CHAPTER 2

EXPERIMENTAL

2.1 CHEMICALS

Sodium metasilicate (SRL), cetyltrimethylammonium bromide (CTAB, OTTO Chemie), chromium nitrate nono hydrate (SRL), ferric nitrate nono hydrate (SRL), vanadyl sulphate monohydrate (SRL), manganese (II) acetate (SRL), ethanol, sulphuric acid (Merck), tetralin, o-xylene and p-xylene (Analytical Grade, SRL, India).

2.1.1 Synthesis of Cr-MCM-41

Cr-MCM-41 (Si/Cr = 25) was synthesized by hydrothermal method as reported (Beck et al 1992) using sodium metasilicate (CDH) as silica source, and cetyl trimethyl ammonium bromide (CTAB, OTTO Chemie) as the structure-directing agent. In a typical synthesis, 21.32 g of sodium metasilicate and 1.20 g of chromium nitrate nono hydrate were dissolved in 60 g of water. The reaction mixture was allowed to stir for 2 h. Meanwhile, 5.47g of CTAB was dissolved in 20 g of water. Then, the resultant mixture of sodium metasilicate and chromium nitrate nono hydrate was added drop wise into CTAB solution. The final mixture was stirred for 1 h. The pH of the gel was adjusted to 10.5-11 using 4 N sulfuric acid followed by stirring for 3 h. The obtained gel was placed into an autoclave and heated to 413 K under static condition for 12 h. The resultant precipitate was filtered, washed with deionized water and dried in air at 375 K and then finally calcined at 773 K.
for 1 h in N$_2$ flow and for 12 h in CO$_2$ - free air flow. Mono metallic M-MCM-41 with various ratios of Si/M = 25, 50, 75 and 100 (M=Cr, Fe, V and Mn) and bimetallic M-M-MCM-41 Si/(M + M) = 100 (M+M=Cr+Fe and V+Mn) were also synthesized in a similar manner wherein only the ratio of metal sources was adjusted. The molar gel composition is given below.

**Cr-MCM-41 catalysts**

<table>
<thead>
<tr>
<th>SiO$_2$</th>
<th>Cr$_2$O$_3$</th>
<th>CTAB</th>
<th>H$_2$O</th>
<th>(Si/Cr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>0.20</td>
<td>160</td>
<td></td>
<td>25</td>
</tr>
<tr>
<td>0.02</td>
<td>0.20</td>
<td>160</td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>0.013</td>
<td>0.20</td>
<td>160</td>
<td></td>
<td>75</td>
</tr>
<tr>
<td>0.01</td>
<td>0.20</td>
<td>160</td>
<td></td>
<td>100</td>
</tr>
</tbody>
</table>

**Fe-MCM-41 catalysts**

<table>
<thead>
<tr>
<th>SiO$_2$</th>
<th>Fe$_2$O$_3$</th>
<th>CTAB</th>
<th>H$_2$O</th>
<th>(Si/Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>0.20</td>
<td>160</td>
<td></td>
<td>25</td>
</tr>
</tbody>
</table>

**V-MCM-41 catalysts**

<table>
<thead>
<tr>
<th>SiO$_2$</th>
<th>V$_2$O$_5$</th>
<th>MnO</th>
<th>CTAB</th>
<th>H$_2$O</th>
<th>(Si/V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>0.02</td>
<td>0.20</td>
<td>160</td>
<td></td>
<td>25</td>
</tr>
<tr>
<td>0.02</td>
<td>0.02</td>
<td>0.20</td>
<td>160</td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>0.013</td>
<td>0.02</td>
<td>0.20</td>
<td>160</td>
<td></td>
<td>75</td>
</tr>
<tr>
<td>0.01</td>
<td>0.02</td>
<td>0.20</td>
<td>160</td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>0.02</td>
<td>0.20</td>
<td>160</td>
<td></td>
<td>50</td>
<td></td>
</tr>
</tbody>
</table>

**Cr-Fe-MCM-41 Catalyst (Si/(Cr+Fe)=100)**

<table>
<thead>
<tr>
<th>SiO$_2$</th>
<th>Cr$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CTAB</th>
<th>H$_2$O</th>
<th>(Si/(Cr+Fe)=100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>0.013</td>
<td>0.20</td>
<td>160</td>
<td></td>
<td>(Cr+Fe)</td>
</tr>
</tbody>
</table>

