CHAPTER 3

RESULTS AND DISCUSSION

3.1 SYNTHESIS AND CHARACTERIZATION

Pure silica MCM-41 showed limited catalytic applications. Therefore, incorporation of transition metal in the silicate framework is necessary for their use in catalytic applications. Hence, isomorphous substitution of silicon with a transition metal is an excellent strategy in creating catalytically active sites and anchoring sites for reactive molecules in the design of new heterogeneous catalysts. The present work describes synthesis of mono and bimetal (Cr, Fe, V and Mn) incorporated MCM-41 by direct hydrothermal method (DHT). All the materials have been characterized and the results are discussed below in detail.

3.1.1 XRD

The X-ray diffractograms of the calcined Cr-MCM-41 samples with (a) Si/Cr =100, 75, 50, and 25, (b) V-MCM-41 with Si/V =100, 75, 50, and 25 and (c) V-Mn-MCM-41(V:Mn=25:75), V-Mn-MCM-41(V:Mn=50:50) and V-Mn-MCM-41 (V:Mn=75:25) were recorded are shown in Figures 3.1, 3.2 and 3.3 respectively.

A strong intense peak in the 2θ range 2.21-2.35° for all synthesized samples is due to the reflection from (1 0 0) plane. Apart from this, low intensity peaks in the 2θ range 3-5°, corresponding to the higher order reflections such as (1 1 0) and (2 0 0) planes were also observed in all the
catalysts, which confirms the mesoporous nature of the samples. The unit cell parameter \( a_0 \) was calculated using the formula \( a_0 = 2d_{100} / \sqrt{3} \), and d spacing values were obtained using the Bragg's equation \( 2d\sin\theta = n\lambda \), where \( \lambda = 1.54 \) Å for Cu Kα radiation and corresponding data are summarized in Table 3.1 and 3.2. The long-range regularity of hexagonal arrays of mesopores of MCM-41 is evident from the intensity of diffraction peaks after the introduction of transition metal by direct hydrothermal methods (DHT). However, when metal content was increased, the intensity of the diffraction peaks decreased largely, indicating the structural irregularity of the mesopores at higher metal content as reported in literature (Wang et al 2003). In other words, the order of the hexagonally arranged pores decreased due to the incorporation of the transition metal in framework position. The increasing d-spacing and unit cell parameter values observed with increasing metal-ion content suggest an incorporation of metal in the framework location (luan et al 1996).

3.1.2 Nitrogen adsorption-desorption isotherms

The \( \text{N}_2 \) adsorption–desorption isotherms of the calcined Cr-MCM-41 catalysts (a) with Si/Cr = 100, 75, 50, and 25, (b) V-MCM-41 with Si/V = 100, 75, 50, and 25, (c) V-Mn-MCM-41(V:Mn=25:75), V-Mn-MCM-41(V:Mn=50:50) and V-Mn-MCM-41 (V:Mn=75:25) samples measured at liquid nitrogen temperature (77 K) are shown in Figures 3.4, 3.5 and 3.6 respectively.

A typical type IV isotherm for mesoporous materials (Sing et al 1985) were obtained for all the samples. At initial low relative pressure, \( \text{N}_2 \) uptake increase sharply as the \( \text{N}_2 \) pressure increases. It points out that the samples have a high surface area and also a sharp inflection between relative pressures \( P/P_O = 0.2 \) and 0.3 corresponding to capillary condensation within the mesopores.
Figure 3.1 X-ray diffraction patterns of (a) Cr-MCM-41 (Si/Cr=100), (b) Cr-MCM-41 (Si/Cr=75), (c) Cr-MCM-41 (Si/Cr=50) and (d) Cr-MCM-41 (Si/Cr=25) catalysts
Figure 3.2  X-ray diffraction patterns of (a) V-MCM-41 (Si/V=100), (b) V-MCM-41 (Si/V=75), (c) V-MCM-41(Si/V=50) and (d) V-MCM-41(Si/V=25) catalysts.
Figure 3.3 X-ray diffraction patterns of (a) V-Mn-MCM-41(V:Mn=25:75), (b) V-Mn-MCM-41(V:Mn=50:50), and (c) V-Mn-MCM-41(V:Mn=75:25)
Figure 3.4 $\text{N}_2$ adsorption-desorption isotherms of catalysts
(a) Cr-MCM-41 (Si/Cr=100), (b) Cr-MCM-41 (Si/Cr=75),
(c) Cr-MCM-41 (Si/Cr=50) and (d) Cr-MCM-41 (Si/Cr=25)
Figure 3.5  $N_2$ adsorption-desorption isotherms of catalysts

(a) V-MCM-41 (Si/V=100),  (b) V-MCM-41 (Si/V=75),
(c) V-MCM-41 (Si/V=50) and (d) V-MCM-41 (Si/V=25)
Figure 3.6  $N_2$ adsorption-desorption isotherms of catalysts
(a) V-Mn-MCM-41(V:Mn=25:75), (b) V-Mn-MCM-41 (V:Mn=50:50) and (c) V-Mn-MCM-41(V:Mn=75:25)
The sharpness and height of the capillary condensation curves are indicative of uniform pore size as suggested by Wang et al (2001). Increase in metal content led to decrease in the surface area, pore volume and pore diameter (Tables 3.1 and 3.2).

3.1.3 Thermogravimetric analysis

The thermo gravimetric analysis of the as-synthesized sample of SiMCM-41 (100) is performed between 208 to 1073 K. The curve shows weight losses in three stages as shown in Figure 3.7. The initial weight loss below 448 K is assigned to the loss of water. The second weight loss around 473 K is attributed to the decomposition of the template. The third weight loss between 673 K and 873 K may be attributed to the condensation of silanol hydroxyl groups. An average weight loss of 52 wt. % during the thermo gravimetric analysis also confirms the mesoporous nature of the synthesized material (Beck et al 1992).

