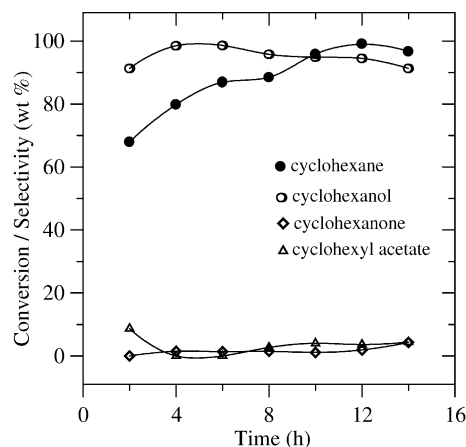
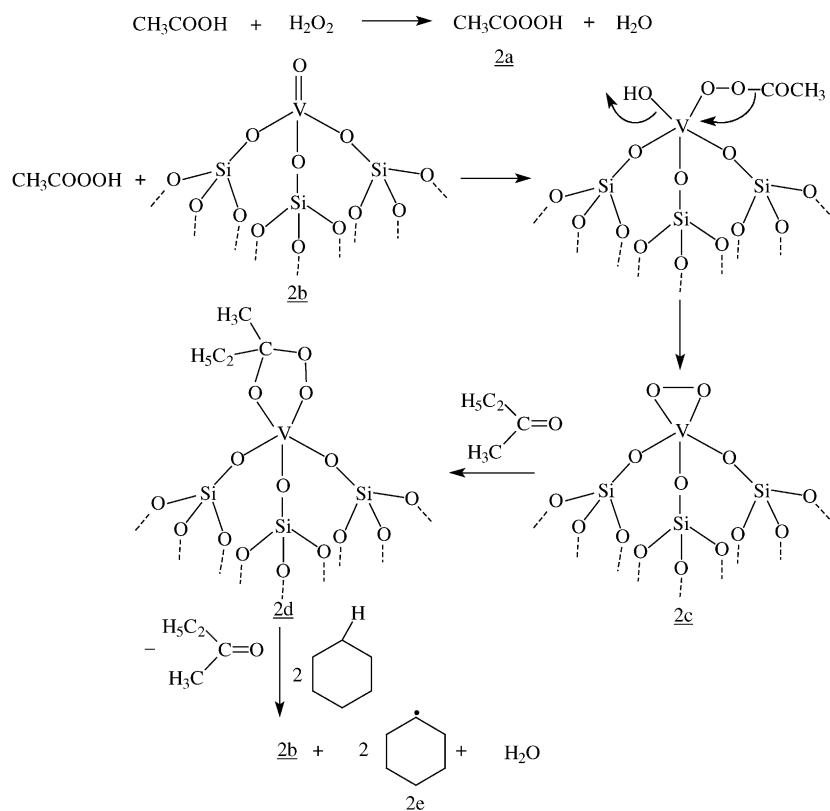


Fig. 6. Effect of reaction time on the conversion and selectivity over VMCM-41 (reaction conditions: substrate:oxidant ( $\text{H}_2\text{O}_2$ ) = 1:1;  $T = 373$  K; catalyst = 3.3 wt.%).





Scheme 2.

tween unreacted cyclohexyl and acetoxy radicals and/or by a possible reaction of cyclohexanol with excess acetic acid in the presence of VMCM-41 (see Schemes 2 and 3). Fig. 7 shows the effect of reaction temperature on cyclohexane reaction. In all cases, cyclohexanol was obtained as the major product, and only small amounts of other products, viz., cyclohexanone, cyclohexyl acetate, etc., were observed. Further, it can also be seen from the figure that the cyclohexane conversion increases with increase in reaction temperature, and that a maximum conversion was obtained at 373 K. However, beyond this temperature, e.g., at 383 K, a decrease in conversion and selectivity was observed, which could be attributed to a possible decomposition of  $\text{H}_2\text{O}_2$  [6] as well as to the formation of cyclohexyl acetate by interaction of cyclo-

