Chapter 5

PREPARATION AND CHARACTERIZATION OF SUPPORTED NICKEL CATALYSTS.

5.1 Preparation of supports
5.1.1 Preparation of \(\alpha\)-Al\(_2\)O\(_3\)
5.1.2 Preparation of \(\gamma\)-Al\(_2\)O\(_3\)
5.1.3 Preparation of MgO
5.2 Preparation of supported nickel catalysts-impregnation deposition
5.3 Characterization techniques
5.3.1 Chemical analysis- AAS
5.3.2 Thermal studies on precursors
5.3.3 N\(_2\) physisorption
5.3.4 Powder XRD
5.3.5 UV-vis DRS
5.3.6 TCD-TPR
5.3.7 TG-TPR
5.3.8 H\(_2\) chemisorption
5.3.9 TPD of CO\(_2\)
5.3.10 TPD of cyclohexylamine
5.3.11 Scanning Electron Micrographs
5.4 Activity studies
5.4.1 Benzene hydrogenation, Cyclohexane dehydrogenation
5.4.2 Cyclohexanol decomposition
5.4.3 Reactions of n butanal and hydrogen
5.5 References

This chapter deals with the preparation of supports, supported nickel catalysts and the details of the characterization methods used in subsequent chapters.

5.1 Preparation of supports

5.1.1 Preparation of \(\alpha\)-Al\(_2\)O\(_3\)

Nano crystalline \(\alpha\)-alumina was made by solution combustion synthesis [1]. Al(NO\(_3\))\(_3\)·9H\(_2\)O (Merck 99+%) (20g) and Urea (BDH India 99+%) (8g) (oxidant (metal salt) /fuel (urea) ratio =1) were together dissolved in 75 mL distilled water
and was then evaporated to a syrupy solution. This solution was then placed in a preheated furnace (450 °C) for five minutes, which yielded the fluffy product. The α-alumina derived by this process is phase pure as indicated by XRD (Figure 1a) (surface area = 5.9 m² g⁻¹, Average crystallite size = 37 nm and pore volume <0.1 mL g⁻¹). Scanning electron micrograph (SEM) (Figure 1b) indicated the formation of sheet like structures.

![Figure 1. (a) XRD and (b) SEM of α-Al₂O₃](image1)

5.1.2 Preparation of γ-Al₂O₃

The γ-Al₂O₃ used was a gift sample from Research and Development Division of Sud Chemie India Ltd. The sample had a surface area of 199 m² gm⁻¹, pore volume 0.57 mL gm⁻¹ and an average pore diameter of 96 Å. The XRD pattern and adsorption desorption isotherm are given in Figure 2 (a) and (b).

![Figure 2. (a) XRD and (b) Adsorption-desorption isotherm of γ-Al₂O₃](image2)
5.1.3 Preparation of MgO

Magnesium hydroxide (Mg(OH)$_2$) was precipitated from 0.1 molar solution of magnesium nitrate at a constant pH of 9 and temperature of 70 °C using 20% ammonia solution. The precipitate was then washed well to remove the nitrate ions, and then dried in an air oven at 120 °C overnight. The dried cakes were then powdered and calcined at 600 °C in a muffle furnace for four hours to obtain crystalline MgO. The XRD pattern and the SEM of calcined MgO are given in Figure 3 (a) and (b).

5.2 Preparation of supported nickel catalysts-impregnation deposition

Metal loading was fixed to be 20 wt% nickel on all the catalysts. The method of catalyst preparation is outlined in the following block diagram (Figure 4). Solutions of the nickel complexes were prepared first. To this solution (volume of the solution should be much larger than pore volume) calcined support (which was dried at 200 °C for two hours prior to the preparation of catalyst) was added and stirred well. The slurry was then slowly dried on a water bath with occasional stirring to obtain dried cakes. It was then dried in an air oven at 120 °C overnight. The cakes were then powdered well and calcined in a muffle furnace at 600 °C for four hours. The heating program was set in such a way that material was heated from room temperature to 600 °C at the rate of 6 °C min$^{-1}$. 
This method of preparation enables loading of higher metal percentages on the support and the targeted metal loading is easily achieved. During the preparation, the following events take place

1. As the supports are dried, pore volume impregnation (filling of void volume with impregnating solution) takes place.
2. An excess solution (much more than pore volume) is used to make impregnating solution, so some nickel complex ions will be ion exchanged with the surface groups.
3. The remaining metal salts (complexes) will be deposited on the surface during the drying step.