3.1.4 Fourier transform infrared spectroscopy

The FT-IR spectra of calcined V-Mn-MCM-41(V:Mn=25:75), V-Mn-MCM-41(V:Mn=50:50) and V-Mn-MCM-41(V:Mn=75:25) samples show the absorption bands at 1050 and 790, 2921 and 2851, 3500, 1623-1640, 960 and 970, 1057 and 1223 cm⁻¹ (Figure 3.8a-c). The bands at 1050 and 790 cm⁻¹ are due to asymmetric and symmetric stretching vibration of framework Si-O-Si. The absorption bands around 2921 and 2851 cm⁻¹ corresponding to symmetric C-H and asymmetric CH₂ vibrations of the surfactant molecules. However, the intensity of these two bands are much less when compared with uncalcined sample. This confirms complete loss of organic molecules from the surfactant.
Figure 3.7 TGA and DTA curves of SiMCM-41 sample
Table 3.1  Physico-chemical characteristics of the Cr, Fe incorporated MCM-41 catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cr content&lt;sup&gt;a&lt;/sup&gt; Wt %</th>
<th>Fe content&lt;sup&gt;a&lt;/sup&gt; Wt %</th>
<th>d-spacing&lt;sup&gt;b&lt;/sup&gt; (Å)</th>
<th>Unit cell Parameter&lt;sup&gt;b&lt;/sup&gt; a&lt;sub&gt;o&lt;/sub&gt; (Å)</th>
<th>Surface area&lt;sup&gt;c&lt;/sup&gt; (m&lt;sup&gt;2&lt;/sup&gt;/g)</th>
<th>Pore diameter&lt;sup&gt;c&lt;/sup&gt; (Å)</th>
<th>Pore volume&lt;sup&gt;c&lt;/sup&gt; (cm&lt;sup&gt;3&lt;/sup&gt;/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr-MCM-41(25)</td>
<td>1.93</td>
<td>-</td>
<td>40.01</td>
<td>46.20</td>
<td>654</td>
<td>24.03</td>
<td>0.86</td>
</tr>
<tr>
<td>Cr-MCM-41(50)</td>
<td>1.17</td>
<td>-</td>
<td>39.50</td>
<td>45.61</td>
<td>796</td>
<td>24.04</td>
<td>0.89</td>
</tr>
<tr>
<td>Cr-MCM-41(75)</td>
<td>0.75</td>
<td>-</td>
<td>38.41</td>
<td>44.36</td>
<td>871</td>
<td>24.05</td>
<td>0.88</td>
</tr>
<tr>
<td>Cr-MCM-1(100)</td>
<td>0.59</td>
<td>-</td>
<td>37.57</td>
<td>43.38</td>
<td>924</td>
<td>24.05</td>
<td>0.90</td>
</tr>
<tr>
<td>Fe-MCM-41(25)</td>
<td>-</td>
<td>2.39</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cr-Fe-MCM-41 Si/(Cr+Fe)=100</td>
<td>1.93</td>
<td>0.73</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tbody>
</table>

<sup>a</sup> Results obtained from ICP-AES analysis

<sup>b</sup> Results obtained from XRD data

<sup>c</sup> Results obtained from N<sub>2</sub> adsorption-desorption isotherms.
### Table 3.2  Physico-chemical characteristics of the V, Mn incorporated MCM-41 catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>d-spacing(^a) (Å)</th>
<th>Unit cell Parameter(^a)</th>
<th>Surface area(^b) (m(^2)/g)</th>
<th>Pore diameter(^b) (Å)</th>
<th>Pore volume(^b) (cm(^3)/g)</th>
</tr>
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<tbody>
<tr>
<td>V-MCM-41(25)</td>
<td>40.01</td>
<td>46.20</td>
<td>814</td>
<td>28.10</td>
<td>0.76</td>
</tr>
<tr>
<td>V -MCM-41(50)</td>
<td>39.60</td>
<td>45.73</td>
<td>893</td>
<td>28.40</td>
<td>0.79</td>
</tr>
<tr>
<td>V -MCM-41(75)</td>
<td>39.50</td>
<td>45.61</td>
<td>976</td>
<td>28.60</td>
<td>0.81</td>
</tr>
<tr>
<td>V -MCM-41(100)</td>
<td>39.30</td>
<td>45.38</td>
<td>1013</td>
<td>28.70</td>
<td>0.82</td>
</tr>
<tr>
<td>V-Mn-MCM-41 (V:Mn=75:25)</td>
<td>36.94</td>
<td>42.66</td>
<td>743</td>
<td>28.46</td>
<td>0.84</td>
</tr>
<tr>
<td>V-Mn-MCM-41 (V:Mn=50:50)</td>
<td>37.48</td>
<td>43.28</td>
<td>765</td>
<td>28.31</td>
<td>0.81</td>
</tr>
<tr>
<td>V-Mn-MCM-41 (V:Mn=25:75)</td>
<td>38.41</td>
<td>44.36</td>
<td>754</td>
<td>28.78</td>
<td>0.83</td>
</tr>
</tbody>
</table>

\(^a\) Results obtained from XRD data.

\(^b\) Results obtained from \(N_2\) adsorption-desorption isotherms.
Figure 3.8  FT-IR Spectra of calcined (a) V-Mn-MCM-41(V:Mn=25:75), (b) V-Mn-MCM-41(V:Mn=50:50) and (c) V-Mn-MCM-41 (V:Mn=75:25)
The broad band around 3500 cm\(^{-1}\) may be attributed to surface silanol groups and water molecules, whose deformational vibrations cause the absorption band between 1623-1640 cm\(^{-1}\) (Kiseler and Lygin 1992). The peak between 960 and 970 cm\(^{-1}\) is assigned to the incorporation of metal into the framework. Actually this band is assigned to a stretching vibration of Si-O-M linkage.

### 3.1.5 DRUV-Vis spectroscopy

Cr-MCM-41 catalysts are initially green in colour and changed to yellow upon calcination. The former is due to the presence of trivalent chromium ions and the latter is due to the presence of hexavalent chromium ions, viz. chromate and/or polychromate ions. The DRUV-Vis spectra of the calcined Cr-MCM-41 with different Si/Cr ratio and spent catalyst (after the catalytic run) are shown in Figure 3.9(a-e). Typical absorption bands with \(\lambda_{\text{max}}\) ~ 445 and 375 nm corresponding to polychromate and chromate species respectively (Mahalingam et al 1999; Weckhuysen et al 1997) are seen in addition to the band at 270 nm due to trivalent chromium in octahedral co-ordination (Figure 3.9 (a-d)). Also it is evident from the spectra that as the ratio of Si/Cr increased, there is a corresponding decrease in the intensity of the peaks due to chromium. Typical spectrum is recorded for the spent Cr-MCM-41(25) catalyst (Figure 3.9e). In the DRUV-Vis spectrum of spent catalyst only two absorption bands were observed with \(\lambda_{\text{max}}\) 350 and 275 nm. These bands may be assigned due to Cr\(^{5+}\) and Cr\(^{4+}\) species respectively. The peaks corresponding to Cr\(^{3+}\) and Cr\(^{6+}\) states are absent.