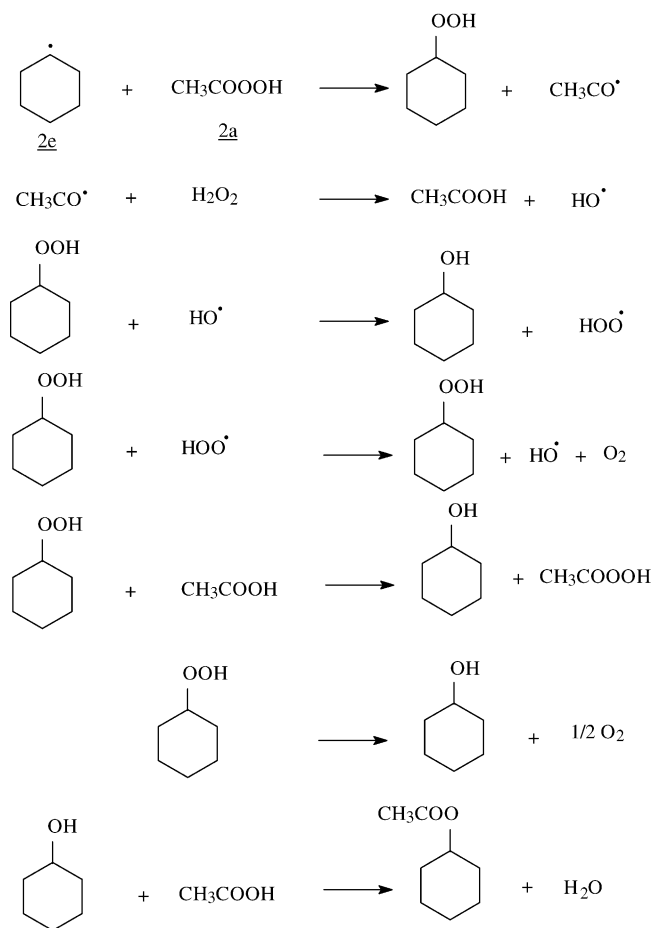
hexyl and acetoxy radicals and/or due to the reaction between cyclohexanol with excess acetic acid (see Schemes 2 and 3).

Fig. 8 shows the effect of vanadium content on the reaction. It can be seen from this figure that the (cyclohexane) conversion increases with vanadium content and that a maximum conversion was obtained for the Si/V ratio of 50. However, the observed decrease in conversion at higher vanadium content (Si/V = 25) could be due to the presence of excess amount of vanadium, which leads to competent interaction of metal oxo-species with both alkylperoxy species and cyclohexane [31], thus inhibiting the catalytic reaction. While cyclohexanol selectivity decreases as a consequence of the formation of ring-oxidized products such as hexanoic acid, which was identified using GC-MS. Fig. 9 presents the ef-

Table 2  
Recycling study over calcined and washed VMCM-41 catalysts<sup>a</sup>

Catalyst	Conversion (wt.%)	Selectivity (%)			
		Cyclohexanol	Cyclohexanone	Cyclohexyl acetate	Others
Calcined VMCM-41	99.0	94.5	1.9	3.6	–
First recycle	93.2	96.1	3.6	0.3	–
Second recycle	92.0	92.4	6.3	1.3	–
Third recycle	91.2	93.4	2.5	4.1	–
Washed VMCM-41	93.4	90.0	4.5	5.5	–
First recycle	89.8	95.0	2.1	2.9	–
Second recycle	90.8	96.9	1.1	2.0	–
Third recycle	90.1	93.8	2.2	4.0	–

<sup>a</sup> Reaction conditions: substrate:oxidant ( $\text{H}_2\text{O}_2$ ) = 1:1; catalyst = 3.3 wt.%;  $T = 373 \text{ K}$ ;  $t = 12 \text{ h}$ .



fect of catalyst concentration on the reaction. It can be seen from this figure that, as the catalyst concentration increases, the cyclohexane conversion increases. At the 3.3 wt.% concentration, maximum substrate conversion and cyclohexanol selectivity was observed. However, above this concentration, a slight decrease in cyclohexane conversion and cyclohexanol

