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Catalytic activity of highly ordered mesoporous VMCM-48

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Abstract

Mesoporous VMCM-48 molecular sieves with Si/V (molar) ratios of 25–200 were synthesized hydrothermally and systematically characterized by various analytical and spectroscopic techniques, viz., XRD, N₂ sorption, TG-DTA, TEM, EPR, ⁵¹V MAS-NMR, FT-IR, and DRUV-VIS. XRD studies suggest that the substitution of vanadium occurs in the silicate framework structure of MCM-48. TEM and ED investigations confirm the highly ordered cubic structure of VMCM-48. EPR and ⁵¹V NMR studies indicate the presence of pentavalent vanadium ions in tetrahedral framework positions, while DRUV-VIS spectra show their existence in two different environments. The catalytic activity of these well-characterized (both in the calcined and the washed forms) materials was evaluated for cyclohexane oxidation under mild reaction conditions. All these catalysts gave high substrate conversion and excellent product (cyclohexanol) selectivity. Furthermore, unlike many other vanadium-based heterogeneous catalysts reported, the mesoporous VMCM-48 catalysts show minimal leaching of the active vanadium species. This was confirmed by washing, recycling and quenching experiments where only a small amount of vanadium ions leaches out in the case of calcined samples, while vanadium was not detected for the washed ones. Finally, the catalytic activity of VMCM-48 was also compared with mesoporous VMCM-41 as well as microporous VS-1 catalyst. The results indicate that the former showed superior activity to those of the latter two, such superiority could, however, be directly related to the amount of vanadium incorporated in MCM-48 being larger than the amounts in MCM-41 and MFI structures.

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1. Introduction

Vanadium-containing microporous molecular sieves, in general, have been found to be active catalysts for a number of oxidation reactions [1,2]. However, the activity and selectivity of these materials have been noticed to be sensitive on the preparation methods [3]. Furthermore, vanadium leaching has also been reported from the microporous matrix during the liquid phase oxidation reactions; the actual reaction is taking place under homogenous medium rather than heterogeneous conditions [1–4]. In addition, the microporous materials have yet another drawback, viz., the smaller pore size, which often restricts the accessibility of active sites to larger substrate molecules. On the other

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hand, the discovery of mesoporous materials, designated as M41S family [5] and consisting of thermally stable hexagonal MCM-41 and cubic MCM-48 structures have overcome the difficulties encountered by their microporous analogues, because they possess large pore diameters (2–20 nm), high surface areas (700–1500 m² g⁻¹) and substantial amounts of silanol (defect sites) groups (30–40%).

It is, however, noteworthy here that despite the successful development of the one-dimensional porous VMCM-41 catalysts, [6–17] only little is known about the three-dimensional porous VMCM-48 [18–20]. One of the main reasons is the difficulty encountered in the preparation of high quality samples having MCM-48 structure owing to a narrower homogeneity region of the phase [21]. On the other hand, the three-dimensional pore opening of MCM-48 is promising from the viewpoint of potential application of these materials owing to the resistance to pore blocking. As a

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consequence, it entails more agitated flow, which in turn increases the number of interactions between reactants and catalytic sites compared to the corresponding one-dimensional pore opening of MCM-41. As a consequence, the former exhibits much higher catalytic activity than the latter [22–28]. Moreover, the presence of ample amounts of silanol groups in MCM-48 [29] can stabilize vanadium in the matrix to a larger extent. Indeed, a similar observation was made earlier for chromium containing MCM-48 [27]. Thus, the study of VMCM-48 is of great importance with respect to its synthesis, characterization and properties.

Furthermore, realizing the importance of MCM-48 structure as well as its possible implication in catalysis, we selected cyclohexane oxidation reaction was selected for the evaluation of its performance. 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 [30]. In view of the importance of this reaction as well as the promising characteristics of MCM-48 structure, in this study, a systematic investigation was attempted to prepare high quality VMCM-48 and used it as a heterogeneous catalyst for the chosen reaction. Further, the performance, as well as the resistance against leaching of active vanadium species under reaction conditions, were assessed in comparison with the performances of frequently reported mesoporous VMCM-41 and microporous vanadium silicalite-1 (VS-1) catalysts.

