

# The effect of vanadium sources on the synthesis and catalytic activity of VMCM-41

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## Abstract

Mesoporous VMCM-41 was synthesized hydrothermally using various vanadium sources, viz, tetravalent vanadium such as vanadyl sulfate and vanadyl acetylacetonate, as well as pentavalent vanadium like sodium vanadate and ammonium vanadate. The influence of different vanadium sources on the framework substitution of vanadium, as well as their catalytic activity for the oxidation of cyclohexane, was investigated. Among the different vanadium stocks, the tetravalent vanadium sources showed maximum vanadium incorporation in the silicate framework of MCM-41. As a consequence, these catalysts gave much higher substrate conversion and excellent product selectivity. On the other hand, the catalysts prepared from pentavalent vanadium sources showed lower activity owing to the smaller amounts of vanadium in the matrix. Although the activity of the catalyst slightly decreased after first recycle as due to leaching of small amounts of active vanadium species, it however remained nearly the same even after several recycles. This was further confirmed by washing experiments wherein non-framework vanadium ions were removed upon ammonium acetate treatment; the washed catalysts showed a similar activity to those of the recycled catalysts. Thus, recycled/washed VMCM-41 behaves truly as heterogeneous catalyst. Furthermore, the influence of pore size of the catalyst was tested for the oxidation of bulkier substrate, viz, cyclododecane.

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## 1. Introduction

Vanadium containing microporous molecular sieves were found to be active in a number of oxidation reactions [1,2]. However, the activity of these catalysts depends strongly on the preparation methods as well as the choice of vanadium sources for the synthesis [2–6]. Furthermore, vanadium leaching is one of the main problems in the liquid phase oxidation reactions; thus the actual reaction is taking place under homogeneous conditions rather than heterogeneous catalysis [1,2,6–8]. In addition, microporous-based molecular sieves have yet another drawback of smaller pore size, which restricts the accessibility of active sites to large substrate molecules. However, the discovery of mesoporous molecular sieves, designated as M41S family [9] consisting

of thermally stable hexagonal MCM-41 and cubic MCM-48 materials, overcomes many of these difficulties as these materials possess a larger pore diameter (2–10 nm), high surface area (700–1500 m<sup>2</sup> g<sup>-1</sup>) and substantial amount of silanol (defect sites) groups (30–40%) [9,10]. The large surface area and high concentration of silanol groups in the mesoporous materials stabilize the vanadium ions in a facile manner to that of the corresponding microporous analogues [11–14].

Several attempts have been made to incorporate vanadium in mesoporous MCM-41 type silicate framework, via isomorphous substitution [15–18], impregnation [19,20], ion-exchange [21], and chemical vapour deposition [22], as well as hexagonal mesoporous silica (HMS) matrix [23,24]. Substitution of vanadium in hexagonal mesoporous aluminophosphate (HMA) network has also been reported [25]. Although several reports have appeared on the incorporation of vanadium in MCM-41, only a few of them address

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the influence of vanadium sources on the extent of incorporation of vanadium in the framework vis-à-vis the catalytic activity. Reddy et al. [23,24] have investigated the leaching of active vanadium species from VHMS matrix and found that the leaching depends, in addition to the experimental conditions, on the nature of vanadium sources used in the synthesis of catalysts, the type of solvent, substrate, oxidant, etc. On the other hand, Deng et al. [26] have also documented the leaching of vanadium species from amorphous vanadium containing porous silica, which also depends on the nature of solvent, substrate, oxidant, etc. Therefore, in this investigation, an attempt has been made to study systematically the effect of various vanadium sources, viz, vanadyl sulfate, vanadyl acetylacetonate, sodium vanadate and ammonium vanadate, on the synthesis and catalytic activity of VMCM-41, as well as to evaluate the leaching behavior of the catalyst. In this regard, we chose cyclohexane oxidation reaction owing to the importance of the oxidation products, viz, cyclohexanol and cyclohexanone, in the production of adipic acid and caprolactam as they are the key intermediates in the manufacture of nylon-6 and nylon-66 polymers [27]. Furthermore, the influence of the mesoporosity of the catalysts was also tested for the oxidation of bulkier substrates such as cyclododecane.

## 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), vanadium sulfate hydrate trihydrate ( $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$ , 99%, Aldrich), vanadyl acetylacetonate ( $\text{VO}(\text{acac})_2$ , 97%, Lancaster), sodium vanadate ( $\text{NaVO}_3$ , 98%, Loba), ammonium vanadate ( $\text{NH}_4\text{VO}_3$ , 98%, Loba), sodium hydroxide ( $\text{NaOH}$ , 98%, Loba), sulfuric acid ( $\text{H}_2\text{SO}_4$ , 98%, BDH), cyclohexane (99.5%, Merck), hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30%, Qualigens), acetic acid (99.5%, Fischer), methyl ethyl ketone (MEK, 99%, SD). All the reagents used in this study were in as-received form.

