CHAPTER 4

CATALYTIC OXIDATION REACTIONS
4.1 INTRODUCTION

The presence of transition metal sites in a molecular sieve has potential for generating oxidation catalysts with shape selective properties. Unlike the conventional aluminosilicate zeolites, the titanium analogs, TS-1 and TS-2 (with MFI* and MEL* structures, respectively) are effective in oxidation reactions such as hydroxylation of aromatics5-7, oxidation of alkanes8,9, ammoximation of cyclohexanone10,11, selective oxidation of alcohols5,6, epoxidation of olefins6,12 with aqueous hydrogen peroxide as oxidant and oxidative dehydrogenation of ethanol to acetaldehyde in presence of molecular oxygen13. The first commercial process using titanium silicate (TS-1) as catalyst was the hydroxylation of phenol to hydroquinone and catechol introduced by Enichem, Italy. Vanadium incorporated molecular sieves are also expected to have interesting properties in various oxidation reactions particularly, since $V^{5+} \leftrightarrow V^{4+}$ transition is possible for the lattice vanadium. They are found to catalyze various oxidation reactions in presence of aqueous hydrogen peroxide14-17.

Vanadium containing molecular sieves are reported to be active in the conversion of methanol to hydrocarbons18,19, reduction of nitrogen oxides and ammoxidation of xylenes20-23, oxidation of butadiene to furan24-26, ammoxidation of propane to acrylonitrile27, oxidative dehydrogenation of propane to propylene28 and aqueous ethanol to acetaldehyde in the presence of molecular oxygen29.

This Chapter presents the studies carried out on the catalytic properties of vanadium silicates in the following reactions:

1. Oxyfunctionalization of alkanes
2. Hydroxylation of benzene and phenol
3. Oxidation of alkyl aromatics
4. Oxidation of aniline and
5. Oxidation of sulfides

4.2 EXPERIMENTAL

4.2.1 PREPARATION OF CATALYSTS

Details of the synthesis of vanadium silicates of different Si/V ratios and their characterization were presented in Chapters II and III. The calcined vanadium silicate samples were treated with 1N ammonium acetate and recalcined at 753 K in air for 6 h before use in catalytic
reactions. For comparison, vanadium impregnated silicalite-2, silicalite-2, ZSM-11 and titanium silicates (TS-1 and TS-2), have also been investigated in the oxidation reactions. They were prepared following the procedures reported in the literature. Vanadyl sulfate was used to prepare vanadium impregnated silicalite-2 samples.

4.2.2 CATALYTIC REACTIONS

4.2.2.1 Alkane oxidation

The oxidation of alkanes was carried out in a stirred autoclave (Parr Instrument, USA) of 300 ml capacity at 373 K under autogenous pressure. Typically, 0.1 g of the catalyst, 2.53 g of 26% (by wt.) aqueous H₂O₂ (alkane/H₂O₂ = 3 moles) and 5 g of alkane were mixed in 25 ml of acetonitrile (solvent) and the reaction was carried out for 8 h. After the completion of the reaction, 25 ml of acetone was added to the products, which were then separated from the catalyst by filtration and analyzed by GC (HP 5880) using a capillary (crosslinked methylsilicone gum) column and flame ionization detector. The identity of the products was confirmed by GC mass spectroscopy (Shimadzu GCMS-QP 2000A) using standard compounds.

Oxidation of cyclohexane was carried out in a similar way except that the amount of catalyst used was 0.5 g.

4.2.2.1 Oxidation of aromatics, substituted aromatics and sulfides

The oxidation of benzene, phenol, toluene, and aniline as well as the oxidation of sulfides were carried out in batch reactors. In a typical reaction, 100 mg of catalyst was dispersed in a solution containing 1 g of reactant and 10 g of solvent. The mixture was vigorously stirred and H₂O₂ was then added. After completion of the reaction, the products were separated from the catalyst and analyzed by GC (HP 5880) using a capillary (crosslinked methylsilicone gum) column and flame ionization detector (FID).

4.3 RESULTS AND DISCUSSION

4.3.1 OXYFUNCTIONALIZATION OF ALKANES

The introduction of oxygen containing functional groups in alkanes proceeds with low selectivities over most homogeneous and heterogeneous catalysts. The catalysts used in alkene oxidation are ineffective for alkanes. Many transition metal complexes, on the other hand, are very effective in C-C bond cleavage leading to complete oxidation to respective acids.
Oxyfunctionalization with high selectivities was reported on natural and synthetic metalloporphyrin systems\textsuperscript{35,36} and on vanadium (V) oxo peroxo complexes\textsuperscript{38}. The use of zeolites and molecular sieve-based catalysts in the oxidation reactions has been reported in recent times. Titanium silicates exhibiting a pentasil structure (both TS-1 and TS-2) have been found to catalyze the oxidation of a variety of organic substrates with an aqueous solution of $H_2O_2$\textsuperscript{14} and are selective in the oxidation of alkanes\textsuperscript{8,9}.

Vanadium silicate molecular sieves can oxidize unactivated alkanes under mild conditions with aqueous hydrogen peroxide. Unlike titanium silicates, vanadium analogs are able to oxidize also the primary carbon atoms of alkanes as well to corresponding primary alcohols and aldehydes\textsuperscript{16,17}.

A. Activity of different catalysts

A comparison of the activity of VS-2, silicalite-2, Al-ZSM-11, vanadium-impregnated silicalite-2 and titanium silicate (TS-2) (all crystalline samples with MEL structure) in the oxidation of $n$-hexane is given in Table 1. The major products of the reaction are 2- and 3-hexanols and hexanones. In addition, 1-hexanol and 1-hexanal were also detected on VS-2. Small quantities of other products with more than one functional group (e.g. dihydroxyalkanes) and lactones were also detected but were not analyzed in detail. The results show that the most active catalysts are TS-2 and VS-2 ($n$-hexane conversions 15.9 and 14.6 mole % respectively), which are also the most selective for the formation of monofunctional compounds. On all the other samples (not containing V or Ti in framework positions), including the vanadium impregnated silicalite-2 sample, both the activity and the selectivity are very low (hexane conversions 2.8 - 3.6 mole %). Between TS-2 and VS-2, the oxyfunctionalization of the primary carbon atoms leading to the formation of primary alcohols and aldehydes is observed only with the vanadium silicate. It has also been observed that in addition to VS-2, other vanadium silicates such as VS-1 (with MFI structure) and V-NCL-1 (the vanadium silicate analogue of NCL-1, a novel large pore molecular sieve\textsuperscript{17}) also exhibit this unique catalytic property of oxyfunctionalizing the primary carbon atom in alkanes and in the side chain alkyl groups of aromatics. Toluene, for example, yields benzyl alcohol and benzaldehyde in addition to cresols\textsuperscript{14,16}.

An examination of the product distribution shows that the activation of the carbon atom at the second position is preferred to others and the activation follows the order, $2 > 3 > 1$ on vanadium silicates. Investigation of the oxidation kinetics revealed that the ratio of (aldehyde
Table 1

Oxidation of n-hexane on different molecular sieve catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>conversion (mole %)</th>
<th>( \text{H}_2\text{O}_2 ) selectivity</th>
<th>Product distribution (mole %)</th>
<th>Product selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1-ol</td>
<td>2-ol</td>
</tr>
<tr>
<td>VS-2</td>
<td>14.6</td>
<td>57.1</td>
<td>3.7</td>
<td>9.2</td>
</tr>
<tr>
<td>S-2</td>
<td>3.6</td>
<td>4.4</td>
<td>-</td>
<td>9.5</td>
</tr>
<tr>
<td>ZSM-11</td>
<td>2.8</td>
<td>5.2</td>
<td>-</td>
<td>3.8</td>
</tr>
<tr>
<td>V-imp-S-2</td>
<td>3.5</td>
<td>3.6</td>
<td>-</td>
<td>8.0</td>
</tr>
<tr>
<td>TS-2</td>
<td>15.9</td>
<td>58.6</td>
<td>-</td>
<td>19.1</td>
</tr>
</tbody>
</table>

* Reaction conditions: catalyst (g) = 0.1; n-hexane (g) = 5; temperature (K) = 373; n-hexane/\( \text{H}_2\text{O}_2 \) (mole ratio) = 3; solvent = acetonitrile; reaction duration = 8 h.

b VS-2: Si/V = 79; S-2: Si/Al = \ (>2000); ZSM-11: Si/Al = 82; V-imp S-2 : Si/V = 80; TS-2: Si/Ti = 77.

c \( \text{H}_2\text{O}_2 \) utilized for monofunctional product formation.

d 1-ol = 1-hexanol; 2-ol and 3-ol = 2 and 3 hexanol; 1-al = hexanaldehyde; 2-one and 3-one = 2 and 3 hexanone.

e Oxygenates with more than one functional group and lactones, methyl cyclopentane and unidentified oligomeric material

f (alcohols, aldehyde and ketones/alkane reacted)X 100, mole/mole
+ ketones) to alcohol increased with time as shown in Fig.4.1. This suggests that the aldehydes and ketones are secondary products from the corresponding primary and secondary alcohols. After 8 h, the product distribution levelled off. A higher (aldehyde + ketone) to alcohol ratio in the product distribution in the case of VS-2 compared to TS-2 (2.77 and 1.27, respectively, Table 1) indicates a greater oxidation ability of the vanadium silicates compared to titanium silicates in the secondary oxidation reaction.

