6 INTRODUCTION

The use of metal complexes as precursors for the preparation of the supported metal catalysts is gaining importance; as such precursors dramatically influence the final properties of the catalysts. The solid-state reactions occurring between active phase and support during calcinations are crucial in controlling the structural properties or the reactivity of supported oxide catalysts. Nickel supported on α-alumina are versatile catalysts used in steam reforming of hydrocarbons [1]. The global demand for processes like GTL (gas to liquid) and DME (dimethyl ether) has renewed interest in improvement of steam reforming catalysts. Steam reforming of gaseous hydrocarbons is seen as a potential way to provide fuel for fuel cells. The high temperature (700 – 1100 °C) of steam reforming requires robust catalyst and α-Al₂O₃ is a best option. α-Alumina is a refractory oxide formulated at high temperatures. They have low surface area, but have high mechanical and thermal stability suitable for the demanding conditions of steam reforming.
Co-precipitation route yields Ni catalysts with some of the active species getting converted to “hard to reduce” nickel aluminate. The most convenient method for preparation is impregnation with nickel salts, followed by calcination to oxide precursors. α-Alumina is considered to be an ‘inert support’ which provides little or no interaction to the metal supported on it. The stable structure of α-Al₂O₃ prevents migrations of metal ions into it. However calcinations at high temperature can force the NiO and α-Al₂O₃ to react to form refractory NiAl₂O₄. Gavalas et al. conducted a series of studies on impregnated 2.2 wt% NiO/α-Al₂O₃, employing hydrogen chemisorption, scanning electron microscopy and X-ray photoelectron spectroscopy [2, 3]. The studies indicated that above 850 °C a precursor of NiAl₂O₄ forms which is insoluble in acid and difficult to reduce. Molina et al. and Richardson et al. have reported NiAl₂O₄ formation at low temperatures [4, 5]. They argue that during impregnation, a part of Al₂O₃ dissolves in the impregnating solution and gets incorporated to NiO structure. Even by low temperature calcinations this can transform to NiAl₂O₄ like species.

Mostly nickel nitrate salt is used to prepare the NiOₓ₋₀.₁₋₁/Al₂O₃ catalysts by impregnation method. Multiple impregnations are required to achieve the required metal concentrations. Conversion to nickel aluminate cannot be avoided even in these cases. In high temperature applications, the nickel particles agglomerate and reduce the active surface area for the reaction. So there is much interest in preparing easily reducible, highly active and stable NiOₓ/α-Al₂O₃ catalysts. Previously reported studies have established that chelating ligands of the acetyl acetonate are good candidates for the preparation of easily reducible nickel and vanadia catalysts [6, 7].

Use of ethylenediamine metal complexes to prepare supported metal catalysts is gaining much importance because of the ease of preparation of the complexes and formation of smaller metal particles, which are held strongly to the support [8, 9]. Che et al. [10-12] have conducted a series of studies on impregnation
and drying of these nickel complexes on silica and gamma alumina. However, the reports on the catalytic activities are very rare [13].

In the present chapter the structure and reactivity of NiOₓ/α-Al₂O₃ composite catalysts prepared by the wet impregnation of ethylenediamine complexes of nickel(II) is discussed. The main objective was to study the influence of counter ions on the physiochemical properties of the final catalyst and their influence on activity. Benzene hydrogenation and cyclohexanol decomposition were carried out on the catalysts. Benzene hydrogenation reaction has been used as a test reaction to check the metal support interaction [14].

