A novel route to produce phthalic anhydride by oxidation of $o$-xylene with air over mesoporous V-Mo-MCM-41 molecular sieves

M. Selvaraj *, T.G. Lee

Yonsei Center for Clean Technology, Yonsei University, Seoul 120-749, South Korea

Received 29 July 2004; received in revised form 18 February 2005; accepted 27 May 2005

Abstract

Mesoporous V-Mo-MCM-41 with Si/(V + Mo) ratio equal to 46, 92, 184 and 230 were synthesized using cetyltrimethylammonium bromide surfactant as template under hydrothermal conditions while the mesoporous materials were characterized using several techniques e.g., ICP-AES, XRD, N$_2$-adsorption, FTIR, TG/DTA, $^{51}$V-MAS-NMR, $^{95}$Mo-MCM-41, $^{29}$Si-MAS-NMR, SEM and TEM. The d-spacing value and unitcell parameter in the V-Mo-MCM-41 increases by increasing the metal ions content. FTIR studies showed that V- and Mo-ions were incorporated into the hexagonal mesoporous MCM-41 materials, however, the wavenumber of the anti-symmetric Si–O–Si vibration bands (1097 cm$^{-1}$) in V-Mo-MCM-41 are higher than those in Si-MCM-41 (1081 cm$^{-1}$). These bands should be due to the increase of the mean Si–O distance in the wall caused by the substitution of the small ionic radii of silicon by the larger ionic radii of vanadium and molybdenum. The surface area, pore diameter, pore volume, hydrothermal stability and acid sites in the V-Mo-MCM-41 decreases by increasing the metal ions content. The incorporated metal ions as V$^{5+}$ and Mo$^{6+}$ in V-Mo-MCM-41 are coordinated to Si(IV) by tetrahedral environments. The synthesized V-Mo-MCM-41 materials were found to be effective as catalysts in the oxidation of alkyl aromatics, e.g., in the oxidation of $o$-xylene using O$_2$ gas as the oxidizing agent for the production of phthalic anhydride. The effect of reaction temperature, feed flow rate ratio ($o$-xylene:O$_2$ gas), contact time and recyclability on the selectivity of phthalic anhydride were studied. Thus, the selectivity of phthalic anhydride in the presence of V-Mo-MCM-41(46) catalyst was higher than that of other V-Mo-MCM-41 catalysts due to increasing the catalytic activity on the inner side pores of silica surface.

© 2005 Elsevier Inc. All rights reserved.

Keywords: V-Mo-MCM-41; Acidity; Recyclability; Oxidation of $o$-xylene; Conversion of $o$-xylene; Selectivity of phthalic anhydride

1. Introduction

Phthalic anhydride has been used in the manufacture of phthaleins, phthalates, benzoic acid, synthesis of indigo and artificial resins (glyptal). Before 1970, there have been a large number of investigations on the kinetics of $o$-xylene oxidation. In general potassium sulfate promoted catalysts have been investigated [1–3]. Although calderbank [4] has used an unpromoted silicon carbide for the supported catalyst in his investigations. During an investigation of the oxidation of $o$-xylene in a transported bed reactor [5] it became apparent that a silica gel supported catalyst had very poor selectivity for phthalic anhydride formation. This result was somewhat unexpected since two groups active in the field of hydrocarbon oxidation kinetics has reported the use of a silica gel supported catalyst.

In the former case [1,2] the low selectivity to phthalic anhydride might have been thought to be due to the low conversions (less than 5%) investigated. In the latter investigation [3], the only detail given for the used catalyst while the catalyst is commonly SiO$_2$-supported and doped V$_2$O$_5$. Normal selectivity to phthalic anhydride was obtained in the study. Because of these somewhat
conflicting results a more extensive review of the catalyst literature was made. It was found that a Japanese group [6–9] had conducted a considerable amount of research into o-xylene and naphthalene oxidation. The oxidation of o-xylene and naphthalene was carried out using silica gel and titania-supported catalysts. The phthalic anhydride has been synthesized using several catalysts viz., Aero PAA [10], 902 catalyst, Von Heyden WO and V₂O₅/Sb₂O₃ on TiO₂ by Wainwright and Hoffmann. The phthalic anhydride maximum yield was 30% over Aero PAA at 399 °C, 50% over 902 catalyst at 350 °C, 70% over Von Heyden WO at >370 °C and 80% over V₂O₅/Sb₂O₃ on TiO₂ at 370 °C for 100% conversion of o-xylene. The yield and selectivity of phthalic anhydride in the above catalysts are low because of having small surface areas. So the zeolites materials as catalysts have been instead to use for the synthesis of phthalic anhydride.