B. Oxidation of n-heptane, n-octane and cyclohexane.

In addition to n-hexane, the oxidation of n-heptane, n-octane and cyclohexane has been studied on a VS-2 sample, with Si/V = 79 at 373 K (Table 2). The results are similar to those observed in the case of n-hexane. The oxyfunctionalization of the secondary carbon atom is preferred eventhough significant quantities of primary alcohols and aldehydes are formed with both C₇ and C₈ substrates. The product distribution is in the order, 2C > 3C > 4C > 1C. No regio selectivity has been observed in these cases. Oxidation of cyclohexane, on the other hand, leads to cyclohexanol and cyclohexanone with very small concentration of oxygenates with more than one functional group. The product selectivity is, therefore, considerably higher than observed in the oxidation of n-alkanes. However, the oxidative conversions and the H₂O₂ selectivities decreased in the order n-C₆ > n-C₇ > n-C₈ > cyclohexane (Table 2). This order is consistent with the observed large decrease in the diffusivity of these alkanes in zeolites with increasing chain length and molecular size.

C. Influence of solvent

The effect of solvent on the oxidation of n-hexane in the presence of VS-2 (Si/V = 79) has been studied by employing other less-polar solvents than acetonitrile. In methanol and acetone, the conversions are lower i.e. 9.1 and 5.4 mole %, respectively (Table 3). Acetonitrile is found to be the most effective solvent with the highest selectivity to monosubstituted products. The activity and H₂O₂ selectivity seems to be related to the polarity of the solvent and decreased in the order, acetonitrile > methanol > acetone. The product distribution, however, in both methanol and acetone is similar to that in acetonitrile. A change of solvent from the non-polar acetone to mixtures of acetone and acetonitrile and then finally to the more polar acetonitrile increases both the conversion and H₂O₂ selectivity (Table 3). On titanium silicate, on the other hand, the rates are not influenced by the polarity of the solvents. Indeed, in non-polar solvents
Fig. 4.1. Oxidation of n-hexane over VS-2 (Si/V = 79) at 373 K in the presence of aqueous acetone. Other conditions as given in Table 4.1. Curves a to c represent, hexane conversion, ketones + aldehydes and alcohols, respectively.
Table 2
Oxidation of alkanes over vanadium silicate molecular sieves*

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Conversion (mole %)</th>
<th>H₂O₂ selectivity</th>
<th>Product distribution (mole %)</th>
<th>Product selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1-ol</td>
<td>2-ol</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>14.6</td>
<td>57.1</td>
<td>3.7</td>
<td>9.2</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>14.3</td>
<td>50.1</td>
<td>3.1</td>
<td>6.8</td>
</tr>
<tr>
<td>n-Octane</td>
<td>12.8</td>
<td>43.4</td>
<td>4.6</td>
<td>5.9</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>8.4</td>
<td>32.7</td>
<td>33.3</td>
<td></td>
</tr>
</tbody>
</table>

* Reaction conditions: catalyst (g) = 0.1 (Si/V = 79); alkane (g) = 5; temperature (K) = 373; alkane/H₂O₂ (mole ratio) = 3; solvent = acetonitrile; reaction duration = 8 h.

b Moles of alkane converted/total no. of moles of alkane X 100
c H₂O₂ utilized for monofunctional product formation.

1-ol = 1-alcohol; 2-ol = 2-alcohol; 3-ol = 3-alcohol; 4-ol = 4-alcohol; 1-al = 1-aldehyde; 2-one = 2-ketone; 3-one = 3-ketone and 4-one = 4-ketone of corresponding alkanes.

* Mostly oxygenates with more than one functional group and lactones
f (alcohols, aldehyde and ketones/alkane reacted) X 100, mole/mole

* Cyclohexanol and b Cyclohexanone.
Table 3

Influence of solvent on n-hexane oxidation over vanadium silicate molecular sieves

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Conversion (mole %)</th>
<th>H₂O₂ selectivity</th>
<th>Product distribution (mole %)</th>
<th>Product selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>14.6</td>
<td>57.1</td>
<td>3.7 9.2 8.2 7.2 26.3 25.0 21.4</td>
<td>79.5</td>
</tr>
<tr>
<td>Methanol</td>
<td>9.1</td>
<td>30.3</td>
<td>3.0 11.9 10.9 4.9 18.8 18.8 31.7</td>
<td>68.3</td>
</tr>
<tr>
<td>Acetone</td>
<td>5.4</td>
<td>18.9</td>
<td>1.8 9.3 9.3 1.9 22.2 24.1 31.4</td>
<td>68.6</td>
</tr>
<tr>
<td>Acetonitrile +</td>
<td>8.4</td>
<td>29.1</td>
<td>3.6 8.3 8.3 3.7 21.4 22.6 32.1</td>
<td>67.9</td>
</tr>
<tr>
<td>Acetone (1:1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetonitrile +</td>
<td>11.8</td>
<td>42.6</td>
<td>4.2 8.5 9.3 3.4 22.9 22.9 28.8</td>
<td>71.2</td>
</tr>
<tr>
<td>Acetone (4:1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Reaction conditions: catalyst (g) = 0.1 (Si/V = 79); n-hexane(g) = 5; temperature (K) = 373; alkane/H₂O₂ (mole ratio) = 3; reaction duration = 8 h.

* Moles of hexane converted/total no. of moles of hexane X 100

* H₂O₂ utilized for monofunctional product formation.

* 1-ol = 1-hexanol; 2-ol and 3-ol = 2 and 3 hexanol; 1-al = hexanaldehyde; 2-one and 3-one = 2 and 3 hexanone.

* Mostly oxygenates with more than one functional group and lactones

* (alcohols, aldehyde and ketones/alkane reacted)X 100, mole/mole
such as acetone, fairly high conversions (of the order of 20 to 25 mole %) and high \( \text{H}_2\text{O}_2 \) selectivities have been reported both on TS-1 and TS-2 samples\(^6\). Moreover, a changeover to more polar solvents retarded the rate of oxidation on titanium silicates\(^6\).

D. Influence of vanadium content

The oxidation of \( \text{n-hexane} \) was carried out over three VS-2 samples with different vanadium contents (\( \text{Si}/\text{V} = 79, 122 \) and 161, respectively) under identical conditions. The results are given in Table 4. As expected, the conversion and selectivity of the samples increased with vanadium content. However, the increase in the activity is not linearly proportional to the vanadium content of the samples. The alcohol to (aldehyde + ketone) ratio is higher on the two low vanadium containing samples showing that the secondary oxidation from alcohol to aldehydes and ketones is slower on these samples. The higher vanadium in the sample with \( \text{Si}/\text{V} = 79 \) leads to a more extensive secondary oxidation. Interestingly, the oxyfunctionalization of the primary carbon atom is enhanced at higher vanadium content as seen from increasing concentration of (1-ol and 1-al) in the product with increasing vanadium content in the catalyst.