6.1 Thermal decomposition of dried precursors, chemical analysis and surface area

The TG curves of the thermal decomposition of the dried precursors are shown in Figure 1. The decomposition of Ni-α-B-d is complete before 300 °C and this type of exothermic decomposition of complexes is because of the close proximity of NO₃⁻ counter ion and ethylenediamine ligand. The total weight loss corresponds to the removal of ethylenediamine ligands and NO₃⁻ ions in a rapid oxidation-reduction reaction. For the precursor with chloride counter ion (Ni-α-D-d), the decomposition was complete only at high temperature 590 °C. Ni-α-A-d followed almost a same decomposition pattern as the parent compound, nickel nitrate (Chapter 2). The DTG-DTA patterns of the precursors are given from Figures 2 to 5. A small weight increase corresponding to the oxidation of nickel can be found for Ni-α-B-d. This indicates metallic nickel has been formed during the decomposition. The decomposition of Ni-α-B-d is complete in a single step which is highly exothermic. The decomposition of Ni-α-C-d is also exothermic, but in two stages. Endothermic and exothermic weight losses are registered in the DTG-DTA pattern of Ni-α-D-d.

The counter ions present can influence the heat generated or absorbed, amount of heat energy and speed of the decomposition. During decompositions the
nickel ions can interact with the support and the strength of decomposition will be affected by above factors. The differences in decomposition patterns will affect the interactions of nickel ions with the support affecting the final structure and activity of the catalyst.

![Figure 1. TG curves of dried precursors](image1.png)

![Figure 2. DTG-DTA of Ni-α-A-d](image2.png)

![Figure 3. DTG-DTA of Ni-α-B-d](image3.png)

![Figure 4. DTG-DTA of Ni-α-C-d](image4.png)

![Figure 5. DTG-DTA of Ni-α-D-d](image5.png)
The results of chemical analysis and surface area for the calcined catalysts are given in Table 1.

Table 1. Chemical analysis and BET surface areas of calcined catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m$^2$ g$^{-1}$)</th>
<th>Ni (weight %)</th>
<th>Cl (weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Support</td>
<td>5.9</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>Ni-α-A-c</td>
<td>7.5</td>
<td>19.8</td>
<td></td>
</tr>
<tr>
<td>Ni-α-B-c</td>
<td>23.8</td>
<td>19.6</td>
<td></td>
</tr>
<tr>
<td>Ni-α-C-c</td>
<td>11.0</td>
<td>20.1</td>
<td></td>
</tr>
<tr>
<td>Ni-α-D-c</td>
<td>3.6</td>
<td>20.0</td>
<td>0.9</td>
</tr>
</tbody>
</table>

The highest surface area obtained was for Ni-α-B-c. The surface areas for Ni-α-A-c, Ni-α-B-c and Ni-α-C-c were higher than the support. The increase of surface can be of two reasons; i) the formed NiO are of high surface area ii) the α-Al$_2$O$_3$ would have dissolved during impregnation and formed high surface area forms like gamma or eta alumina. The single stage exothermic decomposition of Ni-α-B-d resulted in formation of high surface area NiO supported on α-Al$_2$O$_3$. This decomposition happens at low temperatures compared to others. Also the process is very fast and the heat developed can dissipate fast avoiding the thermal sintering of the formed nickel oxide crystallites. The low surface area obtained for Ni-α-D-c is due to the exothermic decompositions at high temperatures (Figure 5 indicates decomposition of Ni-α-D-d is complete only at 590 °C) which might have resulted due to sintering.

6.2 XRD and UV-vis DRS studies

The XRD patterns of the support and samples before and after reduction are shown in Figure 6, and the crystallite sizes and lattice parameters are given in Table 2. The most intense NiO reflections are at 37.3° due to NiO (111) and 43.3° due to NiO (200). In the present system they are almost completely overlapped with the
(113) and (104) reflections of \( \alpha \)-alumina at 37.8° and 43.4° respectively. Therefore the XLBA (X-ray line broadening analysis) was done on the 62.8° (220) peak of NiO for the calcined samples. The XLBA was done for the reduced catalysts for the peaks at 44.4° \( \text{Ni}^{(0)}(111) \) and at 51.8° \( \text{Ni}^{(0)}(200) \). The Ni-\( \alpha \)-B-c derived from nitrate anion has the smallest crystallite for NiO and shows the maximum change in the lattice parameter also. The low crystallite size might have achieved because of the single stage exothermic decomposition during the calcination step. Ni-\( \alpha \)-D-c derived from chloride anion has the largest crystallite size. The crystallite sizes for the reduced Ni systems did not vary much except for the Ni-\( \alpha \)-D-r sample which shows a larger crystallite size. The Ni-\( \alpha \)-D system shows no variation from the theoretical value thus indicating the formation of bulk NiO and Ni grains in this system. None of the catalysts showed reflections due to nickel aluminate formation.

