Chapter 4

STUDIES ON NiO/TiO$_2$ CATALYST

Group VIII metals, especially nickel, are excellent catalysts for hydrogenation of olefins and CO to synthesize saturated hydrocarbons. SiO$_2$ and Al$_2$O$_3$ are the commonly used support materials for Ni catalyst, since they possess high surface area.$^{279}$ Extensive work has been reported recently on Ni supported on TiO$_2$ as a catalyst for CO hydrogenation with better activity compared to the other supports. But limited methods are only reported for the preparation of this catalyst. Traditional methods like, wet-impregnation and ion-exchange on crystalline TiO$_2$ were found to be employed in most of the investigations. In both the above methods, Ni atoms are introduced in to the TiO$_2$ crystal lattice by heating crystalline TiO$_2$ in presence of nickel salt solution at different temperatures, These methods would obviously reduce the surface area of TiO$_2$, enhance the phase transformation and affect adversely on the homogeneous dispersion of the active metal on it. This may cause much greater diffusion of active metal particles towards the bulk of titania during reduction$^{100}$ and thus reduce the number of surface exposed active metal atoms.

Hydrazine hydrate precipitation is a new method described in literature for the preparation of nano sized metal oxides used for electronic applications. The preparation of catalysts by this method is yet to be reported. Hydrazine hydrate can quantitatively precipitate certain
metals by complexing with them. These complexes undergo decomposition upon calcination resulting in high surface area metal oxides.

Titania, in the amorphous state possesses high surface area and hence can incorporate large quantities of other metal oxides. Also, while loading metal oxides on crystalline titania, there is an increased chance for rutilation. Hence, amorphous titania was used for ion-exchange and wet-impregnation methods. The ion-exchange method is based on zero point charge of titania, which is reported to be pH 5-5.6$^{57,78}$ and above which cations can be exchanged as reported. The negative charge is built up on the aqueous dispersion of hydrated TiO$_2$ due to proton transfer from hydrated TiO$_2$ to the water. On increasing the pH above zero point charge, this proton transfer would also be increased leaving behind the electrons in the partially bonded oxygen atoms.$^{280}$ NH$_4^+$ ions get attached to this negatively charged oxygen atoms and while refluxing in presence of Ni$^{2+}$ solution, the NH$_4^+$ ions get exchanged by nickel atoms. Schematic representation for ion exchange is given below:

\[
\begin{align*}
\text{Ti} - \text{OH} & \quad \xrightarrow{\text{-H}^+} \quad \text{Ti} - \text{O}^- \\
\text{Ti} - \text{O}^- & \quad \xrightarrow{+ \text{NH}_4^+} \quad \text{Ti} - \text{ONH}_4 \\
2\text{Ti} - \text{ONH}_4 & \quad \xrightarrow{+ \text{Ni}^{2+}} \quad (\text{Ti} - \text{O})_2\text{Ni}
\end{align*}
\]
The samples prepared by co-precipitation were labeled as CN1, CN2 and CN3. Likewise IN1, IN2 and IN3 for ion exchanged and WN1, WN2 and WN3 for wet-impregnated ones. The percentage of NiO in each sample is shown in Table 4.1.

4.1 XRD studies

XRD patterns are shown in Figs 4.1 – 4.6. Well-defined and sharp peaks were obtained for ion-exchanged and wet-impregnated

Fig. 4.1. XRD pattern of NiO/ TiO$_2$ samples prepared by co-precipitation method 1) CN3 calcined at 350$^\circ$C / 6hrs., 2) CN1, 3) CN2, 4) CN3 calcined at 450$^\circ$C / 6hrs. and 5) CN3 after catalysis. (A = anatase).
samples calcined at 350°C for 6 hrs, but co-precipitated one was amorphous at this temperature. It has become crystalline only at 450°C. All the peaks were those of anatase in all the samples, except in WN3, where a small peak of NiO was observed. There were no peaks due to rutile or NiTiO$_3$ in any of the sample. The absence of NiO peaks clearly discloses the fine nature of NiO, which can not be detected using XRD.
Fig. 4.3 XRD pattern of NiO/ TiO$_2$ samples prepared by wet-impregnation method - calcined at $350^\circ$C / 6hrs. 1) WN1, 2) WN2, 3) WN3 and 4) WN3 after catalysis. (A = anatase and N = NiO).