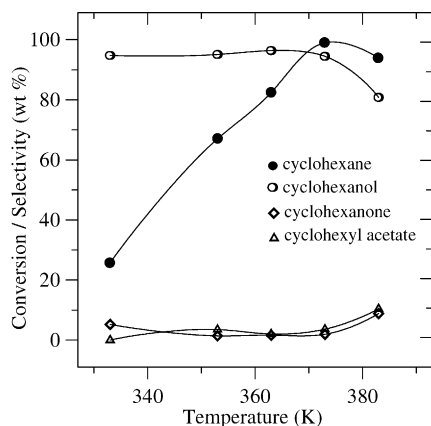


Fig. 7. Effect of reaction temperature on the conversion and selectivity over VMCM-41 (reaction conditions: substrate:oxidant ( $\text{H}_2\text{O}_2$ ) = 1:1;  $t$  = 12 h; catalyst = 3.3 wt.%).

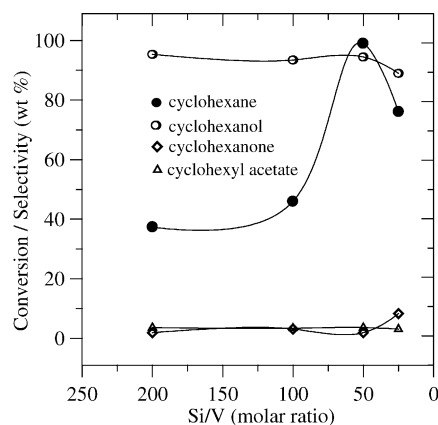


Fig. 8. Effect of Si/V molar ratio on the conversion and selectivity over VMCM-41 (reaction conditions: substrate:oxidant ( $\text{H}_2\text{O}_2$ ) = 1:1;  $T$  = 373 K;  $t$  = 12 h; catalyst = 3.3 wt.%).

selectivity was noticed. This could be attributed to the competent interaction of metal oxo-species in MCM-41 matrix with alkylperoxy species and cyclohexane [32].

Table 2 lists the results of recycling runs over calcined and washed VMCM-41 catalysts. In both the catalysts, cyclohexanol was obtained as the major product with small amounts of other products, viz., cyclohexanone and cyclohexyl acetate. It can also be seen from the table that the calcined catalyst showed high activity while a slight decrease in activity was noticed during the first run owing to the leaching of active vanadium ions under reaction condition. However, the activity is nearly the same in the subsequent cycles. Likewise, it is also interesting to note that the washed catalyst also showed a result similar to that of the recycled catalyst. The observation of loss of vanadium content upon recycling/washing is well supported by DRUV-VIS studies where a slight decrease in absorption band intensity was noted for the recycled/washed catalysts as compared to the calcined catalyst (Fig. 5a). However, the spectra remain nearly the same even after the treatment for the washed and recycled samples (Fig. 5b–d). On

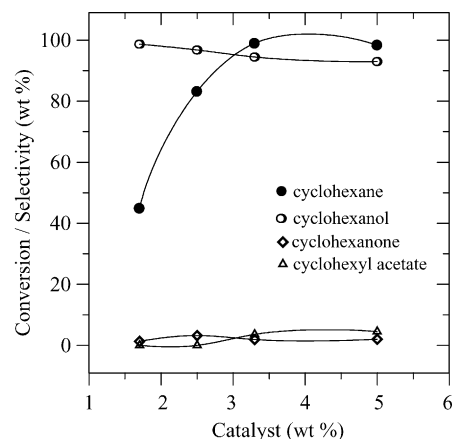


Fig. 9. Effect of catalyst concentration on the conversion and selectivity over VMCM-41 (reaction conditions: substrate:oxidant ( $\text{H}_2\text{O}_2$ ) = 1:1;  $T$  = 373 K;  $t$  = 12 h).

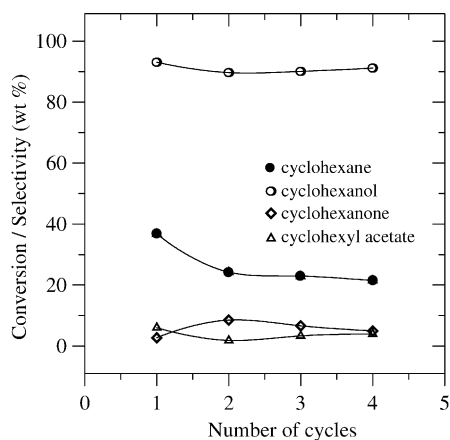


Fig. 10. Effect of recycling of calcined VS-1 catalyst (reaction conditions: substrate:oxidant ( $\text{H}_2\text{O}_2$ ) = 1:1;  $T = 373 \text{ K}$ ;  $t = 12 \text{ h}$ ; catalyst = 3.3 wt.%).