E. Influence of \( \text{n-hexane} \) to \( \text{H}_2\text{O}_2 \) ratio

While maintaining the concentration of \( \text{n-hexane} \) constant (0.058 moles), the concentration of hydrogen peroxide in the reaction mixture was varied during the oxidation of \( \text{n-hexane} \). The results are given in Table 5. Conversion, as expected, increases with increasing \( \text{H}_2\text{O}_2 \) content. The selectivity for alcohols, ketones and aldehydes decreases marginally (80.4 to 75.7 %) due to the formation of polyoxygenated products. The \( \text{H}_2\text{O}_2 \) selectivity also decreases at higher \( \text{H}_2\text{O}_2 \) concentrations due to the formation of polyoxygenated compounds and greater loss of \( \text{H}_2\text{O}_2 \) by decomposition into \( \text{H}_2\text{O} + \text{O}_2 \).

F. Influence of temperature

Conversion increases with temperature. On a given VS-2 sample (\( \text{Si}/\text{V} = 79 \)), the observed conversions of \( \text{n-hexane} \) at 353, 373 and 393 K are 9.0, 14.6 and 16.8 mole %, respectively (Table 6). Beyond 373 K, the selectivity for monooxygenated products decreases. A marginal decrease in \( \text{H}_2\text{O}_2 \) selectivity was also observed. In the product distribution, the 2/3 ratio (2-substituted/ 3- substituted products) decreased from 1.4 to 1.0 with increase in reaction temperature.
Table 4

Influence of vanadium content on oxidation of n-hexane over vanadium silicate molecular sieves*

<table>
<thead>
<tr>
<th>Si/V ratio</th>
<th>Conversion (mole %)*b</th>
<th>H2O2 selectivity*e</th>
<th>Product distribution (mole %)*d</th>
<th>Product selectivity*f</th>
</tr>
</thead>
<tbody>
<tr>
<td>79</td>
<td>14.6</td>
<td>57.1</td>
<td>3.7  9.2  8.2  7.2  26.3  25.0  21.4</td>
<td>79.5</td>
</tr>
<tr>
<td>122</td>
<td>10.0</td>
<td>36.6</td>
<td>5.0  10.0 11.1  3.0  21.1  24.1  25.7</td>
<td>74.3</td>
</tr>
<tr>
<td>161</td>
<td>7.0</td>
<td>24.6</td>
<td>4.2  8.6 10.1  2.8  20.0  24.3  30.0</td>
<td>70.0</td>
</tr>
</tbody>
</table>

* Reaction conditions: catalyst (g) = 0.1; n-hexane (g) = 5; temperature (K) = 373; solvent = acetonitrile; reaction duration = 8 h.

b Moles of hexane converted/total no. of moles of hexane X 100

c H2O2 utilized for monofunctional product formation.

d 1-ol = 1-hexanol; 2-ol and 3-ol = 2 and 3 hexanol; 1-al = hexanaldehyde; 2-one and 3-one = 2 and 3 hexanone.

e Mostly oxygenates with more than one functional group and lactones

f (alcohols, aldehyde and ketones/alkane reacted) X 100, mole/mole
Table 5

Effect of $\text{H}_2\text{O}_2$ concentration on oxidation of n-hexane over vanadium silicate molecular sieves

<table>
<thead>
<tr>
<th>Hexane/$\text{H}_2\text{O}_2$ mole ratio</th>
<th>Conversion (mole %)$^b$</th>
<th>$\text{H}_2\text{O}_2$ selectivity$^c$</th>
<th>Product distribution (mole %)$^d$</th>
<th>Product selectivity$^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1-ol</td>
<td>2-ol</td>
</tr>
<tr>
<td>1.5</td>
<td>23.0</td>
<td>42.2</td>
<td>3.4</td>
<td>7.5</td>
</tr>
<tr>
<td>3.0</td>
<td>14.6</td>
<td>57.1</td>
<td>3.7</td>
<td>9.2</td>
</tr>
<tr>
<td>4.5</td>
<td>10.2</td>
<td>61.7</td>
<td>5.9</td>
<td>9.8</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: catalyst (g) = 0.1 (Si/V = 79); n-hexane (g) = 5; solvent = acetonitrile; reaction duration = 8 h.

$^b$ Moles of hexane converted/total no. of moles of hexane X 100

$^c$ $\text{H}_2\text{O}_2$ utilized for monofunctional product formation.

$^d$ 1-ol = 1-hexanol; 2-ol and 3-ol = 2 and 3 hexanol; 1-al = hexanaldehyde; 2-one and 3-one = 2 and 3 hexanone.

$^e$ Mostly oxygenates with more than one functional group and lactones

$^f$ (alcohols, aldehyde and ketones/alkane reacted)X 100, mole/mole
Table 6
Effect of temperature on oxidation of n-hexane over vanadium silicate molecular sieves*

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Conversion (mole %)(^{b})</th>
<th>H(_2)O(_2) selectivity(^{c})</th>
<th>Product distribution (mole %)(^{d})</th>
<th>Product selectivity(^{f})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1-ol</td>
<td>2-ol</td>
</tr>
<tr>
<td>353</td>
<td>9.0</td>
<td>35.8</td>
<td>2.3</td>
<td>8.3</td>
</tr>
<tr>
<td>373</td>
<td>14.6</td>
<td>57.1</td>
<td>3.7</td>
<td>9.2</td>
</tr>
<tr>
<td>393</td>
<td>16.8</td>
<td>56.4</td>
<td>6.0</td>
<td>11.3</td>
</tr>
</tbody>
</table>

*Reaction conditions: catalyst (g) = 0.1 (Si/V = 79); n-hexane (g) = 5; alkane/H\(_2\)O\(_2\) (mole ratio) = 3; solvent = acetonitrile; reaction duration = 8 h.

\(^{b}\)Moles of hexane converted/total no. of moles of hexane X 100

\(^{c}\)H\(_2\)O\(_2\) utilized for monofunctional product formation.

\(^{d}\)1-ol = 1-hexanol; 2-ol and 3-ol = 2 and 3 hexanol; 1-al = hexanaldehyde; 2-one and 3-one = 2 and 3 hexanone.

\(^{e}\)Mostly oxygenates with more than one functional group and lactones

\(^{f}\)(alcohols, aldehyde and ketones/alkane reacted)X 100 mole/mole
G. Mechanism of Oxidation

Vanadium(V) peroxo complexes in non-protic solvents are effective oxidants of olefins (to epoxides), aromatics (to phenols) and alkanes (to alcohols and ketones)\textsuperscript{38}. This reactivity was attributed to a peroxo radical $V^{4+}-O-O^-$ species generated from peracid-like forms, which adds to double bonds or aromatic nuclei and abstracts hydrogen from alkanes to give a carbon radical intermediate\textsuperscript{38}. The peroxo complexes are derived from the reaction of the $V=O$ groups with $H_2O_2$ and may be represented as:

\begin{align*}
&\text{(a)} & &\text{(b)} & &\text{(c)} & &\text{(d)} & &\text{(e)} \\
&\text{O} & &\text{O} & &\text{O} & &\text{H} & &\text{H} \\
&\text{V} & &\text{+} & &\text{O} & &\text{O} & &\text{O} \\
&\text{O} & &\text{V} & &\text{V} & &\text{V} & &\text{V} \\
&\text{H} & &\text{O} & &\text{O} & &\text{O} & &\text{O} \\
&\text{H} & &\text{O} & &\text{O} & &\text{O} & &\text{O}
\end{align*}

In the homogeneous medium, the oxidation is usually carried out in non-protic solvents such as $CH_3CN$, the reaction rate being retarded in protic solvents like $CH_3OH$. Protic solvents probably inhibit the formation of intramolecular hydrogen-bonds. The formation of the peroxo radical was detected (an ESR signal with $g = 1.987$), when VS-2 was added to a mixture of $n$-octane and $H_2O_2$. This signal was not observed in the absence of VS-2. The intensity of the signal increased up to 30 min and then decreased. The formation of the radical and its subsequent decay by reaction with the alkane molecules may be envisaged to proceed as given below:

\begin{align*}
&\text{(c)} & &\text{(g)} & &\text{(f)} \\
&\text{O} & &\text{O} & &\text{O} \\
&\text{V} & &\text{O} & &\text{OH} \\
&\text{V} & &\text{+} & &\text{n-C}_n \\
&\text{V} & &\text{+} & &\text{n-C}_n-OH
\end{align*}
In this scheme, a hydrogen atom of the alkane is abstracted by the diradical, \( c \) to give an intermediate carbon radical. The latter combines with a hydroxyl radical coming from \( V^{+} - O - O - H \) (species \( f \)) to give an alcohol molecule and the \( V^{+} \)oxo complex (\( g \)). Peroxo species like \( c \) may be generated by the rearrangement of the intramolecularly hydrogen-bonded oxo-hydroperoxide species like \( e^{38} \). Only isolated \( V^{+} \) species are probably involved in the formation of such peroxo moieties and hence, it is not surprising that the vanadium impregnated silicalite sample (which probably contains vanadium clusters) are inactive in this reaction.