### 2.2. Synthesis of VMCM-41

The VMCM-41 samples were synthesized hydrothermally using various vanadium sources with different Si/V (molar) ratio as per the procedure described elsewhere [18,28] with a typical molar gel composition of:  $\text{SiO}_2$ :0.135 (CTA) $_2\text{O}$ :0.13  $\text{Na}_2\text{O}$ :0.075 (TMA) $_2\text{O}$ :68  $\text{H}_2\text{O}$ :(0.02–0.0025)  $\text{V}_2\text{O}_5$ . The pH of the gel was adjusted to 11.5 and it was subjected to hydrothermal treatment at 373 K for 3 d. The final solid product, designated as as-synthesized VMCM-41, obtained was filtrated and dried for overnight. The samples were prepared from various vanadium sources,

viz, vanadyl sulfate, vanadyl acetylacetonate, sodium vanadate and ammonium vanadate. The as-synthesized samples are designated as VMCM-41(AVS), VMCM-41(AVA), VMCM-41(ASV), and VMCM-41(AAV), respectively. All as-synthesized VMCM-41 samples were 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. The calcined samples were designated in a way similar to that of the as-synthesized samples, i.e., VMCM-41(CVS), VMCM-41(CVA), VMCM-41(CSV), and VMCM-41(CAV), respectively. Unless otherwise stated, the VMCM-41 catalyst used in the present study was with Si/V ratio of 50.

For a comparison, microporous vanadosilicate or vanadium silicalite-1 (VS-1) was synthesized as per literature procedure using vanadyl sulphate as vanadium source [5]. The catalyst was prepared hydrothermally in a Teflon-lined stainless steel autoclave with a typical molar gel composition of:  $\text{SiO}_2$ :0.165(TPA) $_2\text{O}$ :22 $\text{H}_2\text{O}$ :0.01 $\text{V}_2\text{O}_5$ . First, aqueous solution of vanadyl sulphate was added to tetraethylorthosilicate and the mixture was stirred for 30 min. To this, tetrapropyl ammonium hydroxide was added and the mixture was stirred for 1 h to achieve homogenization of gel. The resulting gel was transferred into Teflon-lined stainless-steel autoclaves and kept in an air oven for crystallization at 443 K for 48 h. The solid product obtained was washed, filtered and dried at 383 K for 12 h. The resulting as-synthesized samples were calcined at 823 K for 12 h under oxygen. This sample is designated as VS-1(CVS). In addition, mesoporous siliceous MCM-41 was also prepared, for both loading of vanadium oxide as well as for a blank reaction, according to the procedure described earlier [29]. Vanadium oxide supported MCM-41 ( $\text{V}_2\text{O}_5/\text{MCM-41}$ ) was prepared by incipient wetness method. For this purpose, first, an aqueous solution of vanadyl sulphate ( $5 \times 10^{-3} \text{ M}$ ) was added dropwise to 1 g preactivated calcined MCM-41 and was kept under mild stirring for 3 h at room temperature. The resulting sample was repeatedly washed, dried and calcined in air for 8 h at 773 K. This sample is referred to as  $\text{V}_2\text{O}_5/\text{MCM-41}$  (CVS).

### 2.3. Characterization

All the samples were systematically characterized by various analytical and spectroscopic techniques such as low angle powder X-ray diffraction (XRD, Rigaku), thermogravimetry-differential thermal analysis (TG-DTA, Dupont 9900/2100), transmission electron microscopy (TEM, Philips CM 200 operated at 160 kV), nitrogen sorption (Sorpomatic 1990), Fourier transform-infrared spectroscopy (FT-IR, Nicolet Impact-400),  $^{29}\text{Si}$  magic angle spinning nuclear magnetic resonance ( $^{29}\text{Si}$  MAS-NMR, Varian 300X), diffuse reflectance ultraviolet-visible spectroscopy (DRUV-vis, Shimadzu UV-260), 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% H<sub>2</sub>O<sub>2</sub> (18 mmol) as oxidant and acetic acid as solvent medium (10 ml). The reaction was performed both in the presence and in the absence of methyl ethyl ketone (MEK, 5 mmol) as initiator at 373 K for 12 h. Oxidation of cyclododecane (12 mmol) was carried out under similar conditions as mentioned above for cyclohexane reaction with the only change of cyclododecane mixed solvents (5 ml acetic acid + 5 ml CH<sub>2</sub>Cl<sub>2</sub>) being utilized to make a homogeneous reaction mixture. After the reaction, the catalyst was separated and the products were extracted with diethyl ether and analyzed by gas chromatography (GC, Nucon 5700) with carbowax column. Further confirmation of oxidation products was made by GC-MS (Hewlett Packard G1800A) equipped with a HP-5 capillary column.

