CHAPTER 3

PHYSICO-CHEMICAL CHARACTERIZATION
3.1 INTRODUCTION

Several researchers have studied the introduction of vanadium into the zeolites and aluminophosphate molecular sieves. Reports have appeared recently on the synthesis of vanadium containing zeolites with MFI structure and their interesting catalytic properties. The location and the state of vanadium in these zeolites are, however, still ambiguous. Recently, Rigutto et al. and Fejes et al. have reported synthesis and characterization of vanadium containing silicalite with MFI structure. It was postulated that vanadium ions are located at defect sites. Earlier Komatowskii et al. had also reported synthesis of vanadium silicate with MFI structure. In a recent report, Centi et al. have identified more than three different vanadium species, which contained extractable and occluded vanadium in the pore structure. V-silicalite and V-ZSM-5 samples have also been prepared recently by chemical vapor deposition of VOCl3 on silicalite and HZSM-5. High temperature interaction of V2O5 with ZSM-5 zeolite leads to the formation of VO2+ species which replaced both strong acid protons and terminal Si-OH groups located on the surface. Fejes et al. have proposed a square pyramid ligand field symmetry in dehydrated vanadium oxide-zeolite mixture and square bipyramid coordination after adsorption of water or ammonia.

This Chapter describes the detailed characterization of vanadium silicates with MEL structure. Evidence for the incorporation of vanadium ions into the zeolite framework has been obtained from X-ray diffraction (XRD), Infra-red (IR and FT-IR), electron spin resonance (ESR), and NMR techniques. Additional support is obtained from surface area and sorption studies. The catalytic activity in various oxidation reactions (which will be discussed in the next chapter) also confirm the presence of vanadium at framework positions.

3.2 EXPERIMENTAL

3.2.1 X-RAY DIFFRACTION

The samples were analyzed by X-ray diffraction to study the crystallinity and phase purity. Rigaku (model D/MAX III VC, Japan) X-ray diffractometer, with Ni filtered Cu-Kα radiation (λ = 1.5404 Å) was used to record powder diffraction profile. The samples were scanned from 2θ, 5 to 50° at a scan rate of 2° min⁻¹. Phase purity of the samples was worked out from the X-ray diffraction pattern reported by Fyfe et al. for MEL structure. Based on the preliminary
experiments, a sample with highest crystallinity was taken as reference sample and was used to check phase purity and crystallinity. Peak areas were calculated from the collected data, using a semiquantitative software programme provided with the instrument.

Silicon was used as internal standard for calibrating the 2θ values. The unit cell parameters were calculated for calcined samples from x-ray diffraction pattern scanned at a rate of 0.25° min⁻¹.

3.2.2 INFRARED SPECTROSCOPY

The infrared spectra of the as-synthesized samples were recorded in FT-IR Perkin Elmer spectrometer in the frequency range of 450 - 1400 cm⁻¹ using the Nujol mull technique. KCN was used as the internal standard.

The spectra in the range of 4000- 1300 cm⁻¹, were recorded in a Nicolet 60 SXB FT-IR spectrometer using self supported wafers. For in-situ studies, a cell in which the temperature can be varied from liquid nitrogen temperature to 773 K was fabricated and used. This cell was connected to a volumetric adsorption apparatus (Micromeritics, USA, Model: Accusorb-2000 E).

The cell was basically a DEWAR flask with a modification as shown in Fig.3.1. The sample was pressed under pressure of 5 ton/inch² into a thin pellet (5-6 mg/cm²) and mounted in the sample holder (SH). It was then placed inside the heating compartment of the cell (HC) and aligned with the IR beam. The cell was sealed at both the ends by potassium bromide windows (KW) with the help of elastometer "O" rings. A thermocouple is placed in close vicinity of the sample to measure the temperature of the sample. The side tube at the top of the cell was connected to the vacuum system. Cold water was constantly circulated through the cooling coil provided near the KBr windows. The sample was heated to 673 K with a heating rate of 5 K min⁻¹, under vacuum. The spectra were recorded by averaging more than 100 scans with 2 cm⁻¹ resolution. Vapors of ammonia, pyridine and benzene were admitted to the sample through the adsorption manifold of the system.

3.2.3 ELECTRON SPIN RESONANCE SPECTROSCOPY

Electron spin resonance spectra were recorded using Bruker ER-200 D spectrometer at 9.7 GHz (X-band) with a rectangular cavity ST₄ₓ₄. Modulation at 100 KHz with intensity 1.25
Fig. 3.1  FT-IR transmittance cell.
GPP and time constant $10^3$ m sec. was used. The h.f. power was chosen small enough to prevent any signal saturation. The spectra were recorded at 300 K. A constant weight of 0.1 g of the sample was taken to record the spectra.