### 4.3.2 OXYFUNCTIONALIZATION OF CYCLOHEXANE

Among the alkane oxidation reactions, the conversion of cyclohexane to cyclohexanol and cyclohexanone is industrially important. At present, oxidation of cyclohexane is carried out over transitional metal catalysts\(^{39} \). In a recent report, titanium silicate-2 (TS-2) was found to be selective for this reaction\(^{40} \).

Table 7 illustrates the oxidation of cyclohexane using aqueous hydrogen peroxide on vanadium silicate, VS-2. In all the experiments, the major products were cyclohexanol and cyclohexanone. Small amounts of compounds with more than one functional group were also detected. Increasing temperatures also favour the formation of cyclohexanone. Increase in the content of \( H_{2}O_{2} \) favours the formation of higher amounts of cyclohexanol with an increase in the cyclohexane conversion. Hydrogen peroxide selectivity, however, decreases.

The activity and selectivity of \( H_{2}O_{2} \) increases with vanadium content suggesting that the vanadium ions are active centers. Conversion of cyclohexane on three catalysts with different Si/V ratios of 79, 122, 161, are 13.0, 8.6 and 7.0 mole \( \% \), respectively. Increase in the amount of catalyst also increases the cyclohexane conversion.

### 4.3.3 HYDROXYLATION OF BENZENE

The hydroxylation of benzene to phenol in the liquid phase using many metallic systems such as Fenton’s reagent (\( Fe^{2+} - H_{2}O_{2} \))\(^{41} \), the Udenfriend system (\( Fe^{2+} \)-EDTA-ascorbic acid-\( O_{2} \) or \( H_{2}O_{2} \))\(^{42} \) and Hamilton’s reagent (\( Fe^{3+} \)-catechol-\( H_{2}O_{2} \))\(^{43} \) was well studied. Kinoshita \( et \) \( al. \)\(^{44} \) reported that benzene was hydroxylated by air under ambient conditions in the presence of cuprous chloride. Orita \( et \) \( al. \)\(^{45} \) oxidized benzene with the cuprous-chloride-dioxygen catalytic
<table>
<thead>
<tr>
<th>Si/V</th>
<th>Amount of Catalyst (g)</th>
<th>Moles of $\text{H}_2\text{O}_2$</th>
<th>Conversion$^b$ (mole, %)</th>
<th>$\text{H}_2\text{O}_2$ Selectivity$^c$</th>
<th>Product distribution (mole %)</th>
<th>Product selectivity$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cyclohexanol</td>
<td>Cyclohexanone</td>
</tr>
<tr>
<td>79</td>
<td>1.0</td>
<td>0.0198</td>
<td>14.0</td>
<td>52.2</td>
<td>52.9</td>
<td>35.7</td>
</tr>
<tr>
<td>79</td>
<td>0.5</td>
<td>0.0198</td>
<td>13.0</td>
<td>48.6</td>
<td>47.7</td>
<td>38.5</td>
</tr>
<tr>
<td>79</td>
<td>0.25</td>
<td>0.0198</td>
<td>8.1</td>
<td>32.4</td>
<td>46.9</td>
<td>43.2</td>
</tr>
<tr>
<td>79</td>
<td>0.1</td>
<td>0.0198</td>
<td>7.1</td>
<td>28.5</td>
<td>43.6</td>
<td>45.0</td>
</tr>
<tr>
<td>122</td>
<td>0.5</td>
<td>0.0198</td>
<td>8.6</td>
<td>35.1</td>
<td>50.0</td>
<td>43.0</td>
</tr>
<tr>
<td>161</td>
<td>0.5</td>
<td>0.0198</td>
<td>7.0</td>
<td>27.6</td>
<td>48.6</td>
<td>41.4</td>
</tr>
<tr>
<td>79</td>
<td>0.5</td>
<td>0.0397</td>
<td>19.2</td>
<td>36.9</td>
<td>40.4</td>
<td>43.8</td>
</tr>
<tr>
<td>79</td>
<td>0.5</td>
<td>0.0132</td>
<td>8.5</td>
<td>47.8</td>
<td>60.7</td>
<td>32.1</td>
</tr>
</tbody>
</table>

* Reaction conditions: cyclohexane (g) = 5; temperature (K) = 373; solvent = acetonitrile; reaction duration = 5 h.

$^b$ Conversion = \(\frac{\text{No. of moles of cyclohexane converted}}{\text{Total no. of moles of cyclohexane}}\) X 100

$^c$ $\text{H}_2\text{O}_2$ utilized for cyclohexanol and cyclohexanone formation

$^d$ Mostly oxygenates with more than one functional group and lactones

$^e$ (cyclohexanol + cyclohexanone/cyclohexane reacted) X 100 mole/mole
system. Vapor phase hydroxylation of benzene using nitrous oxide on acidic zeolites such as ZSM-5, FeZSM-5\textsuperscript{46,47} has been reported. A direct catalytic hydroxylation of benzene efficiently using titanium silicate (TS-1) has recently been reported\textsuperscript{7}.

Table 8 compares the activities of VS-2, Silicalite-2, V impregnated silicalite-2, V\textsubscript{2}O\textsubscript{5}, and TS-2 in the hydroxylation of benzene. The active catalysts for hydroxylation of benzene are vanadium and titanium silicates. Apart from phenol, the presence of secondary oxidation products such as para-benzoquinone was also observed in the products. No hydroxylated products were observed in this reaction on pure silicalite-2, on vanadium impregnated silicalite-2, or on vanadium pentoxide and in blank experiments. This shows that as in the case of titanium silicates only those vanadium ions, which are probably in the framework positions, are able to catalyze the hydroxylation of benzene. However, the selectivity of H\textsubscript{2}O\textsubscript{2} on vanadium silicates is lower compared to titanium silicates. This may be due to the faster decomposition of H\textsubscript{2}O\textsubscript{2} on the active vanadium centers compared to titanium ions.

\[
\begin{array}{c}
\text{Table 9 illustrates the influence of various solvents on the catalytic activity of the vanadium silicates in the hydroxylation of benzene in presence of aqueous hydrogen peroxide. The activity of the vanadium silicates increases with increase in polarity of the solvent. The activity in the hydroxylation reaction decreases in the following order:}
\end{array}
\]

acetonitrile > methanol > acetone

It was reported that the hydroxylation of benzene over titanium silicate proceeds with the formation of an appreciable amount of para-benzoquinone as secondary oxidation product\textsuperscript{7}, while only phenol was the product on pure acidic zeolites (Al-ZSM-5 and Fe-ZSM-5) when reaction was carried out at room temperature in the absence of the solvent. In the case of
Table 8

Hydroxylation of benzene on different catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion(^c) (mole, %)</th>
<th>(\text{H}_2\text{O}_2) selectivity(^d)</th>
<th>Product distribution (mole, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Phenol</td>
</tr>
<tr>
<td>VS-2</td>
<td>7.2</td>
<td>18.2</td>
<td>90.3</td>
</tr>
<tr>
<td>S-2</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>V-imp-S-2</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\text{V}_2\text{O}_5)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TS-2</td>
<td>17.1</td>
<td>42.2</td>
<td>88.2</td>
</tr>
</tbody>
</table>

\(^a\) Reaction conditions: benzene/catalyst (wt. ratio) = 10; benzene/\(\text{H}_2\text{O}_2\) (mole ratio) = 3; temperature (K) = 333; reaction duration (h) = 8


\(^c\) Conversion = \(\frac{\text{No. of moles benzene converted}}{\text{Total no. of moles of aniline in reaction mixture}}\) X 100

\(^d\) \(\text{H}_2\text{O}_2\) utilized for the formation phenol and \textit{para}-benzoquinone