On comparing with crystallization temperatures of bare TiO$_2$ prepared by hydrazine precipitation and thermal hydrolysis, no change was observed in crystallization temperature in presence of NiO.
In order to investigate clearly the effect of NiO on rutilation, the XRD analysis of all the samples calcined at different temperatures were carried out. Well-defined rutile peaks were obtained in the sample CN3 calcined at 600°C (Fig. 4.4), but in IN3 and WN3, the rutile peaks appeared only after calcination at 700°C (Figs 4.5 and 4.6). So, it is apparent from the XRD data that the onset temperature of rutilation was

![XRD patterns](image)

Fig. 4.4. XRD patterns of CN3 calcined at 1) 600, 2) 800 and 3) 900°C / 6hrs. (A = anatase, R = rutile and NT = NiTiO$_3$).
lower in co-precipitated ones. When the calcination temperature was increased to 800°C, the intensity of rutile peaks increased and that of anatase decreased. On increasing further to 900°C in CN3 and 1000°C in IN3 and WN3, all the anatase peaks disappeared and rutile peaks became more predominant. Marked changes could be seen in the characteristic peaks of anatase at d-value 3.52Å and that of rutile at d-value 3.23Å. The percentage of rutile in CN3, IN3 and WN3 was calculated and the

Fig. 4.5: XRD patterns of IN3 calcined at 1) 700, 2) 800 and 3) 1000°C / 6hrs. (A = anatase, R = rutile & NT = NiTiO₃).
results are shown in Fig. 4.7. Among all the samples, the co-precipitated one has highest rutile percentage at any temperature and lowest for ion-exchanged one. So, the preparation method and NiO percentage have marked influence on rutile phase formation.

On comparing with bare TiO₂, where the onset and completion temperatures of rutilation were 700°C and 1000°C in TiO₂ prepared by thermal hydrolysis and 800°C and 1200°C in TiO₂ prepared
by hydrazine precipitation, it is very clear that in ion exchanged and wet-impregnated ones there were no changes in these temperatures, whereas in co-precipitated one, both the onset and completion temperatures were reduced much.

It is noteworthy that, at the onset of rutilation, some peaks due to NiTiO$_3$ were also present in the pattern. On increasing the calcination temperature, the intensity of these peaks also increased.
The XRD pattern of CN3, IN3 and WN3 after catalysis is given in Figs 4.1 – 4.3. No phase changes could be observed in any of the sample. This reflects the thermal stability of these catalysts under the conditions adopted.

The crystallite size of anatase (not particle size) calculated from XRD data are given in Table 4.1. Crystallite size calculations were

Table 4.1 Variation in crystallite size of anatase with calcination temperature of NiO/TiO₂ samples.

<table>
<thead>
<tr>
<th>Method of preparation</th>
<th>NiO (%)</th>
<th>Sample label</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>350°C</td>
</tr>
<tr>
<td>Co-pption</td>
<td>4.98</td>
<td>CN1</td>
<td>10.98</td>
</tr>
<tr>
<td></td>
<td>9.93</td>
<td>CN2</td>
<td>10.26</td>
</tr>
<tr>
<td></td>
<td>14.96</td>
<td>CN3</td>
<td>9.63</td>
</tr>
<tr>
<td>I.E</td>
<td>4.96</td>
<td>IN1</td>
<td>10.26</td>
</tr>
<tr>
<td></td>
<td>9.98</td>
<td>IN2</td>
<td>10.26</td>
</tr>
<tr>
<td></td>
<td>14.94</td>
<td>IN3</td>
<td>10.26</td>
</tr>
<tr>
<td>W.I</td>
<td>4.92</td>
<td>WN1</td>
<td>10.26</td>
</tr>
<tr>
<td></td>
<td>9.95</td>
<td>WN2</td>
<td>10.26</td>
</tr>
<tr>
<td></td>
<td>14.97</td>
<td>WN3</td>
<td>10.26</td>
</tr>
</tbody>
</table>
done only at certain calcination temperatures at which drastic changes occurred. No change in crystallite size was observed in ion-exchanged and wet-impregnated samples on increasing NiO percentage, while in co-precipitated ones, the crystallite size decreased on increasing NiO percentage. It would be due to the suppression of titania grain growth by extremely fine NiO particles uniformly dispersed on TiO\textsubscript{2}. On increasing the calcination temperature, the crystallite size was also increased in all the samples, but to different extent. In co-precipitated ones, at the onset of rutilation, the crystallite size was 11.82nm, while in ion-exchanged one it was 15.37nm and in wet-impregnated one 17.1nm. So, the rutilation takes place after the enlargement of anatase crystallites and the growth in crystallite size is highly dependent on method of preparation. The anatase crystallites are larger in NiO loaded samples than that in bare titania.