Figure 6. XRD patterns of support, calcined and reduced catalysts.

* NiO   # Ni
Table 2. Crystallite sizes and lattice constants of calcined and reduced samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Crystallite size NiO nm</th>
<th>Crystallite size Ni nm</th>
<th>Cell constant NiO nm</th>
<th>Cell constant Ni nm</th>
<th>% Change in lattice parameter NiO</th>
<th>% Change in lattice parameter Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-α-A-c</td>
<td>17</td>
<td>--</td>
<td>0.4175</td>
<td>--</td>
<td>0.034</td>
<td>--</td>
</tr>
<tr>
<td>Ni-α-B-c</td>
<td>9</td>
<td>--</td>
<td>0.4184</td>
<td>--</td>
<td>0.197</td>
<td>--</td>
</tr>
<tr>
<td>Ni-α-C-c</td>
<td>14</td>
<td>--</td>
<td>0.4179</td>
<td>--</td>
<td>0.068</td>
<td>--</td>
</tr>
<tr>
<td>Ni-α-D-c</td>
<td>20</td>
<td>--</td>
<td>0.4176</td>
<td>--</td>
<td>0.001</td>
<td>--</td>
</tr>
<tr>
<td>Ni-α-A-r</td>
<td>--</td>
<td>20</td>
<td>--</td>
<td>0.3526</td>
<td>--</td>
<td>0.046</td>
</tr>
<tr>
<td>Ni-α-B-r</td>
<td>--</td>
<td>18</td>
<td>--</td>
<td>0.3535</td>
<td>--</td>
<td>0.322</td>
</tr>
<tr>
<td>Ni-α-C-r</td>
<td>--</td>
<td>20</td>
<td>--</td>
<td>0.3524</td>
<td>--</td>
<td>0.012</td>
</tr>
<tr>
<td>Ni-α-D-r</td>
<td>--</td>
<td>33</td>
<td>--</td>
<td>0.3525</td>
<td>--</td>
<td>0.039</td>
</tr>
</tbody>
</table>

Theoretical NiO lattice parameter- 0.4176 nm
Theoretical Ni lattice parameter- 0.3524 nm

The UV-vis DRS spectra (Figure 7) of the calcined samples exhibit charge transfer band at 280 nm and the d-d transitions, $^3A_{2g} \rightarrow ^1T_{1g}$, $^3A_{2g} \rightarrow ^3T_{1g}(P)$ and $^3A_{2g} \rightarrow ^3T_{1g}$ (F) at 377 nm, 425 nm and 714 nm respectively. These transitions are due to nickel(II) in octahedral structure [15]. The transitions at 590 and 620 nm are not seen indicating the absence of Ni(II) in tetrahedral structures. This again points out the non formation of nickel aluminate, which is in agreement with the observation from XRD. The peaks of Ni-α-D-c are intense than others and it’s less intense charge transfer band indicates the formation of bulk NiO. TPR and SEM results agree with this observation. The high intensity of charge transfer band, high absorption along the entire wavelength and low intensity of Ni[O] bands suggest the formation of black Ni$_2$O$_3$ on the Ni-α-C-c sample [16]. In general the DRS spectrum reveals the formation of NiO with less interaction with the support and is similar to the spectrum obtained by Lisboa et al. for the Ni/α-alumina catalysts [17]. Due to
the dark color and high absorbance in the entire range, more information could not be extracted from UV-vis DRS spectra.