3.2.4 $^{51}$V MAS-NMR SPECTROSCOPY

The wide-line solid state $^{51}$V MAS NMR measurements of vanadium silicate samples were recorded on a Bruker MSL-400 FT-NMR spectrometer at 105 MHz. The spectral width was 2.5 MHz and 200 m.sec repetition time was used. The spectra were from accumulation of 10,000 to 20,000 transients. Liquid VOCl$_3$ was chosen as reference to measure the chemical shift.

3.2.5 THERMAL ANALYSIS

Simultaneous TG-DTA-DTG analyses of as-synthesized and dried vanadium silicate samples were carried out in a computer controlled thermal analyzer instrument (Setaram, France TG-DTA92). A linear rate of heating of 10$^\circ$ min$^{-1}$ in the range from room temperature to 900 $^\circ$C in air flow at a rate of 30 ml min$^{-1}$ was used to find out the temperature of decomposition of template and hence the calcination temperature required for the samples. A sample volume of about 30 mg was taken with an inert $\alpha$-alumina as a reference. Detailed analysis of weight loss due to decomposition of template and accompanying heats of decomposition have been calculated from stored data of each TG-DT analysis using software programme available with the instrument.

3.2.6 UV-VIS SPECTROSCOPY

The UV-VIS diffuse reflectance spectra of the sample were recorded in a Pye Unichem SP-8-100 UV-Visible spectrometer.

3.2.7 ION-EXCHANGE STUDIES

The calcined samples were treated with 0.05 N NaCl for 3 h at 323 K to exchange protons with Na. The Na form was exchanged with 0.05 N KCl for 3 h at 323 K. The solid was filtered, washed thoroughly with deionized water and dried at 373 K for 10 h. The resultant material was analyzed for K$^+$ and vanadium ions.
3.2.8 ADSORPTION STUDIES

The sorption measurements for water, cyclohexane and n-hexane were carried out gravimetrically in a recording electromicrobalance (Model: Cahn-2000 G). The calcined sample of about 60 mg was pressed into a pellet and weighed into an aluminium bucket which was attached to the balance. The system was evacuated down to pressure of $10^{-6}$ torr at 673 K. After two hours, the temperature was lowered to the desired value. The sorbate was admitted into the sample at a constant pressure and temperature and the weight gain was recorded as a function of time. After adsorption was over, the catalyst was heated to 673 K under vacuum in the order of $10^{-4}$ torr and used for the next measurement.

3.2.9 SURFACE AREA MEASUREMENTS

Omnisorb 100 CX (supplied by COULTER Corporation, USA) unit was used for the measurement of nitrogen adsorption to determine apparent surface area. The samples were activated at 673 K for 2 h in high vacuum ($10^{-5}$ mm). After the treatment, the anhydrous weight of the sample was taken. The samples were then cooled to 94 K using liquid nitrogen. After cooling, the sample was allowed to adsorb nitrogen gas. From the adsorption isotherm the micropore area (by BET method) and mesopore area (by t-method) were calculated.

3.2.10 STEAMING EXPERIMENTS

The zeolite samples were treated in a muffle furnace to the desired temperature at a heating rate of 2.5 K min$^{-1}$. Then the samples were cooled to room temperature and kept in a desiccator over saturated ammonium chloride solution. The hydrothermal treatment was carried out in a tubular furnace with steam (100 %) at atmospheric pressure.

3.3 RESULTS AND DISCUSSION

3.3.1 X-RAY DIFFRACTION

The X-ray diffraction patterns of vanadium silicates (VS-2) sample were similar to that of silicalite-$2^{27,28}$ (Fig.3.2). The structure belonged to tetragonal space group $I4_{1}m2$ [119]. The crystalline VS-2 was found to be free from any MFI type impurity. In the XRD pattern of VS-2, the lines at $2\theta = 9.05^\circ$ and $24.05^\circ$ (both these lines are characteristic of MFI structure) are completely absent. Further, a peak at $2\theta = 45^\circ$ is present as a singlet.
Fig. 3.2. X-ray powder patterns of Silicalilte-2 (A) and VS-2 (B) calcined at 823 K.
The unit cell parameters increased uniformly and regularly with the vanadium content in the sample (Table 3.1 and Fig.3.3 A-C curve 1) suggesting the incorporation of vanadium in the framework of the MEL structure. On steaming the samples at 873 K for 2 h, all the vanadium silicates exhibited a reduction in the unit cell parameters to values typical of silicalite-2 (Fig.3.3 A-C curve 2), evidently due to the removal of vanadium from the framework to non-framework positions. Silicalite-2 itself did not show any decrease in the unit cell parameters after similar steam treatment. The results of steaming experiments thus suggest that in the VS-2 samples the vanadium ions are in the framework positions.