**V-Mn-MCM-41 Catalyst (Si/(V+Mn)=100**

<table>
<thead>
<tr>
<th>SiO$_2$</th>
<th>V$_2$O$_5$</th>
<th>MnO</th>
<th>CTAB</th>
<th>H$_2$O</th>
<th>(Si/(V+Mn))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>0.02</td>
<td>0.20</td>
<td>160</td>
<td></td>
<td>100</td>
</tr>
</tbody>
</table>


2.1.2 Synthesis of M-ZSM-5 (M = V and Mn)

Chemicals: Sodium metasilicate, tetra propyl ammonium bromide (TPAB), vanadyl sulphate monohydrate (SRL), manganese (II) acetate, sulphuric acid and water.

The M-ZSM-5 (M = V and Mn) was synthesized hydrothermally using the following molar gel composition \( \text{SiO}_2:0.18 \text{ Na}_2\text{O}: 0.025 \text{ TPAB}:35 \text{ H}_2\text{O}: x (\text{M}) \). 28.5 g Sodium metasilicate and respective metal source (vanadyl sulphate monohydrate and manganese (II) acetate) diluted with 60 ml of water were stirred well for 1h. Solution of aluminium sulphate 1.3g in 20 ml water was added drop wise to the sodium metasilicate solution and stirred well for 1h. Tetra propyl ammonium bromide (3g dissolved in 20 ml water) is added drop by drop to the above solutions with mechanical stirring. After 1h stirring, 4N \( \text{H}_2\text{SO}_4 \) was added drop by drop to the mixture till the formation of gel and the pH of the gel was adjusted to 10.5 by adding \( \text{H}_2\text{SO}_4 \) solution, then stirred well for 30 min. The milky gel was transferred to a 300 ml stainless steel autoclave, sealed and placed in a hot air oven maintained at 150°C for 3-4 days. At the end of crystallization, the product was filtered, washed and dried at 120°C for 12h. The synthesized and dried materials were calcined at 550°C for 7h to remove the template molecules. V-ZSM-5 catalysts with the ratio of \( \text{Si}/\text{V} = 50 \) and V-Mn-ZSM-5 \( \text{Si}/(\text{V} + \text{Mn}) = 100 \) were also synthesized in a similar manner wherein only the ratio of metals sources was adjusted.

2.1.3 Synthesis of M-HT (M=V and Mn)

Hydrotalcites (HT) were prepared by co-precipitation method. This technique allows homogeneous distribution of the starting materials, where
two or more elements can be intimately mixed together resulting in synergetic effects which can be favorably employed in catalysis. Two methods are generally employed for preparing hydrotalcites. One is precipitation at high supersaturation and the other is precipitation at low supersaturation.

2.1.4 At high supersaturation with interlayer CO$_3^{2-}$(HTA-HTD)

Hydrotalcite was prepared according to the method described by Reichle et al (1986). Solution A was prepared by dissolving 256 g of Mg(NO$_3$)$_2$.6H$_2$O, 187.5 g of Al(NO$_3$)$_3$.9H$_2$O and in 700 cm$^3$ of distilled water. Solution B was prepared by dissolving 280 g of 50% NaOH (140 g NaOH in 140 cm$^3$ distilled water) and 100 g of Na$_2$CO$_3$ in 1000 cm$^3$ of distilled water. HTA was prepared by adding solution A to solution B in 3-4 h at pH (11-13) and crystallized at 333 K for 18 h. Another HT sample was prepared by adding solution A into solution B in 8-9 h. The resulting slurry was divided into three parts and crystallization was carried out at 333, 373 and 423 K for 18 h. The samples were termed as HTB, HTC and HTD respectively. The samples were filtered and washed several times with hot distilled water until the filtrate showed neutral pH. The sample was then dried at 373 K for 12 h and then calcined at 723 K for 18 h. $x = \text{Al(III)}/\text{Al(III)}+\text{Mg(II)} = 0.33$ for all the samples (HTA-HTD).