This method thus involves impregnation and deposition.

---

**Figure 4.** Scheme for the preparation of supported catalysts

Procedure for the preparation (for 5g of support) is as follows. The impregnating solution of \([\text{Ni(H}_2\text{O)}_6]\)(NO\(_3\))\(_2\) (Ni-A), was prepared by dissolving 4.956g Ni(NO\(_3\))\(_2\).6H\(_2\)O in 100mL distilled water. The impregnating solution of \([\text{Ni(en)}_2(\text{H}_2\text{O})_2]\)(NO\(_3\))\(_2\) (Ni-B) was prepared by adding ethylenediamine at a mol
Preparation and Characterization of Supported Nickel Catalysts

ratio of en/Ni = 2 to a solution of Ni(NO$_3$)$_2$.6H$_2$O (4.956 g) dissolved in distilled water (100 mL). The impregnating solutions, Ni-C and Ni-D were prepared in a similar way by using Ni(CH$_3$COO)$_2$.4H$_2$O (4.240g) or NiCl$_2$.6H$_2$O (4.050g) respectively. As an example for the preparation of α-Al$_2$O$_3$ supported catalysts, 5g of α-Al$_2$O$_3$ was added to the impregnating solution Ni-A, slowly evaporated to dryness with constant stirring on a water bath. It was then dried at 120 °C overnight in an air oven and the resulting sample was named as Ni-α-A-d. It was then calcined in a static furnace at 600 °C for 4 hours, with a heating rate of 6 °C min$^{-1}$ and the resulting sample was named as Ni-α-A-c. Further the sample was reduced at 500 °C for four hours and was named as Ni-α-A-r. The other supported Ni/NiO catalysts were named in a similar way and the nomenclatures for the catalysts are as follows.

en= ethylenediamine

<table>
<thead>
<tr>
<th>Metal Complex</th>
<th>NiO</th>
<th>Ni/α-Al$_2$O$_3$</th>
<th>Ni/γ-Al$_2$O$_3$</th>
<th>Ni/MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="NO$_3$">Ni(H$_2$O)$_6$</a>$_2$ (A)</td>
<td>NiO-A</td>
<td>Ni-α-A-x</td>
<td>Ni-γ-A-x</td>
<td>Ni-M-A-x</td>
</tr>
<tr>
<td><a href="NO$_3$">Ni(en)$_2$(H$_2$O)$_2$</a>$_2$ (B)</td>
<td>NiO-B</td>
<td>Ni-α-B-x</td>
<td>Ni-γ-B-x</td>
<td>Ni-M-B-x</td>
</tr>
<tr>
<td><a href="CH$_3$COO">Ni(en)$_2$(H$_2$O)$_2$</a>$_2$ (C)</td>
<td>NiO-C</td>
<td>Ni-α-C-x</td>
<td>Ni-γ-C-x</td>
<td>Ni-M-C-x</td>
</tr>
<tr>
<td>[Ni(en)$_2$(H$_2$O)$_2$]Cl$_2$ (D)</td>
<td>NiO-D</td>
<td>Ni-α-D-x</td>
<td>Ni-γ-D-x</td>
<td>Ni-M-D-x</td>
</tr>
</tbody>
</table>

x = d for dried, c for calcined, and x = r for reduced

5.3 Characterization techniques

5.3.1 Chemical analysis- AAS

The metal percentages on the calcined catalysts were estimated by atomic absorption spectrophotometry (AAS) on a Thermo Electron Corporation MMK$_2$ system. The catalyst (0.5g) was mixed well with potassium hydrogen sulphate
(KHSO₄, 3g) in a small china dish. It was then fused in a muffle furnace set at 450 °C. The fused mixture was extracted by boiling with dilute sulfuric acid (50:50 solution) and was made up to 200 mL with distilled water. The solution was then analyzed for nickel content on AAS.

