Chapter 7

STUDIES ON V₂O₅/TiO₂ CATALYSTS

Vanadium oxide based catalysts are widely used for oxidation of hydrocarbons, SO₂, etc. Vanadia supported on TiO₂ was reported to have superior properties than that supported on other supports like SiO₂, Al₂O₃, etc.¹⁻² It is highly active and selective in oxidation processes of industrial importance.¹⁻⁴

Very few methods are described in literature for the preparation of V₂O₅/TiO₂ catalysts. In this Chapter our studies on the effect of preparation method on rutilation, physical properties and toluene oxidation activity are presented.

The samples prepared by co-precipitation are labeled as CV1, CV2 and CV3, those prepared by ion-exchange as IV1, IV2 and IV3 and those prepared by wet-impregnation as WV1, WV2 and WV3. The percentage of V₂O₅ in each sample is given in Table 7.1.

7.1 XRD studies

Figs 7.1 – 7.3 show the XRD pattern of co-precipitated, ion-exchanged and wet-impregnated ones respectively. Co-precipitated one calcined at 350°C was not crystalline, whereas ion-exchanged and wet-impregnated ones calcined at 350°C exhibit well-defined sharp peaks of anatase. The co-precipitated sample showed crystalline nature only by calcination at 450°C, like NiO/TiO₂ and CeO₂/TiO₂ samples. Here also there were no peaks due to V₂O₅. Any other phases of vanadium oxide were also not seen in any of the pattern.
Interesting feature of these samples was that, the rutilation started at a very low temperature, i.e. at 450°C in the samples CV3, IV3 and WV3, irrespective of the method of preparation. No peaks of rutile were observed in the samples containing lower percentages of V$_2$O$_5$. 

Fig. 7.1. XRD pattern of V$_2$O$_5$/ TiO$_2$ samples prepared by co-precipitation method 1) CV3 calcined at 350°C / 6hrs. 2) CV1, 3) CV2, 4) CV3 calcined at 450°C / 6hrs. and 5) CV3 after catalysis. (A = anatase and R = rutile).
Hence, for convenience, the XRD pattern of the samples, where rutilation started are only given in Figs 7.4 – 7.6. As the calcination temperature was increased to 600°C, the rutilation progressed. In co-precipitated sample CV3, calcined at 650°C, there were no anatase peaks seen in the pattern, whereas in IV3 and WV3, the anatase peaks disappeared.
completely only at 800°C and 700°C respectively. So, here also, the co-precipitated one was converted completely to rutile at a lower temperature. The rutilation was started and completed at a very low temperatures in all these samples compared to bare TiO₂. Hence, it is
Fig. 7.3. XRD pattern of V$_2$O$_5$/TiO$_2$ samples prepared by wet­impregnation method - calcined at 350$^0$C / 6hrs. 1) WV1, 2) WV2, 3) WV3 & 4) WV3 after catalysis (A = anatase)

completely only at 800$^0$C and 700$^0$C respectively. So, here also, the co-precipitated one was converted completely to rutile at a lower temperature. The rutilation was started and completed at a very low temperatures in all these samples compared to bare TiO$_2$. Hence, it is
obvious that quantity of $V_2O_5$ has a marked effect on rutilation, in addition to method of preparation and calcination temperature. The rutile percentage plotted against calcination temperature is shown in Fig 7.7. It
reflects clearly that, the co-precipitated one has highest rutile percentage at any temperature and the ion-exchanged one has the lowest rutile percentage.

In the samples calcined at 600°C and above, V₂O₅ peaks and some peaks of V₂Ti₃O₉ were also present along with peaks due to rutile.
at the onset of rutilation, no peaks of \( V_2O_5 \) or \( V_2Ti_3O_9 \) were seen, but, as the intensity of rutile peaks increased on increasing calcination temperature, \( V_2O_5 \) and \( V_2Ti_3O_9 \) peaks also appeared in the pattern. On further calcination these peaks were seen to be more intense, revealing the growth of \( V_2O_5 \) crystals during high temperature calcination. The appearance of \( V_2Ti_3O_9 \) peaks (instead of \( V_2TiO_7 \), by reacting \( V_2O_5 \) with
\( \text{TiO}_2 \) mirrored the fact that some non-stoichiometric titania \( (\text{TiO}_{1.33}) \) having some oxygen vacancies were formed on \( \text{TiO}_2 \) surface, when calcined in presence of \( \text{V}_2\text{O}_5 \). This might be the reason, for the easy rutilation of these samples. This is in accordance with the literature reports\(^5\)-\(^7\) which states that, the formation of oxygen vacancies are the basic reason for rutilation (as it enhances the rupture of \( \text{Ti} \) — \( \text{O} \) bonds of anatase).