V and Mn were loaded onto the support by incipient wet impregnation method, with an aqueous solution of metal source acidified with HCl to effect the complete dissolution of the salt. Metal source (vanadyl sulphate monohydrate as vanadium source and manganese (II) acetate as manganese source) was taken as the precursor so as to obtain the desired metal (M = V and Mn) concentration in support and the solution was mixed with support in distilled water. The resulting slurry was subjected to
continuous stirring and subsequently dried in an oven at 373 K for 12 h. The solid residue was then crushed and calcined in air at 723 K for 5 h. The catalysts M-HT with the ratio of Si/V=50 (M=V) and M-M-ZSM-5 Si/(M+M)=100 (M+M= V+Mn) were also synthesized in a similar manner wherein only the ratio of metal sources was adjusted. V-HT catalysts with the ratio of Si/V=50 and V-Mn-HT Si/(V + Mn) = 100 were also synthesized in a similar manner.

2.2 CHARACTERIZATION OF THE CATALYSTS

The study of physico chemical properties of metal incorporated catalysts is a challenging task and many analytical methods are applied to characterize the catalysts. It is very important to know the surface and structural properties of the support which is vital in deciding the metal dispersion. The surface area, pore volume, different phases and impurities present in the support can affect the dispersion and thereby, the activity and selectivity of the catalyst. The techniques described in the following sections are employed to characterize the support and the catalyst to know the properties of these supported metal systems in detail.

2.2.1 X-ray diffraction (XRD)

X-ray diffraction (XRD) pattern of the all synthesized catalysts were recorded on a Rigaku Miniflex X-ray diffractometer. Liquid nitrogen cooled germanium solid state detector with CuKα radiation source was used (λ = 1.5406 Å). The diffractograms were recorded in the 2θ range 1.5˚ to 60˚ with a step size of 0.05˚. The count time was 4 s over each step. From the 2θ values read from the diffractograms, the interplanar spacing d, were calculated using Bragg’s equation, nλ = 2d sinθ where n is the order of
reflection, \( \lambda \) the wavelength of the radiation used and \( \theta \) the angle of diffraction along with the corresponding unit cell parameter calculated from 
\[ a_0 = 2d_{100}/\sqrt{3}. \]
The peak height gives the intensity of the corresponding peak.

### 2.2.2 Textural analysis

The textural characteristics of the synthesised materials were analysed by nitrogen adsorption method. Nitrogen adsorption and desorption isotherms were measured at 77 K on an Belsorpmini II surface area analyzer (BEL Japan. Inc). All the samples were initially degassed at 473 K for 2-3 h under vacuum in the degas port of the analyzer. The specific surface area was calculated following the BET procedure. The pore size distribution of the materials were calculated from the desorption branch of the nitrogen isotherm following the BJH method.

### 2.2.3 Thermal Analysis

Thermal analysis is widely used to study the structural stability of as-synthesised forms of molecular sieves. It provides information about the temperature required for the removal of adsorbed water, decomposition of the occluded organic cations in the pores and channels of molecular sieves. Data obtained form TG, DTA and DTG study are useful in evaluating the thermal properties of molecular sieves. The shape and splitting of the endotherms (low temperature) help to identify the location of water molecules. The temperature at which an exotherm appears in the DTA after the loss of water molecules, gives helpful information about the temperature required to remove the template molecules from the pores of the molecular sieves during calcination. Phase transformations (if any) can also be understood from the exotherms obtained at higher temperatures. TGA samples were performed on Mettler TA
3000 system. The thermogram of the samples was recorded under the following conditions.

- Weight of the sample = 20 – 30 mg
- Heating rate = 10 K/min
- Atmosphere (flowing air) = 25 mL/min

2.2.4 ICP-AES

Inductively coupled plasma (ICP) optical emission spectroscopy was used for the determination of the metal content in each sample synthesized above. The measurements were performed with a Perkin-Elmer OPTIMA 3000. The sample was dissolved in a mixture of HF and HNO₃ before the measurement.

2.2.5 Diffused Reflectance Spectroscopy (DRS)

The coordination environment of chromium, iron, vanadium and manganese containing MCM-41 catalysts was examined by diffuse reflectance UV-vis spectroscopy. The spectra were recorded between 200-800 nm on a Shimadzu UV-vis spectrophotometer (Model 2450) using BaSO₄ as the reference.