The chloride content on the catalysts was determined by titration with standardized silver nitrate solution following Volhard’s method [2].

5.3.2 Thermal studies on precursors

The thermal decomposition patterns of the dried precursors were recorded on a Pyris Diamond TG of Perkin Elmer make. An air flow of 200 mL min⁻¹ was maintained and the heating rate employed was 10 °C min⁻¹ from 100 °C to 800 °C. The same instrument measured the DTA responses simultaneously.

5.3.3 N₂ physisorption

The adsorption desorption characteristics of the calcined catalysts were determined on a Micromeritics Tristar Surface area Analyzer. Prior to adsorption, the samples were degassed in the Flowprep unit of the system at a temperature of 350 °C for three hours under nitrogen flow.

5.3.4 Powder XRD

X-ray diffraction patterns of the calcined and reduced catalysts were recorded on Bruker model D8 (CuKα source) and X-ray line broadening analysis (XLBA) was done with the well known Scherrer equation.

5.3.5 UV-vis DRS

The UV-vis diffuse reflectance spectra were recorded on a Labomed UV-Vis spectrophotometer equipped with a diffuse reflectance accessory and integrating sphere in the range 200 to 900 nm. BaSO₄ was used as blank for the measurements. The percentage reflectance values were converted to absorbance using the Kubelka Munk function (equation) [3].
Preparation and Characterization of Supported Nickel Catalysts

5.3.6 TCD-TPR

The temperature programmed reduction (TPR) of NiO/α-Al₂O₃ (chapter 6) and NiO/MgO catalysts (chapter 8) were done on Micromeritics Pulse Chemisorb 2705 system. The calcined samples were heated in a flow of helium at 300 °C for two hours to remove any adsorbed moisture. It was then cooled to room temperature. The gas was switched to 5% H₂ in helium and the temperature was raised to 950 °C. A heating rate of 5 °C min⁻¹ was used for NiO/α-Al₂O₃ and a heating rate of 10 °C min⁻¹ was used for NiO/MgO catalysts. A thermal conductivity detector (TCD) was used to measure the hydrogen consumption. Moisture from the reduction reaction was trapped by a moisture trap before passing the gases through TCD. The TCD was calibrated by injecting pulses of pure hydrogen gas.

5.3.7 TG-TPR

The reduction characteristics of NiO/γ-Al₂O₃ catalysts (chapter 7) were studied by the technique of TG-TPR. The weight change accompanying the reduction reaction is monitored by a thermogravimetric balance. This method has been used by some researchers to identify the nickel species on supported nickel catalysts [4, 5].

The experiment was done on a Pyris Diamond TG of Perkin Elmer make. The sample was dried ex situ in flowing nitrogen at 200 °C for three hours. The sample (20-22 mg) was weighed in to the alumina crucible of the TG balance. Temperature was raised to 200 °C for 30 minutes to remove any adsorbed moisture and then it was increased at a rate of 10 °C min⁻¹ to 800 °C in flow of 10% H₂ in N₂ (200 cc hr⁻¹) gas. Weight loss corresponding to the reduction was measured.

\[
F(R_\alpha) = \frac{(1 - R_\alpha)^2}{2R_\alpha}
\]

\(R_\alpha = \text{reflectance of sample}\)
Chapter 5

5.3.8 H$_2$ Chemisorption

The hydrogen chemisorption studies were done on a Quantachrome Autosorb system. Around 0.1g of catalysts was loaded into the reactor and was reduced in a flow of hydrogen (20 vol %) at 500 °C for two hours. It was allowed to cool to 40 °C in a flow of Argon. After one hour, hydrogen chemisorption was done at 40 °C to determine the monolayer uptake in μmols of hydrogen adsorbed per gram of catalyst. From the monolayer uptake, % metal dispersion and active metal surface area were calculated as

\[
\text{% dispersion} = \left( \frac{\text{Ni}_{\text{surface}}}{\text{Ni}_{\text{total}}} \right) \times 100
\]

\[
\text{Active metal surface area} = \text{Ni surface area (m}^2 \text{ gm}^{-1}) = m \times N \times 2 \times a / 10^{20}
\]

\[
\text{Ni}_{\text{surface}} = \text{number of surface nickel atoms} = \mu\text{mols of hydrogen adsorbed} \times 10^{-6} \times 2 \times N
\]

\[
\text{Ni}_{\text{total}} = \text{no of total nickel atoms} = \text{wt of catalyst} \times N \times \% \text{ Ni loading} / (\text{mol wt of nickel (58.69)} \times 100
\]

\[N = 6.022 \times 10^{23} \text{ molecules}\]