The discovery of mesoporous molecular sieves designated as MCM-41 have been reported by researchers at Mobil [11]. V-MCM-41 mesoporous molecular sieves were synthesized using vanadate salts such as ammonium vanadate [12], vanadyl sulfate [13–16] or vanadium chloride [13] for catalytic oxidation of organic compounds using H₂O₂, TBHP and 2,6-DTBP as oxidizing agent by several researchers. Zhang et al. synthesized Mo-MCM-41 mesoporous molecular sieves using ammonium molybdenate as the template. The phthalic anhydride has been synthesized using sodium metasilicate (Na₂SiO₃·5H₂O), vanadyl sulfate, ammonium molybdenate, cetyltrimethylammonium bromide (C₁₆H₃₃(CH₃)₃N⁺Br⁻) and sulfuric acid (H₂SO₄). The synthesis of phthalic anhydride was carried out using the reagents, o-xylene. The used all chemicals were purchased from M/s Aldrich & Co., USA.

2.2. Synthesis of V-Mo-MCM-41

For the synthesis of the V-Mo-MCM-41 (Si/(V + Mo) = 46), 21.2 g (1 mol) sodium metasilicate (44–47% SiO₂, dissolved in 50 g of deionized water) was mixed with 0.226 g (0.0125 mol) of vanadyl sulfate (dissolved in 10 g of deionized water) and 1.544 g (0.0125 mol) of ammonium molybdenate (dissolved in 10 g of deionized water). This mixture was stirred for 30 min using a mechanical stirrer at a speed of about 250 rpm and in order to reduce the pH to 10.8, 1 N of sulfuric acid was added with continuous stirring for another 30 min at a speed of about 250 rpm until the gel formation. After that, 9.1 g (0.25 mol) of cetyltrimethylammonium bromide was added drop by drop (30 ml/h) by the dual syringe pump so that the gel was changed into suspension. After further stirring for 1 h the resulting synthesis gel of composition 1SiO₂/0.01125V₂O₅/0.0125MoO₃/0.25CTMABr/100H₂O, was transferred into Teflon-lined steel autoclave and heated at 165 °C for 48 h. After cooling to room temperature, the material was recovered by filtration, washed with deionized water and ethanol and finally calcined at 540 °C for 6 h in air.

The different V-Mo-MCM-41 catalysts (Si/(V + Mo) = 92, 184 and 230) were also synthesized in an above similar manner wherein only the ratio of sodium metasilicate, vanadyl sulfate and ammonium molybdenate was adjusted and the input in gel molar compositions 1SiO₂/xV₂O₅/yMoO₃/0.25CTMABr/100H₂O (x = 0.00625–0.0025; y = 0.00625–0.0025).

2.3. Hydrothermal treatment of V-Mo-MCM-41

V-Mo-MCM-41 samples were treated in boiling water in polypropylene bottles and retained at 100 °C for 1 week in order to evaluate the hydrothermal stability of the mesoporous structure of MCM-41 materials.

2.4. Physicochemical characterization

The vanadium and molybdenum content in V-Mo-MCM-41 samples were recorded using ICP-AES with allied analytical ICAP 9000.

The crystalline phase identification and phase purity determination of the calcined V-Mo-MCM-41 samples were carried out by XRD (Philips, Holland) using nickel filtered CuKα radiation (λ = 1.5406 Å). The samples were scanned from 0.5° to 7° (20) angles in steps of 0.5°, with a count of 5 s at each point. In order to pro-
tect the detector from the high energy of the incident and diffracted beam, slits were used in this work.

The surface areas and pore properties of V-Mo-MCM-41 samples before and after hydrothermal treatments were analyzed using a NOVA-1000 (QUANTA-CHROME, version 5.01) sorptometer. The calcined samples were dried at 130 °C and evacuated overnight for 8 h in flowing argon at flow rate of 60 ml min\(^{-1}\) at 200 °C under vacuum. Surface area, pore size, pore volume and wall thickness was obtained from these isotherms using the conventional BET and BJH equations.

Infra red spectra were recorded with a Nicolet Impact 410 FTIR Spectrometer in KBr pellet (0.005 g sample with 0.1 g KBr) scan number 36, resolution 2 cm\(^{-1}\). The data was treated with Omnic Software.

The weight loss, dehydration and dehydroxylation for as-synthesized V-Mo-MCM-41 samples was evaluated by a thermogravimetric–differential thermal analysis (TG/DTA) in a Rheometric scientific (STA 15HT) thermobalance. 10–15 mg of as-synthesized MCM-41 was placed in a platinum pan and heated from room temperature to 1273 K at a heating rate of 2 K/min in air with flow rate of 50 ml/min. For comparison experiments, samples were dried at 323 K for the same period. The data were collected at 30-s intervals using on-line PC.

The \(^{29}\text{Si}\) MAS-NMR spectra were recorded at frequency of 59.627 MHz and a spinning rate of 2.5 kHz in a Brucker double-air bearing probes with a pulse length of 4 μs, a pulse interval of 8 s and approximately 8000 scans.