The DRUV-Vis spectra of calcined Fe-MCM-41(25) and Cr-Fe-MCM-41 (Si/(Cr+Fe)=100) are shown in Figure 3.10a and 3.10b. An absorption band at around 265 nm is seen in the spectrum of Fe-MCM-41(25), similar to that observed for ferrisilicate containing tetrahedrally coordinated iron species. This band could be assigned to the d\(_{\Pi}\)p\(_{\Pi}\) charge
transfer between Fe and O atoms in the framework of Fe-O-Si as in the case of zeolites (Echchahed et al 1997). But this band is shifted to longer wavelength from 265 to 285 nm when chromium is incorporated with Fe-MCM-41 catalyst (Figure 3.10a). This shift towards longer wavelength can be attributed to the reorientation of the electrons between Cr-Fe bonds. Since chromates and polychromates pull electrons from Fe in the framework, the framework Fe possesses high degree of positive charge. Hence, the absorption maximum of Fe in the bi metal catalyst is shifted to longer wavelength due to charge transfer of Fe-O bond. This observation illustrates clearly that there is interaction of Fe with chromium in the bimetal catalyst. Peaks due to Cr\(^{6+}\) oxidation state remain unaffected.

For vanadium containing mesoporous materials, direct information about the oxidation state and the possible dispersion of vanadia species can be derived from the DRUV-Vis spectroscopy. Upon calcination, the colour of V-MCM-41 samples changed from light green to white due to oxidation of small amount of VO\(^{2+}\) to V\(^{5+}\) ions. Interestingly, the DRUV-Vis spectra of V-MCM-41(Si/V ratio =25, 50, 75 and 100) catalysts (Figure 3.11(a-d)) show the presence of bands at 260 and 340 nm for the tetrahedral V\(^{5+}\) ions in framework and non framework position respectively (Shylesh and Singh 2005). These bands appear to have relatively higher intensity for higher vanadium loading. They are assigned to the low-energy charge transfer transitions between tetrahedral oxygen ligands and the central V\(^{5+}\) ion (Chenite et al 1995; Morey et al 1996). Based on this assignment, it can be concluded that the charge transfer bands at 260 and 340 nm are due to V\(^{5+}\) ions in tetrahedral environment with a short V=O double bond and three longer V-O bonds as reported elsewhere (Reddy et al 1994; Chenite et al 1995).
Figure 3.9 DRUV-Vis spectra of calcined catalysts
(a) Cr-MCM-41(25), (b) Cr-MCM-41 (50),
(c) Cr-MCM-41 (75), (d) Cr-MCM-41 (100) and
(e) Cr-MCM-41 (25) spent
Figure 3.10 DRUV-Vis spectra of calcined catalysts (a) Fe-Cr-MCM-41 (Si/(Cr+Fe)=100) and (b) Fe-MCM-41(25)
Figure 3.11  DRUV-Vis spectra of calcined catalysts (a) V-MCM-41(25), (b) V-MCM-41 (50), (c) V-MCM-41(75) (d) V-MCM-41(100) and (e) V-MCM-41 (50) spent
Figure 3.12  DRUV-Vis spectra of catalysts calcined (a) Mn-MCM-41(50) and (b) V-MCM-41(50)
Figure 3.13  DRUV-Vis spectra of calcined catalysts

(a) V-Mn-MCM-41 (V:Mn=25:75),
(b)V-Mn-MCM-41(V:Mn=50:50) and
(c) V-Mn-MCM-41(V:Mn=75:25)
It is also evident from the DRUV-Vis spectra of calcined catalysts that as the ratio of Si/V increases, there is a corresponding decrease in the intensity of the peaks due to decrease in the vanadium content. Typical spectrum is recorded for the spent V-MCM-41 (50) catalyst (Figure 3.11(e)) and no absorption bands were observed indicating that the absence of V$^{5+}$ species in the spent catalyst.

The DRUV-Vis spectra of V-MCM-41 (50), Mn-MCM-41 (50) V-Mn-MCM-41(V:Mn=25:75), V-Mn-MCM-41(V:Mn=50:50) and V-Mn-MCM-41 (V:Mn=75:25) MCM-41 calcined samples are shown in Figure 3.12(a & b) and 3.13(a-c). The two absorption bands at 260 and 340 nm are observed for V-MCM-41(Figure 3.12b). These bands are due to framework and non-framework V$^{5+}$. Two bands observed for Mn-MCM-41 at 270 and 500 nm are assigned to framework Mn$^{2+}$ (Figure 3.12a), as reported by Velu et al (1999). But, in the case of V-Mn-MCM-41 samples (Figure 3.13(a-c)) a broad band observed from 500 to 250 nm is due to the combination of V$^{5+}$ and Mn$^{2+}$.

3.1.6 EPR spectroscopy

The electron paramagnetic resonance (EPR) spectra of the as-synthesized, calcined Cr-MCM-41(25) and spent catalysts recorded at room temperature are shown in Figure 3.14(a-c). Both the catalysts exhibited similar spectral features. The g value calculated is 1.98 which corresponds to Cr$^{3+}$. It appears that chromium might be present as Cr$^{3+}$ even after calcination, and this is in good agreement with previous reports (Weckhuysen et al 1997; Zhu et al 1999). The g value obtained for the spent catalyst was found to be different from that of Cr$^{3+}$ indicating the utilisation of Cr$^{3+}$ for reaction.
The EPR spectra of the calcined V-MCM-41 samples with varying Si/V atomic ratio were recorded at room temperature and are shown in Figure 3.15a-d. The EPR signal corresponding to vanadyl species (V^{4+}) almost disappeared as the V content increased from Si/V=100 to 25 (Figure 3.15 d-a), indicating oxidation of all VO^{2+} ions to V^{5+} (d^0) (Yuan et al 2001). In other words, with increasing V content in MCM-41 there is a possibility for formation of V^{5+}. This is in concurrence with the DRUV-Vis spectra of V-MCM-41 (Figure 3.11a-d) as discussed above. The EPR spectra of as-synthesized, calcined and spent vanadium containing mesoporous materials recorded at room temperature are shown in Figure 3.16 a-c. The as-synthesized V-MCM-41 exhibited its characteristic EPR signal corresponding to the vanadyl sulfate (Figure 3.16a.). Comparison of this spectrum with that of the calcined form (Figure 3.16b) clearly indicates major oxidation of V^{4+} to V^{5+}.