Figure 7. UV-vis diffuse reflectance spectra of calcined catalysts

6.3 TCD-TPR

Metal support interactions appreciably affect the surface properties of these catalysts and, hence, their catalytic properties. It is well known that the interaction between nickel oxide and support can affect the reduction temperature [18]. The reduction temperature mainly depends on the support interaction, Ni species, particle size and rate of nucleation of metallic nickel. The nickel species having weak interaction can be reduced at low temperature than those having strong interaction. Small particle sizes generally result in high reduction temperatures than large particle sizes. The TPR spectra of Ni-α-A-c and Ni-α-B-c (Figure 8) show major peaks at 620 and 450 °C. The peak at 620 °C is due to surface nickel aluminate, while the peak at 450 °C is due to small NiO crystallites having interaction with the support (supported NiO). The peak at 390 °C for Ni-α-D-c is due to the reduction of bulk NiO [19].
The reduction peak of Ni-α-C-c at 320 °C agrees with that reported for the pure Ni$_2$O$_3$ by Ho et al. who calcined their catalysts at low temperature and under inert atmosphere [20]. Such low reduction peak is very uncommon in nickel supported systems and is attributed to the formation of Ni$_2$O$_3$ in which Ni is in the +3 state. The samples Ni-α-A-c and Ni-α-B-c also show the presence of this Ni$^{3+}$ species by the low intense peaks below 300 °C. Table 3 shows the different species present on the catalysts. It can be seen that the major species present on Ni-α-B-c is supported NiO crystallites. The use of ethylenediamine ligands in general resulted in formation of easily reducible nickel species. This may be due to the presence of chelating ligands which favour the formation of bulk NiO. During decomposition, the chelating ligands protect the nickel ions from interacting with the support.
Table 3. Different nickel species present on calcined catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Nickel Species</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni$_2$O$_3$ (320 °C)</td>
</tr>
<tr>
<td>Ni-α-A-c</td>
<td>√</td>
</tr>
<tr>
<td>Ni-α-B-c</td>
<td>√</td>
</tr>
<tr>
<td>Ni-α-C-c</td>
<td>√ (major)</td>
</tr>
<tr>
<td>Ni-α-D-c</td>
<td>√ (major)</td>
</tr>
</tbody>
</table>

6.4 SEM

SEM results (Figure 9) show a striking difference in the morphologies of reduced catalysts. The SEM image of support indicates sheet like structures. Ni-α-A-r and Ni-α-A-r show smaller Ni grains embedded on the sheet like surface of α-alumina thus giving the support a rough nature. Morphology of Ni-α-D-r shows bulk Ni grains with nearly cubic shapes; whereas Ni-α-C-r contains flower shaped Ni grains which seems to be formed by loose aggregates of nickel crystallites. Both Ni-α-C-r and Ni-α-D-r are loosely bound to support surface resulting in very low metal support interaction. TPR results are in accordance with this observation. Variations in morphologies of NiO on changing the metal precursors were also noted by Estelle et al. [21].
Structure and Reactivity of Ni/\alpha-\text{Al}_2\text{O}_3 Catalysts.

Figure 9. Scanning Electron Micrographs of reduced catalysts and support

$\text{Ni-}\alpha\text{-A-r}$ $\text{Ni-}\alpha\text{-B-r}$

$\text{Ni-}\alpha\text{-C-r}$ $\text{Ni-}\alpha\text{-D-r}$

$\alpha\text{-Al}_2\text{O}_3$ - support

Figure 9. Scanning Electron Micrographs of reduced catalysts and support
6.5 Benzene hydrogenation

The results of benzene hydrogenation on reduced catalysts are shown in Figure 10. Ni-α-C-r shows the highest conversion. The catalyst with lowest crystallite size, Ni-α-B-r did not show much activity. The special flower like morphology present on Ni-α-C-r may be the reason for its high activity.