\(^{31}\text{V}\)-MAS-NMR spectra were acquired at 131.375 MHz with 5.0 μs recycle delays using SiN rotors 5 mm in diameter without spinning and with spinning at 3 kHz. The chemical shifts are reported relative to 1 M VOCl\(_3\). All spectra were recorded at room temperature.

\(^{95}\text{Mo}\)-MAS-NMR spectra were acquired at 131.375 MHz with 5.0 μs recycle delays using SiN rotors 5 mm in diameter without spinning and with spinning at 3 kHz. The chemical shifts are reported relative to 1 M ammonium heptamolybdate. All spectra were recorded at room temperature.

The SEM microscope of a typical sample of MCM-41 materials were obtained on a JEOL JEM-2010 microscope operating at 200 kV from a thin film dispersed on a holly carbon film supported on a Cu grid. The samples were briefly heated under tungsten filament light bulb in air before transfer into the specimen chamber. The images were recorded at magnifications of 100,000×.

2.5. Oxidation of o-xylene—experimental procedure for vapor phase catalytic reaction

Reactions were carried out in an ordinary fixed bed flow-type reaction apparatus. 0.2 g of catalyst was mixed with porcelain beads 4 mm diameter vertical and being packed above and below with cotton wool on either side of the catalyst bed. The reactor was placed coaxially in the cylindrical ceramic tube furnace of internal diameter 3.5 cm, coated with a thin layer of asbestos and wound uniformly with nichrome wire. The furnace temperature was raised to the requisite level by adjusting the variance. When the reaction temperature attained a constant value, the syringe was filled with the feed material (o-xylene) and attached to the dual syringe pump (microcomputer model) and oxygen gas was connected with catalyst packed reactor for flowing while the needle was connected to the reactor. The liquid and gas product collected for the first 15 min of each run, which normally covers an hour was discarded and only the products collected after interval was analyzed. This was done to ensure the attainment of a steady state for the reaction over the catalyst and also to set right temperature fluctuations, if any, due to the starting of the reaction. The products in the outlet stream were first condensed, and the residual gaseous flow was scrubbed in acetone. The products were analyzed by gas chromatograph (Hewlett Packard 5890) equipped with a HP-5 capillary column (FID) for condensable products and with a Carbosieve S column (TCD) for oxygen and carbon oxides. The identification of products was performed on Shimadzu GC–MS-QP1000EX (gas chromatography–mass spectrometer).

After reusing the MCM-41 its activity decreases and the catalyst needs to be regenerated by calcinations. The catalysts were regenerated by burning away the coke deposit formed on them from the previous reaction by passing a stream of pure dry air at a temperature of 500 °C for 8 h. The catalysts were used continuously to study the effects of various parameters viz., reaction temperature, feed flow rate ratio and contact time.

3. Results and discussion

3.1. ICP-AES

The vanadium and molybdenum ions content in V-Mo-MCM-41 have been observed using ICP-AES. The observed vanadium and molybdenum ions content in the samples have been presented in Table 1.
3.2. XRD

Fig. 1 shows the X-ray powder diffraction patterns of calcined V-Mo-MCM-41 samples having different Si/(V + Mo) ratios. The X-ray diffractograms of V-Mo-MCM-41 after calcinations in air at 540 °C for 6 h, contain, a sharp d100 reflection line in the range 2θ = 2.45–2.7°. Physicochemical properties of these mesoporous materials are summarized in Table 1. For example, the pore-to-pore distance of V-Mo-MCM-41 could be determined by the XRD patterns. The XRD patterns of calcined V-Mo-MCM-41(46) with characteristic peaks of hexagonal (p6mm) symmetry and with d100 of 36.73 Å are shown in Fig. 1. The repeating distance (d00) between pore centers was 42.41 Å. The hexagonal unit cell parameter (a0) was calculated using the formula as 

\[ a_0 = \frac{2d_{100}}{\sqrt{3}} \]

from d100, which was obtained from the peak in the XRD pattern by Bragg’s equation (2d sinθ = λ, where \( \lambda = 1.5406 \, \text{Å} \) for the CuKα line). The value of a0 was equal to the internal pore diameter plus one pore wall thickness. These peaks reflections were indexed based on the hexagonal unit cell as described by Beck et al. [11]. The XRD peaks shifted to lower 2θ values for the rest of the samples. The higher d-spacing and unit cell parameter values observed with increasing metal-ions content suggest an incorporation of metal in the framework locations [18] because of its (V–O (~1.5893 Å) and Mo–O (~1.658 Å)) longer bonding length with oxygen than Si–O (~1.509 Å). However, there is no regular rule in MCM-41 as it has an amorphous structure where both bond length and angle may be change. The perturbation of d-spacing and unit cell parameter is hypothesized to be dependent on the metal substitution state resulting from the sample preparation method, i.e., coordination number of metal with OH groups and also along with bond length and bond angle of metal ion on the silica surface.