![Graph](image)

**Fig. 7.7.** Variation in rutile % with calcination temperature of \( \text{V}_2\text{O}_5/\text{TiO}_2 \) catalysts prepared by different methods.
The crystallite size of anatase was calculated after calcinations of these samples at temperatures when drastic changes in physical properties took place. The results are given in Table 7.1. No change was observed in crystallite size, on increasing the percentage of V$_2$O$_5$ in any of the samples, except in CV3, where the anatase crystallites were seen to grow to a size of 17.1nm (in this sample 30.9 % of anatase was irreversibly converted to rutile). So, it is noteworthy that, like NiO/TiO$_2$, Fe$_2$O$_3$/TiO$_2$ and CeO$_2$/TiO$_2$, as the rutile percentage increased, the anatase crystallite size also increased, but to different extent, depending on the method of preparation.

Table 7.1. Variation in crystallite size of anatase with calcination temperature of V$_2$O$_5$/TiO$_2$ samples

<table>
<thead>
<tr>
<th>Method of prepn</th>
<th>Sample label</th>
<th>V$_2$O$_5$ (%)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>350°C</td>
</tr>
<tr>
<td>Co-pptn</td>
<td>CV1</td>
<td>4.96</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CV2</td>
<td>9.95 Amorphous</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CV3</td>
<td>14.97</td>
<td></td>
</tr>
<tr>
<td>I.E</td>
<td>IV1</td>
<td>4.95</td>
<td>11.82</td>
</tr>
<tr>
<td></td>
<td>IV2</td>
<td>9.96</td>
<td>11.82</td>
</tr>
<tr>
<td></td>
<td>IV3</td>
<td>14.94</td>
<td>11.82</td>
</tr>
<tr>
<td>W.I</td>
<td>WV1</td>
<td>4.92</td>
<td>10.98</td>
</tr>
<tr>
<td></td>
<td>WV2</td>
<td>9.91</td>
<td>10.98</td>
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<tr>
<td></td>
<td>WV3</td>
<td>14.98</td>
<td>10.98</td>
</tr>
</tbody>
</table>
7.2 Surface area studies

Figs 7.8 – 7.10 show the surface area values plotted against calcination temperature. The surface area decreased with increasing V$_2$O$_5$ percentage and this decrease was more noticeable in co-precipitated and wet-impregnated ones. For CV1, CV2 and CV3, the values are 110.2 m$^2$/g, 102.7 m$^2$/g and 56.4 m$^2$/g respectively. In the case of ion-exchanged samples, IV1, IV2 and IV3, the values are 84.1 m$^2$/g, 83.5 m$^2$/g

![Graph showing the effect of calcination temperature on surface area of V$_2$O$_5$/TiO$_2$ catalysts prepared by co-precipitation method.](image)

Fig. 7.8. Effect of calcination temperature on surface area of V$_2$O$_5$/TiO$_2$ catalysts prepared by co-precipitation method
and 82.1 m²/g respectively. Whereas in wet-impregnated samples, WV1, WV2 and WV3, the surface area values are 106.8 m²/g, 84.8 m²/g and 71.2 m²/g respectively. The co-precipitated ones have the largest surface area and the ion-exchanged ones have the lowest values. On increasing further the calcination temperature to 600°C, the surface area decreased very much and it became 18.3 m²/g, 15.7 m²/g and 10.12 m²/g in CV1, CV2 and CV3; 22.7 m²/g, 19.45 m²/g and 17.8 m²/g in IV1, IV2 and IV3;

Fig. 7.9. Effect of calcination temperature on surface area of V₂O₅/TiO₂ catalysts prepared by ion-exchange method
18.4 m²/g, 16.51 m²/g and 13.7 m²/g in WV1, WV2 and WV3 respectively. These changes could be clearly seen in Figs 7.8 – 7.10.

When the TiO₂ support was fully transformed to rutile (at 650°C in co-precipitated ones, at 800°C in ion-exchanged ones and at 700°C in wet-impregnated ones), the surface area was reduced markedly in all the samples. Surface area became 9.81 m²/g, 6.8 m²/g and 4.23 m²/g in CV1, CV2 and CV3 respectively; 2.32 m²/g, 2.21 m²/g and 2.17 m²/g in IV1, IV2 and IV3 and 4.83 m²/g, 4.35 m²/g and 4.1 m²/g in WV1, WV2 and WV3 respectively.