2. Experimental

2.1. Starting materials

The following starting materials, viz., cetyltrimethylammonium bromide (CTAB; Aldrich; 99%), tetraethyl orthosilicate (TEOS; Aldrich; 98%), vanadium sulfate hydrate (VOSO₄·3H₂O; Aldrich; 98%), and sodium hydroxide (NaOH; Loba; 98%), were used as sources for template, silicon, vanadium, and alkali, respectively for the synthesis of VMCM-48. In addition, fumed silica (SiO₂; Aldrich; 99.8%) was used as the silica source for the synthesis of VMCM-41 and VS-1. In the case of VMCM-41, tetramethylammonium hydroxide (TMAOH; Aldrich; 25 wt.%) was used as a base while tetrapropyl ammonium bromide (TPAB; Merck; 99%) was used as the template for the synthesis of VS-1.

2.2. Synthesis

A series of vanadium-containing MCM-48 samples were synthesized under hydrothermal conditions as per the following procedure: First, a solution of vanadyl sulfate in water was added to TEOS and the mixture was stirred for 15 min. An aqueous solution of CTAB (25 wt.%) was added to NaOH and the mixture was stirred for 30 min. The latter was added to the first mixture and stirred for another 30 min for homogenization. The resulting gel was transferred into Teflon-lined stainless steel autoclaves and kept in an air oven at 373 K for 10 days. The solid product obtained was washed with distilled water, filtered and dried at 353 K for 12 h. The synthesis gel had a chemical (molar) composition of: SiO₂:0.25 Na₂O:0.3 $(CTA)_2O:xV_2O_5:60$ H₂O (x = 0.0025-0.02). The assynthesized samples were calcined in a flow of oxygen at 823 K for 12 h; the resulting sample was designated as calcined VMCM-48. For a comparison, mesoporous VMCM-41 [15] and microporous VS-1 [3] catalysts were also synthesized hydrothermally as per the reported procedures with the following typical gel composition: VMCM-41:SiO₂:0.135 (CTA)₂O:0.075 (TMA)₂O:0.13 Na₂O:68 H₂O:0.005 V₂O₅ and VS-1:SiO₂:0.5 Na₂O:0.5 (TPA)₂O:100 H₂O:0.005 V₂O₅. In addition, vanadium-free siliceous MCM-41 and MCM-48 samples were also prepared and characterized as per the procedure outlined previously with typical gel (molar) compositions of: SiO₂:0.135 (CTA)₂O:0.075 (TMA)₂O:0.13 Na₂O:68 H₂O for the former, and $SiO_2:0.3$ (CTA)₂:0.25 Na₂O:60 H₂O for latter [31].

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 nickel filtered Cu Ka radiation ($\lambda = 1.5418$ Å) and a step size of 0.02°. TEM and ED analysis were carried out on a Philips CM 200 operating at 200 kV (structural resolution of 0.23 nm). The image and the diffraction pattern were recorded with GATAN CCDcamera. The calcined VMCM-48 samples were used for TEM and ED studies. The sample was dispersed in ethanol with sonication (Oscar ultra sonics), and then a drop of it was placed on a carbon-coated grid (300 mesh; Sigma-Aldrich). 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} mbar) . 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 N2 adsorbed at $P/P_0 = 0.5$. Diffuse reflectance ultraviolet and visible (DRUV-VIS) spectra were recorded on JASCO-V 570 spectrophotometer with barium sulfate as standard. Electron spin resonance (ESR; Varian E-112) spectra were recorded at both room temperature and liquid N₂ temperature. FT-IR spectra of the were recorded on a Nicolet Impact 400 instrument with a 4 cm^{-1} resolution and 128 scans in the mid IR (400–4000 cm^{-1}) region using the KBr pellet technique. Inductively coupled plasmaatomic emission (ICP-AES; Labtam Plasma Lab 8440) analysis was used to detect the vanadium concentration in the catalysts. ⁵¹V MAS-NMR data were acquired at 131.37 MHz with spinning at 3 kHz on a Varian VXR-300S spectrometer.