\text{chemisorption stoichiometry; one mol of hydrogen = 2 mols of nickel = 2}

\[m = \mu\text{mols of hydrogen adsorbed gm}^{-1}\]

\[\text{surface area of nickel atom} = 6.49 \text{ Å}^2 = a\]

\[\text{Total area} = \text{number of nickel atoms} \times \text{surface area of one nickel atom}\]

\textbf{NB:} As precursors change, the morphology (shape) of the particles changes; so no attempt was done to calculate the Ni crystallite diameter, as such calculations include the assumptions about the shape of the crystallites.

5.3.9 TPD of CO$_2$

The temperature programmed desorption of carbon dioxide (for NiO/MgO catalysts, Chapter 8) was done on Micromeritics Pulse Chemisorb 2705 system under Helium atmosphere. The sample (= 0.1 g) was heated under helium flow at 300 °C for two hours to remove and adsorbed gases. It was then cooled to room
temperature. Three pulses of pure CO\textsubscript{2} (size of 100\,\mu\text{L}) was injected consecutively through the injection port to the sample. The sample was then allowed to stabilize under helium flow for another one hour. It was then heated from room temperature to 600 °C with a heating rate 10 °C min\textsuperscript{-1}. The desorbed CO\textsubscript{2} was monitored by TCD response. Quantitative calibration of CO\textsubscript{2}-TPD peak area was made by monitoring the decomposition of known amounts of CaCO\textsubscript{3}.

5.3.10 TPD of cyclohexylamine

The acidity of Ni/\gamma-\text{Al}_2\text{O}_3 catalysts (Chapter 7) was determined by temperature programmed desorption of cyclohexylamine (CHA) using thermogravimetry. The sample was treated with liquid cyclohexylamine for 20 minutes. It was then slowly heated to 150 °C in oven for two hours, cooled and 20 mg was weighed to the TG balance. Desorption thermograms were recorded at a heating rate of 10 °C min\textsuperscript{-1} under nitrogen flow (200 cc hr\textsuperscript{-1}). The mass loss between 200 and 420 °C was used to determine the acid content of the samples (in mmols CHA g\textsuperscript{-1} adsorbent) [6].

5.3.11 Scanning Electron Micrographs

The Scanning electron micrographs (SEM) of the samples were taken on a scanning electron microscope, model Jeol JSM-6390 LA. The powdered samples were spread on a carbon tape and then mounted on the microscope. The details of the magnification are present on the micrographs.

5.4 Activity studies

The details of the reaction conditions of vapor phase reactions are given in this section. Exploratory experiments were done to arrive at the reaction conditions.

5.4.1 Benzene hydrogenation / cyclohexane dehydrogenation

The benzene hydrogenation reaction (for Ni/\alpha-\text{Al}_2\text{O}_3 catalysts, Chapter 6) was performed in a conventional glass reactor (10mm id) operated at atmospheric pressure. Benzene (99+%; Loba Chemie, India) was introduced with a precalibrated
syringe pump and H\textsubscript{2} flow was controlled by Bronkhaurst mass flow controller. Before the activity tests, the catalysts were reduced at atmospheric pressure with H\textsubscript{2} (flow rate 40mL min\textsuperscript{-1}) at 500 °C for 4 hours. The liquid products were collected at the bottom of the reactor in an ice cooled trap. Products were analysed after 30 min (to ensure mass balance) on a gas chromatograph (Chemito 8510) equipped with a carbowax column and flame ionization detector. The selectivity was 100% towards cyclohexane. (Reaction conditions were: WHSV = 2.8 hr\textsuperscript{-1}, mol ratio \([\text{H}_2]/[\text{C}_6\text{H}_6] = 4\), temperature 220 °C).