#### 2.5. Washing studies

In order to check the stability of vanadium ions in the mesoporous matrix, we treated the calcined samples, e.g., VMCM-41(CVS), with 1 M ammonium acetate solution. That is, about 100 mg of the calcined sample was stirred with 30 ml of the ammonium acetate solution for 12 h at room temperature and then it was filtered and washed repeatedly with distilled water; the solid residue was dried at 373 K. Further, the dried sample was calcined at 723 K for 6 h in air so as to decompose the residual organics; such samples were designated as washed catalysts, VMCM-41(WVS).

#### 2.6. Recycling studies

To check the stability and recycling ability as well as leaching of vanadium ions from the mesoporous matrix under reaction conditions, several recycling experiments were carried out for all the catalysts as per the procedure outlined elsewhere [30]. After the reaction was over, the catalyst was separated from the reaction mixture and washed

with acetone followed by drying at 353 K. Then, in order to remove the adsorbed molecules, the catalyst was activated at 823 K for 6 h in air. The reaction was then carried out on the recycled catalyst. The following catalysts, viz, VMCM-41(CVS), VMCM-41(CSV), V<sub>2</sub>O<sub>5</sub>/MCM-41(CVS), and VS-1(CVS), were used for the recycling purpose. The recycled catalysts were designated as VMCM-41(RVS), VMCM-41(RSV), V<sub>2</sub>O<sub>5</sub>/MCM-41(RVS), and VS-1(RVS), respectively.

### 3. Results and discussion

All as-synthesized and calcined VMCM-41 samples, irrespective of the vanadium sources and vanadium content, were white. However, the color of the calcined samples upon exposure to air at room temperature turns slowly into faint yellow, which further intensifies with increase in vanadium content. This could be attributed to the additional coordination of water molecules to form hexacoordinated vanadium ions in the mesoporous matrix [16]. Furthermore, the white color of the as-synthesized samples and the yellow color of the calcined samples suggest the pentavalent nature of vanadium in the mesoporous network. Powder XRD patterns (not reproduced here) of the various as-synthesized and calcined VMCM-41 obtained from different vanadium sources show characteristic diffraction patterns [28], which are typical of hexagonal mesoporous MCM-41 structure [9,10]. Table 1 summarizes the XRD, ICP-AES and nitrogen sorption data of different VMCM-41 samples having different Si/V (molar) ratios. As expected, for all the samples, an increase in the *d*-spacing (or *a*<sub>0</sub> values) was observed as compared to the siliceous analogue, MCM-41. The pragmatic expansion in the unit cell dimension with increase in Si/V ratio could possibly be attributed to a larger (crystal) radius of V<sup>5+</sup> (0.495 Å) than that of Si<sup>4+</sup> (0.40 Å) [31], and/or the longer V–O bond distance (1.8 Å) as compared to Si–O distance (1.6 Å) [15]. This clearly indicates a possible substitution of pentavalent vanadium ions in the framework structure of MCM-41. A similar observation was made earlier of vana-

Table 1  
XRD, ICP-AES, and N<sub>2</sub> sorption data of VMCM-41 synthesized using vanadyl sulfate as vanadium source

VMCM-41(AVS)		VMCM-41(CVS)		Vanadium <sup>d</sup> (wt%)	Pore volume (ml g <sup>-1</sup> )	Pore diameter (Å)	Surface area (m <sup>2</sup> g <sup>-1</sup> )
Si/V ratio <sup>a</sup>	<i>a</i> <sub>0</sub> <sup>b</sup> (Å)	<i>a</i> <sub>0</sub> <sup>b</sup> (Å)	Si/V ratio <sup>c</sup>				
25	49.67	48.02	35	1.23	0.69	24	892
50	49.05	46.08	70	0.76	0.85	29	919
100	48.26	43.62	130	0.32	0.81	27	980
200	47.34	41.30	240	0.21	0.86	26	1012
∞ <sup>e</sup>	46.64	40.84	∞ <sup>f</sup>	–	0.91	27	1040

<sup>a</sup> Nominal Si/V ratios in the synthesis gel.

<sup>b</sup> XRD data; average unit cell parameter calculated using the relation:  $1/d^2 = 4/3[(h^2 + hk + k^2)/a^2] + [l^2/c^2]$ .