4.2 Surface area studies

The results are shown in Figs 4.8 – 4.10. The co-precipitated samples have got largest surface area even though prepared at 450\textdegree{}C. The surface area increased in co-precipitated and ion-exchanged ones and decreased in wet-impregnated samples on increasing the percentage of NiO, which is in agreement with crystallite size results given in Table 4.1. In sample CN1 the surface area was 94.39 m\textsuperscript{2}/g and it increased to 119.06 m\textsuperscript{2}/g in CN2 and 130.2 m\textsuperscript{2}/g in CN3. Similarly, in sample IN1 the surface area was 78.4 m\textsuperscript{2}/g, in IN2 it became 87.2 m\textsuperscript{2}/g and in IN3 it again increased to 90.3 m\textsuperscript{2}/g. While in sample WN1, it was 91.8 m\textsuperscript{2}/g, but it decreased in WN2 to 80.5 m\textsuperscript{2}/g and to 65.26 m\textsuperscript{2}/g in WN3. Hence the
change in surface area with increase in NiO percentage is highly influenced by preparation method.

On increasing calcination temperature, there occurred a marked decrease in surface area in all the samples. When the calcination temperature was increased to 600°C, in sample CN1, the surface area became nearly half of the earlier value, i.e. 43.8 m²/g, like wise, in the case of CN2 and CN3, it became 50.12 m²/g and 55.28 m²/g respectively. In ion exchanged and wet-impregnated samples, the surface area became
one third when the calcination temperature was increased to 600°C and it again decreased at 700°C at which the rutileation was started. On increasing the temperature further to 800°C, the surface area was reduced very much in all the samples. At 900°C, when the TiO$_2$ was fully converted to rutile in co-precipitated samples, the surface area of CN1, CN2 and CN3 became 2.01 m$^2$/g, 2.32 m$^2$/g and 2.74 m$^2$/g respectively. Similarly at 1000°C the surface area was reduced to 1.12 m$^2$/g, 1.71 m$^2$/g and 1.97 m$^2$/g in samples IN1, IN2 and IN3 respectively and 1.8 m$^2$/g,
1.12 m²/g and 0.98 m²/g in samples WN1, WN2 and WN3 samples respectively. Even though no direct relation between crystallite size and surface area could be made, surface area decreased significantly along with marked increase in crystallite size. It is also evident that a very smaller change in crystallite size does not always necessarily involve a change in surface area. There was a decrease in surface area at the onset and completion of rutilation due to sintering and fusion of TiO₂ and NiO, to form NiTiO₃, which is in agreement with XRD data.
On comparing with surface area of bare TiO$_2$, (vide Fig 3.1) surface area decreased on loading NiO. It is obvious from the above observations that the surface area decreased drastically during rutilation, which in turn is dependent on method of preparation, calcination temperature and NiO percentage. The decrease in surface area during rutilation was also greater in presence of NiO compared to bare TiO$_2$.

4.3 Dispersion studies

The results are shown in Table 4.2. Determination of dispersion of the catalytically active component on the surface of the support is one of the best ways to characterize supported catalysts. The dispersion was carried out at room temperature after reducing the sample at 390$^\circ$C for 1 hr. Comparatively better dispersion was obtained for co-precipitated samples, since they are precipitated from a homogeneous solution. As the NiO percentage was increased the dispersion decreased in all the samples. This reflects that a slight diffusion of Ni particles towards the bulk of the pellets would have occurred during reduction and the chance for such diffusion is obviously higher on increasing the percentage of NiO. Dispersion of 22.18% was obtained in sample CN1 and it decreased to 19.33% in CN2 and 16.64% in CN3. Similarly it decreased from 13.28% to 10.07% in ion exchanged ones and from 21.16% to 13.18% in wet-impregnated ones on increasing the NiO%.

The surface average crystallite size of Ni calculated from dispersion data showed that it increased on increasing NiO percentage and nickel is present as very fine particles on the surface with size range
in nanometers. These results are in line with XRD data. No peaks due to NiO were seen, since the NiO particles were present in very fine form.