3.3. N2-adsorption

Fig. 2 shows the isotherm of nitrogen adsorption by calcined V-Mo-MCM-41 samples measured at liquid nitrogen temperature (77 K). Three well-defined stages may be identified: (1) a slow increase in nitrogen uptake at low relative pressure, corresponding to monolayer-multilayer adsorption on the pore walls; (2) a sharp step at intermediate relative pressures indicative of capillary condensation within mesopores; and (3) a plateau with a slight inclination at high relative pressures associated with multilayer adsorption on the external surface of the crystals [19]. A fourth stage, characterized by a sharp rise in N2 uptake filling all other available pores as the pressure reaches saturation (P/P0 = 1.0), may be identified in some isotherms. Each isotherm showed type IV character, which is a typical shape for mesoporous MCM-41. The third stage of the isotherm shifts slightly toward higher relative pressure with the incorporation of transition metal (V + Mo). The hysteresis loop broadened with an increase in the metal content suggesting some disorder in the pore system arising from metal.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>V-contenta</th>
<th>Mo-contenta</th>
<th>d-Spacingb (Å)</th>
<th>Unit cell parameterb, a0 (Å)</th>
<th>Surface area2 (m²/g)</th>
<th>Pore sizec, D (Å)</th>
<th>Pore volumec (cm³/g)</th>
<th>Wall thicknessd (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-Mo-MCM-41(46)</td>
<td>0.125</td>
<td>0.875</td>
<td>36.73</td>
<td>42.41</td>
<td>824</td>
<td>33.0</td>
<td>0.48</td>
<td>9.41</td>
</tr>
<tr>
<td>V-Mo-MCM-41(92)</td>
<td>0.062</td>
<td>0.438</td>
<td>34.61</td>
<td>39.97</td>
<td>930</td>
<td>33.1</td>
<td>0.49</td>
<td>6.87</td>
</tr>
<tr>
<td>V-Mo-MCM-41(184)</td>
<td>0.031</td>
<td>0.219</td>
<td>33.31</td>
<td>38.45</td>
<td>972</td>
<td>33.2</td>
<td>0.50</td>
<td>5.25</td>
</tr>
<tr>
<td>V-Mo-MCM-41(230)</td>
<td>0.025</td>
<td>0.170</td>
<td>32.46</td>
<td>37.48</td>
<td>1080</td>
<td>33.3</td>
<td>0.51</td>
<td>4.18</td>
</tr>
</tbody>
</table>

a The results obtained from ICP-AES.

b Values obtained from XRD studies.

c Values obtained from N2-adsorption results.

d Wall thickness (t) = Unit cell parameter (a0) – pore size (D).
incorporation. Incorporation of metal in MCM-41 has significant effect on these parameters. The surface area, pore size and pore volume values decreased but the wall thickness value increases with increasing metal-ions content and are also listed in Table 1. Generally, in the crystalline zeolites, the pore size decreases by metal-ion incorporation because of its longer bonding length with oxygen than Si–O. However, there is no regular rule in MCM-41 as it has an amorphous structure where both bond length and angle may change. Usually, it has been observed that the pore size of MCM-41 is decreased after metal incorporation, but there is no clear explanation for this observation. MCM-41 has thin pore walls relative to zeolites so that the incorporated metal cannot be substituted into the silica framework completely. That is, a part of the metal will be exposed on the pore wall surface so that it might have properties similar to impregnated metal complexes on the MCM-41 walls. The incorporated metal may interact with surface hydroxyl groups and may contract the pore wall when combined with two or three hydroxyl groups, so that the pore size will be decreased as previous similar report [20,21,15]. In the context, the surface area, pore size in V-Mo-MCM-41 might be decreased with increasing metal content.

The remarkable improvement of hydrothermal stability due to the higher metal incorporation is further evidenced by the measurement of N2 adsorption. The surface areas of all the MCM-41 materials were measured after they had been treated in boiling water for 1 week. The surface areas slightly decreased from 1080–930 to 1005–910 m²/g in Si/(V + Mo) ratios of 230–92 in V-Mo-MCM-41 samples, but the surface area does not decrease in V-Mo-MCM-41(46). The Si–O–V and Si–O–Mo bonds are relatively stable to further attack from boiling water [16]; the presence of Mo 6+ and V 5+ creates a negative charge on the surface of the pore walls, repelling OH–/C0 ions and therefore preventing the hydrolysis of siloxane bonds and also resulting in an increase in the number of acid sites. The surface area in the V-Mo-MCM-41 (Si/V + Mo = 92–230) samples decreased due to low metal incorporation/nonframework as it does not create sufficient negative charges on the surface of the pore walls. But the surface area of V-Mo-MCM-41(46) samples does not decrease due to the higher repelling OH– ions on the pore walls. Hence, it is concluded that V and Mo is irreversibly incorporated into the structure of V-Mo-MCM-41 samples. Thus, the hydrothermal stability is higher in V-Mo-MCM-41(46) than that in other V-Mo-MCM-41 samples.