Figure 10. Percentage conversion for benzene hydrogenation on reduced catalysts

Such special morphology has found to give unexpected activity in nickel supported systems [22, 23]. For supported catalysts, when metal supported interaction is more, the benzene hydrogenation activity will be less [14].

6.6 Cyclohexanol dehydrogenation

The results of cyclohexanol dehydrogenation on the bare support, calcined samples and reduced catalysts are shown in the Table 4. All the catalysts yielded cyclohexanone and cyclohexene as the major products; however, using reduced catalysts trace quantities of benzene, cyclohexane and phenol were also obtained. These trace secondary products were less than 1%; so they were neglected in
selectivity and yield calculations. The calcined catalysts are highly selective towards cyclohexanone even though their activities were low.

**Table 4.** Results of cyclohexanol dehydrogenation

<table>
<thead>
<tr>
<th>Sample</th>
<th>% (wt) conversion of Cyclohexanol</th>
<th>% selectivity</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cyclohexanone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Support</td>
<td>2</td>
<td>72</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>Ni-α-A-c</td>
<td>8</td>
<td>98</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Ni-α-B-c</td>
<td>6</td>
<td>97</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Ni-α-C-c</td>
<td>7</td>
<td>96</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Ni-α-D-c</td>
<td>6</td>
<td>96</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Ni-α-A-r</td>
<td>28</td>
<td>95</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Ni-α-B-r</td>
<td>45</td>
<td>99</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Ni-α-C-r</td>
<td>18</td>
<td>98</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Ni-α-D-r</td>
<td>12</td>
<td>98</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

The increase in selectivity on these calcined catalysts, compared to the bare support is due to introduction of NiO, which always gives more selectivity towards cyclohexanone [24]. The reduced catalysts are reasonably active towards the dehydrogenation reaction. The Ni-α-B-r with the smallest nickel crystallite size and largest BET surface area gave the maximum yield for cyclohexanone, while the Ni-α-C-r gave least yield.

The TPR data indicate that different types of NiO having different interactions with the support has been formed, while XRD shows different crystallite size formation on the alpha alumina surface. Even though these different NiO did not show any difference in their performance for their reaction, upon reduction they yielded nickel metal crystallites differing in size and strength of interaction with support. The evolution of the active phase from the precursors during the
calcination stage determines the final properties of the catalysts. Cyclohexanol dehydrogenation to cyclohexanone is a reaction which depends on the metal crystallite size [25]. The high activity of Ni-α-B-r sample derived from the [Ni(en)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ for cyclohexanol dehydrogenation to cyclohexanone is because of its low metal crystallite size and high surface area. And this low crystallite size resulted from the exothermic decomposition of the ligands in single step at a low temperature compared with the conventional preparation method. However, this highly exothermic decomposition resulted in formation of supported NiO crystallites with moderate interaction with the support.

The difference in reactivity of Ni-α-B-r and Ni-α-C-r towards the studied reactions indicate the difference in reactivity of the species present. Ni-α-C-r which have high amount of ‘free Ni’, having special flower like morphology is highly active for hydrogenation. Ni-α-B-r which contains high amount of ‘Ni interacting moderately with support’ (or small Ni crystallites) is highly active for cyclohexanol dehydrogenation. Thus, change of counterions resulted in formation of different types of nickel species on alpha alumina with varying activities towards chemical transformations.

6.7 Conclusions

i.) TG studies of dried precursors indicate that low temperature exothermic decomposition for Ni-α-B-d, results in formation of catalyst with high surface area and small supported NiO crystallites.

ii.) The acetate counter ion results in formation of nickel metal with special morphology highly active for benzene hydrogenation

iii.) The use of different counter ions results in catalysts with different metal-support interactions.

iv.) The model reactions studied indicate that aromatic hydrogenation sites are different from the sites for cyclohexanol dehydrogenation.
References


Chapter 6


Structure and Reactivity of Ni/\(\alpha\)-Al\(_2\)O\(_3\) Catalysts.


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