The EPR spectra of calcined Mn-MCM-41(50) and V-Mn-MCM-41 (V:Mn=75:25), V-Mn-MCM-41 (V:Mn=50:50) and V-Mn-MCM-41 (V:Mn=25:75) samples were recorded at liquid nitrogen temperature and are shown in Figure 3.17 and 3.18(a-c) respectively. Six hyperfine lines centered on g = 2.00 corresponding to Mn^{2+} in octahedral environment is observed (Figure 3.17) in Mn-MCM-41 catalysts. Similar observations were also made for Mn-MCM-41 (Xu et al 1998) and Mn-ALPO-5 (Levi et al 1991) with the manganese species incorporated in the framework. But bimetallic V-Mn-MCM-41 (Figure 3.18a) catalyst shows EPR signal at g = 2.01 with hyperfine coupling, which could be attributed to distorted octahedral Mn^{2+} species. The hyperfine lines are slightly broader in the case of V-Mn-MCM-41 (V:Mn=50:50) (Figure 3.18b) and V-Mn-MCM-41 (V:Mn=25:75) (Figure 3.18c) due to low Mn content.
Figure 3.14 EPR spectra of Cr-MCM-41 (25) (a) as synthesized, (b) calcined and (c) spent catalyst recorded at room temperature.
Figure 3.15  EPR spectra of catalysts recorded at room temperature (a) V-MCM-41(25), (b) V-MCM-41(50), (c) V-MCM-41(75) and (d) V-MCM-41(100)
Figure 3.16 EPR spectra of catalysts recorded at room temperature
(a) as synthesised V-MCM-41(50),
(b) calcined V-MCM-41(50) and (c) V-MCM-41(50) spent
Figure 3.17 EPR spectra of calcined Mn-MCM-41 (Si/Mn =50) recorded at liquid Nitrogen temperature.
Figure 3.18  EPR spectra of calcined catalysts recorded at liquid nitrogen temperature

(a) V-Mn-MCM-41 (V:Mn=75:25),
(b) V-Mn-MCM-41(V:Mn=50:50) and
(c) V-Mn-MCM-41(V:Mn=25:75)
3.1.7 Scanning Electron Microscopic studies

SEM images of the calcined Cr-MCM-41 samples with varying Si/Cr atomic ratios (100, 75, 50, and 25) are shown in Figures 3.19 a-b and 3.20 c-d. Same morphology was observed. The SEM images of Fe-MCM-41 (25) and Cr-Fe-MCM-41(Si/(Cr+Fe) =100), V-MCM-1(50) and V-Mn-MCM-41(V:Mn =50:50) are also shown in Figures 3.21 e&f and 3.22 g & h. No morphological change was noticed on the introduction of bimetal on mono metal MCM-41 (Mahendiran et al 2007).

3.1.8 Transmission Electron Microscopic studies

TEM images of the calcined V-MCM-41 samples with Si/V atomic ratios of 100, 75, 50, and 25 are shown in Figure 3.24(c-d) and 3.25(e-f) and that of Fe-MCM-41(25) and Cr-Fe-MCM-41((Si/ (Cr + Fe) =100) are shown in Figure 3.23 (a) and (b). Highly ordered mesoporous framework with hexagonal array of cylindrical channels is confirmed from TEM images. These are virtually regular hexagonal arrays of fine pore arrangement existing in these samples. The ordered arrangement, typical for the MCM-41 material is further confirmed. The TEM pictures indicate that the structural regularity of the mesopores decreased largely as the V content is increased. It can be concluded that incorporation of vanadium into the framework of MCM-41 affects the long-range order of the mesopores depends on the vanadium content (Der-Sing Lee and Tsung- Kwei 2002).
Figure 3.19 SEM images of calcined (a) Cr-MCM-41(100), and (b) Cr-MCM-41(75)
Figure 3.20 SEM images of calcined (c) Cr-MCM-41(50) and (d) Cr-MCM-41 (25)
Figure 3.21 SEM images of calcined (e) Fe-MCM-41(25) and (f) Cr-Fe-MCM-41(Si/Cr+Fe) =100
Figure 3.22 SEM images of calcined (g) V-MCM-41(50) and (h) V-Mn-MCM-41 (V:Mn=50:50)
Figure 3.23 TEM images of calcined (a) Cr-MCM-41(25) and (b) Cr-Fe-MCM-41(Si/Cr+Fe) =100
Figure 3.24 TEM images of calcined (c) V-MCM-41(100) and (d) V-MCM-41(75)
Figure 3.25 TEM images of calcined (e) V-MCM-41(50) and (f) V-MCM-41(25)
3.2 CATALYTIC OXIDATION OF TETRALIN TO 1-TETRALONE

Oxidation of tetralin to 1-tetralone is an industrially important reaction. 1-tetralone is an intermediate for the production of important chemicals such as carboryl, sertaline and 18-methyl norethisterone which are used as insecticide, anti-depressant and contraceptive respectively. The reaction scheme is given below.

\[
\text{Tetralin} + O_2 \xrightarrow{\text{Catalyst}} 1\text{-tetralone}
\]

The catalytic activity of chromium and iron incorporated MCM-41 catalysts is evaluated for vapour phase oxidation of tetralin to 1-tetralone. In order to optimise the reaction conditions for maximum selectivity, the following reaction parameters viz., temperature, effect of flow rate, weight of the catalyst, weight hourly space velocity (WHSV) and time on stream studies have been studied and their corresponding results are discussed below.

3.2.1 Effect of reaction parameters on 1-tetralone formation

Influences of various reaction parameters have been studied on the conversion of tetralin in order to optimize the reaction conditions. Oxidation of tetralin to 1-tetralone is studied in the temperature range 523–673 K (Figure.3.26) using Cr-MCM-41(25) catalyst. As temperature is increased from 523–623 K, the conversion is increased and decreased beyond
623K. The selectivity also followed similar trend as that of the conversion. Increase in conversion from 523–623 K is due to activation energy demanding but decrease above 623 K is due to blocking of active sites by coke formation.