3.3.2 INFRARED SPECTROSCOPY

Additional support for the location of vanadium is suggested by the observation of an absorption band at around 965 cm$^{-1}$ in the IR spectra of VS-2 samples$^{29,30}$ (Fig.3.4). Bands in this region are characteristic of metal oxygen stretching vibrations. Titanium silicates (both TS-1 and TS-2) containing titanium in the lattice positions and vanadium silicate with MFI structure also exhibit this band around 960 cm$^{-1}$ due to Si-O-Ti linkages$^{31,32}$. This band is absent in the IR spectra of pure silicalite-2 as well as silicalite-2 impregnated with oxides of vanadium (or titanium$^{33,35}$). The intensity of this IR band increased linearly with vanadium content in VS-2. The ratio of 965 to 550 cm$^{-1}$ band also increases with unit cell parameters (Fig.3.3 D). The band at 550 cm$^{-1}$ is characteristic of the MEL framework structure. IR spectroscopic results, thus, lend additional support to the presence of vanadium in framework positions.

Fig.3.5 illustrates the IR spectra of the calcined samples in the hydroxyl stretching region (4000 - 2800 cm$^{-1}$) after outgassing in vacuum at 673 K. A sharp band at 3728 cm$^{-1}$ and a broad band at 3532 cm$^{-1}$ can be seen. The former is due to terminal silanol groups and the latter is assigned to H- bonded hydroxyl groups$^{36}$. The sharp peak due to isolated silanols, probably located on the external surface, is present in pure silicalite-2 also (Fig.3.5 curve d). The broad band at 3532 cm$^{-1}$ is found in all vanadium silicate samples, their intensity increasing with the vanadium content. Centi et al.$^{24}$ have in addition reported a band at 3682 cm$^{-1}$, attributed to less thermally stable -OH groups. This band is also present but as a shoulder in our samples (Fig.3.5). The band ascribable to V-OH vibration, however, is not clearly distinguished due probably to the broad nature of the 3532 cm$^{-1}$ band and the low vanadium content in the samples. It was earlier suggested that the vanadium ions are probably at surface defect sites where the Si-OH
Table 3.1

Physico-chemical properties of vanadium silicates

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/V sample&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Si/V sample&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Na/V&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Surface area (m²/g)</th>
<th>Unit cell volume&lt;sup&gt;d&lt;/sup&gt;</th>
<th>ESR signal intensity&lt;sup&gt;e&lt;/sup&gt;</th>
<th>Sorption capacity, (wt. %)</th>
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<td></td>
<td></td>
<td></td>
<td>n-hexane</td>
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<td>VS-2</td>
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<td>0.61</td>
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<td>5367.5</td>
<td>24</td>
<td>8.0</td>
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<tr>
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<td>554</td>
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<tr>
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<td></td>
<td>548</td>
<td>5354.4</td>
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<td>8.0</td>
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<sup>a</sup> as-synthesized sample

<sup>b</sup> after treating the calcined sample with 0.5 M ammonium acetate solution at room temperature

<sup>c</sup> after treating the calcined sample with 0.05 M NaCl solution at room temperature

<sup>d</sup> Unit cell volume of the calcined samples (in Å<sup>3</sup>) calculated from XRD parameters.

<sup>e</sup> ESR signal intensity (arbitrary units) due to V<sup>4+</sup> ions in the as-synthesized samples.
Fig. 3.3. The unit cell parameters $a = b$ (A), $c$ (B) and volume, $V$ (C) and ratio of intensities of 965/550 cm$^{-1}$ IR bands vs mole fraction of vanadium ($x$) (D) in various VS-2 samples.
Curve 1, calcined samples in air at 753 K and curve 2, after steaming the calcined samples at 873 K for 1 hr in 100% steam.
Fig. 3.4. Framework IR spectra of VS-2 samples (calcined 753 K). Curves a to e represent samples with Si/V 41, 79, 122, 161 and 302, respectively and silicalite-2 (curve f).
concentration is likely to be high. That the formation of such sites could be enhanced by the presence of vanadium during the hydrothermal synthesis is indicated by the linear increase in the total integrated intensity of the absorption in the region 3850 to 3150 cm$^{-1}$ with the vanadium content in the three samples, (inset in Fig.3.5). Irrespective of the differences in the preparation of vanadium silicates, this correlation supports the model proposed for V-MEL$^{29}$ and V-MFI$^{22,24}$ molecular sieves for the possible environment of vanadium in the pentasils.