3.4. FTIR

Infra red spectroscopy had been used extensively for the characterization of transition-metal cation modified zeolites. The as-synthesized V-Mo-MCM-41 samples exhibit absorption bands around 2921 and 2851 cm⁻¹ corresponding to n–C–H and δC–H vibrations of the surfactant molecules. The broad bands around 3500 cm⁻¹ may be attributed surface silanols and adsorbed water molecules, while deformational vibrations of adsorbed molecules cause the absorption bands at 1623–1640 cm⁻¹ [22] (the results of peaks have not shown in figures). The substitution of silicon by vanadium and molybdenum causes shifts of the lattice vibration bands to lower wavenumbers. Compared to
the Si-MCM-41, the wavenumber of the anti-symmetric Si–O–Si vibration band of V-MCM-41 [16] and V-Mo-
MCM-41 samples decreases to 1086 and 1097 cm$^{-1}$, respectively (Fig. 3). Theses shifts should be due to the in-
crease of the mean Si–O distance in the walls caused by the substitution of the small silicon (radius 40 pm) by
the larger size of Mo$^{5+}$ (radius 41 pm) and V$^{5+}$ (radius 36 pm) [23]. The observed shifts, which depend as well
on the change in the ionic radii as on the degree of sub-
stitution, are comparatively small. Therefore, only a low
degree of substitution is suggested. Interestingly, the wavenumber shifts decrease in the series V-MCM-
41 > V-Mo-MCM-41, although the ionic radius of van-
dium is smaller than those of molybdenum. While the wavenumber of the anti-symmetric Si–O–V and Si–O–
Mo vibration bands of V-Mo-MCM-41 and only Si–
O–V of V-MCM-41 [16] samples decreases to 967 and
962 cm$^{-1}$, receptively (Fig. 3). Upon introduction of
higher metal content, most of the bands shifted to higher
wavenumbers, consistent with their incorporation in lat-
tice positions. Additionally, an absorption band in the
range 960–967 cm$^{-1}$ assigned to a stretching vibration
of Si–O$^–$M$^+$ linkage was observed. This is generally
considered to be a proof of the incorporation of the heter-
oatom into the framework as reported the similar
stretching vibrations of Si–OH groups present at defect
sites [24]. By the disappearing peaks at 2851 and
2921 cm$^{-1}$, one could conclude that calcination of the
original framework was complete and the identity of or-
ganic molecule completely disappeared from the cal-
cined M-MCM-41.

### 3.5. TG/DTA

Thermogravimetric analysis of the MCM-41 mater-
ials show distinct weight losses that depend on frame-
work composition. Representative thermograms are
given in Fig. 4 (V-Mo-MCM-41). Generally, when the
metal content increases, there is a decrease in organic
content and increase in water content [24]. Three distinct
regions of weight loss are noted in the temperature range
50–150 °C, 150–350 °C and 350–550 °C. The first weight
loss (~4.6% to 16.61%) corresponds to the desorption
and removal of the water and/or ethanol molecules physisorbed on the external surface of the crystallites or occluded in the macropores and mesopores present between the crystallites aggregates. A second weight loss (~38.58% to 40.5%), between 150 and 350 °C is attributed to the removal of the organic template. Finally, a third weight loss (~1.51% to 1.9%) between 350 and 550 °C is related to water loss from the condensation of adjacent silanol groups to form siloxane bond. The all samples were almost no exothermal peak after 550 °C, which is indicated that the surfactant has been removed completely from the porous materials [25]. The total weight loss at 1000 °C of the V-Mo-MCM-41 samples is in the 44.69–59.01% range. However, the distribution of successive weight loss depends on the framework or substituted silicon to metal ratio [16]. Thus, weight loss was higher in the low metal contents of MCM-41 materials than that in the high metal contents of MCM-41 materials.

3.6. MAS-NMR

The $^{51}$V NMR experiments were carried out to determine the V substitution state in V-Mo-MCM-41 samples (Si/(V + Mo) = 46, 92, 184 and 230) and the results are shown in Fig. 5. All samples show a similar resonance pattern and the main signals are around −525 to −530 ppm which are assigned to tetrahedral coordinated V [26]. Octahedral coordination of V ions is not detected in these samples (chemical shift around −300 ppm). Thus, most of the incorporated V is substituted into the silica framework of V-Mo-MCM-41 samples and assumes tetrahedral coordination with surrounding oxygen anions. However, all the main resonance peaks exhibit quite patterns compared to previously reported only V-impregnated or -incorporated catalysts [27–29]. This result indicates that all samples prepared in this study have tetrahedral coordination of V, so they show sharp resonance peaks compared to the only V-containing MCM-41 samples [16]. The intensity of resonance peaks in the V-Mo-MCM-41 materials are increased with increasing V-ions content. From the above results it was concluded that the $V^{5+}$ ions are tetrahedrally coordinated to inner side pores on the silica surface.