\(^e\) PBQ = \textit{para}-benzoquinone
Table 9

Hydroxylation of benzene on vanadium silicate molecular sieves

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Conversion</th>
<th>( \text{H}_2\text{O}_2 ) selectivity</th>
<th>Product distribution (mole, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Phenol</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>7.2</td>
<td>18.2</td>
<td>90.3</td>
</tr>
<tr>
<td>Methanol</td>
<td>4.2</td>
<td>10.1</td>
<td>81.0</td>
</tr>
<tr>
<td>Acetone</td>
<td>3.6</td>
<td>9.3</td>
<td>88.9</td>
</tr>
</tbody>
</table>

* Reaction conditions: catalyst = VS-2, Si/V = 79; benzene/catalyst (wt. ratio) = 10; benzene/\( \text{H}_2\text{O}_2 \) (mole) = 3; temperature (K) = 333; reaction duration (h) = 8.

\[ \text{Conversion} = \frac{\text{No. of moles benzene converted}}{\text{Total no. of moles of aniline in reaction mixture}} \times 100 \]

\( \text{H}_2\text{O}_2 \) utilized for the formation phenol and \textit{para}-benzoquinone

\( \text{PBQ} = \textit{para}-\text{benzoquinone} \)
vanadium silicate molecular sieves also \( p \)-benzoquinone is formed during the reaction. A similar type of oxidation mechanism is probably involved, both on vanadium and titanium silicate molecular sieves.

\[
\begin{align*}
\text{OH} & + \text{HgO} \\
\text{OH} & + \text{C}_6\text{H}_6
\end{align*}
\]

A free radical mechanism involving hydroxycyclohexadienyl radical intermediates was proposed for metal ion catalyzed hydroxylation of benzene with hydrogen peroxide\(^8\). Olah and Onishi\(^9\) have suggested an ionic mechanism in the case of super acid catalyzed hydroxylation of benzene with hydrogen peroxide. The hydroxylation of benzene and phenol over TS-1 has been postulated to occur by the formation of titanium peroxy species which facilitate the direct insertion of the oxygen into the aromatic ring\(^6\). On vanadium silicates a similar mechanism to that on titanium silicates with the formation of vanadium peroxy species may be involved in the hydroxylation of aromatics.

4.3.4 HYDROXYLATION OF PHENOL

The direct catalytic hydroxylation of phenol is an industrially important reaction, catalyzed by strong mineral acids such as HClO\(_4\). Titanium silicate molecular sieves, (TS-1 and TS-2)\(^6,7\) are effective in catalytic hydroxylation of phenol to hydroquinone and catechol. The first commercial process utilizing titanium silicate (TS-1) as a catalyst was the hydroxylation of phenol, introduced by Enichem, Italy\(^2,5,6\). Several reports have since appeared on the influence of the various parameters, such as titanium content, feed ratio, influence of solvent, \textit{etc.} on the conversion and product distribution\(^7,52-55\). This reaction is frequently used as a test reaction to show the presence or absence of titanium ions at framework positions\(^52\). The vanadium analog of ZSM-11, namely VS-2 also possesses such catalytic activity in the hydroxilation of phenol to catechol and hydroquinone\(^15\). It is postulated that as in the case of titanium silicate molecular sieves only those vanadium ions which are in the framework catalyze this reaction.
A. Influence of vanadium content

Hydroxylation of phenol did not take place in the absence of catalyst. Neither pure silicalite nor silicalite-2 impregnated with vanadium was active in the reaction. The introduction of vanadium even at a very low concentration in the silicalite lattice made the catalysts active in the hydroxylation of phenol. This is similar to the observation made on titanium silicates, where hydroxylation of phenol and benzene has frequently been used as a test reaction to characterize the presence or absence of Ti\textsuperscript{4+} ions in the framework positions\textsuperscript{52}. Table 10 reports the catalytic activity of vanadium silicates (VS-2) with different Si/V mole ratios in the hydroxylation of phenol using water as solvent. Phenol conversion marginally increased up to 27.8 mole % on increasing the catalyst concentration. Large amounts of para-benzoquinone (PBQ) are present at a catalyst concentration of 0.01 - 0.02 g in the reaction mixture. Depending upon the concentration of the catalyst in the reaction mixture, the amount of the quinones decreased with time. For a given duration of the run (8 h) the decrease was found to be rapid, when the catalyst
Table 10
Influence of vanadium content/catalyst concentration on hydroxylation of phenol over vanadium silicates

<table>
<thead>
<tr>
<th>Si/V</th>
<th>Catalyst amount (g)</th>
<th>Conversion(\text{a}) (mole, %)</th>
<th>(\text{H}_2\text{O}_2) Sel(\text{b}) (%)</th>
<th>Product distribution (mole,%)(\text{d})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HQ</td>
</tr>
<tr>
<td>79</td>
<td>0.01</td>
<td>13.4</td>
<td>19.0</td>
<td>13.6</td>
</tr>
<tr>
<td>79</td>
<td>0.02</td>
<td>18.7</td>
<td>34.5</td>
<td>21.8</td>
</tr>
<tr>
<td>79</td>
<td>0.05</td>
<td>24.2</td>
<td>53.9</td>
<td>41.0</td>
</tr>
<tr>
<td>79</td>
<td>0.010</td>
<td>25.8</td>
<td>58.7</td>
<td>42.2</td>
</tr>
<tr>
<td>79</td>
<td>0.020</td>
<td>27.8</td>
<td>62.9</td>
<td>44.3</td>
</tr>
<tr>
<td>122</td>
<td>0.010</td>
<td>25.0</td>
<td>58.0</td>
<td>41.1</td>
</tr>
<tr>
<td>161</td>
<td>0.010</td>
<td>24.1</td>
<td>55.3</td>
<td>36.7</td>
</tr>
</tbody>
</table>

\(\text{a}\) Reaction conditions: catalyst = VS-2; phenol (g) = 1; solvent = water (10 ml); temperature (K) = 353; phenol/\(\text{H}_2\text{O}_2\) (mole ratio) = 3; reaction duration (h) = 8.

\(\text{b}\) Conversion = \(\frac{\text{No. of moles of phenol converted}}{\text{Total no. of moles of phenol in the reaction mixture}}\) X 100

\(\text{c}\) \(\text{H}_2\text{O}_2\) selectivity = \(\frac{\text{No. of moles of } \text{H}_2\text{O}_2 \text{ consumed in the formation of dihydroxy benzenes}}{\text{Total no. of moles of } \text{H}_2\text{O}_2 \text{ added}}\) X 100

\(\text{d}\) Break-up (in mole %) of products excluding tars. HQ = hydroquinone; CAT = catechol; PBQ = \textit{para}-benzoquinone.
concentration was greater than 5% in the reaction mixture i.e. > 0.05 g for 1 g of phenol. Irrespective of the catalyst concentration in the reaction mixture, all the H$_2$O$_2$ initially taken is transformed and no H$_2$O$_2$ was detected after completion of the reaction.

B. Influence of Solvent

The solvent used in this reaction is known to have a profound influence on the phenol conversion, H$_2$O$_2$ selectivity and the ratio of catechol to hydroquinone over both vanadium and titanium silicates$^{5,15,57}$. The influence of various solvents on vanadium silicate-2 (VS-2) is illustrated in Table 11. Phenol conversion increases with increase in the polarity of the solvent (7.0, 13.9 and 24.3 mole % in acetone, acetonitrile and water, respectively) with a corresponding increase in the efficiency of H$_2$O$_2$ utilization. Under identical conditions, maximum phenol conversion is observed in water. Interestingly, no hydroxylation products were obtained in methanol. Even an increase in the temperature up to 353 K or a higher concentration of the catalyst in the reaction mixture did not lead to the formation of any dihydroxylated product from phenol. Similarly no oxidation products are formed from aniline when methanol is the solvent. However, vanadium silicates are active in the oxidation of alkanes, benzene and toluene even when methanol is used as solvent. This observation is in contrast to that observed with titanium analogs. In case of the latter, high H$_2$O$_2$ selectivity (of the order of 80%) has been observed in methanol solvent$^{57}$.