<sup>c</sup> Actual Si/V ratio in the catalyst.

<sup>d</sup> ICP-AES data.

<sup>e</sup> Vanadium-free as-synthesized sample, MCM-41(A).

<sup>f</sup> Vanadium-free calcined sample, MCM-41(C).

Table 2  
XRD, ICP-AES, and N<sub>2</sub> sorption data results of various VMCM-41(50)<sup>a</sup> prepared using various vanadium sources

Sample	$a_0^b$ (Å)	Sample	$a_0^b$ (Å)	Vanadium content <sup>c</sup> (wt%)	Pore volume (ml g <sup>-1</sup> )	Pore diameter (Å)	Surface area (m <sup>2</sup> g <sup>-1</sup> )
VMCM-41(AVS)	49.05	VMCM-41(CVS)	46.08	0.76	0.85	29	919
VMCM-41(AVA)	48.76	VMCM-41(CVA)	45.50	0.66	0.75	27	945
VMCM-41(ASV)	46.97	VMCM-41(CSV)	43.89	0.46	0.78	28	960
VMCM-41(AAV)	46.80	VMCM-41(CAV)	43.82	0.35	0.76	28	930

<sup>a</sup> Number in parenthesis is nominal Si/V molar ratio in synthesized gel.

<sup>b</sup> XRD data; average unit cell parameter calculated using the relation:  $1/d^2 = 4/3[(h^2 + hk + k^2)/a^2] + [l^2/c^2]$ .

<sup>c</sup> ICP-AES data.

dium incorporated zeolite- $\beta$  [32] and HMS [24]. Table 2 presents XRD, ICP-AES and nitrogen sorption data of various VMCM-41 samples synthesized, with a Si/V (molar) ratio of 50, using different vanadium sources. However, it is interesting to note that a considerable variation in the diffraction data is observed for the same initial (gel) composition, which could be accounted for the very different amounts of vanadium incorporated in the framework. This is well supported by the ICP-AES results wherein distinct vanadium content is noticed for all these samples under consideration. TEM studies (not reproduced here) of VMCM-41(CVS) having Si/V ratio of 50 showed a regular hexagonal array of uniform channels [28] typical of MCM-41 structure. ED investigation (not reproduced here) performed on the same sample also confirms the periodicity and high crystallinity [28] of VMCM-41. Both the TEM and ED results are consistent with XRD data, thus validating the hexagonal structure of the samples [10].

Fig. 1 which depicts the nitrogen adsorption–desorption isotherms of VMCM-41(CVS), shows reversible type IV adsorption isotherms [33]. A sharp inflection between relative pressure  $P/P_0 \sim 0.3$  corresponds to capillary condensation within the mesopores (see the inset of Fig. 1). The sharpness of this step reflects the uniformity of the pores. Further, the isotherms also confirm the absence of any mi-

cropore filling at low  $P/P_0$ . The pore volume, surface area and pore diameter deduced from N<sub>2</sub> sorption isotherms for all the VMCM-41 samples are compiled in Tables 1 and 2. All the results corroborate the mesoporous nature of catalysts [9,10]. Table 2 also presents the vanadium analysis data. It is clear from this table that relatively low vanadium incorporation was observed in the case of pentavalent vanadium as the starting sources. On the contrary, tetravalent vanadium sources favor high vanadium incorporation in the matrix. The very different influence of these two sources on the vanadium incorporation in the MCM-41 network may be explained as follows: Under the same synthesis conditions and initial vanadium concentration, the tetravalent vanadium sources form monomeric VO<sub>4</sub><sup>3-</sup> species while the pentavalent vanadium sources produce both monomeric VO<sub>4</sub><sup>3-</sup> and dimeric V<sub>2</sub>O<sub>7</sub><sup>2-</sup> species [34]. It seems likely that the dimeric species hinder the incorporation of vanadium in the matrix, and hence part of the vanadium ions remains in solution.