The effect of catalyst weight is also studied at 623 K and the results are illustrated in Figure 3.27. Conversion increased with the increase in weight of Cr-MCM-41(25) up to 0.3g and decreased after attaining a steady level between 0.3 and 0.4g of the catalyst weight. However, the selectivity of 1-tetralone increased gradually with increasing catalyst weight and levelled off at 0.3 g. Formation and subsequent conversion of tetralol depend on its diffusion length of the catalyst bed.

The effect of flow rate of tetralin on the conversion and 1-tetralone selectivity was studied at 623 K with 0.3 g of Cr-MCM-41(25). The results are presented in Figure 3.28. The selectivity and conversion gradually decreased with increase in flow rate of tetralin. Since the formation of 1-tetralone involves consecutive oxidation of tetralin to tetralol and then to 1-tetralone, adequate contact time is necessary. Maximum selectivity of 1-tetralone was observed at low flow rate WHSV = 6.46 h⁻¹. Decrease in selectivity at high flow rates may be attributed to rapid diffusion of tetralol.

The time on stream study was carried out for the vapour phase oxidation of tetralin at 623 K with the flow rate of tetralin 6.46 h⁻¹ (WHSV) and with the flow of CO₂ - free air 0.02 mol h⁻¹ to test the stability of the catalyst. The plot of tetralin conversion and 1-tetralone selectivity vs. time on stream is shown in Figure 3.29. Initially an increase in conversion was observed up to one hour and then decrease with the increase in time. The selectivity also followed similar trend as that of the conversion. The decrease in conversion may be due to the formation of Cr⁵⁺ which is not reactivated to
Cr$^{6+}$ sites during the course of reaction. In order to verify this, DRUV-Vis spectral analysis of both the spent and fresh catalysts was undertaken. The spectra are shown in Figure 3.9a and 3.9e. In the spectrum of the spent catalyst, complete loss of polychromate and chromate species is observed. This analysis therefore confirms the necessity of polychromate and chromate for oxidation and also their regeneration. But they are not instantaneously regenerated.

3.2.2 Effect of the Si/Cr ratio of MCM-41 on the oxidation of tetralin

The vapour phase oxidation of tetralin was carried out in the presence of CO$_2$ – free air at atmospheric pressure on Cr-MCM-41 catalysts with different Si/Cr ratio (Si/Cr= 25, 50, 75 and 100). The effect of Si/Cr ratio on the conversion of tetralin and product selectivity was studied at the optimized reaction conditions viz., at 623 K, 0.3 g weight of the catalyst with (6.46 h$^{-1}$ WHSV) flow rate of tetralin being and 0.02 mol h$^{-1}$ of oxygen. The results are presented in Figure 3.30. Oxidation of tetralin involves consecutive oxidation of tetralin to tetralol and then to 1-tetralone. It is seen from the results that tetralin conversion decreased with the increase in Si/Cr ratio and the selectivity to 1-tetralone remained close to 100% on all the catalysts. DR-UV-vis spectra of the catalysts (Figure 3.9) with different Si/Cr ratio also show that there is a corresponding decrease in the intensity of the absorption bands corresponding to Cr$^{3+}$ and Cr$^{6+}$ species. The decrease in activity of Cr-MCM-41 with an increase in Si/Cr ratio may be attributed to the decrease in the level of Cr$^{3+}$ and Cr$^{6+}$ species.
Reaction conditions: Catalyst: Cr-MCM-41(25), Catalyst Weight = 0.3 g, WHSV = 6.46 h$^{-1}$ and Flow rate of air = 0.02 mol h$^{-1}$

Figure 3.26 Effect of temperature on the oxidation of tetralin
Reaction Conditions: Catalyst: Cr-MCM-41(25), Temperature = 623 K, WHSV = 6.46 h\(^{-1}\) and Flow rate of air = 0.02 mol h\(^{-1}\)

Figure 3.27 Effect of catalyst weight on tetralin oxidation
Reaction Conditions: Catalyst: Cr-MCM-41(25), Temperature = 623 K, Catalyst Weight = 0.3 g and Flow rate of air 0.02 mol h⁻¹

Figure 3.28 Effect of flow rate on the oxidation of tetralin
Reaction Conditions: Temperature = 623 K, Weight of Cr-MCM-41 (25) = 0.3 g, WHSV = 6.46 h\(^{-1}\) and Flow rate of air = 0.02 mol h\(^{-1}\)

**Figure 3.29** Effect of reaction time on the oxidation of tetralin
Reaction Conditions: Temperature = 623 K, Catalyst Weight = 0.3 g, WHSV = 6.46 h\(^{-1}\) and Flow rate of air 0.02 mol h\(^{-1}\)

**Figure 3.30** Effect of Si/Cr ratio of Cr-MCM-41 on the oxidation of tetralin
3.2.3 Comparison of activity of the Cr-MCM-41 catalyst with Fe-MCM-41 and Cr-Fe-MCM-41 catalysts

The activity of Cr-MCM-41 (25) was compared with Fe-MCM-41 and Cr-Fe-MCM-41 catalysts in order to study the influence of other metals on the oxidation of tetralin (Figure 3.31). All the three catalysts exhibited different levels of conversion. Among the three different catalysts, Cr-MCM-41(25) showed maximum activity for vapor phase oxidation of tetralin. However, the activity of Cr-Fe-MCM-41 was not equal to the sum of the activities of Cr-MCM-41 and Fe-MCM-41. Instead it is less than that of Cr-MCM-41(25). The decrease in the activity of Cr-Fe-MCM-41 catalyst is due to the interaction of Fe with Cr in the framework of MCM-41 there by decreasing the activity of Cr. The interaction is evident by shift in wave length towards longer wavelength (Figure 3.10) due to the charge transfer in Fe-O bond. Hence, from this study, it is well understood that both co-existence of Fe and Cr and Fe alone are not beneficial for the vapor phase oxidation of tetralin under these experimental conditions.