Fig. 6 shows solid-state $^{95}$Mo-MAS spectra of V-Mo-MCM-41 of different Si/(V + Mo) = 46, 92, 184 and 230 ratios. Each spectrum in all MCM-41 samples shows a strong and sharp signal at 23 ppm regardless of the Mo content. The intensity of the resonance peaks are increased with increasing Mo-ions content. The signal at 23 ppm could be assigned to tetrahedrally coordinated framework Mo(VI) ion (T$_{d}$-Mo) in V-Mo-MCM-41 as similar in heptamolybdate (Mo$_7$O$_{24}$O$_{6}$) [30].

$^{29}$Si MAS-NMR spectra (Fig. 7) of the as-synthesized sample consist of some broad peaks. On the basis of the chemical shifts the peak at −109 ppm has to be assigned
to the Si(OSi)$_4$ ($Q_4$) sites and the line at $-102$ ppm is attributed to the Si–(OSi)$_3$OH ($Q_3$) site. The observed spectrum was relatively poor in comparison to that of Si-MCM-41. There was a progressive reduction in the intensity of $Q_3$ (because of the large number of silanol groups in Si-MCM-41, $Q_3$ intensity is always higher) sites with increasing vanadium content. It strongly supports metal promoted cross-linking of the mesoporous wall.

3.7. Scanning electron microscopy

All calcined V-Mo-MCM-41 materials are having micellar rod-like shape hexagonal or spherical edges, as shown in Fig. 8 (V-Mo-MCM-41(46)). Each rod itself transformed into the MCM-41 hexagonal-phase mesostructure. Because all materials have been synthesized using cetyltrimethyammonium bromide as surfactant in the liquid crystal template mechanism, Steel et al. [31] postulated that CTMABr surfactant molecules assembled directly into the hexagonal liquid crystal phase upon addition of the silicate species, based on $^{14}$NMR spectroscopy.

3.8. Transmission electron microscopy

The TEM image of all calcined V-Mo-MCM-41 (Fig. 9 for V-Mo-MCM-41(46)) samples exhibit ordered hexagonal arrays of mesopores with uniform pore size [11]. The corresponding electron diffraction pattern also shows reflections contrast in the TEM image of the sample, the distance between mesopores are estimated, in good agreement with the value determined from XRD and N$_2$-adsorption measurements values.

Both pore channels and hexagonal symmetry can be clearly identified in the TEM image for a large number of V-Mo-MCM-41 samples which indicates that the MCM-41 samples have only one uniform phase as inferred from the XRD results. The pore sizes as observed by TEM analysis are in agreement with the results obtained from N$_2$-adsorption measurements.

3.9. Mechanism of oxidation of o-xylene

The oxidation of o-xylene with O$_2$ is an intramolecular oxidative dehydrogenation (nucleophilic oxidation) on the aromatic ring. The byproducts are carbon oxides, o-tolualdehyde, phthalide and maleic anhydride. In the first step one methyl group is oxidized to tolualdehyde as the main intermediate product, which is then oxidized.
further to phthalic anhydride. Maleic anhydride is the side product made by direct oxidation of \( o\)-xylene, and phthalide is a side product formed from tolualdehyde. Carbon oxides may be formed either directly from \( o\)-xylene, from any of the intermediates, or by consecutive oxidation of the final product. The reaction scheme is illustrated in Fig. 10. Experiments in which \( o\)-xylene with \( ^{14}\text{C}\)-labelled methyl groups and phthalic anhydride \((-^{14}\text{CO})\) were oxidized over V-Mo-MCM-41 catalyst [32] and also showed that maleic anhydride is formed only from carbon atoms of the nucleus. This indicates that maleic anhydride results from an attack by electrophilic oxygen on the \( \pi\)-system of the benzene ring. The oxidation of \( o\)-xylene in the presence of oxygen and in its absence provided evidence [10] that it is lattice oxygen, which is provided in the formation of phthalic anhydride.

The \( o\)-xylene oxidation has been extensively studied because of the industrial importance of this reaction. The process is usually carried out at various temperatures, feed flow rate ratio and contact time. The reaction of \( o\)-xylene oxidation is shown in Fig. 10 and discussed below.