TG of as-synthesized VMCM-41 samples (not reproduced here) showed > 50 wt% weight loss [28] attributed to the removal of adsorbed water and surfactant molecules. On the other hand, the calcined sample showed a relatively large weight loss (not reproduced here) of > 20 wt% [28] suggesting that part of the silanol groups in the matrix may possibly be consumed for stabilization of vanadium ions in a similar manner to that reported for chromium incorporated MCM-41 [35]. DTA traces (also not reproduced here) showed the corresponding endothermic/exothermic transitions characteristic of mesoporous MCM-41 materials. The above conjecture is well supported by <sup>29</sup>Si MAS-NMR studies (not reproduced here) of as-synthesized MCM-41( $\infty$ ) and VMCM-41(AVS) with a Si/V ratios of 25–100, wherein the spectra showed three signals at –110.0 (Q<sub>4</sub>), –100.0 (Q<sub>3</sub>), and –90.1 (Q<sub>2</sub>) ppm corresponding to Si(OSi)<sub>4</sub>, Si(SiO)<sub>3</sub>(OH), and Si(OSi)<sub>2</sub>(OH)<sub>2</sub>, respectively [28]. The spectra also confirmed the presence of large number of internal silanol groups (defect sites  $\equiv$ Si–OH; Q<sub>3</sub> sites) in the case of siliceous MCM-41 [36]. However, as the vanadium content in the sample increases, the intensity of the Q<sub>3</sub> sites decreases, or the intensity ratio of Q<sub>4</sub>/Q<sub>3</sub> sites increases. This implies that there is an interaction between vanadium ions and hydroxyl groups of the silicate MCM-41 matrix. That is, during the synthesis, in addition to the isomorphous substitution, vanadyl species

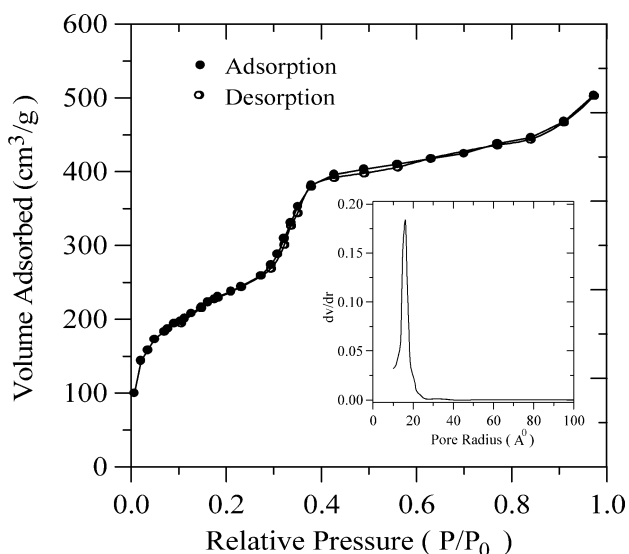


Fig. 1. N<sub>2</sub> sorption isotherms of VMCM-41(CVS). The inset shows pore size distribution.

(VO<sub>2</sub><sup>2+</sup>) may also bind to the surface termination groups (≡Si–OH) in the MCM-41 matrix via condensation to form (SiO)<sub>3</sub>V=O type units [13,14,18].

DRUV–vis spectra of various as-synthesized vanadium samples (Fig. 2a–d) prepared from different vanadium sources show two intense absorption bands at 275 nm and 340 nm. These bands are attributed to charge transfer transitions associated with O<sup>2–</sup> to V<sup>5+</sup> [37]. Further, the absence of *d–d* transitions in the region 600–800 nm, and of a tetravalent vanadium EPR signal (not reproduced here) confirms the above assignment [16]. While the charge transfer bands at 275 nm are consistent with V<sup>5+</sup> in tetrahedral environment, the other charge transfer band at 340 nm is attributed to V<sup>5+</sup> with V=O double bond and V–O single bonds [24,38]. Indeed, these bands closely resemble those of NH<sub>4</sub>VO<sub>3</sub> (Fig. 2i) indicating isolated tetrahedral environment of V<sup>5+</sup> in the mesoporous VMCM-41 matrix, which is in good agreement with literature [38]. On the other hand, the bands at 275 nm and 340 nm may also be assigned to distorted tetrahedral arrangement of V<sup>5+</sup> (as a result of anchoring/grafting on the pore walls of MCM-41) in a way similar to that reported for various vanadium-loaded/grafted amorphous/mesoporous silica materials [30,38]. Hence, it is highly difficult to distinguish between these two types of species and DRUV–vis, and therefore only an averaged