Table 4.2. Results of dispersion studies

<table>
<thead>
<tr>
<th>Method of preparation</th>
<th>Sample label</th>
<th>Oxygen chemisorbed (μmol / g)</th>
<th>Dispersion (%)</th>
<th>Surface average crystallite size of Ni (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-pptition</td>
<td>CN1</td>
<td>147.88</td>
<td>22.18</td>
<td>3.61</td>
</tr>
<tr>
<td></td>
<td>CN2</td>
<td>256.99</td>
<td>19.33</td>
<td>4.14</td>
</tr>
<tr>
<td></td>
<td>CN3</td>
<td>333.28</td>
<td>16.64</td>
<td>4.81</td>
</tr>
<tr>
<td>I.E</td>
<td>IN1</td>
<td>88.19</td>
<td>13.28</td>
<td>6.02</td>
</tr>
<tr>
<td></td>
<td>IN2</td>
<td>144.44</td>
<td>10.81</td>
<td>7.40</td>
</tr>
<tr>
<td></td>
<td>IN3</td>
<td>201.43</td>
<td>10.07</td>
<td>7.94</td>
</tr>
<tr>
<td>W.I</td>
<td>WN1</td>
<td>139.39</td>
<td>21.16</td>
<td>3.78</td>
</tr>
<tr>
<td></td>
<td>WN2</td>
<td>203.02</td>
<td>15.24</td>
<td>5.25</td>
</tr>
<tr>
<td></td>
<td>WN3</td>
<td>264.17</td>
<td>13.18</td>
<td>6.06</td>
</tr>
</tbody>
</table>

4.4 SEM analysis

SEM analysis of CN3, IN3 and WN3 samples before rutilation and CN3 after rutilation were carried out and the micrographs are shown in Figs 4.11 and 4.12. Only titania particles could be seen, which mirrors the presence of NiO as very fine particles, as supported by XRD and dispersion studies. The particles were all in a shapeless nature and were aggregated. The aggregation of particles is an evidence for the
Fig. 4.11 Scanning electron micrographs of NiO/TiO$_2$ catalysts

A) IN3 and B) WN3 (calcined at 350°C)
Fig. 4.12 Scanning electron micrographs of NiO/TiO₂ catalysts

A) CN3 (calcined at 450°C and B) CN3 (calcined at 900°C)
fineness of the sample, because it has been reported that\textsuperscript{281} the individual particles in a fine powder would be in an aggregated form (i.e. assemblages of particles which are loosely coherent). No appreciable change in particle size was observed between the three samples prepared through different methods, even though the surface area values and other physical properties were different. So, it is apparent that a very small change in particle size, which could not be detected in SEM, can also cause a larger alteration in surface area. The particles were in much more agglomerated state (i.e. assemblages of particles which are rigidly joined) when the TiO\textsubscript{2} was fully converted to rutile, which would be due to cementation and sintering of individual particles, which is in agreement with XRD and surface area studies.

4.5 Methanation activity studies

Carbon monoxide hydrogenation is a profoundly important process widely exploited by many chemical industries to produce a wide variety of organic compounds like, alcohol, methane, gasoline and other higher hydrocarbons.\textsuperscript{160} There is a long history for this reaction, beginning from 1902, with the investigations of Sebatier and Senderens, who succeeded in producing methane from CO and hydrogen mixture over Ni catalyst. For this contribution and his work on catalytic hydrogenation, Sebatier won the Nobel Prize in Chemistry in 1912.\textsuperscript{160} One year later, the German, Badische- Anilin- und Soda Fanrik (BASF) started to fabricate longer chain hydrocarbons and oxygenated hydrocarbons with the aid of Co-Os catalyst promoted with alkali metals. In 1923, BASF performed the first successful exclusive methanol
synthesis and three years later, Fischer and Tropsch described the formation of longer chain hydrocarbons from CO and hydrogen at 200°C and at atmospheric pressure using Fe-Co catalysts doped with K and Cu as promoters.\textsuperscript{160} It is a highly efficient method for producing fuels with high heating value from coal. By means of suitable choices of catalyst materials, one can control and direct the reaction to obtain the desired product. Hence it is an intensely pursued reaction even today. Methane is reported to form selectively over Ni catalyst.\textsuperscript{160}

The results of methanation activity studies are shown in Figs 4.13-4.16. To optimize the reaction temperature the activity studies were
carried out at different temperatures ranging between 275°C and 375°C using the sample CN3, which is shown in Fig 4.13. Only 40% conversion was obtained at 275°C and the percentage conversion increased with increasing temperature of reaction. At 350°C, 98% conversion was obtained and on further increasing the reaction temperature the percentage conversion decreased to 83%. So, the activities of all the other samples were tested at 350°C. The percentage conversion was strongly influenced by temperature of reaction and maximum conversion was obtained at 350°C (vide Fig 4.13).