In order to study the surface acidity of the above samples, adsorption of ammonia was performed on vanadium silicate (Si/V = 79). The spectra on desorption of ammonia from the calcined sample at various temperatures are shown in Fig.3.6. Two bands at 1680 cm$^{-1}$ and 1450 cm$^{-1}$ due to ammonium ions ($\delta_\alpha$ and $\delta_\beta$ of NH$_4^+$, respectively) indicate the presence of Brønsted acid sites$^{37-39}$. The intensity of these bands decreased drastically on evacuation even at 373 K indicating the presence of only weak Brønsted acid sites. At 373 K when most of the bands due to Brønsted acidic sites have disappeared, a distinct band at 1620 cm$^{-1}$ is seen clearly. This band is due to ammonia coordinatively bonded to Lewis acid sites$^{37}$. Brønsted acid sites, were not observed in pure silicalite. These observations are in broad agreement with the recent report of Centi et al.$^{24}$ on vanadium silicate (Si/V = 262) with MFI structure. However, the presence of a distinct band at 1620 cm$^{-1}$ after evacuation at 373 K had not been observed earlier.

The spectra of the adsorbed pyridine after evacuation at 323 K for the three vanadium silicates and pure silicalite-2 are presented in Fig.3.7 (curves a to d, respectively). Fig.3.8 illustrates the spectra of adsorbed pyridine on vanadium silicate (Si/V = 79) after evacuation at 323, 373 and 423 K (curves a, b and c), respectively. A weak band at 1581 cm$^{-1}$ observed in the spectra supports the presence of H-bonded pyridine$^{37,40}$. In addition, a weak band at 1547 cm$^{-1}$ due to Brønsted acid sites (due to the formation of pyridinium ions) is seen in the vanadium silicate samples. This 1547 cm$^{-1}$ band is absent in pure silicalite-2 and . The intensity of this band increases with the vanadium content. The pyridinium ions on vanadium silicates are unstable on evacuation at 423 K (Fig.3.8). Hence, only weak Brønsted acid sites are present in the vanadium silicates. They are probably related to V-OH species. This is in agreement with the sodium ion-exchange behavior of the samples reported earlier (Table 3.1)$^{22,24,29}$.

Centi et al.$^{24}$ using adsorption probe molecules such as ammonia, pyridine, dureted acetonitrile and tert-butylcyanide reported the presence of stronger Brønsted acid sites in the
Fig. 3.5. FT-IR spectra of vanadium silicate-2 and silicalite-2 samples. Curves a to c refer to VS-2 samples with Si/V mole ratios of 79, 122 and 161, respectively and curve d for silicalite-2. Inset: correlation between integrated intensity of IR absorbance in the range 3850-3150 cm$^{-1}$ and mole fraction of vanadium in various VS-2 samples.
Fig. 3.6. FT-IR spectra of VS-2 (Si/V = 79) sample after adsorption of ammonia at 303 K and evacuation at 303, 323 and 373 K (curves 'a' to 'c' respectively).
Fig. 3.7. FT-IR spectra after adsorption of pyridine at 303 K and evacuation at 323 K. Curves a to c refer to VS-2 samples with Si/V = 79, 122 and 161, respectively and curve d for silicalite-2.
Fig. 3.8. FT-IR spectra of VS-2 (Si/V = 79) sample after adsorption of pyridine at 303 K and evacuation at 323, 373 and 423 K (curves a' to c' respectively).
vanadium silicate-1 (V-MFI) compared to pure silicalite-1. They have also reported that very weak Lewis acids are present on the external surface of both VS-1 and pure silicalite, but additional stronger Lewis site are present inside the zeolite channels in VS-1. Our results on vanadium silicate with MEL structure are in agreement with those proposed for vanadium silicate for MFI structure.