2.4. Washing treatment

In order to check the stability of vanadium ions, we treated the calcined samples with ammonium acetate solution as per the procedure reported earlier [32]. For this purpose, about 100 mg of the calcined VMCM-48 was stirred with 30 ml of 1 M ammonium acetate solution for 12 h at room temperature. Then it was filtrated and washed repeatedly with distilled water and the solid residue was dried at 353 K for 12 h. Further, the dried sample was calcined at 773 K for 6 h in air in order to decompose the residual organics; such samples were designated as washed samples. In this way, the non-framework vanadium ions, if any present in the mesoporous VMCM-48 matrix, were also removed.

2.5. Reaction procedure

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 (calcined, washed, and recycled) with H₂O₂ (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. The products were analyzed by GC (Nucon 5700) with carbowax column.

2.6. Recycling/quenching

In order to check the leaching of vanadium ions (under reaction conditions) from the mesoporous matrix, we carried out several recycling and quenching experiments, as per the procedure reported elsewhere [32] on both calcined and washed catalysts. Each recycle experiment was done as per the following procedure. After the reaction, the catalyst was separated from the reaction mixture, washed with acetone, and was dried at 353 K. Then the catalyst was calcined at 823 K for 6 h in oxygen atmosphere, in order to remove the adsorbed molecules. The reaction was then carried out on the recycled catalyst. The filtrate experiment was carried out by separating the catalyst from the reaction mixture at room temperature and then the reaction was followed on both filtrate and catalyst. Each quenching experiment was carried out by separating the catalyst from the reaction mixture under the reaction conditions and the reaction was followed on the filtrate solution.

Fig. 1. XRD patterns of VMCM-48(100): (a) calcined; (b) washed; (c) calcined and recycled; (d) washed and recycled (inset shows the expanded of (c)).

3. Results and discussion

Both the as-synthesized and calcined samples were white. However, the color of the calcined sample upon exposure to air at room temperature turns into light yellow, which further intensifies as the vanadium content increases. The white color of the as-synthesized or the calcined samples suggests the presence of pentavalent vanadium ions in the matrix. XRD patterns of the as-synthesized (not reproduced here) and calcined VMCM-48 (Fig. 1) exhibit well-resolved reflections, which are typical characteristic of the cubic MCM-48 structure [5]. The computed average unit cell parameters, a_0 , for all samples are given in Table 1. It is interesting to note from this table that an increase in the a_0 value was observed for VMCM-48 as compared to its siliceous analogue. The shift in the reflections or the deviations of the a₀ values of VMCM-48 from MCM-48 could be attributed to the crystal radius of V^{5+} (0.495 Å) being larger than that of Si^{4+} (0.40 Å) [33] as well as to the V-O bond length being longer that of Si-O [6]. Such differences indicate a possible substitution of pentavalent vanadium ions in the silicate framework of MCM-48.

TG of as-synthesized VMCM-48 shows the total weight loss 60%, which corresponds to the removal of adsorbed water and/or gas molecules (5-7%, <373 K), removal of surfactant molecules (40%, 393-673 K) and condensation of silanol groups (5–6%, >673 K). These processes are supported by the corresponding endothermic and exothermic transitions in DTA. On the other hand, TG of calcined, washed and recycled VMCM-48 (Fig. 2) shows around 22-25% weight loss, accompanied by an endothermic peak at 369 K, which could be attributed to the removal of adsorbed water occluded within the mesopores. The typical behavior

(c) (b) (a) 2 4 6 8 2θ (deg.)



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Catalyst ^a	$a_0 (\text{\AA})^{\text{b}}$		Si/V (molar) ratio ^c		N ₂ sorption data						
	As-synthesized	Calcined	Synthesis gel	Calcined	Pore volume (ml g^{-1})	Pore diameter (Å)	Surface area $(m^2 g^{-1})$				
MCM-48	92.72	80.07	_	_	0.85	34	1220				
VMCM-48(200)	93.62	82.76	200	270	0.80	30	1130				
VMCM-48(100)	94.15	84.30	100	150	0.82	30	1180				
VMCM-48(100) ^d	94.15	83.46	100	175	0.80	29	1110				
VMCM-48(50)	95.86	86.12	50	67	0.78	28	1070				
VMCM-48(25)	97.11	88.01	25	34	_	_	_				

Table 1 XRD, ICP-AES, and N₂ sorption analysis results of various VMCM-48 samples

^a Number in parentheses is Si/V molar ratio in synthesis gel.