Fig. 7.10. Effect of calcination temperature on surface area of V₂O₅/TiO₂ catalysts prepared by wet-impregnation method
In all these samples, even though, no direct relation between crystallite size and surface area could be made, a marked decrease in surface area could be seen along with a significant increase in crystallite size. It was also noted that, a very small change in crystallite size does not necessarily involve a change in surface area. The surface area of sample CV3 was very low compared to its siblings IV3 and WV3, because of the presence of 30.9% rutile in this sample. Figs 7.8 - 7.10 clearly show the decrease in surface area at the onset of rutilation and severe decrease when rutilation was complete, due to sintering. This is consistent with XRD data. On comparing with the surface area of pure TiO$_2$, shown in Fig 3.1, the surface area decreased on loading V$_2$O$_5$. It is very clear from all these observations that the surface area decreased noticeably during rutilation, which in turn is dependent on preparation method and calcination temperature. The decrease was greater compared to pure TiO$_2$. So, V$_2$O$_5$ is enhancing the reduction in surface area during calcination.

7.3 **SEM studies.**

Figs 7.11A and 7.11B are the scanning electron micrographs of the samples IV3 and WV3 respectively. The micrographs of sample CV3 is shown in Fig. 7.12A. The individual particles were with a size ranging between 0.1 to 0.75\(\mu\)m in CV3 and IV3 samples and in WV3 the particle size was between 0.5 to 2\(\mu\)m. All the particles were more or less spherical in shape in all the samples with much aggregation. In CV3, even though, there is 30.9% rutile present, no appreciable change in particle size could be seen. In any of the micrographs, V$_2$O$_5$ particles
Fig. 7.11 Scanning electron micrographs of $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts

A) IV3 and B) WV3 (calcined at $350^\circ\text{C}$)
Fig. 7.12 Scanning electron micrographs of V$_2$O$_5$/TiO$_2$ catalysts

A) CV3 (calcined at 450°C and B) CV3 (calcined at 650°C)
could not be seen. This is in line with XRD data, where no peaks of V₂O₅ were seen due to the very fine nature of V₂O₅.

In order to understand the changes in particle shape and size upon rutilation, the SEM analysis of CV3 calcined at 650°C (when all the anatase was completely converted to rutile), was carried out. Particles with sharp octahedral and needle like structures were present in the micrograph shown in Fig7.12B. The octahedral particles could be rutile with approximate size 8μm. The needle like structure could be V₂Ti₃O₉, formed by the fusion between individual particles.

7.4 Dispersion studies

The dispersion was carried out at 370°C after reducing the catalyst samples at 370°C, because at this temperature V⁵⁺ species present on the surface of TiO₂ gets reduced to V³⁺ species and bulk phase reduction and the reduction of TiO₂ will not take place at this temperature.⁸⁻¹⁰ During oxygen chemisorption, the V³⁺ species chemisorbs one molecule of oxygen to regain V⁵⁺ state.⁸⁻¹⁰ The results are shown in Table 7.2. Comparatively better dispersion was obtained for co-precipitated samples. The dispersion of V₂O₅ was found to be increased on increasing V₂O₅ percentage, due to the increased chemisorption of oxygen (vide Table 7.2). The surface average crystallite size of vanadium atom calculated from chemisorption data is also included in Table 7.2. In all samples the vanadium atoms have the size less than 7nm. Maximum size of 6.97nm was seen in WV1 and minimum size of 4.56nm was observed in CV3. It decreased on increasing V₂O₅ percentage. It is very interesting to note that as the anatase crystallite size increased, the surface
average crystallite size of vanadium atom was decreased. Because of the very smaller size of vanadium atom in all these samples, peaks due to $V_2O_5$ were not observed in XRD pattern.

Table 7.2. Results of dispersion studies

<table>
<thead>
<tr>
<th>Method of prepn</th>
<th>Sample label</th>
<th>Oxygen chemisorbed ($\mu$mol / g)</th>
<th>Dispersion (%)</th>
<th>Surface average crystallite size of V atom (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-ppn</td>
<td>CV1</td>
<td>76.84</td>
<td>14.1</td>
<td>5.67</td>
</tr>
<tr>
<td></td>
<td>CV2</td>
<td>168.69</td>
<td>15.43</td>
<td>5.18</td>
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<td></td>
<td>CV3</td>
<td>288.51</td>
<td>17.54</td>
<td>4.56</td>
</tr>
<tr>
<td>I.E</td>
<td>IV1</td>
<td>64.18</td>
<td>11.8</td>
<td>6.78</td>
</tr>
<tr>
<td></td>
<td>IV2</td>
<td>150.04</td>
<td>13.71</td>
<td>5.83</td>
</tr>
<tr>
<td></td>
<td>IV3</td>
<td>233.1</td>
<td>14.2</td>
<td>5.63</td>
</tr>
<tr>
<td>W.I</td>
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</tr>
<tr>
<td></td>
<td>WV3</td>
<td>254.46</td>
<td>15.46</td>
<td>5.17</td>
</tr>
</tbody>
</table>