3.3.3 ELECTRON SPIN RESONANCE SPECTROSCOPY

The ESR spectra of both the as-synthesized and the calcined samples have been recorded at room temperature. In the as-synthesized form, the spectra (Fig.3.9) are characteristic of atomically dispersed and immobile V^{4+} ions. The anisotropic 8-line hyperfine splitting caused by the ^{51}V nucleus is very well resolved in all the cases, without the presence of any superimposed broad singlet. The g-values and hyperfine coupling constants (g_|| = 1.932; g_\perp = 1.981; A_\perp = 185 G and A_\parallel = 72 G), are notably different from those observed for VO_2^+ exchanged into ZSM-5. They are assigned to V^{4+} in framework positions. The latter are typical of vanadyl complexes.

Similarly, the integrated intensities of ESR signals of samples of different Si/V ratios (after completion of the crystallization) were calculated. A linear increase in the ESR signal intensities with increasing vanadium content in the samples and a corresponding parallel increase in the unit cell volume (calculated from the XRD data) of the synthesized samples, as presented in Fig.3.10 A, strongly suggest that V^{4+} ions are incorporated at framework positions.

Identical spectra were obtained at 298 K and 77 K indicating that V^{4+} ions are not in tetrahedral symmetry positions (Fig.3.9 curve a). On calcination of the samples in air at 753 K, the samples did not exhibit any ESR spectra either at 298 or at 77 K (Fig.3.9 curve b). The V^{4+} ions are probably oxidized to the V^{5+} (d^0) state on calcination. The complete oxidation of V^{4+} to V^{5+} indicates the absence of any polymeric vanadium clusters. On reducing the calcined samples at 673 K in H_2, the typical spectrum of V^{4+} reappeared (Fig.3.9 curve c) indicating the reversibility of the V^{4+} <-> V^{5+} transition. This is further confirmed by the observation of V^{4+} ESR signals for the sample after catalytic reaction with hydrocarbons (Fig.3.9 curve d). Table 3.2 compares the 'g' values and hyperfine coupling constants ('A') observed in VS-2 with those observed in other but similar matrices. In the closely related vanadium silicalite-1 (VS-1) system, Rigutto and van Bekkum concluded that vanadium is five coordinate (square pyramidal), probably at defect sites. The different ESR signal response with the magnetic field for samples
Fig. 3.9. ESR spectra of as-synthesized vanadium silicalite-2 (a), calcined (b), calcined and reduced (c) and after use in catalytic reaction (d).
with $\text{VO}^{2+}$ in ion-exchanged positions and $\text{V}^{4+}$ in the framework positions of ZSM-5 has recently been discussed by Fejes et al. In their study, notable differences were observed in the parallel component of the 'g' tensor and the elements on the main diagonals of the hyperfine coupling tensors of $\text{VO}^{2+}(\text{ex})$-ZSM-5 (vanadium at exchangeable cation positions) and $\text{V}^{4+}(\text{f})$-ZSM-5 (vanadium at framework positions) zeolites, due to a displacement of the $\text{V}^{4+}(\text{f})$-ZSM-5 spectrum to higher fields as shown in Fig.3.10 B. The shift of the first parallel lines was 51.9 gauss which diminished to 15.5 gauss for the 8th line, due to the greater width of $\text{VO}^{2+}(\text{ex})$-ZSM-5 spectrum. The observed 'g' values in our samples are consistent with the argument that the $\text{V}^{4+}$ ions are in the framework positions in addition to being well dispersed and immobile. In the case of VAPO-5 system, Montes et al. proposed that vanadium in as-synthesized VAPO-5 is $\text{V}^{4+}$ in a vanadyl like environment and that upon calcination in $\text{O}_2$ at 773 K most of the vanadyl species were converted to $\text{V}^{5+}$ in framework positions. This transition was found to be reversible on reduction.

The calcined samples at higher temperatures are white in color. However, in contact with water vapor they turn yellow in color. At higher temperatures, the net positive charge of the framework caused by the presence of $\text{V}^{5+}$ ions can be compensated by $\text{O}^{2-}$ ions only (Fejes et al. reported ESR signal due to $\text{O}^{2-}$ ion radical with $g = 2.0027$ for incompletely oxidized samples, in contact with oxygen, confirming the interaction of framework elements with gaseous oxygen). In contact with water vapor they undergo hydration causing the change in color from white to yellow. This indicates that the yellow color is caused by the hydration and not by the oxidation state of vanadium ions.

$$\{\text{V}^{4+}\text{O}_2\} + \text{O}_2 \rightarrow \{\text{V}^{5+}\text{O}_2\}^* \text{O}_2^-.$$

$$[2\{\text{V}^{4+}\text{O}_2\}]\text{O}^2^- + \text{H}_2\text{O} \rightarrow 2\{\text{V}^{4+}\text{O}_2\}^* \text{.OH}^-.$$

The $\text{H}^+$ ion of these $\text{V}$-OH groups can be exchanged with $\text{Na}^+$ ions. Based on the adsorption studies of ammonia and pyridine described earlier, they are weakly acidic in nature.