^b Average unit cell parameter (a₀) calculated using $1/d = \sqrt{(h^2 + k^2 + l^2)/a}$.

° ICP-AES.

^d After reaction.

of both the as-synthesized and calcined/washed/recycled samples suggests the mesoporous nature of VMCM-48. N₂ adsorption–desorption isotherms of calcined VMCM-48 (not reproduced here) shows a reversible type IV isotherm, which is also a typical presentation of mesoporous materials [34]. A sharp inflection noticed at pressure $P/P_0 = 0.2$ and 0.3 corresponds to capillary condensation within uniform mesopores. In addition, the inflection also confirms the absence of any micropore filling at low P/P_0 . Furthermore, no defined hysteresis loop was obtained in the adsorption and desorption cycle upon pore condensation. The pore volume, surface area and pore diameter deduced from N₂ sorption isotherms for all VMCM-48 samples are summarized in Table 1.

Fig. 3 depicts the TEM image and ED pattern of calcined VMCM-48. TEM shows a large area of pore structure with a cubic-type ordering on the (1 1 0) cubic plane, thus



Fig. 2. TG-DTA spectra of VMCM-48(100): (a) calcined; (b) washed; (c) calcined and recycled; (d) washed and recycled.

suggesting the ordered cubic MCM-48 structure. Further, that ED shows the regular cubic patterns confirms the good quality of the sample; the results are in good agreement with earlier reports of siliceous MCM-48 [35,36]. The vanadium content in different VMCM-48 samples were analyzed by



Fig. 3. (a) TEM and (b) ED of calcined VMCM-48(100).



Fig. 4. FT-IR spectra of VMCM-48(100): (a) as-synthesized; (b) calcined; (c) washed; (d) calcinded and recycled; (e) washed and recycled.

ICP-AES, and the results are also presented in Table 1. It can be seen from the table that the calcined samples have a deficiency of vanadium in comparison with the vanadium content in the synthesis gel. This observation may, however, be due to the fact that vanadium partly remains as soluble hydroxides (bluish-green color) in mother liquor under postsynthesis conditions; these were removed during filtration and washing treatment, therefore giving a lower vanadium content in the calcined samples.

FT-IR spectra of various VMCM-48 samples are presented in Fig. 4. It is clear from this figure that, upon calcination, the bands characteristic of template ν_{C-H} (2940 and 2889 cm^{-1}) disappears indicating complete removal of the surfactant molecules from the matrix. The major bands at 1220, 1080, 794 and 460 cm^{-1} are assigned to symmetric and asymmetric stretching of Si-O-Si vibrations. The band at 960 cm^{-1} is, in general, assigned to Si–O stretching vibrations of Si–O[–] R⁺ groups in the as-synthesized state, while it is assigned to Si-OH in the calcined state [37]. However, this band can also be assigned to the Si-O-V groups. Further, the intensity of the 960 cm^{-1} band, though not shown here, enhances with an increase in the vanadium content in all the as-synthesized, calcined, washed and recycled samples. This could be attributed to the presence of non-extractable Si–O–V linkage in the mesoporous matrix. On the other hand, non-framework species, e.g., V_2O_5 , present if any, may also give this band due to V-O-V bridges. However, the characteristic band of V-O-V (or V=O) in V₂O₅ is generally observed at around 830- 850 cm^{-1} , which is absent in these samples. Hence 960 cm^{-1} band may be assigned to Si–O–V linkage. Further, DRUV-VIS spectra indicate the absence of bands beyond 400 nm, which further confirms the absence of V_2O_5 . The broad band in the range of 3200–3800 cm⁻¹ is assigned to the surface internal hydroxyl groups, and the band around 1680 cm^{-1} is attributed to the bending of water



Fig. 5. ⁵¹V MAS-NMR of calcined VMCM-48(100).

molecules, δ_{OH} (H₂O). All these signatures are characteristic of mesoporous MCM-48 structure. Furthermore, there is no appreciable change in spectrum before and after reaction (see Fig. 4d). This indicates the intactness of the mesoporous structure during several treatment and catalytic runs, which is well supported by the XRD results (see also Fig. 1).