The cyclohexane dehydrogenation (for Ni/\(\gamma\)-Al\textsubscript{2}O\textsubscript{3} catalysts, Chapter 7) was done in same apparatus as mentioned above. After reduction with hydrogen, the gas was changed to pure nitrogen at a flow rate of 20 mL min\textsuperscript{-1}. The cyclohexane feed rate was set at 2.4 mL hr\textsuperscript{-1} and temperature of the reaction was set at 300 °C. The catalyst weight used was 1.5g. The products were analyzed with the same GC used for benzene hydrogenation. The time on stream was only 30 minutes (Exploratory experiments indicated there was rapid deactivation for this reaction).

**5.4.2 Cyclohexanol decomposition**

The cyclohexanol dehydrogenation was performed on calcined and reduced samples of Ni/\(\alpha\)-Al\textsubscript{2}O\textsubscript{3}, reduced Ni/\(\gamma\)-Al\textsubscript{2}O\textsubscript{3} and reduced Ni/MgO, in a conventional glass reactor (10 mm id, fixed bed, down flow) operated at atmospheric pressure. Cyclohexanol was introduced with a pre calibrated syringe pump (at a flow rate of 3 mL hr\textsuperscript{-1}), and a flow of N\textsubscript{2} (20 mL min\textsuperscript{-1}) was maintained in the reactor by Bronkhaurst mass flow controller. The amount of catalyst was 0.8g. For the reactions on reduced catalysts, prior to the reaction the samples were reduced at atmospheric pressure with H\textsubscript{2} (flow rate 40 mL min\textsuperscript{-1}) at 500 °C for 4 hours. However, for Ni/MgO catalysts (Chapter 8) the reduction was done at higher temperature of 550 °C for 4 hours. The reaction was done at a temperature of 270 °C for Ni/\(\alpha\)-Al\textsubscript{2}O\textsubscript{3} and Ni/\(\gamma\)-Al\textsubscript{2}O\textsubscript{3} catalysts, and at 350 °C for Ni/MgO catalysts. The reaction was conducted for two hours and the integral conversion was measured. The liquid products were collected at the bottom of the reactor in an ice cooled trap.
Products were analysed after 30 minutes (to ensure mass balance) on a gas chromatograph (Chemito 8510) equipped with a carbowax column and flame ionization detector.

5.4.3 Reactions of n-butanal and hydrogen

The Ni/MgO samples (Chapter 8) were reduced in a flow of hydrogen (20 mL min\(^{-1}\)) prior to the reaction at 550 °C for four hours. It was then cooled to the reaction temperature. n-Butanal was injected with the precalibrated syringe pump at a flow rate of 3.2 mL h\(^{-1}\). Catalyst weight was fixed as 1.0g. The exploratory experiments indicated that a higher contact time increases the trimers. Increase of temperature resulted in formation of light fractions (mainly C3’s). The reaction conditions selected were WHSV = 2.78 hr\(^{-1}\), mol ratio [H\(_2\)]/[C\(_6\)H\(_6\)] = 6 (H\(_2\) flow = 80 mL min\(^{-1}\)); temperature = 150 °C, and time on stream (TOS) = 45 minutes. The outlet of the reactor was connected to a condenser followed by ice trap. The condenser was circulated with a super cooled water-ethylene glycol mixture (70-30) and the ice trap was filled with sodium chloride and crushed ice. The condensed products were analyzed by a gas chromatograph (Chemito 8510) equipped with a 15% carbowax (on DMDS) column (1/8”, 12 ft) and flame ionization detector. The temperature conditions of the GC were

Carrier gas N\(_2\) pressure = 0.8 bar; injector temperature = 210 °C; detector temperature = 260 °C; oven programme = 90 °C (for 8 minutes) — 2 °C min\(^{-1}\) to 120 °C — stay at 120 °C (10 minutes) — 5 °C min\(^{-1}\) to 180 °C — stay at 180 °C (10 minutes).

Occasionally the products were identified on a GC-MS (Shimadzu, Model – QP2010, equipped with universal capillary column).
References


…….*…….