The influence of the solvent on the product distribution is more complex. Para-benzoquinone is obtained (4 to 5%) in all the three solvents (acetone, acetonitrile and water). Surprisingly only hydroquinone is observed when acetone was used as the solvent. The products of hydroxylation of phenol on titanium silicates, on the other hand consist almost of equimolar mixture of catechol and hydroquinone$^5$. Tuel et al.$^{57}$ have recently reported enhanced yields of catechol in this reaction over TS-1, on changing the solvent from methanol to acetone.

C. Influence of phenol to H$_2$O$_2$ ratio.

The results of the influence of concentration of hydrogen peroxide on the phenol conversion and utilization of H$_2$O$_2$ are presented in Table 12. As expected, the efficiency of utilization of H$_2$O$_2$ increases at higher phenol to H$_2$O$_2$ molar ratios. A H$_2$O$_2$ selectivity of 71.5% was observed at a ratio of phenol/H$_2$O$_2$ of 10 using water as solvent. The ratio of hydroquinone to catechol shifted marginally in favor of hydroquinone with an increase in phenol to H$_2$O$_2$ ratio.
Table 11
Influence of solvent on the hydroxylation of phenol over vanadium silicates

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Conversion(^b) (mole, %)</th>
<th>(\text{H}_2\text{O}_2) Sel.(^c) (%)</th>
<th>Product distribution (mole, %)(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>HQ</td>
</tr>
<tr>
<td>water</td>
<td>24.3</td>
<td>55.7</td>
<td>44.1</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>13.9</td>
<td>29.7</td>
<td>55.4</td>
</tr>
<tr>
<td>Acetone</td>
<td>7.0</td>
<td>12.7</td>
<td>95.1</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
</tr>
<tr>
<td>Acetone + water (1:1)</td>
<td>12.5</td>
<td>27.8</td>
<td>53.6</td>
</tr>
<tr>
<td>Acetone + water (1:3)</td>
<td>18.8</td>
<td>42.1</td>
<td>51.4</td>
</tr>
</tbody>
</table>

\(^a\) Reaction conditions: Catalyst = VS-2 (Si/V = 79); temperature (K) = 333; phenol/VS-2 (wt. ratio) = 10; phenol/\(\text{H}_2\text{O}_2\) (mole ratio) = 3; reaction duration (h) = 8.

\(^b\) Conversion = \(\frac{\text{No. of moles of phenol converted}}{\text{Total no. of moles of phenol in the reaction mixture}}\) \times 100

\(^c\) \(\text{H}_2\text{O}_2\) selectivity = \(\frac{\text{No. of moles of \(\text{H}_2\text{O}_2\) consumed in the formation of dihydroxy benzenes}}{\text{Total no. of moles of \(\text{H}_2\text{O}_2\) added}}\) \times 100

\(^d\) Break-up (in mole %) of products excluding tars. HQ = hydroquinone; CAT = catechol; PBQ = \textit{Para}-benzoquinone.
Table 12

Influence of H$_2$O$_2$ concentration on the hydroxylation of phenol over vanadium silicates*

<table>
<thead>
<tr>
<th>Phenol/H$_2$O$_2$ (moles)</th>
<th>Conversion$^b$ (mole, %)</th>
<th>H$_2$O$_2$ Sel.$^c$ (%)</th>
<th>Product distribution (mole, %)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>HQ</td>
</tr>
<tr>
<td>3</td>
<td>25.8</td>
<td>58.7</td>
<td>42.2</td>
</tr>
<tr>
<td>5</td>
<td>17.4</td>
<td>65.7</td>
<td>45.0</td>
</tr>
<tr>
<td>10</td>
<td>9.5</td>
<td>71.5</td>
<td>49.6</td>
</tr>
</tbody>
</table>

* Reaction conditions: catalyst = VS-2 (Si/V = 79); phenol/VSS-2 (wt. ratio) = 10; temperature (K) = 353; reaction duration (h) = 8; solvent (10 ml) = water

$^b$ Conversion = No. of moles of phenol converted
Total no. of moles of phenol in the reaction mixture

$^c$ H$_2$O$_2$ selectivity = No. of moles of H$_2$O$_2$ consumed in the formation of dihydroxy benzenes
Total no. of moles of H$_2$O$_2$ added

consumption for quinones and tars excluded

$^d$ Break-up (in mole %) of products excluding tars. HQ = hydroquinone; CAT = catechol; PBQ = para-benzoquinone.
D. Comparison with titanium silicates

A comparison of the activities of VS-2 and titanium silicates, TS-1 and TS-2 in hydroxylation of phenol under similar operating conditions has been made. The phenol conversion, H$_2$O$_2$ selectivity and product distribution as a function of time on VS-2, TS-2 and TS-1 are presented in Fig.4.2. A, B and C respectively. The reactions were carried out using water as solvent at 353 K and phenol to H$_2$O$_2$ mole ratio of 3.0. 100 mg of each of three catalyst having almost similar Si/M ratios was used in the batch reaction. At the end of a 8 h run, the phenol conversions are 25.8, 26.7 and 30.1 mole % with H$_2$O$_2$ selectivities of 58.7 62.3 and 72.2 % for VS-2, TS-2, and TS-1 respectively. A fairly large difference observed in phenol conversions on VS-2 on the one hand and the titanium silicates on the other, in solvent acetone is not discernible when the reactions were carried out in protic solvent such as water. Fig.4.2 shows that the initial activity of VS-2 is much lower compared to those of TS-1 and TS-2. The rates follow the order, TS-1> TS-2> VS-2. The difference in the product distributions at the end of the run on three catalysts is seen from the catechol to hydroquinone ratios, which are 1.3, 1.1 and 0.9 for VS-2, TS-2 and TS-1, respectively.

4.3.5 OXIDATION OF ALKYL AROMATICS

The common reaction of aromatic derivatives with H$_2$O$_2$ in the liquid phase in presence of metals$^{33}$, super acid catalysts$^{49}$, or pyridinium polyhydrogen fluoride$^{58}$ catalyst is the hydroxylation of the aromatic ring. Insertion of oxygen atom in the alkyl group was achieved either by autoxidation in the presence of metal catalyst, typically in a polar solvent$^{59}$, or by application of stoichiometric oxidants (e.g. cerium sulfate$^{60}$, cerium ammonium nitrate$^{61}$) or peroxo sulfate$^{62}$. Oxidation of side chain alkyl group was also reported using H$_2$O$_2$-manganese phoryrin-imidazole system and Ru(III) complex$^{63}$.

Oxidation of toluene to benzaldehyde was well studied both in liquid phase using hydrogen peroxide and in vapor phase oxidation using air as oxidant. Oxidation of toluene to benzaldehyde was reported on (acetylacetonato) oxovanadium catalyst with H$_2$O$_2$ in CF$_3$COOH$^{64}$. Ru(III) complex$^{65}$ also catalyzed this reaction. Titanium silicates both TS-1 and TS-2 catalyze hydroxylation of toluene to cresols and are inactive in the oxidation of the alkyl substituent. Vanadium silicates are active in both the hydroxylation of the aromatic nucleus and the oxidation of the alkyl substituent.
Fig. 4.2. Comparison of hydroxylation of phenol over VS-2 (A), TS-2 (B) and TS-1 (C) catalysts. Solvent = water, temperature (K) = 353, phenol/H$_2$O$_2$ (mole ratio) = 3. (▼) : phenol conversion, (△) : H$_2$O$_2$ selectivity, (○) : para benzoquinone, (▽) : catechol, (●) : hydroquinone.
The oxidation of toluene over vanadium silicate samples is illustrated in Table 13. For comparison the activities of V-free silicalite-2, vanadium impregnated silicalite and titanium silicate (TS-2) are also included in Table 13. The products of the oxidation of toluene on vanadium silicates are mainly benzyl alcohol, benzaldehyde (formed by the secondary oxidation of benzyl alcohol), o- and p-cresol. The formation of benzaldehyde as the major product in the product distribution indicates that vanadium silicates are more effective in the oxidation of the side chain alkyl group. The formation of significant quantities of benzyl alcohol and benzaldehyde is in contrast to the observation on titanium silicates wherein the products are only o- and p-cresols. Silicalite-2 is completely inactive in the oxidation of toluene either to benzaldehyde or to cresols. It may be also mentioned that vanadium impregnated silicalite-2 showed negligible activity in the above oxidation reaction.