Fig. 5 shows the ⁵¹V MAS-NMR of calcined VMCM-48, which gives a signal at -576 ppm characteristic of pentavalent vanadium in tetrahedral environment [6,20]. It is important to note that the ⁵¹V MAS-NMR gives no indication of the presence of V2O5, which normally appears at -300 ppm. The absences of EPR signal at room temperature (300 K) and at liquid nitrogen (77 K) temperature for the as-synthesized samples indicate the complete aerial oxidation of tetravalent to pentavalent during synthesis and subsequent hydrothermal treatment (Fig. 6a), as such conversion of lowervalent to highervalent is known to occur rapidly in alkaline medium [38]. As expected, no EPR signal was observed for calcined and recycled samples (see Fig. 6b and c), thus suggesting that the vanadium is predominantly present as pentanvalent species in the framework structure.

Fig. 7 shows the DRUV-VIS spectra of various assynthesized vanadium samples. All the samples show two intense absorption maxima around 275 nm and at 340 nm, which are attributed to the charge transfer band associated with O^{2-} to V^{5+} in tetrahedral environment [6,7,9,13]. A similar observation was also noticed for VMCM-41 [6,7,9,11,13,14] and related mesoporous molecular sieves [39–41]. Further, in the visible region, no absorption band appeared for the as-synthesized sample, thus supporting the presence of V^{5+} in the matrix. Upon calcination and hydration, the spectra broadens (Fig. 8) towards lower energy (i.e., in the range of 350–550 nm). It is now generally accepted that the broadening of the spectra is due to the reversible coordination of water molecules to the pentava-



Fig. 6. EPR spectra of VMCM-48(100): (a) as-synthesized; (b) calcined; (c) washed; (d) calcined and recycled. The solid line (—) spectra were recorded at 300 K, while the dashed line (- -) spectra were recorded at 77 K.

lent vanadium ions present in the tetrahedral framework structure. It is, therefore, likely that a part of the pentavalent vanadium (Scheme 1), located preferably near the pore mouth, may be susceptible for such transformation. At this juncture, it should also be noted that the bands at around 330 and 480 nm, which are typical of bulk V_2O_5 (Fig. 8d), are absent for the calcined VMCM-48 (Fig. 8a), suggesting that the vanadium is mainly present in the framework of the



Fig. 7. DRUV-VIS spectra of as-synthesized VMCM-48: (a) Si/V = 200; (b) Si/V = 100; (c) Si/V = 50; (d) Si/V = 25.



Fig. 8. DRUV-VIS spectra of VMCM-48: (a) Si/V = 100; (b) Si/V = 50; (c) Si/V = 25; (d) V_2O_5 . The solid line (—) spectra represent the calcined samples, while the dotted line (- -) spectra represent the washed samples.

MCM-48 structure. However, the broadening is pronounced in the case of samples with higher vanadium content, which may be due to the water coordination as well as the presence of small amounts of non-framework vanadium. The latter may easily be removed by washing. Indeed, the washed samples confirm the above conjecture, as the broadening is considerably reduced for the washed samples (Fig. 8b and c).

Table 2 summarizes the results of cyclohexane oxidation over VMCM-48 along with the results of VMCM-41(100) and VS-1(100). It can be seen from this table that the activity is highest for VMCM-48 with a Si/V ratio of 100. However, a decrease in activity was observed for higher or lower vanadium contents. In the case of the latter, it is quite understandable that the amount of vanadium present in the matrix is insufficient for the reaction, while the former may lead to competing interaction of metal oxo-species with both alkylperoxy species and cyclohexane, thus inhibiting the catalytic reaction [42]. Fig. 9 depicts the results of the recycling studies performed over various vanadium-containing catalysts. One can see from this figure that VMCM-48 shows the conversion nearly the same even after third run indicating very little leaching of the active vanadium species under reaction conditions. This is in good agreement with the ICP-AES results of the recycled catalyst (0.69% vanadium) where only a small loss in vanadium was noticed after the second recycling (or third run) experiments as compared to the calcined catalyst (0.73% vanadium). In addition, these results are well supported by ICP-AES analyses of the filtrates of both calcined and washed samples. Furthermore, the reaction carried out over the quenched and filtrate solutions of the washed catalysts show



Scheme 1. Nature of vanadium in calcined VMCM-48.