3.2.4 The reaction scheme for oxidation of tetralin

Based on the above investigation on the vapour phase oxidation of tetralin, a reaction scheme is suggested as shown in scheme-1. According to the scheme, oxidation of tetralin proceeds through two steps. In the first step tetralin is oxidized to tetralol followed by oxidation of tetralol to 1-tetralone, Cr$^{3+}$ is required for the oxidation of tetralin to tetralol and Cr$^{6+}$ is required for the tetralol to 1-tetralone. Based on the above fact it is suggested that this reaction requires the co-existence of Cr$^{3+}$ and Cr$^{6+}$ which is more at the Si/Cr ratio = 25 than at other Si/Cr ratios as it is clear from intensity of the DRUV-Vis peaks at 350 and 275 nm corresponding to Cr$^{6+}$ and Cr$^{3+}$ (Figure 3.9). The reaction was also studied with N$_2$ in place of air. It was
found that tetralin remained unreacted. This observation establishes the requirement of molecular oxygen as oxidant. However, molecular oxygen might not be adsorbed and activated by Cr\textsuperscript{6+}. It is the Cr\textsuperscript{3+} species which can adsorb and activate O\textsubscript{2}. Hence, presence of Cr\textsuperscript{3+} is necessary for the vapour phase oxidation of tetralin with molecular oxygen as the oxidant as shown in the reaction scheme-1. DRUV-Vis spectra of all the catalysts indicate that there is a large proportion of Cr\textsuperscript{6+} in comparison with Cr\textsuperscript{3+}. Since it is proposed in the reaction Scheme-1, that Cr\textsuperscript{6+} is responsible for 1-tetralone formation, one would expect maximum probability for the conversion of tetralol to 1-tetralone. This may be the reason for 100% selectivity observed in all the cases for 1-tetralone formation.

During the oxidation of tetralin with air Cr\textsuperscript{3+} adsorbs and activates molecular oxygen leading to the formation of peroxide. One of the peroxide oxygens is inserted between C-H bond of tetralin to give tetralol. Now Cr\textsuperscript{3+} might become Cr\textsuperscript{5+}. Tetralol is oxidized to tetralone by framework Cr\textsuperscript{6+}. Tetralol makes a nucleophilic attack on Cr\textsuperscript{6+} to give an intermediate which rapidly decomposes to 1-tetralone and water. This process facilitates the formation of Cr\textsuperscript{4+} species. In the DRUV-Vis spectrum of spent catalyst (Figure 3.9(e)), two absorption bands were observed with \( \lambda \) max at 350 and 275 nm, which are assigned to Cr\textsuperscript{5+} and Cr\textsuperscript{4+} species, respectively (Shi et al 1999). The suggested scheme for the formation 1-tetralone is in good agreement with the DRUV-Vis spectral features. As discussed in the reaction scheme-1, for oxidation of every tetralol molecule to 1-tetralone, two hexavalent chromium sites are required. From the above result it is established that oxidation of tetralin requires Cr\textsuperscript{6+} species either in the form of chromate or polychromate.
Reaction conditions: Temperature = 623 K, Weight of the Catalyst = 0.3 g, WHSV = 6.46 h\(^{-1}\) and Flow rate of air = 0.02 mol h\(^{-1}\)

**Figure 3.31** Comparison of activity of the catalysts for the oxidation of tetralin
Reaction scheme 1

\[
\begin{align*}
\text{tetralin} & \quad \rightarrow \quad \text{tetralol} \\
& \quad + \\
& \quad 1\text{-tetralone}
\end{align*}
\]
3.3 CATALYTIC OXIDATION OF O-XYLENE TO PHTHALIC ANHYDRIDE

Phthalic anhydride is an industrially important chemical produced by the oxidation of o-xylene. This is widely employed as a raw material in manufacture of phthalate plasticizers, poly ester and alkyl resins, paints, lacquers, insecticides; phthalic anhydride is the basis of vat dyes and other chemical synthesis such as production of benzoic acid. Phthalic anhydride is formed from o-xylene as shown below.

\[
\begin{align*}
\text{CH}_3 & \\
\text{CH}_3 & \\
\text{CH}_3 & \\
\text{O} & \\
\text{O} & \\
\text{O} & \\
\text{O} & \\
\text{O} & \\
n\text{o-Xylene} & \xrightarrow{\text{O}_2, \text{catalyst}} \text{Phthalic anhydride}
\end{align*}
\]

Vanadium and manganese incorporated MCM-41 catalysts have been chosen for vapour phase oxidation o-xylene to phthalic anhydride. The role of V and coexistence of V-Mn metals has been studied. In order to compare the performance of the catalysts, the reaction conditions viz., temperature, flow rate, weight of the catalyst and time on stream studies are optimised and the results are discussed below. The products formed during the oxidation are o-tolualdehyde, phthalic anhydride and trace amounts of carbon oxides.
3.3.1 Optimization of the reaction parameters

Experiments were carried out on the vapour phase oxidation of o-xylene by varying the temperature from 523–623 K, catalyst weight from 0.1–0.5 g, flow rate of o-xylene from 5.87–14.66 h⁻¹ (WHSV) in the presence of CO₂ free air flow of 0.02 mol h⁻¹ on V-MCM-41(Si/V=50). The time on stream study was carried out over V-MCM-41(50) for the vapor phase oxidation of o-xylene at the optimized reaction conditions viz., temperature at 573 K, 0.3 g weight of the catalyst with the flow rate of o-xylene 5.87 h⁻¹ (WHSV) and CO₂-free air flow of 0.02 mol h⁻¹, to test the stability of the catalyst. The results are depicted in Figure 3.32. The conversion increased from 60 to 120 min and then decreased up to 300 min. After 5h of the reaction, the catalyst attained steady state. A similar trend was observed on the selectivity of phthalic anhydride. The initial increase in conversion from 60 to 120 min is attributed to oxidation of V⁴⁺ to V⁵⁺ which is necessary for oxidation. It has also been reported that V⁵⁺ is the actual active site for dehydrogenation of isobutane to isobutene (Jia et al 2004). Hence the V⁵⁺ might be the active site for the oxidation of o-xylene also. The DRUV-Vis spectral analysis of spent and fresh V-MCM-41 (50) showed the presence of V⁵⁺ and only V⁴⁺ respectively (Figure 3.11). During the oxidation process, V⁴⁺ ions are oxidized to V⁵⁺.