### 3.9.1. Selectivity of phthalic anhydride

The oxidation of \( o\)-xylene over V-Mo-MCM-41 catalysts at 350 °C with contact time \((W/F_0) = 24.41\) h in the presence of 0.016:200 cc flow rate ratio of \( o\)-xylene:oxygen gas per minute was carried out for the highly selective synthesis of phthalic anhydride while the results have been depicted in Table 2. On increasing the Si/(V + Mo) ratio of V-Mo-MCM-41 catalyst from 46 to 230, the conversion of \( o\)-xylene, selectivity of phthalic anhydride decreased because the number of Lewis acid sites in V-Mo-MCM-41 catalysts are found to decrease almost linearly with increasing Si/(V + Mo) ratios. Hence the selectivity of the final product as phthalic anhydride which depends on the rate of oxidation, in turn, on substrate and catalyst features (pore structure, active sites depends upon the Lewis acid sites on the silica surface) was found to be the highest in V-Mo-MCM-41(46). The catalysts not only retain the high surface area and the regular mesoporosity associated with the MCM-41 structure but also disperse the active V and Mo atoms on the surface of MCM-41 very well because the larger number of V\(^{5+}\) [33] and Mo\(^{6+}\)-ions [34] are coordinated tetrahedrally with surrounding oxygen anions in the structure of the catalyst. This isolated tetrahedral coordinated vanadium or molybdenum ion conceivably produces three active sites. Our material characterization suggests that this hydrothermal method can generate solid supported molecular ‘akin’ species, which were highly dispersed with maximum conformity of the surface morphology [35]. It is generally accepted that oxidation reaction using oxygen gas as oxidizing agent involves formation and transfer of electrophilic oxygen over active metal species. Thus, the formation of phthalic anhydride is higher in V-Mo-MCM-41(46) than that in other V-Mo-MCM-41 catalysts.

---

**Fig. 10. Reaction scheme for the formation of phthalic anhydride from \( o\)-xylene.**
3.9.2. Effect of different Si/(V + Mo) ratios of V-Mo-MCM-41

The conversion of o-xylene (90.2%) and selectivity of phthalic hydride (87.3%) was the higher at reaction temperature of 350 °C in the presence of 0.016:200 cc flow rate ratio of o-xylene:oxygen gas per minute with contact time \((W/F_0) = 24.41\) h using V-Mo-MCM-41(46). The conversion of o-xylene and selectivity of phthalic anhydride in V-Mo-MCM-41(46) is higher than that of other V-Mo-MCM-41 catalysts due to increasing the catalytic activity along with the higher number of Lewis acid sites on the surface of the catalyst by the \(V = O\) and \(Mo = O\) complex species supported on the surface of the catalysts and the results are shown in Table 2. The superior catalytic activity of V-Mo-MCM-41(46) catalyst towards o-xylene oxidation is attributed to their active oxygen with a high electron affinity (electrophilic) for the attack of the methyl group (electron-donating group) of the o-xylene molecule. Hence the higher selectivity of phthalic anhydride and conversion of o-xylene using V-Mo-MCM-41(46) depicts its superiority in performance compared to other V-Mo-MCM-41.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Conversion of o-xylene (mol%)</th>
<th>Selectivity (mol%)</th>
<th>OTA</th>
<th>PA</th>
<th>PI</th>
<th>MA</th>
<th>Carbon oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-Mo-MCM-41(46)</td>
<td>90.2</td>
<td>10.2</td>
<td>87.3</td>
<td>0.6</td>
<td>1.5</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>V-Mo-MCM-41(92)</td>
<td>73.3</td>
<td>26.4</td>
<td>60.3</td>
<td>3.8</td>
<td>7.8</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>V-Mo-MCM-41(184)</td>
<td>63.2</td>
<td>28.7</td>
<td>57.6</td>
<td>4.0</td>
<td>8.2</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>V-Mo-MCM-41(230)</td>
<td>50.8</td>
<td>37.3</td>
<td>48.6</td>
<td>4.2</td>
<td>8.5</td>
<td>1.4</td>
<td></td>
</tr>
</tbody>
</table>

Reaction conditions: 0.2 g of catalyst; feed flow rate ratio (0.016 cc, o-xylene:200 cc, oxygen gas per minute); contact time \((W/F_0) = 24.41\) h; reaction temperature, 350 °C; OTA—o-tolualdehyde; PA—phthalic anhydride; PI—phthalide; MA—maleic anhydride and carbon oxide—CO + CO2. Contact time \((W/F_0)\) in hour = weight of catalyst in g/(volume × density/molecular weight).

3.9.3. Effect of reaction temperature

The oxidation of o-xylene was carried out using reactant as 0.016:200 cc flow rate ratio of o-xylene:oxygen gas per minute for a duration time \((W/F_0)\) of 24.41 h at various temperatures in the presence of different Si/(V + Mo) ratios of V-Mo-MCM-41 and the results are shown as in Fig. 11. The optimum temperature was found to be 350 °C. Deviation to either side of the required temperature showed a decrease in the conversion of o-xylene and selectivity of phthalic anhydride. Lower temperatures (<350 °C) do not favor the formation of phthalic anhydride because the byproducts as o-tolualdehyde (intermediate) and phthalide increases with increasing V- and Mo-ions content while the catalytic activity of all catalysts are less. At higher temperature (>360 °C), the conversion of o-xylene and selectivity of phthalic anhydride decreased. This may be due to the formation of byproduct as maleic anhydride and carbon oxide \((CO_2 + CO)\) involving carbon–carbon bond cleavage from the aromatic ring of the o-xylene or other byproducts. The selectivity of phthalic anhydride was found to be 87.3% at 350 °C for 24.41 h in the presence of V-Mo-MCM-41(46). Thus, the selectivity of phthalic anhydride in V-Mo-MCM-41(46) is higher than that in other V-Mo-MCM-41 catalysts.
3.9.4. Effect of feed flow rate ratio