7.5 Toluene oxidation studies

The results are shown in Figs 7.13 – 7.15. Air oxidation of toluene to form benzoic acid by $V_2O_5/TiO_2$ has not yet been reported in literature. The activity studies were carried out after calcination of these samples at temperatures when drastic change occurred in physical
properties. In ion-exchanged samples, the percentage conversion increased on increasing $V_2O_5$ percentage, while in co-precipitated and wet-impregnated ones, the percentage conversion decreased. Out of all these samples, better conversion was obtained with co-precipitated ones with low $V_2O_5$ loading. With sample CV1, percentage conversion was 67.5, while with CV2 and CV3 it was 66.2% and 40.6% respectively. The reduction in activity of CV3 to 40.6%, even though the dispersion of
$V_2O_5$ was very high, would be due to the presence of 30.9% rutile in this sample. The very low surface area of this sample would also affect the activity. With ion-exchanged ones IV1, IV2 and IV3 the percentage conversion was 63.2, 64.15 and 66.2 respectively and with WV1, WV2 and WV3 the percentage conversion was 65.1, 64.0 and 62.0 respectively.

In order to investigate the changes occurring in activity along with rutilation, the activity studies of co-precipitated ones calcined

![Graph showing variation in toluene oxidation activity with calcination temperature](image)

**Fig. 7.14.** Variation in toluene oxidation activity with calcination temperature of $V_2O_5/TiO_2$ catalysts prepared by ion-exchange method
at 600°C and 650°C were carried out. Similarly the activity studies of ion-exchanged ones calcined at 450°C, 600°C and 800°C and wet-impregnated ones calcined at 450°C, 600°C and 700°C were also carried out.

A severe decrease in activity was observed with these samples on increasing the calcination temperature. In co-precipitated ones CV1, CV2 and CV3 calcined at 600°C, the percentage conversion became 19.4, 20.1 and 18 respectively. On further calcination at 650°C at

![Graph](image-url)

Fig. 7.15. Variation in toluene oxidation activity with calcination temperature of V₂O₅/TiO₂ catalysts prepared by wet-impregnation method
which the TiO$_2$ was fully transformed to rutile, the percentage conversion was reduced to 9.7, 10.1 and 10.1 respectively. With ion-exchanged ones IV1, IV2 and IV3 calcined at 450$^\circ$C (which was the onset temperature of rutilation), the activity became 54.3%, 56.5% and 47.9% respectively and the activity reduced noticeably on every rise in calcination temperature. At calcination temperature when rutilation was complete, the percentage conversion became 8.1, 8.3 and 8.3 respectively. Similarly with wet-impregnated ones WV1, WV2 and WV3 calcined at 450$^\circ$C, the percentage conversion was reduced to 58.1, 53 and 48.1 respectively and on further increasing the calcination temperature, the conversion became nearly 20% with all the samples. When these samples were calcined at 700$^\circ$C (at which the TiO$_2$ support was fully converted to rutile), the percentage conversion became 8.6, 8.9 and 9.4 respectively. All these changes could be clearly seen in Figs 7.13 – 7.15.

Dramatic change in percentage conversion could be seen when the TiO$_2$ was fully converted to rutile. The lack of enough V$_2$O$_5$ sites, lower surface area, presence of rutile phase as the support and presence of V$_2$Ti$_3$O$_9$ would be the reason for the reduced activity.

7.6 Conclusions

From all the above observations the following conclusions can be made.

- On loading V$_2$O$_5$ and during rutilation significant reduction in surface area was observed.
The onset and completion temperatures of rutilation were much lower compared to all other samples.

Quantity of $V_2O_5$ and percentage play a major role in rutilation.

$V_2Ti_3O_9$ phase formed at above $600^0C$, which indicate the presence of some non-stoichiometric titania.

Crystallite size enlargement of anatase take place during rutilation and $V_2O_5$ loading.

Better surface area, dispersion and activity were obtained with co-precipitated samples.

Order of activity for toluene oxidation with these samples is: co-precipitated > ion exchanged > wet-impregnated ones.

All of these samples were stable under the conditions adopted.

The significant decrease in percentage conversion upon rutilation would be due to lower surface area and shortage of free $V_2O_5$ particles.