### 3.3.4 $^{51}\text{V}$ MAS-NMR SPECTROSCOPY

The $^{51}\text{V}$ NMR spectrum of a vanadium silicate sample (Si/V = 79) is shown in Fig.3.11 a. The spectrum is quite complex due to simultaneous line-broadening effects arising from second order quadrupolar and chemical shift anisotropy interactions. The spectrum shows a main signal at -573 ppm (relative to VOCl$_2$). The observed line width at half-height (approximately 50 ppm) is much narrower than that reported (around 250 ppm) for other supported
Fig. 3.10 A. Correlation between vanadium content and integrated ESR signal intensities (a) and the corresponding unit cell volumes (b).

Fig. 3.10 B. Term scheme for $\text{VO}_2(\text{ex})$ and $\text{V}^{4+}(\text{f})$. (Ref. 23)
Table 3.2

Principal Values of $g$ and $A$ for $V^{4+}$ in some host matrices.

| S.No | Sample               | Temp. (K) | $g_{||}$ | $g_{\perp}$ | $A_{||}$ | $A_{\perp}$ | ref. |
|------|----------------------|-----------|----------|-------------|----------|-------------|------|
| 1.   | VS-2                 | 298       | 1.932    | 1.981       | 185      | 72          | 29, 30 |
|      | As-synthesized       | 77        | 1.935    | 1.981       | 185      | 70          |      |
|      | Reduced in Hydrogen  | 298       | 1.933    | 1.972       | 185      | 71          |      |
|      |                      | 77        | 1.929    | 1.975       | 185      | 69          |      |
| 2.   | VS-1                 | 298       | 1.935    | 1.994       | 183      | 69          | 22   |
|      | As-synthesized       | 298       | 1.935    | 1.996       | 179      | 65          |      |
|      | Reduced in benzene   | 298       | 1.949    | 1.990       | 185.8    | 72.5        | 23   |
|      |                      | 300       | 1.963    | 2.007       | 190.8    | 75.4        |      |
| 3.   | $V^{4+}$ (f) - ZSM-5  | 300       | 1.932    | 1.983       | 198      | 78          | 20   |
|      | As-synthesized       | 77        | 1.932    | 1.983       | 198      | 78          |      |
|      | $V^{4+}$ (ex)-ZSM-5   | 300       | 1.932    | 1.983       | 198      | 78          | 20   |
| 4.   | VAPO-5               | 300       | 1.932    | 1.983       | 198      | 78          | 20   |
|      | As-synthesized       | 77        | 1.932    | 1.983       | 198      | 78          | 20   |
| 5.   | V-ThGeO$_4$          | 77        | 1.831    | 1.980       | 166      | 32          | 50   |
|      | ($V^{4+}$ in $T_d$)  | 77        | 1.831    | 1.980       | 166      | 32          | 50   |
| 6.   | Ga$_2$NaMg$_2$V$_3$O$_{12}$ | 4.7     | 1.855    | 1.980       | 152      | 30          | 51   |
vanadium oxide catalysts. The $^{51}$V NMR spectrum of a vanadium silicate prepared using VCl$_3$ as the source of vanadium (instead of VOSO$_4$) is shown in Fig.3.11 b. The main signal is around -513 ppm, with a line width of about 60 ppm. Monomeric orthovanadates such as Na$_3$VO$_4$ and Mg$_3$(VO$_4$)$_2$ contain isolated tetrahedrally coordinated vanadium ions in a nearly symmetrical environment and show characteristic $^{51}$V NMR spectrum of narrow symmetrical lines centered around -550 ppm. The wide line $^{51}$V NMR spectrum of V$_2$O$_5$, which has a square pyramidal geometry around V is, on other hand, dominated by a central line around -300 ppm. The absence of an absorption band around -300 ppm shows that no V$_2$O$_5$-like phase is present in our samples.