Table 14 illustrates the activity of the vanadium silicates with different Si/V ratios. Both the conversion and the hydrogen peroxide selectivity increased with the content of the vanadium. For the samples with Si/V ratios 79, 122 and 161, the toluene conversions are 11.7, 8.2 and 6.9, respectively and the hydrogen peroxide selectivities are 49.5, 32.4 and 23.4 respectively. With an increase in the content of the vanadium in the sample, the oxidation of the side chain methyl group is more favoured.
Table 13
Oxidation of toluene over vanadium silicate molecular sieves

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (mole, %)</th>
<th>Selectivity</th>
<th>H₂O₂</th>
<th>Product distribution, (mole, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Benzyl alcohol</td>
</tr>
<tr>
<td>VS-2</td>
<td>11.7</td>
<td>49.5</td>
<td>7.7</td>
<td>52.2</td>
</tr>
<tr>
<td>S-2</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>V-imp-S-2</td>
<td>1.2</td>
<td>0.4</td>
<td>-</td>
<td>5.2</td>
</tr>
<tr>
<td>TS-2</td>
<td>13.2</td>
<td>38.0</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* Reaction conditions: catalyst = VS-2, (Si/V = 79); toluene (g) = 1; toluene/catalyst (wt. ratio) = 10; toluene/H₂O₂ (mole ratio) = 3; temperature (K) = 353; solvent = acetonitrile; reaction duration = 12 h.


c Conversion = No. of moles of toluene converted
              Total no. of moles of Toluene in reaction mixture X 100

d H₂O₂ utilized in the formation of benzyl alcohol, benzaldehyde and cresols.
Table 14

Oxidation of toluene over vanadium silicate molecular sieves*

<table>
<thead>
<tr>
<th>Si/V</th>
<th>Conversion&lt;sup&gt;b&lt;/sup&gt;</th>
<th>H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt; Selectivity</th>
<th>Product distribution (mole, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(mole, %)</td>
<td></td>
<td>Benzyl alcohol</td>
</tr>
<tr>
<td>79</td>
<td>11.7</td>
<td>49.5</td>
<td>7.7</td>
</tr>
<tr>
<td>122</td>
<td>8.2</td>
<td>32.4</td>
<td>17.0</td>
</tr>
<tr>
<td>161</td>
<td>6.9</td>
<td>23.4</td>
<td>17.7</td>
</tr>
</tbody>
</table>

* Reaction conditions: catalyst = VS-2, (Si/V = 79); toluene (g) = 1; toluene/catalyst (wt. ratio) = 10; tolene/H<sub>2</sub>O<sub>2</sub> (mole ratio) = 3; temperature (K) = 353; solvent = acetonitrile; reaction duration = 12 h.

<sup>b</sup> Conversion = \( \frac{\text{No. of moles of toluene converted}}{\text{Total no. of moles of Toluene in reaction mixture}} \) X 100

<sup>c</sup> H<sub>2</sub>O<sub>2</sub> utilized in the formation of benzyl alcohol, benzaldehyde and cresols.
Vanadium silicate are also active in the oxidation of xylenes and trimethylbenzenes. Both ring hydroxylation and side chain oxidation occur. The relative rates of conversions are, toluene (3.6) > p-xylene (2.4) > m-xylene (1) = o-xylene (1) = 1 3 5 trimethylbenzene (1). The trend parallels the diffusivity of these molecules in the MEL molecular sieves and indicates that the vanadium sites are located inside the channel system.

The influence of solvents on the catalytic activity of the vanadium silicates in the oxidation of toluene is presented in Table 15. The highest activity is found in acetonitrile and follows the order: acetonitrile > methanol > acetone. Unlike in the case of the oxidation of phenol and aniline, vanadium silicates are active even when methanol is used as solvent. However the product selectivity is much lower compared to that in acetonitrile and acetone.

4.3.6 OXIDATION OF ANILINE

Several methods for the oxidation of aniline are reported in the literature. Azobenzene is obtained using MnO₂ as stoichiometric oxidant⁶⁶. Aqueous peracids oxidize aniline to azo and azoxy benzenes⁶⁷, while anhydric peracids oxidize aniline to nitrobenzene⁶⁸. Vanadium and molybdenum complexes⁶⁹ in the presence of tert-butyl hydroperoxide catalyze the oxidation of aniline to nitrobenzene, and titanium complexes⁷⁰ to only azoxybenzene. Tungsten oxide⁷¹ in the presence of hydrogen peroxide oxidizes aniline to nitroso and azoxybenzenes. Recently, oxidation of aniline to either azoxybenzene or to nitrobenzene using ruthenium ternary complexes in the presence of hydrogen peroxide has been reported⁷². Vanadium silicate molecular sieves in the presence of aqueous H₂O₂ catalyze the oxidation of aniline to nitrobenzene, azoxybenzene and hydroxy anilines.
Table 15
Oxidation of toluene over vanadium silicate molecular sieves

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Conversion&lt;sup&gt;b&lt;/sup&gt; (mole, %)</th>
<th>H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt; Selectivity&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Benzyl alcohol</th>
<th>Benzaldehyde</th>
<th>o-Cresol</th>
<th>p-Cresol</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>11.7</td>
<td>49.5</td>
<td>7.7</td>
<td>52.2</td>
<td>19.7</td>
<td>17.1</td>
<td>3.7</td>
</tr>
<tr>
<td>Methanol</td>
<td>7.2</td>
<td>15.0</td>
<td>8.1</td>
<td>21.4</td>
<td>11.7</td>
<td>10.8</td>
<td>48.0</td>
</tr>
<tr>
<td>Acetone</td>
<td>5.2</td>
<td>20.8</td>
<td>10.2</td>
<td>45.0</td>
<td>21.0</td>
<td>19.6</td>
<td>4.2</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: catalyst = VS-2, (Si/V = 79); toluene (g) = 1; toluene/catalyst (wt. ratio) = 10; toluene/H<sub>2</sub>O<sub>2</sub> (mole ratio) = 3; temperature (K) = 353; reaction duration = 12 h.

<sup>b</sup> Conversion = \( \frac{\text{No. of moles of toluene converted}}{\text{Total no. of moles of Toluene in reaction mixture}} \) X 100

<sup>c</sup> H<sub>2</sub>O<sub>2</sub> utilized in the formation of benzyl alcohol, benzoaldehyde and cresols.
The oxidation of aniline was studied using different solvents and VS-2 as catalyst. The oxidation product distribution strongly depends on the solvent used. As shown in the Table 16, nitrobenzene and azoxy benzene along with small amounts of azobenzene are obtained when water is used as solvent. Hydroxy anilines are obtained as major products using acetonitrile as solvent. Aniline condensed with acetone immediately when hydrogen peroxide was added to the reaction mixture (the condensation reaction also occurred in the absence of catalyst). Minor quantities of hydroxylated products on the aromatic nucleus of the condensed product are also obtained. When methanol is used as the solvent, neither oxidation of the amine group nor hydroxylation of the aromatic nucleus took place. Similarly, in the hydroxylation of phenol, no hydroxylated products are obtained when methanol is used as the solvent. However, hydroxylation of alkanes, benzene and alkyl aromatics occurred in methanol solvent.

4.3.7 OXIDATION OF SULFIDES

The oxidation of sulfides to corresponding sulfoxides and sulfones is generally carried out by using hydroperoxides, peracids, diazomethane and \( \text{SO}_2 \) and superoxide anion in stoichiometric quantities. Recently, selective oxidation of sulfides to sulfoxides and sulfones was reported on titanium silicate molecular sieves. Vanadium silicate molecular sieves are more active in the oxidation of sulfides compared to their titanium analogs.
Table 16

Oxidation of aniline on vanadium silicate molecular sieves

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Conversion&lt;sup&gt;b&lt;/sup&gt; (mole, %)</th>
<th>H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt; selectivity&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Product distribution (mole, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>PHA&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>4.3</td>
<td>9.2</td>
<td>21.4</td>
</tr>
<tr>
<td>Water</td>
<td>23.9</td>
<td>48.8</td>
<td>-</td>
</tr>
<tr>
<td>Acetone</td>
<td>18.0</td>
<td>1.4</td>
<td>0.9</td>
</tr>
<tr>
<td>Methanol</td>
<td>19.6</td>
<td>0</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: catalyst = VS-2, Si/V = 79; aniline/catalyst (wt. ratio) = 10; aniline/H<sub>2</sub>O<sub>2</sub> (mole ratio) = 3; temperature (K) = 333; reaction duration (h) = 10

<sup>b</sup> Conversion = \[
\frac{\text{No. of moles aniline converted}}{\text{Total no. of moles of aniline in reaction mixture}} \times 100
\]

<sup>c</sup> H<sub>2</sub>O<sub>2</sub> utilized for the formation hydroxy anilines, nitrobenze and azoxy benzene

<sup>d</sup> \textit{para}-hydroxy aniline and \textit{ortho}-hydroxy aniline

<sup>e</sup> Condensation product of aniline with acetone (also formed in the absence of catalyst) and their hydroxylated products.