the other hand, filtrate and quenching studies carried out on washed catalyst shows no catalytic conversion of cyclohexane and furthermore, ICP-AES analysis yielded no evidence for any leached vanadium in the liquid phase, which is in accordance with literature [33]. Thus, the samples behave truly as heterogeneous catalysts.

The cyclohexane reaction was also carried out over microporous VS-1 catalyst and the results are shown in Fig. 10. It can be seen from this figure that the activity of VS-1 is quite low as compared to mesoporous VMCM-41 (Fig. 11). This could possibly be due to the less diffusivity of cyclohexane molecule (kinetic diameter =  $6 \text{ \AA}$ ) in the MFI pore channels ( $5.4 \text{ \AA}$ ) thereby the accessibility is restricted, which is in good agreement with an earlier report [34]. Further, it can also be noticed from this figure that VS-1 shows a decrease in conversion upon recycling, owing to leaching of active vanadium ions from the microporous matrix. On the other hand, in the absence of catalyst/initiator or in presence of vanadium free MCM-41 the reaction shows only  $\sim 10\%$  conversion while a continuous leaching of vanadium was observed for the  $\text{V}_2\text{O}_5$  supported MCM-41 [16]. Thus, the high activity of various mesoporous vanadium catalysts is due to the stabilization of vanadium ions in the silicate framework of MCM-41 structure.

Scheme 2 depicts the possible reaction pathway over the VMCM-41 catalyst. At first, acetic acid interacts with  $\text{H}_2\text{O}_2$  leading to the formation of peroxy acetic acid **2a**, which fur-

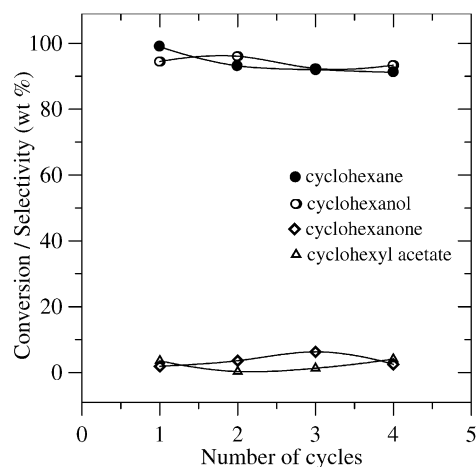


Fig. 11. Effect of recycling of calcined VMCM-41 catalyst (reaction conditions: substrate:oxidant ( $\text{H}_2\text{O}_2$ ) = 1:1;  $T = 373 \text{ K}$ ;  $t = 12 \text{ h}$ ; catalyst = 3.3 wt.%).

ther reacts with vanadyl species **2b** to produce vanadium peroxospecies **2c** [34,35]. The latter then interacts with ketone (initiator) to produce a chelate complex of the type **2d** followed by reaction of cyclohexane leads to cyclohexyl radical **2e**. The cyclohexyl radical in turn reacts with peroxyacetic acid **2a**, and  $\text{H}_2\text{O}_2$  through chain transfer free radical reaction [36] to produce the desired product, viz., cyclohexanol (see Scheme 3). Table 3 presents the results of the influence of various initiators on the reaction. It is noteworthy here that the use of other initiators such as acetaldehyde, acetone and cyclohexanone lowers both the (substrate) conversion and (cyclohexanol) selectivity. On the other hand, the use of MEK resulted in a significant increase in conversion, which could be attributed to the reduction of the induction period [4,37,38] by use of unsymmetrical ketone (MEK) resulted in the formation of chelate complex (**2d**) may easily be cleaved into free radical and thus the initiation of the chain transfer by hydrogen abstraction with cyclohexane takes place [39].