Rigutto et al. have reported a main signal at -500 ppm for their samples (with MFI structure) prepared using vanadyl sulfate. For vanadium silicates (MFI) prepared using VCl$_3$ as the vanadium source, Centi et al., on the other hand, reported a symmetrical spectrum with a line centered at -480 ppm and ascribed the line shape to the presence of V$^{5+}$ sites in a nearly symmetrical tetrahedral environment. The considerable shift in the line position from that normally observed for orthovanadates (-520 to -590 ppm) was attributed by them to the presence of a slightly shorter V-O bond length. For a ZSM-5 (Si/Al = 30) sample treated with VCl$_3$ at 600°C for 48 h., Fejes et al. observed the $^{51}$V NMR signal at -512 ppm. In the same study, vanadium silicate prepared using VO(COO)$_2$ in the synthesis mixture exhibited two signals at -567 ppm (10%) and -575 ppm (90%), respectively. They concluded that at least two different V$^{5+}$ species both in the framework positions of MFI are present in their samples. These results clearly show the difference in the environment of the vanadium in samples synthesized using different vanadium sources and synthesis procedures. The single signal for $^{51}$V observed in our studies (Fig.3.11) indicates that vanadium ions are located in a single structural environment. The value of the chemical shift (-573 ppm) and linewidth (50 ppm) in the sample prepared using vanadyl sulfate as the raw material suggests that the vanadium ions in these samples are located in framework positions with, perhaps, distorted tetrahedral symmetry. More detailed studies using samples prepared under well defined conditions are needed for a definitive assignment of NMR signals of $^{51}$V in vanadium silicates.

3.3.5 UV-VIS SPECTROSCOPY

The optical absorption spectra of VS-2 samples are presented in Fig.3.12. The bands below 400 nm arise from O --> V charge transfer transitions. No significant absorption was
Fig. 3.11. $^{51}$V MAS-NMR spectra of VS-2 samples prepared using VOSO$_4$ (Si/V = 79, spectrum a) and VCl$_3$ (Si/V = 68, spectrum b) as source of vanadium.
observed in the 400 - 800 nm region (consistent with the white color of the material). The absence of any absorption above 550 nm shows that no $V^{4+}$ ions in tetrahedral coordination are present\textsuperscript{19,46}. The electron charge transfer energy is strongly influenced by the number of ligands on the central ion and gives information on the coordination of the vanadium in the clusters\textsuperscript{48,49}. It has been reported that when the number of the ligands on vanadium decreases from 6 to 4, the absorptions shift to shorter wave length and that tetrahedrally coordinated $V^{5+}$ shows absorption around 350 nm\textsuperscript{48,49}. The VS-2 samples show absorption at 310 nm which may indicate distorted tetrahedral environment around $V^{5+}$ ion.

3.3.6 THERMAL ANALYSIS

Simultaneous TG-DTA of samples show that the calcination of the as-synthesized samples in air occurs exothermally (Fig.2.16). The decomposition around 623-633 K, coincides with a weight loss due to template decomposition. There are shoulders around 548 and 723 K, respectively, on either side of the sharp exotherms. The template removal and weight loss occurs endothermally in the presence of argon (Fig.3.13) between 523 and 773 K. The well-resolved exotherms in the presence of air and endotherms in the presence of argon point to diffusional hindrances for the template removal. In argon, a first weight loss occurs between 373 K and 523 K, which corresponds to water removal and is accompanied by a broad DTA endotherm.

3.3.7 ION-EXCHANGE STUDIES

The cation (Na$^+$) exchange capacities of vanadium silicate-2 samples with different Si/V ratios are given in Table 3.1. Ion exchange capacities indicate the presence of exchangeable protons. These are most probably due to V-OH groups.

3.3.8 ADSORPTION STUDIES

The sorption capacities of water, n-hexane, cyclohexane (at $p/p_\text{eq} = 0.5$ and $T = 298$ K) on vanadium silicates with different Si/V ratios and silicalite-2 are given in the Table 3.1.

The values in Table 3.1 are comparable to those reported for silicalite-2 and metallosilicate analogs with MEL structure\textsuperscript{32}. The adsorption capacities for n-hexane and cyclohexane do not vary with of Si/V ratio. However the sorption capacities of water decrease with increase in Si/V ratio. Sorption capacity of water is indicative of the relative hydrophobicity/ hydrophilicity of the molecular sieves and is dependent on Si/V ratios. The equilibrium sorption capacities for the larger molecules of cyclohexane are lower than for the linear n-hexane.
Fig. 3.12. Diffuse reflectance UV-VIS spectra of VS-2 samples. Curve 'a' Si/V = 41 and Curve 'b' Si/V = 161
Fig.3.13. Simultaneous TG-DTA of as-synthesized sample with Si/V = 79 in argon
3.3.9 SURFACE AREA MEASUREMENTS

The low pressure (p/p₀ = 0.001) nitrogen adsorption isotherm at liquid nitrogen temperature is typical of microporous material. The apparent surface area of the vanadium silicates with different Si/V ratios are given in Table 3.1. In VS-2 samples, a high surface area of the order 500 - 550 m²/g and a t area (due to mesoporous impurities) of only 20 - 40 m²/g, indicate that the content of amorphous phase in the samples is very small.