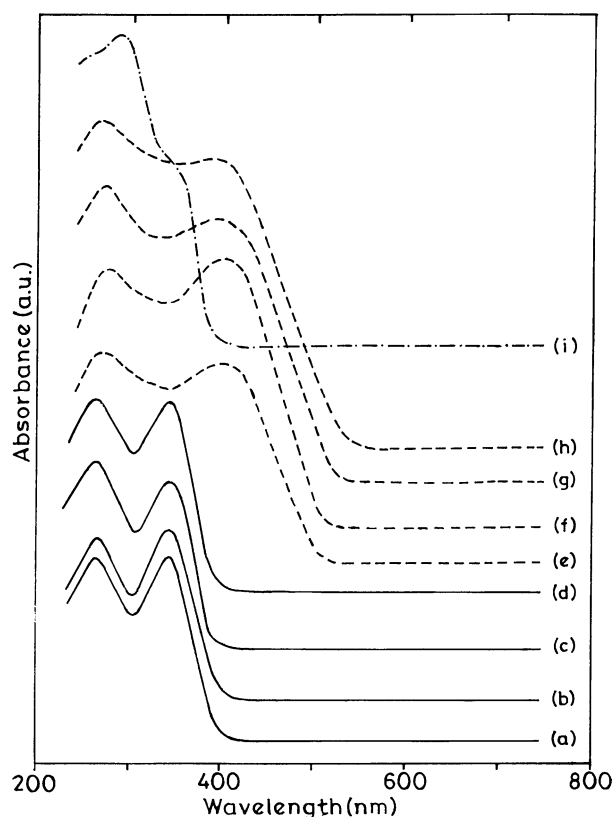


Fig. 2. DRUV–vis spectra of various mesoporous vanadosilicates: (a) VMCM-41(AVS), (b) VMCM-41(AVA), (c) VMCM-41(ASV), (d) VMCM-41(AAV), (e) VMCM-41(C), (f) VMCM-41(CVA), (g) VMCM-41(CSV), (h) VMCM-41(CAV), and (i) NH<sub>4</sub>VO<sub>3</sub>.

structure of the tetrahedral vanadium species can be detected. On the other hand, DRUV–vis studies of the various calcined samples (Fig. 2e–h) prepared from different vanadium sources showed considerable broadening of the spectra towards lower energy (in the region 400–500 nm). Such broadening could be attributed to the additional water coordination of the distorted tetrahedral vanadium species, which results in the formation of hexacoordinated vanadium species in a way similar to the reported for vanadium supported silica [39,40] and vanadium incorporated HMS [24]. This implies that a small part of V<sup>5+</sup> is present on the wall surface as distorted tetrahedral arrangement, while the majority of V<sup>5+</sup> is located mainly in the regular tetrahedral environment in the framework of VMCM-41. Photoluminescence studies [41] have shown evidence for these two different kinds of (regular and distorted) tetrahedral vanadium species in the framework sites, which are accessible and inaccessible to water molecules, respectively.

Table 3 summarizes the cyclohexane oxidation results over various vanadium containing catalysts. It can be seen from this table that the catalysts VMCM-41(CVS) and VMCM-41(CVA) show excellent activity as compared to VMCM-41(CSV) and VMCM-41(CAV). The modest activity of the latter catalysts is accounted for the low vanadium content in the samples. It is however interesting to note that, irrespective of the nature of catalysts, the washed and recycled catalysts show only a small loss in activity as compared to their calcined counterparts due to leaching of non-framework vanadium ions from the mesoporous matrix, which is consistent with vanadium analyses in the samples (cf. Table 3). The observation of loss of vanadium content upon recycling/washing is well supported by DRUV–vis studies [28] where a slight decrease in absorption band intensity was noted for the recycled/washed catalysts as compared to the calcined catalyst (not reproduced here). However, the spectra remain nearly the same even after the treatment for the washed and recycled samples. At this juncture, it is also interesting to note that the reaction carried out in the absence of catalyst or initiator or with vanadium-free MCM-41 showed much lower conversion (Table 3), thus confirming the role of vanadium ions in the reaction. In addition, filtrate and quenching studies, carried out on washed catalyst, show no catalytic conversion of cyclohexane. Thus, the observed high activity of the mesoporous VMCM-41 catalysts is due to the stabilization of vanadium ions in the silicate framework. Moreover, unlike in most cases when extreme reaction conditions such as high pressure and high temperature are adopted, in the present investigation where the use of methyl ethyl ketone as initiator facilitate the reaction under standard experimental conditions.

In order to check the vanadium leaching as well as the repeated use of the catalysts, several recycling runs were performed over VMCM-41(CSV). Fig. 3 illustrates the recycling studies. It can be seen from this figure that during the first recycling experiment (or second run), a decrease in conversion is noticed, and thereafter a minimal or no

Table 3  
Oxidation of cyclohexane over vanadium containing catalysts (Si/V = 50)<sup>a</sup> prepared using various vanadium sources<sup>b</sup>