It is interesting to note that the selectivity trend of phthalic anhydride is reverse of o-tolualdehyde. This indicates that phthalic anhydride formation takes place through the intermediate namely o-tolualdehyde during the oxidation process. The most interesting observation made in this study is the steady conversion and product selectivity even after 300 min. The residual active sites might not promote coke formation even after blocking of some of the active sites.
3.3.2 Effect of vanadium content for oxidation of o-xylene

The effect of V content (Si/V = 25, 50, 75 and 100) on o-xylene conversion and product selectivity was studied with 0.3 g of the catalyst at 573 K with the flow rate of o-xylene 5.87 h\(^{-1}\) (WHSV) and flow of CO\(_2\) free air 0.02 mol h\(^{-1}\). The results are illustrated in Figure 3.33. The o-xylene conversion increased when the Si/V ratio is increased from 25 to 50 and decreased thereafter. V-MCM-41(50) exhibited maximum catalytic activity. As the ratio is increased, the level of vanadium is decreasing. The poor activity of the catalyst with high Si/V ratio may be due to low vanadium content and that of the catalyst with low Si/V ratio may be due to poor dispersion of active sites. Very low intense bands around 260 and 340 nm corresponding to V\(^{5+}\) were observed in the DRUV-Vis spectra of V-MCM-41(25) when compared with V-MCM-41(50) Figure 3.11 (a, b). The decrease in conversion at higher values of Si/V may be attributed to the decrease in the concentration of V\(^{5+}\) active sites. It is evident from the DRUV-Vis spectra that as the Si/V ratio increased from 50 to 100, the absorbance intensity decreased. This observation is also supported by EPR spectral analysis. EPR spectra of V-MCM-41 samples (Figure 3.15) showed the presence of V\(^{5+}\) and V\(^{4+}\) and there is an increase in the formation of more number of V\(^{4+}\) with increase in the Si/V ratio as evident through hyperfine splitting. The absence of hyperfine splitting in V-MCM-41(25) indicates that there is only V\(^{5+}\) ions. Hence, the high activity of V-MCM-41 (50) may be attributed to the availability of more number of V\(^{5+}\) than V-MCM-41(75) and V-MCM-41(100).
3.3.3 Comparison of activity of the V-MCM-41 catalyst with Mn-MCM-41 and V-Mn-MCM-41 catalysts for oxidation of o-xylene

The activity of V-MCM-41(50), Mn-MCM-41(50), V-Mn-MCM-41 (V:Mn=50:50), was measured at 623 K with the WHSV of o-xylene 5.87 h\(^{-1}\) (WHSV). The results are compared to understand the influence of various metals on the oxidation reaction (Figure 3.34). V-MCM-41(50) exhibited maximum activity when compared with Mn-MCM-41 and bimetal V, Mn loaded catalysts. The reason for the high activity of V-MCM-41(50) may be due to the availability of both framework and non framework V\(^{5+}\) in MCM-41 which is evident from DRUV-Vis spectra (Figure 3.11). Framework V\(^{5+}\) was shown to be more active than the non-framework V\(^{5+}\) for dehydrogenation of isobutene to isobutene (Jia et al 2004). Based on the literature, it can be understood that the poor activity of V-Mn-MCM-41 may be due to the presence of few number of framework V\(^{5+}\) in V-Mn-MCM-41 catalyst.

3.3.4 Reaction scheme for oxidation of o-xylene

Based on the above results a reaction scheme is proposed for the vapour phase oxidation of o-xylene (Scheme 2). According to the scheme, oxygen is activated by framework vanadium. The activated O\(_2\) is inserted between carbon and hydrogen bond of methyl group in o-xylene. The resulting alcohol (III) is rapidly oxidized to o-tolualdehyde which is also subsequently oxidized to o-toluic acid. The same process is also repeated on adjacent methyl group to yield phthalic acid. The product is subsequently oxidized to phthalic anhydride.
Reaction Conditions: Temperature = 573 K, Weight of the Catalyst = 0.3 g, WHSV = 5.87h⁻¹ and Flow rate of air 0.02 mol h⁻¹

Figure 3.32  Effect of reaction time on the oxidation of o-xylene
Reaction Conditions: Temperature = 573 K, Weight of the Catalyst = 0.3 g, WHSV = 5.87h⁻¹ and Flow rate of air 0.02 mol h⁻¹

Figure 3.33 Effect of Si/V ratio of V-MCM- 41 on the oxidation of o-xylene
Reaction Conditions: Temperature = 573 K, Weight of the Catalyst = 0.3 g, WHSV = 5.87 h⁻¹ and Flow rate of air 0.02 mol h⁻¹

Figure 3.34 Comparison of activity of the catalysts for the oxidation of o-xylene
Scheme 2

I \xrightarrow{O_2} II

\(\text{O}^{-}V\text{O}^{-}\text{O}^{-}\text{OSiSiSiSi}) \xrightarrow{O_2} (\text{O}^{-}V\text{O}^{-}\text{O}^{-}\text{OSiSiSiSi})\)

\(\text{CH}_2\text{CH}_3\text{H}) \xrightarrow{\text{O-xylene}} \text{CH}_2\text{CH}_3\text{OH}\)

\(\text{CH}_2\text{CH}_3\text{H}) \xrightarrow{\text{fast}} \text{CH}_2\text{CH}_3\text{CHO}\)

\(\text{CH}_2\text{CH}_3\text{H}) \xrightarrow{\text{Repeated}} \text{CH}_2\text{CH}_3\text{COOH}\)

Phthalic anhydride
3.4 CATALYTIC OXIDATION OF P-XYLENE TO TEREPTHALIC ACID

Terephthalic acid (TPA) is one of the most important chemicals used as a raw material for synthesis of polyester. Synthesis of terephthalic acid via eco friendly and economical method is of great importance. Hence, attempts were made to synthesize terephthalic acid selectively using metal incorporated MCM-41 catalysts. Terephthalic acid can be formed by the oxidation of p-xylene.

\[
\text{CH}_3\text{C}_6\text{H}_4\text{CH}_3 + \text{O}_2 \xrightarrow{\text{Catalyst}} \text{COOH}
\]

p-xylene oxidation is carried out in the presence of air using V-Mn-MCM-41(V:Mn=50:50) catalyst and the conditions are optimized. The product formed on oxidation of p-xylene is only phthalic anhydride.