3.4 CONCLUSIONS

The results bearing on the structural identity of the vanadium in the VS-2 samples may be summarized as follows:

1. There is a linear and progressive increase in unit cell parameters (from X-ray diffraction) of the MEL lattice with increase in vanadium content. On hydrothermal treatment the unit cell parameters decrease to values characteristic of vanadium-free silicalite-2, presumably due to exit of vanadium from MEL framework positions.

2. The intensity of the framework IR adsorption band around 965 cm⁻¹ (probably due to Si-O-V linkages) also increases linearly with the vanadium content and the crystalline unit cell volume of the vanadium silicate material (Fig.3.3 and 3.4).

3. There is a correlation between the vanadium content and the concentration of H-bonded hydroxyl groups (Fig.3.5). It is possible that a) the presence of V ions during the hydrothermal synthesis enhances the concentration of such hydroxyl groups and that b) the hydroxyl groups once formed bind the vanadium ions in a coordinative manner to generate VS-2. This observation supports the model for vanadium silicate proposed earlier.⁴⁻⁴⁰⁹

4. There are weak Brønsted and Lewis acid sites on VS-2 as may be seen from the spectra of adsorbed ammonia and pyridine at various temperatures (Fig.3.6 - 3.8). They originate from the modification induced by vanadium in the silicalite structure.

5. The $^{51}$V NMR spectra of VS-2 reveal that the nature of the vanadium species depends strongly on the source of vanadium used in the synthesis. Samples prepared from VOSO₄ contain only one vanadium species with a chemical shift parameter of -573 ppm and
signal linewidth of 50 ppm, similar to those observed in monomeric orthovanadates and contain isolated vanadium ions in distorted tetrahedral coordination. Clusters of vanadium as well as V₂O₅-like phases are absent.

6. ESR experiments indicate that in the as-synthesized samples, the vanadium occurs as atomically dispersed V⁴⁺ ions. On calcination in air the spectra disappear indicating the complete oxidation of V⁴⁺ to V⁵⁺ species. Reduction in H₂ restored the original spectra. The vanadium ions are, hence, accessible to gas molecules and the V⁴⁺ ↔ V⁵⁺ transition is reversible. The complete oxidation of V⁴⁺ to V⁵⁺ upon calcination indicates the absence of any clustered vanadium.

7. The observed 'g' values and hyperfine coupling constants (gₘ = 1.932; gₐ = 1.981; Aₘ = 185 G and Aₐ = 72 G) are notably different from those observed for VO²⁺ exchanged into ZSM-5 and are assigned to V⁴⁺ in framework positions. A linear increase in the integrated intensities of ESR signals and the unit cell volume of the samples with vanadium content (Fig.3.10) suggest that the atomically dispersed vanadium ions observed by ESR spectroscopy are located in the MEL lattice framework positions.

8. Adsorption experiments indicate that the pore volume is free of occluded oxides of vanadium.

9. Vanadium silicate samples have exchangeable protons, as indicated by Na⁺ ion exchange capacity and adsorption of probe molecules.

A possible structure and environment of the vanadium in VS-2 consistent with our results and those of others²²-²⁴ (for other systems like VS-1 and VAPO-5⁵⁰) may be envisaged as shown in Fig.3.14. The proton of the OH group attached to the vanadium can be exchanged for Na⁺ ions (as indeed observed).

The vanadium ions are probably coordinated at defect sites wherein the concentration of SiOH groups is likely to be high. This tentative model is consistent with several of the above observations. During the preparation of pure silicalite, only some silanol groups are present on the external surface due to defects or crystal faults. It is quite possible that specific defects are created by the presence of vanadium during hydrothermal synthesis and that these are associated
with the stabilization of vanadium in the silicalite structure. The linear increase in the integrated intensity of the IR band (3550 cm$^{-1}$) with the vanadium content of the sample supports this hypothesis.
Fig.3.14. Possible environment of vanadium in VS-2, in as-synthesized (A), calcined (B) and calcined and reduced (C) forms.
3.5 REFERENCES

47. Fejes, P. and Nagy, J.B., to be published.