2.2.6 Electron Paramagnetic Resonance Spectroscopy (EPR)

The co-ordination environment of chromium and vanadium was analyzed by EPR spectroscopic technique (varien E112 spectrometer operating in the X-band 9.2 GHz frequency) at room temperature. Samples
were loaded into 2mm i.d x 150mm length suprasil quartz tube. The magnetic field was calibrated with a Varian E-500 gaussmeter.

2.2.6.1 The g factor (Spectroscopic Splitting Factor)

The g factor is one of the most important concepts in electron spin resonance studies. For an atom where $L = 0$ and $S = 1/2$, the $g_J = g_S = 2$; in practice the value now adopted for a free electron is 2.0023. In the crystalline salts of Mn$^{2+}$ and Fe$^{3+}$ the g-value is almost 2.

In general, $g$ approaches the value of 2 when the coupling of the orbital and spin a momentum of electrons with in solids is broken down almost completely by the strong electric field existing with in the solid. However, in some paramagnetic solids the value of $g$ may differ considerably from 2. In the majority of crystalline samples which have an internal electric field, $Lh/2\pi$ and $Sh/2\pi$ are neither totally uncoupled nor totally coupled, and the energy levels consists of a complex admixture of spin and orbital momenta. The experimental g-value is determined by substituting the measured values of $H$ and $\nu$ into the following equation.

$$h\nu = g\beta H$$

where,
- $h$ - Plank’s Constant = $6.626 \times 10^{-27}$ erg sec
- $\beta_e$ - Bohr Magneton of electron = $9.274 \times 10^{-27}$ erg Gauss
- $H$ - Magnetic field strength
- $\nu$ - Micro wave frequency
2.2.7 Fourier-Transform Infrared Spectroscopy (FT-IR)

The atoms in a molecule rotate and vibrate in different ways at certain quantized energy levels. The infrared spectrum of a molecule results due to vibrations and rotations of its atoms producing a change in permanent dipole moment of the molecule. The most commonly used range of infrared spectrum is mid IR range which lies between 4000 cm$^{-1}$ and 400 cm$^{-1}$.

FT-IR spectra provide valuable information about the basic characteristics of the molecule, namely, the nature of the atoms, their spatial arrangement and their chemical linkage forces. Infrared spectroscopy has been extensively used for identifying the various functional groups of the support and active component of the catalysts. FT-IR with modification in the cell compartment can also be used to measure the surface acidity of the catalysts. In FT-IR studies, there are different methods of preparing samples depending on the purpose of study. The catalyst in powder form is generally prepared as a thin pellet in order to be transparent to the infrared beam. In general, KBr pellet is prepared by grinding, 2 mg of catalyst with 200 mg of KBr.

In the present study the FT-IR spectra of metal incorporated MCM-41 catalysts were recorded with a Nicolet Magna 550 IR spectrometer equipped with a MCT detector using 256 scans at a resolution of 4 cm$^{-1}$. The catalyst powder was pressed into a self-supported wafer (~15 mg) and placed into Spectra tech insitu IR cell, equipped with CaF$_2$ windows and double walls with a space for cooling agent.
2.2.8 Scanning Electron Microscope (SEM)

The morphology of samples was investigated using scanning electron microscopy. The samples were suspended in methanol and the specimen stub was dipped into the liquid and removed. The catalyst powder was deposited onto the surface of the stub evenly when methanol got evaporated. This specimen was then coated with gold for 2 min using an ion sputter coater and viewed under SEM model JEOL 640 scanning electron microscope (SEM) at an operating voltage of 10 kV.

2.2.9 Transmission electron microscopy (TEM)

Transmission electron microscopy measurement for the reduced catalysts was carried out in JEOL 200 kV electron microscope operating at 200 kV. Catalyst sample powders were dispersed on to ‘holy carbon’ coated grids, which were then introduced to the microscope column, which was evacuated to less than $1 \times 10^{-6}$ Torr. Specimens were enlarged using thin photographic paper. The size of metal particles visible in the photograph were measured manually and averaged.