The time on stream study was carried out over V-Mn-MCM-41(V:Mn=50:50) at 623 K with the WHSV of p-xylene 5.74 h\(^{-1}\) (WHSV) and CO\(_2\)-free air 0.02 mol h\(^{-1}\) for 360 min to test the stability of the catalyst. The plot of p-xylene conversion and terephthalic acid selectivity Vs time on stream (min) (Figure 3.35) showed that there is a possibility of acquiring steady conversion at the higher value of time on stream. This is concluded from the slow decrease in conversion with increased time on stream above 120 min.
3.4.1 Activity of Bimetal V-Mn-MCM-41 catalyst for oxidation

*p*-xylene to terephthalic acid

The catalytic activity of V-Mn-MCM-41 catalyst with the composition of V:Mn=50:50 (B) is compared with V-Mn-MCM-41 (V:Mn=25:75) (A) and V-Mn-MCM-41 (V:Mn=75:25) (C) under the optimized reactions conditions (Figure 3.37).

Among the three catalysts, catalyst B showed higher activity than other catalysts A&C whereas among the catalysts A & C, catalyst A showed less activity than catalyst C. It is to be emphasised that pure V-MCM41 and Mn-MCM41 are not very efficient for the oxidation of *p*-xylene. The bimetallic MCM 41 showed higher activity than individual metal-MCM 41 catalyst. Vanadium and manganese sites might not be independently exhibiting catalytic activity; the activity appears to be modified by synergistic of vanadium and manganese. Also V-Mn-MCM-41(V:Mn=50:50) Figure 3.18 b showed a hyperfine splitting due to poor delocalization of Mn electrons. However, the high activity of catalyst B can be explained with the results of EPR and DRS. From the results of EPR, it is observed that catalyst B possesses optimum number of unpaired electrons in the 3d shells whereas there are more number of unpaired electrons on catalyst A and less number of unpaired electrons on catalyst C than catalyst B. It can be concluded that there should be sufficient number of unpaired electrons to favour the oxidation reaction. In the case of V-Mn-MCM-41 (V:Mn=25:75) and V-Mn-MCM-41 (V:Mn=75:25) catalysts due to high delocalization of Mn electrons there is very poor hyperfine splitting. The oxidation reaction seems to be favourable on the catalyst with poor delocalization of Mn electrons. Hence the present study confirms the fact that there should be poor delocalisation and hence good hyperfine splitting in order to account for high activity. Hence bimetal catalysts with optimum content of V and Mn is better choice for the oxidation of *p*-xylene than the respective mono metallic catalysts.
Reaction Conditions: Temperature = 623 K, Weight of the Catalyst = 0.3 g,
WHSV = 5.74 h\(^{-1}\) and Flow rate of air = 0.02 mol h\(^{-1}\)

**Figure 3.35** Effect of reaction time on the oxidation of p-xylene
(A) V-Mn-MCM-41 (V:Mn = 25:75)
(B) V-Mn-MCM-41 (V:Mn = 50:50)
(C) V-Mn-MCM-41 (V:Mn = 75:25)

Reaction Conditions: Temperature = 623 K, Weight of the Catalyst = 0.3 g, WHSV = 5.74 h\(^{-1}\) and Flow rate of air = 0.02 mol h\(^{-1}\)

Figure 3.36 Comparison of activity of the catalysts for the oxidation of p-xylene
3.4.2 Influence of support for mono metal V and bimetal V-Mn catalysts on oxidation of hydrocarbons

Interaction of metal with support is also an important aspect in determining the performance of the catalyst for oxidation of hydrocarbons. For the purpose of comparison, Vanadium metal supported on different supports with optimum V content (Si/V=50) and bimetal V-Mn supported on various supports at the optimum composition of V-Mn as 50:50 were prepared and tested for the oxidation of hydrocarbon and the activities are compared.

Vanadium mono metal and V-Mn bimetal incorporated Hydrotalcite (HT), ZSM-5 and MCM-41 were synthesized and characterized by XRD, BET Surface area, DRUV-Vis and EPR spectroscopy and catalytic activities are compared at optimized reaction conditions for the oxidation of o-xylene (Figure 3.37) and p-xylene (Figure 3.38) respectively. Among the three different supported catalysts, MCM-41 supported vanadium and V-Mn bimetal catalyst showed maximum activity. The catalytic activity follows the trend V-MCM-41 > V-HT > V-ZSM-5. This indicates that there is no direct correlation between surface area (Table 3.4) and catalytic activity. However, in the case of MCM-41 supported V catalyst, presence of non framework and frame work $V^{5+}$ is seen from DRUV-Vis (Figure 3.11). It has been reported in literature that, the possibility of V going into the framework is less likely in the case of ZSM-5 and HT than MCM-41, in addition to the diffusion problem within the pores of ZSM-5 (Mercedes Alvaro et al 2003). This may be the reason for poor activity of ZSM-5 and HT supported catalysts. Hence, it can be concluded that framework $V^{5+}$ available in MCM-41 may be responsible for exhibiting high oxidation activity.
Table 3.3  Surface area of the mono metal V and bimetal V-Mn incorporated Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-MCM-41 (50)</td>
<td>893</td>
</tr>
<tr>
<td>V-Mn-MCM-41(V:Mn=50:50)</td>
<td>765</td>
</tr>
<tr>
<td>V-HT(50)</td>
<td>156</td>
</tr>
<tr>
<td>V-Mn-HT (50,50)</td>
<td>143</td>
</tr>
<tr>
<td>V-ZSM-5 (50)</td>
<td>412</td>
</tr>
<tr>
<td>V-Mn-ZSM-5 (50,50)</td>
<td>396</td>
</tr>
</tbody>
</table>
Reaction Conditions: Temperature = 573 K, Weight of the Catalyst = 0.3 g, WHSV = 5.87 h\(^{-1}\) and Flow rate of air = 0.02 mol h\(^{-1}\)

**Figure 3.37 Comparison of activity of the catalysts with various supports for the oxidation of o-xylene**
Figure 3.38 Comparison of activity of the catalysts with various supports for the oxidation of p-xylene

Reaction Conditions: Temperature = 623 K, Weight of the Catalyst = 0.3 g, WHSV = 5.74h\(^{-1}\) and Flow rate of air 0.02 mol h\(^{-1}\)