The methanation activity of co-precipitated and ion-exchanged catalysts increased much on increasing the NiO percentage due to the increase in surface area and increase in number of surface exposed nickel atoms. With sample CN1 90.8% conversion was obtained and it increased to 98% in CN2 and on further increase in NiO% there was no change in activity, i.e. with sample CN3 also 98% conversion was obtained. Much lower percentage conversion was observed with ion-exchanged samples; with IN1 63.8%, with IN2 66.2% and 68.1% with IN3. Whereas in wet-impregnated samples the percentage conversion decreased with increasing NiO%. 73.8% conversion of was obtained with the sample WN1, 71.8% with WN2 and 64.1% using WN3. So, it is very important to note that this reaction is highly influenced by the quantity of nickel atom present on the surface of the catalyst and the surface area of the sample. It has been reported that a significant variation occurs in methanation activity with change in dispersion and metal concentration. But, the activity of wet-impregnated ones decreased
on increasing percentage of NiO due to a noticeable decrease in surface area in these samples on increasing the percentage of NiO. So, it is evident that, the surface area of the catalyst is also equally important as dispersion to enhance the activity. No solid relation could be made between surface average crystallite size of nickel and activity of the catalyst. Hence this reaction can be considered as a structure in sensitive one. This is in line with the literature data.\textsuperscript{283}

In order to investigate the effect of rutilation and changes in physical properties on the activity of these catalysts, the activity studies
were carried out after calcination of these samples at temperatures, when drastic changes in physical properties have occurred. The activity of these catalysts was altered on increasing the calcination temperature. The percentage conversion was nearly halved in co-precipitated ones and it became one third or less in ion-exchanged and wet-impregnated ones at the onset of rutilation. When the samples were fully rutilated the percentage conversion became very much lowered to less than 5% in all the samples as evidenced by Figs 4.14 – 4.16. The severe reduction observed in activity upon rutilation could be due to the following reasons,
Fig. 4.16. Variation in methanation activity with calcination temperature of NiO/TiO₂ catalysts prepared by wet-impregnation method

- the shortage of enough free Ni atoms on the surface due to sintering and NiTiO₃ phase formation,
- the incompleteness of reduction of NiTiO₃ in to Ni and TiO₂ under the conditions adopted,
- the increased possibility for strong-metal-support-interaction in the reduced state during the reduction of NiTiO₃,
- the irreversible conversion of the support to rutile, and
- the much lower surface area of these samples. It has been reported that the strong-metal-support-interaction (SMSI) is drastically changing the properties of Ni/TiO₂ catalyst and it has also been reported that this reaction is significantly influenced by support material.
The product formed was selectively methane. Hence the reaction would have proceeded through dissociative addition mechanism with carbodic carbon intermediate. The proposed reaction is:

\[ \text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \]

Hence, the presence of even a very low percentage of rutile on the support can affect badly the activity of this catalyst. The co-precipitated ones are the best among these catalysts for methanation, even though they have lower onset temperature of rutilation, which is well above the optimum temperature of methanation. So, it is worth to note that, only by using pure anatase as a support, the effect of rutile phase, on activity could be investigated. Most or almost all investigations on this catalyst prepared through other methods described in literature, were found to be carried out on TiO$_2$ having both anatase and rutile phases.

In this investigation, since the 'CO pulse method' was adopted to study the methanation activity (of the samples prepared through different methods and the changes occurring in activity upon rutile phase formation), the percentage conversion was studied instead of the rate of the reaction. For the same reason it was not possible to compare with other studies reported in literature, where the rate and turnover frequency are only mentioned instead of percentage conversion. However, it is apparent from this study that the methanation activity has been reduced much upon rutilation and the activity was strongly influenced by quantity of nickel present on the surface and surface area of the sample, which in turn is dependent on method of preparation. But most of the studies reported in literature do not consider or account for
the presence of rutile phase in TiO₂ support. However, in the case of samples prepared in this study, it is very clear that rutile phase formation take place only at very high temperature, which is well above the optimum temperature of methanation and hence should be superior to the catalysts reported in literature as the properties deteriorate on rutilation.

4.6 Conclusions

- The co-precipitated samples crystallize at 450°C, while ion-exchanged and wet-impregnated ones crystallize at 350°C.
- Onset and completion temperatures of rutilation were found to vary with method of preparation.
- At the onset of rutilation NiTiO₃ phase is also formed.
- Better surface area, dispersion and activity are obtained with co-precipitated ones. Ion-exchange and wet-impregnation methods also gave better properties compared to conventional methods.
- Method of preparation, calcination temperature, rutilation and NiO percentage have greater role in determining surface area.
- Enhancement of rutilation by same metal oxide varies with method of preparation.
- Crystallite size enlargement takes place during rutile phase formation.
- Methanation activity significantly reduces at the onset of rutilation and drastically when the TiO₂ is fully converted to rutile.
All these samples were found to be thermally stable under the conditions adopted for methanation.

The order of methanation activity is: co-precipitated > wet-impregnated > ion exchanged samples.