2.2.10 Gas Chromatography

Gas-liquid chromatography is used for the separation of molecules by partitioning solutes between a mobile phase and a stationary liquid phase held on a solid support. Gas-solid chromatography employs a solid adsorbent as the stationary phase. The sequence of a gas chromatography separation is as follows. A sample containing the solutes is injected into heating block where it is immediately vaporized and swept as a plug of vapor by the carrier gas stream into the column inlet. The solutes are adsorbed at the head of the column by the stationary phase and then desorbed by carrier gas. This
sorption-desorption process occurs repeatedly as the sample is moved by the carrier gas towards the column outlet. Each solute travels at its own rate through the column. Their bands separate to a degree that is determined by the individual partition ratio. The solutes are eluted sequentially in the increasing order of their partition ratios and enter a detector attached to the column exit. Flame ionization detector is used for detecting products in the mixture. The signals appear on the recorder as a peak characteristic for each component. The peak area is proportional to the concentration of the component in the mixture. In this study the samples are analyzed using GC-17A M/s. Shimadzu instruments, Japan. SE-30 column and carbowax column were used for product analysis.

Conversion = fraction of reactants converted into products
Selectivity = Fraction of the individual product that constitutes to the total conversion.

\[
\text{Yield} = \frac{\text{Conversion} \times \text{Selectivity}}{100}
\]

2.3 FLOW UNIT FOR CATALYST ACTIVITY MEASUREMENT

Catalytic reactions were carried out in a differential flow reactor operating at atmospheric pressure; infusion pump being used to displace the reactants from the feeder into the reactor. The unit is shown in Figure 2.1.

The vapour phase oxidation reaction was carried out using a fixed bed down flow quartz reactor (length 40 cm; diameter 15 mm) at atmospheric
pressure in the temperature range of 473-623 K with air flow of 0.02 mol h\(^{-1}\), reactor packed with 0.3 g of the catalyst was preheated in a tubular furnace equipped with a thermocouple. Prior to the reaction, the catalyst was activated at 623 K for 3 h in CO\(_2\) free flow of air. The electrically heated furnace was well insulated with asbestos packing to minimize the heat loss by radiation. The temperature measured using a thermocouple was controlled within ±2 °C using a sunvic regulator. The reaction temperature was measured using a previously calibrated thermocouple. The catalyst was packed inside the reactor between beds of pyrex glass wool (GW) as shown in Figure 2.1. The reaction products were passed through a water-cooled double surface condenser (DSC) attached to the end of the reactor.

The liquid products were collected for the first 15 minutes of each run, (which normally covers one hour) was discarded and only the products collected after this interval was analyzed and gaseous products were collected with a gas tight syringe through a septum. After each run, the catalyst was regenerated by burning away the coke deposit formed from the previous reaction by passing a stream of pure dry air at temperature of 500°C for 5 h.

The regenerated catalyst was used continuously for repeated runs to study the effects of various parameters viz, WHSV, effect of temperature and flow rates. The WHSV was calculated by using the formula

\[
\text{WHSV} = \frac{\text{Weight of the feed (g/h)}}{\text{Weight of the catalyst (g)}}
\]
Figure 2.1 Flow unit for catalytic reactions at atmospheric pressure
2.4 PRODUCT ANALYSIS

The reactants tetralin, \textit{o}-xylene and \textit{p}-xylene and their reaction products were estimated by gas chromatography. The liquid products were identified and estimated using a Shimadzu gas chromatograph fitted with a flame ionization detector (FID) using hydrogen as the carrier gas. A 2 m × 4 mm copper column packed with 20\% SE 30 supported on chromosorb W was used for the analysis of tetralin and its products and carbowax was used for the analysis of \textit{o}-xylene and \textit{p}-xylene. The output of the detector was fed into an automatic recorder after suitable amplification. The constituent products in the reaction mixture were identified by comparison with authentic samples. The identities of the products were confirmed by a GC-MS analysis (PERKIN ELMER CLAURUS-500). The percentage conversion and selectivity calculations are based on GC analysis. The selectivity to a product is expressed as the amount of the particular product divided by the conversion of reactant multiplied by 100.

\[
\text{% Product selectivity} = \frac{\text{% Product}}{\text{% Conversion of reactant}} \times 100
\]