Table 2 Oxidation of cyclohexane over various vanadium-containing molecular sieves^a

Catalyst ^b	Calcined				Washed			
	Vandium content (wt.%)	Cyclohexane conversion (wt.%)	Selectivity (wt.%)		Vanadium content	Cyclohexane conversion	Selectivity (wt.%)	
			Cyclohexanol	Cyclohexanone	(wt.%)	(wt.%)	Cyclohexanol	Cyclohexanone
VMCM-48(25)	1.63	73.3	81.1	10.5	1.32	65.2	80.0	10.6
VMCM-48(50)	1.40	81.7	85.8	10.4	1.20	75.2	86.2	10.7
VMCM-48(100)	0.73	96.4	86.0.	8.0	0.65	90.9	84.5	9.2
VMCM-48(200)	0.42	82.5	93.1	5.5	0.38	80.1	94.0	5.8
VMCM-41(100)	0.32	45.8	93.5	4.5	0.28	43.2	95.4	3.7
VS-1(100)	0.26	20.4	93.7	2.7	0.19	12.8	93.2	3.2
MCM-48	_	10.9	95.1	_	-	_	_	_

^a Reaction conditions: substrate:oxidant = 1:1; 10 ml acetic acid (solvent); MEK = 0.5 ml; catalyst = 3.3 wt.%; temperature = 373 K; time = 12 h. ^b Number in parentheses indicates the nominal Si/V molar ratio in synthesis gel.

a very low conversion, which is nearly the same as that obtained without the use of catalyst or in blank reaction (>10%). Thus, the nearly unaltered catalytic activity after the first recycling suggests a minimal leaching of vanadium from the VMCM-48 matrix. At this juncture, it is also interesting to note that the XRD patterns and N₂ sorption data (cf. Fig. 1 and Table 1) as well as FT-IR spectra (cf. Fig. 4) also show nearly identical behavior even after washing

and recycling studies, suggesting the intactness of the structure.

For comparison, the reaction was also carried out over mesoporous VMCM-41(100) and microporous VS-1(100), see also Table 2. Fig. 10 depicts the recycling results for all the three catalysts. VMCM-48(100) exhibits better conversion than the corresponding VMCM-41(100) and VS-1(100). The very high activity of VMCM-48 could be



Fig. 9. Recycling studies of the oxidation of cyclohexane over VMCM-48(100).



Fig. 10. Effect of recycling runs on the conversion of cyclohexane over various vanadium-containing molecular sieves.

attributed to the incorporation of larger amounts of vanadium than the latter two. On the other hand, the microporous VS-1 catalyst shows much lower activity owing to the leaching of larger amounts of vanadium ions from the matrix; also the lower diffusivity of cyclohexane (kinetic diameter = 6 Å) in the channels of silicalite-1 (pore opening = 5.4 Å) provides less accessibility of active sites, which is in agreement with an earlier study [43]. It can be seen from this figure that the activities of both VMCM-48 and VMCM-41 catalysts remain nearly the same after second recycle, and that much more leaching is observed for the VS-1 catalyst. Finally, the reaction pathway over the VMCM-48 catalyst can be described as follows: At first, acetic acid interacts with H₂O₂ leading to the formation of peroxy acetic acid, which further reacts with vanadyl species to produce vanadium peroxospecies [43,44]. The latter than interacts with ketone (initiator) to produce a chelate complex followed by reaction of cyclohexane leads to cyclohexyl radical. The cyclohexyl radical in turn reacts with peroxyacetic acid and H₂O₂ through chain transfer free radical reaction to produce the desired products.

4. Conclusion

In summary, various analytical and spectroscopic studies show the substitution as well as anchoring of pentavalent vanadium in the silicate framework of MCM-48. Furthermore, for a given initial gel composition, the threedimensional cubic framework of MCM-48 stabilizes much more vanadium than the corresponding one-dimensional hexagonal MCM-41 matrix owing to the high concentration of silanol group in the former, since it is known that the silanol groups can anchor metal ions more efficiently in the mesoporous matrix. It was also demonstrated that the VMCM-48 catalysts exhibited good activity for cyclohexane oxidation than many other vanadium-based molecular sieve catalysts. Further, several recycling and quenching studies indicate the heterogeneous nature of these catalysts.

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