Table 4 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-dioxane due to possible partial decomposition of  $\text{H}_2\text{O}_2$  under the reaction conditions. However, the observed higher catalytic activity in acetic acid can be attributed to the stabilization of  $\text{H}_2\text{O}_2$  as peroxy acetic acid species **2a**

Table 3  
Influence of initiators on the oxidation of cyclohexane<sup>a</sup>

Initiator	Conversion (wt.%)	Selectivity (%)			
		Cyclohexanol	Cyclohexanone	Cyclohexyl acetate	Others <sup>b</sup>
MEK	99.0	94.5	1.9	3.6	–
Cyclohexanone	65.2	64.2	30.2	1.9	3.7
Acetone	61.7	63.8	31.4	1.4	3.4
Acetaldehyde	42.9	89.5	8.6	0.9	1.0

<sup>a</sup> Reaction conditions: substrate:oxidant ( $\text{H}_2\text{O}_2$ ) = 1:1; catalyst = 3.3 wt.%;  $T = 373 \text{ K}$ ;  $t = 12 \text{ h}$ .

<sup>b</sup> Hexanoic acid and cyclohexene.



Table 4  
Oxidation of cyclohexane over VMCM-41 with different solvents<sup>a</sup>

Solvents	Conversion (wt.%)	Selectivity (%)			
		Cyclohexanol	Cyclohexanone	Cyclohexyl acetate	Others <sup>b</sup>
Acetic acid	99.0	94.5	1.9	3.6	–
Methanol	38.9	98.6	–	0.2	1.2
1,4-Dioxan	34.3	98.2	–	0.4	1.4
Acetone	38.6	58.2	40.0	0.7	1.1

<sup>a</sup> Reaction conditions: substrate:oxidant (H<sub>2</sub>O<sub>2</sub>) = 1:1; catalyst = 3.3 wt.%; T = 373 K; t = 12 h.

<sup>b</sup> Hexanoic acid and cyclohexene.

Table 5  
Oxidation of cyclohexane over VMCM-41 with different oxidants<sup>a</sup>

Oxidant	Conversion (wt.%)	Selectivity (%)			
		Cyclohexanol	Cyclohexanone	Cyclohexyl acetate	Others <sup>b</sup>
H <sub>2</sub> O <sub>2</sub>	99.0	94.5	1.9	3.6	–
O <sub>2</sub>	83.1	95.3	–	4.7	–
Air	48.8	98.3	–	1.7	–
TBHP	63.4	–	82.4	7.4	10.2

<sup>a</sup> Reaction conditions: substrate:oxidant = 1:1; catalyst = 3.3 wt.%; T = 373 K; t = 12 h.

<sup>b</sup> Hexanoic acid and cyclohexene.

[6]. The reaction was also carried out with different oxidants, e.g., 70% TBHP, molecular O<sub>2</sub> and air, and the results are listed in Table 5. It can be seen from the table that the use of molecular O<sub>2</sub> and air leads to a decrease in substrate conversion due to milder oxidizing nature as well as difficulty in activation [6]. Although, the use of TBHP decreases the conversion, it produces cyclohexanone as major product with considerable amount of cyclohexyl acetate and other ring oxidized products. The observed higher cyclohexanone selectivity may possibly be due to stronger oxidation efficiency of TBHP [39] thereby leading to secondary reaction, viz., oxidation of cyclohexanol to cyclohexanone, and other ring-oxidation reactions, e.g., hexanoic acid [40], which was confirmed by GC–MS analysis.

#### 4. Conclusion

In summary, it can be concluded that mesoporous VMCM-41 molecular sieve is a very efficient and highly selective catalyst for the cyclohexane oxidation under relatively mild reaction conditions. Among the various oxidants, H<sub>2</sub>O<sub>2</sub> was found to be more suitable for the high substrate conversion and selective formation of cyclohexanol. Likewise, among the various initiators, MEK resulted in considerable increase in activity. Although small amounts of vanadium ions leach out at the initial stages of the reaction, like most other vanadium-based catalysts, however, in the case of VMCM-41, it was only the non-framework ions, which was washed out from the matrix. However, the remaining amount of vanadium ions in mesoporous VMCM-41 remain intact even after several recycling/washing treatments possibly due to the stabilization of vanadium ions in the mesoporous matrix. Thus, VMCM-41 behaves truly as heterogeneous catalyst.

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