The oxidation of o-xylene was carried out with various volume ratio (o-xylene:oxygen) over V-Mo-MCM-41 with different ratios of Si/(V + Mo) for a contact time ($W/F_0$)-24.41 h at 350 °C. The conversion of o-xylene and selectivity of phthalic anhydride in feed flow rate ratio of 0.016 cc of o-xylene:200 cc of oxygen gas per minute was higher than that in other feed flow ratio of o-xylene:oxygen due to the reactants well equilibrating to the active sites in V-Mo-MCM-41(46) and the results are shown as in Fig. 12. But the reactants equilibrium may not be significant at higher feed flow rate ratio while there is a possibility of coke formation in the inner side pores of catalytic surface. The conversion of o-xylene and selectivity of phthalic anhydride are increased with increasing V- and Mo-ions content along with respect to the feed flow rate ratio.

3.9.5. Effect of contact time

The oxidation of o-xylene was carried out with various contact time ($W/F_0$) and feed flow rate ratio (0.016 cc of o-xylene:200 cc of oxygen gas per minute) over V-Mo-MCM-41 with different Si/(V + Mo) ratios at 350 °C and the results are shown as in Fig. 13. The conversion of o-xylene and selectivity of phthalic anhydride is the higher for a contact time of 24.41 h. While the selectivity of o-tolualdehyde as the byproduct at low contact time is high because the catalytic activities of the all catalysts are favorable to it. At higher contact time, the phthalic anhydride product is very low, because, if the phthalic anhydride is further reacted on the catalytic surface, it is decomposed into phthalide, maleic anhydride and carbon oxides. The conversion of o-xylene and selectivity of phthalic anhydride are increased with increasing V- and Mo-content with respect.

---

**Fig. 12.** Variation of feed flow rate ratio with (a) conversion of o-xylene and (b) selectivity of phthalic anhydride.

**Fig. 13.** Variation of contact time with (a) conversion of o-xylene and (b) selectivity of phthalic anhydride.
to the contact time. Thus, the best contact time is 24.41 h for the conversion of o-xylene to phthalic anhydride.

3.9.6. Recyclability
The different Si/(V + Mo) ratios of V-Mo-MCM-41 catalysts were reused for the oxidation of o-xylene in 24.41 h contact time (W/F₀) for feed flow rate ratio (0.016 cc of o-xylene:200 cc of oxygen gas per minute) at 350 °C and the results are shown as in Fig. 14. No loss of catalytic activity was observed after 4 runs in V-Mo-MCM-41(46). Instead, its conversion of o-xylene and selectivity of phthalic anhydride increased with each cycling. But, the conversion and selectivity decreased in other V-Mo-MCM-41 catalysts at the same reaction conditions. This may be due to decreasing the catalytic activity of the catalysts along with decreasing of Lewis acid sites while the V- and Mo-content are decreased (increasing the Si/(V + Mo) ratios) on the inner side pores of the catalysts. Thus, the V-Mo-MCM-41(46) is better and also very suitable catalyst for oxidation of o-xylene to highly selective synthesis of phthalic anhydride.

4. Conclusion
Mesoporous V-Mo-MCM-41 molecular sieves with Si/(V + Mo) ratio equal to 46, 92, 184 and 230 were synthesized using sodium metasilicate, vanadyl sulfate and ammonium molybdenate as reagents, and cetyltrimethylammonium bromide as the template under hydrothermal conditions. From the physicochemical characterization of the materials it was concluded that all the synthesized catalysts have good V-O-Si and Mo-O-Si framework on the silica surface, mild Lewis acid sites, good thermal, hydrothermal stability and high surface area. While the V⁵⁺ and Mo⁶⁺ ions are tetrahedrally coordinated on the silica surface in all V-Mo-MCM-41. From the various catalytic reaction experiment carried out using the above synthesized catalysts, it could be inferred that the selectivity of phthalic anhydride (87.3%) was there high with feed flow rate ratio (0.016 cc of o-xylene:200 cc of oxygen gas per minute at STP) and 24.41 h contact time (W/F₀) at 350 °C reaction temperature over V-Mo-MCM-41(46). Thus, the V-Mo-MCM-41(46) is the best catalyst for the highly selective synthesis of phthalic anhydride.

Acknowledgement
The authors gratefully acknowledge the KOSEF through National Core Research Center for Nanomedical Technology for sponsoring this work (R15-2004-024-00000-0).

References