Catalyst	Vanadium content <sup>c</sup> (wt%)	Conversion (wt%)	Selectivity (wt%)		
			Cyclohexanol	Cyclohexanone	Others <sup>d</sup>
VMCM-41(CVS)	0.76	99.0	94.5	1.9	3.6
VMCM-41(CVS) <sup>e</sup>	0.76	10.9	90.5	1.2	8.3
VMCM-41(RVS) <sup>f</sup>	0.63	93.2	96.1	3.6	0.3
VMCM-41(WVS) <sup>g</sup>	0.65	93.4	90.0	5.5	5.5
VMCM-41(CVA)	0.66	94.0	93.2	4.0	2.8
VMCM-41(CSV)	0.46	72.0	92.5	4.6	2.9
VMCM-41(RSV) <sup>f</sup>	0.37	65.3	88.6	8.9	2.5
VMCM-41(CAV)	0.35	58.0	92.8	5.6	1.6
V <sub>2</sub> O <sub>5</sub> /MCM-41 (CVS)	0.59	97.3	86.3	7.6	6.1
V <sub>2</sub> O <sub>5</sub> /MCM-41 (RVS) <sup>f</sup>	0.32	75.8	99.6	–	0.4
VS-1(CVS)	0.54	36.8	93.9	2.7	2.4
VS-1(RVS) <sup>f</sup>	0.30	24.2	89.7	8.5	1.8
MCM-41(C) <sup>h</sup>	–	11.6	96.4	–	3.6
No catalyst	–	9.0	78.1	–	21.9

<sup>a</sup> Number in parenthesis is nominal Si/V molar ratio in synthesized gel.

<sup>b</sup> Reaction conditions: substrate-to-oxidant (molar) ratio = 1; acetic acid (solvent) = 10 ml; time = 12 h; temperature = 373 K; initiator = MEK (0.5 ml); catalyst amount = 3.3 wt%.

<sup>c</sup> ICP-AES data.

<sup>d</sup> Mainly cyclohexyl acetate.

<sup>e</sup> Without initiator.

<sup>f</sup> Recycled catalyst: first cycle (or second run).

<sup>g</sup> Washed catalyst.

<sup>h</sup> Vanadium-free calcined catalyst.

Table 4  
Oxidation of cyclododecane over mesoporous and microporous vanadosilicates with a Si/V ratio of 50<sup>a</sup>

Catalysts	Vanadium content <sup>b</sup> (wt%)	Conversion (wt%)	Selectivity (wt%)		
			Cyclododecanol	Cyclododecanone	Others
VMCM-41(CVS)	0.76	93.8	80.0	12.0	8.0
VMCM-41(RVS) <sup>c</sup>	0.63	81.6	72.8	20.5	6.7
VS-1(CVS)	0.54	18.0	65.5	17.5	17.0

<sup>a</sup> Reaction conditions: 373 K; 12 h; substrate:oxidant (H<sub>2</sub>O<sub>2</sub>) = 1:1; catalyst = 50 mg (2.48 wt%); solvent = (acetic acid 5 ml + dichloromethane 5ml); MEK = 5 mmol.

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

<sup>c</sup> Third cycle (or fourth run).

loss in activity is observed. The decrease in the conversion during the second run is ascribed to the leaching of small amounts of non-framework vanadium under reaction conditions, which is consistent with ICP-AES results (Table 3) as well as DRUV-vis studies (not reproduced here) of the recycled catalysts, viz, VMCM-41(RSV). In this regard, it is noteworthy here that under a similar reaction conditions, the chromium containing mesoporous molecular sieves leach much higher amounts of chromium ions [35]. Likewise, the washed catalyst, VMCM-41(WVS), was also tested for vanadium leaching and recycling ability. Fig. 4 depicts the results of such a study. It is clear from this figure that the catalytic activity is nearly the same as in the first and subsequent cycles. That is, nearly no change or only a very slight change in the activity is noticed. This is ably supported by ICP-AES analyses, which yielded no evidence for leached vanadium in filtrate solution. Furthermore, the XRD patterns [28] of the catalysts remain nearly the same (not reproduced here) even after recycling or washing experiment,

indicating the intactness of the MCM-41 structure. Thus, the samples behave truly as heterogeneous catalysts.

The catalytic activity of VMCM-41(CVS) was also compared with its microporous analogue, VS-1(CVS) (Table 3). It is clear from this table that the activity of the latter is much lower, which could mainly be attributed to the low diffusivity, and hence little accessibility, of active sites of cyclohexane (kinetic diameter = 6 Å) in the micropore channels of MFI structure [6]. This conjecture is consistent with the results obtained for the bulkier substrates, wherein the microporous catalyst VS-1(CVS) showed meager activity as compared with mesoporous VMCM-41(CVS) catalyst (Table 4). At this juncture, it is also important to mention that the catalyst VS-1(CVS), as well as V<sub>2</sub>O<sub>5</sub>/MCM-41 (CVS), showed a continuous decrease in activity upon cycling, which is attributed to repeated leaching of active vanadium ions from the matrix. Table 4 presents the results of the oxidation of a bulkier cyclododecane over microporous and mesoporous vanadosilicate catalysts. It is inter-