<sup>f</sup> Condensation product of aniline with methanol.
The results of the oxidation of various sulfides, viz., dimethylsulfide, diethylsulfide, phenylmethylsulfide and phenylethylsulfide on vanadium silicate (Si/V = 79) using dilute hydrogen peroxide are summarized in Table 17. Oxidation of (CH₃)₂S was carried out at 298 K and other sulfides at 323 K. The products of the reaction are corresponding sulfoxides and sulfones. No other side products are formed in these reactions. Vanadium silicates have high activity and the oxidation of sulfides was completed within 5 to 30 min. The reactivity of the sulfides followed the order CH₃S > C₂H₅S > PhSCH₃ > PhSC₂H₅. Table 18 compares the activities of VS-2, TS-2, silicalite-2 and ZSM-11 as catalysts in the oxidation of PhSCH₃. The most active catalyst in this sulfoxidation is VS-2. The activity decreased in the order VS-2 > TS-2 > ZSM-11 > silicalite-2. After 30 min of the reaction time under similar conditions the oxidation of methyl phenyl sulfide on VS-2, TS-2, silicalite-2 and ZSM-11 are 100, 22, 15, 16 mole %, respectively. On continuing the reaction for 120 min, complete oxidation of sulfide was achieved on TS-2. However, on silicalite-2 and ZSM-11 the conversion levelled off around 50 mole % even after continuing the reaction for 10 h.
Table 17

Oxidation of sulfides over vanadium silicate molecular sieves

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Conversion(^b), (mole, %)</th>
<th>Product distribution (mole, %)</th>
<th>Sulfoxide</th>
<th>Sulfone</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl sulfide(^c)</td>
<td>100</td>
<td></td>
<td>71</td>
<td>29</td>
<td>-</td>
</tr>
<tr>
<td>Diethyl sulfide</td>
<td>100</td>
<td></td>
<td>81</td>
<td>19</td>
<td>-</td>
</tr>
<tr>
<td>Methyl phenyl sulfide</td>
<td>100</td>
<td></td>
<td>84</td>
<td>16</td>
<td>-</td>
</tr>
<tr>
<td>Ethyl phenyl sulfide</td>
<td>92</td>
<td></td>
<td>81</td>
<td>12</td>
<td>7</td>
</tr>
</tbody>
</table>

\(^a\) Reaction conditions: catalyst = VS-2, Si/V = 79; sulfide/catalyst (wt. ratio) = 10; sulfide/H\(_2\)O\(_2\) (mole ratio) = 1; temperature (K) = 333; solvent = acetonitrile; Reaction duration 5 - 30 min.

\(^b\) Conversion = \( \frac{\text{No. of moles of sulphide converted}}{\text{Total no. of moles of sulphides in the reaction mixture}} \times 100 \)

\(^c\) Temperature (K) = 298.
Table 18

Oxidation of methyl phenyl sulfide on different catalysts

<table>
<thead>
<tr>
<th>Catalyst(^b)</th>
<th>Reaction Time (min.)</th>
<th>Conversion(^c), (mole, %)</th>
<th>Product distribution, (mole, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>PhSCH(_2)O</td>
</tr>
<tr>
<td>VS-2</td>
<td>30</td>
<td>100</td>
<td>84</td>
</tr>
<tr>
<td>S-2</td>
<td>30</td>
<td>15</td>
<td>72</td>
</tr>
<tr>
<td>S-2</td>
<td>120</td>
<td>47</td>
<td>84</td>
</tr>
<tr>
<td>ZSM-11</td>
<td>30</td>
<td>16</td>
<td>84</td>
</tr>
<tr>
<td>ZSM-11</td>
<td>120</td>
<td>44</td>
<td>89</td>
</tr>
<tr>
<td>TS-2</td>
<td>30</td>
<td>22</td>
<td>74</td>
</tr>
<tr>
<td>TS-2</td>
<td>120</td>
<td>100</td>
<td>78</td>
</tr>
</tbody>
</table>

* Reaction conditions: sulfide/catalyst (wt. ratio) = 10; sulfide/H\(_2\)O\(_2\) (mole ratio) = 1; temperature (K) = 333; solvent = acetonirile

\(^b\) VS-2 : Si/V = 79; S-2 : Si/Al = > 2000; ZSM-11 : Si/Al = 82; TS-2 : Si/Ti = 77.

\(^c\) Conversion = \[\frac{\text{No. of moles of sulphide converted}}{\text{Total no. of moles of sulphides in the reaction mixture}}\] \times 100
4.4 CONCLUSIONS

1. Vanadium silicate molecular sieves are active in the oxyfunctionalization of hydrocarbons (hexane, heptane, octane and cyclohexane). Hydroxylation of aromatics (benzene, phenol, toluene, aniline) and sulfoxidation reactions.

2. Like titanium silicates (TS-1 and TS-2), vanadium silicates are active in the oxyfunctionalization of alkanes yielding alcohols, which undergo further oxidation to carbonyl compounds. However, contrary to the observation on titanium silicates, the vanadium silicates are also able to activate the primary C-H bond of the n-alkanes giving primary alcohols and corresponding aldehydes.

3. Solvents have considerable influence on the activity in the oxyfunctionalization of alkanes. Non-protic solvents enhance the rate of reactions. Amongst the non-protic solvents, more polar solvents such as CH$_3$CN are more effective.

4. The formation of a radical-type intermediate has been inferred from ESR observations. A mechanism involving a peroxo vanadium radical which abstracts a H atom from the hydrocarbon molecule to give a carbon radical which is further hydroxylated to the alcohol is proposed. Only isolated vanadium ions (which exist in VS-2 samples) are probably involved in the oxidation reaction.

5. Vanadium silicate molecular sieves are active in hydroxylation of benzene. Neither silicalite-2 nor vanadium impregnated silicalite-2 are active in this reaction. Acetonitrile is the most suitable solvent among acetone, acetonitrile, methanol.

6. Vanadium silicate molecular sieves are also efficient catalysts in the hydroxylation of phenol.

7. The influence of solvent on the product selectivity in hydroxylation of phenol is significantly different from that observed on titanium silicates. Water is the most suitable solvents in which the activity is comparable to that of titanium silicates.

8. No hydroxylated products of phenol were formed when methanol was used as the solvent, though hydroxylation of alkanes, benzene and alkyl aromatics took place in the presence of methanol. When acetone was used as the solvent hydroquinone and para-benzoquinone were the only products; catechol was not formed.
9. In oxidation of toluene, vanadium silicates are active both in ring hydroxylation (to ortho and para cresols) and side chain oxidation (to benzyl alcohol and benzaldehyde). In this respect they differ from titanium silicates which are active in ring hydroxylation of aromatic nucleus only.

10. Shape selectivity was observed in oxidation of alkyl aromatics (xylenes and trimethylbenzene) confirming that most of the vanadium ions are inside the channel system of MEL.

11. In the oxidation of aniline, vanadium silicates are active in both ring hydroxylation (to ortho and para hydroxyl anilines) and amine group oxidation (to nitrobenzene). Hydroxylation of aromatic nucleus occurred in the presence of acetonitrile and oxidation of amine group took place when water was used as solvent.

12. Vanadium silicates are active catalysts in the oxidation of sulfides to sulfoxides and sulfones. Their activity is about 8 times higher than that of the titanium analogs.
4.5 REFERENCES

17. Hari Prasad Rao, P.R., Reddy, K.R., Ramaswamy, A.V. and Ratnasamy, P., 3rd Int. Symp. on Heterogeneous Catalysis and Fine Chemicals, Poitiers, France, April (1993) (Accepted for oral presentation)