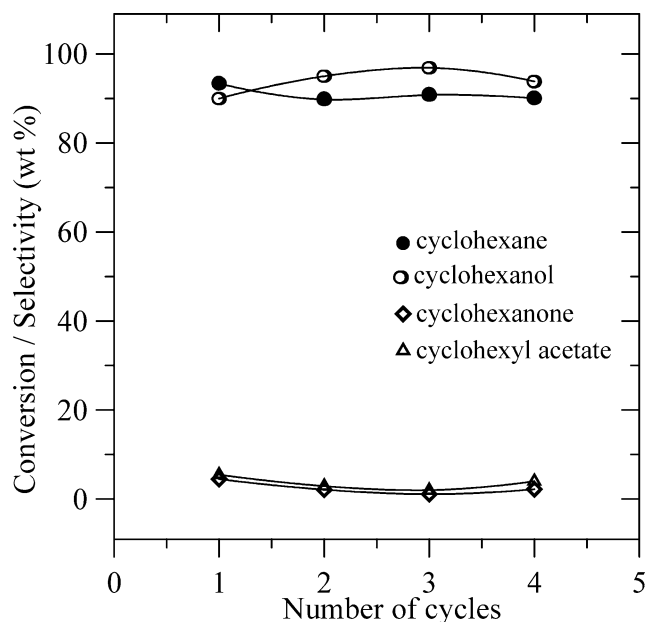


Fig. 3. Recycling studies of VMCM-41(CSV) (reaction conditions: substrate:oxidant = 1;  $T = 373$  K;  $t = 12$  h; catalyst amount = 3.3 wt% of substrate).

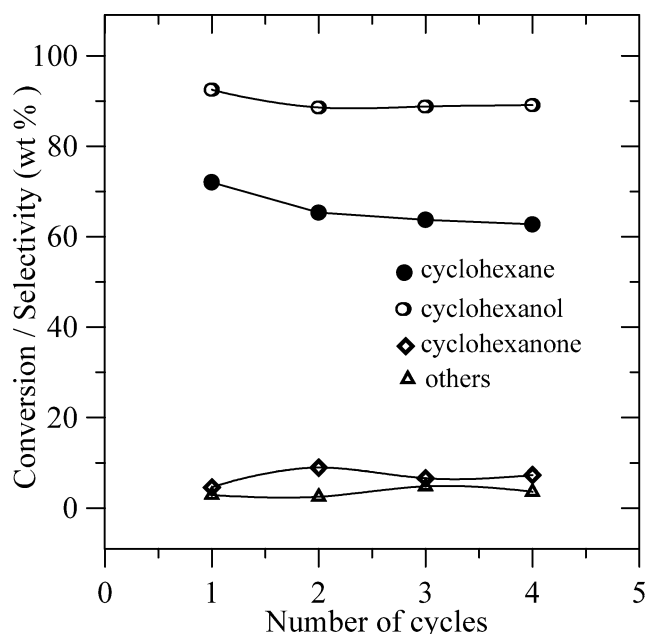


Fig. 4. Recycling studies of VMCM-41(WVS) catalyst (reaction conditions: substrate:oxidant = 1;  $T = 373$  K;  $t = 12$  h; catalyst amount = 3.3 wt% of substrate).

esting to note that VMCM-41(CVS) showed good activity for the cycloalkane oxidation, while VS-1(CVS) catalyst showed fairly small activity owing to their pore size restriction. Furthermore, it is noteworthy that the mesoporous catalyst showed much higher activity as compared to many other catalysts reported for the oxidation of cyclododecane [15,42].

#### 4. Conclusion

In summary, it is clear from this study that the use of different vanadium sources for the synthesis of VMCM-41 significantly influences the extent of vanadium incorporation in the mesoporous matrix and therefore the catalytic activity. Under similar synthesis conditions, the tetravalent vanadium sources incorporate more vanadium due to the formation of monomeric  $\text{VO}_4^{3-}$  species, while the use of pentavalent vanadium sources results in the formation of both monomeric  $\text{VO}_4^{3-}$  and dimeric  $\text{V}_2\text{O}_7^{2-}$  species. Further, the recycling and washing studies also showed very little or no loss in activity; thus the vanadium containing mesoporous MCM-41 behaves as truly heterogeneous catalysts irrespective of vanadium sources employed for the preparation. On the other hand, the yield is directly related to the vanadium content. In this regard, the tetravalent sources are preferred for the synthesis as they facilitate vanadium incorporation much more efficiently than the pentavalent vanadium. Finally, this investigation also demonstrates that the VMCM-41 catalysts are a promising alternative for the oxidation of bulkier molecules.

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