CATALYST SYNTHESIS AND ANALYSIS

(Ni,W,Cu) supported on kieselguhr catalyst, earlier described for hydrogenolysis of sucrose[82] was used for the present investigation.

6.1 Catalyst Synthesis:

The synthesis of this catalyst is briefly described below:

A slurry of 178.4 gm nickel nitrate, 3.82 gm cupric nitrate and 40 gm kieselguhr in 200 ml distilled water, was digested for 15 min. at 80°C with constant stirring. A milky suspension of 13 gm. tungstic acid and 180 ml. conc. ammonium hydroxide, heated on a steam bath, was then added to this slurry over a period of 30 min., and thereafter digested for an hour at 80°C.

After digestion, a solution of 60.2 gm anhydrous sodium carbonate in 150 ml distilled water, was added over a period of 30 min. at 80°C. After further digestion for 30 min. at 90°C, the green catalyst slurry was filtered and was washed with two litre of hot distilled water to remove any free nickel present in it. Absence of nickel was confirmed by lack of appearance of even slightest pink colour, when a little amount of ammonia and 1% alcoholic solution of dimethyl glyoxime were added to the washings. The green catalyst thus obtained, was then dried under vacuum at 120°-130°C and was ground to pass a 200 mesh screen. The wt. % composition of the catalyst given by its chemical analysis is shown in table 6.1.

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>31.5</td>
</tr>
<tr>
<td>Tungsten</td>
<td>11.2</td>
</tr>
<tr>
<td>Copper</td>
<td>1.2</td>
</tr>
</tbody>
</table>
6.2 **Electron microscopy of the catalyst**:  

The coprecipitated and the reduced catalysts were examined under **JEOL, JSM-8408** scanning electron microscope. Scanning electron micrographs of these catalysts are shown in Figs. 6.1 - 6.4. Unreduced catalyst is seen in Fig. 6.1 to contain about 15 μM size round clusters of smaller particles of about 4 μM size. These clusters are mixed with about 20 μM long rod shaped particles. The unreduced catalyst also contains small number of square disc type particles (Fig.6.2) of size approximately 20 μM. On reduction the morphology of the particles changes. The clusters are broken and approximately 10 μM long rectangular particles (Fig.6.3) are formed. Formation of some flower like clusters of petal shaped particles of about 1μM size are also seen in Fig. 6.4.

X-ray spectra of the unreduced catalyst, obtained using EDAX attachment in scanning electron microscope, is shown in Fig. 6.5. The spectra confirms the presence of nickel, tungsten and copper in the catalyst. Approximate analysis of these components (Table 6.2) obtained using EDAX attachment matches closely with the chemical analysis given in Table 6.1.

**TABLE 6.2**

Approximate analysis of catalyst's constituents using EDAX attachment in scanning electron microscope.

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>30.7</td>
</tr>
<tr>
<td>Tungsten</td>
<td>11.7</td>
</tr>
<tr>
<td>Copper</td>
<td>1.5</td>
</tr>
</tbody>
</table>

6.3 **Chemical analysis of Ni, Cu and W in the catalyst**:  

Gravimetric method was used for catalyst analysis.
Fig. 6.1: Scanning electron micrograph of unreduced catalyst showing long rod shaped particles.
Fig. 6.2: Scanning electron micrograph of unreduced catalyst showing square disc type particles.
Fig. 6.3: Scanning electron micrograph of reduced catalyst showing long rectangular particles.
Fig. 6.4: Scanning electron micrograph of reduced catalyst showing petal shaped particles.
Fig. 6.5: X-ray spectra of un-reduced (Ni, W, Cu)/kieselguhr catalyst.
Prepared catalyst & filtrates obtained during the synthesis were analysed for amounts of copper, nickel and tungsten. Sum total of amount of these components in the catalyst and filtrate should be equal to the amounts originally taken for synthesis. This provides a check for the accuracy of the analysis.

(i) Gravimetric analysis of the catalyst:

One gram of the catalyst was mixed with 20 ml conc. HCl and 5 ml. conc. HNO₃ in a beaker and was digested for 2 hours. After digestion, the contents were evaporated to get a dry residue. This was stirred vigorously with 50 ml distilled water. The slurry so obtained was filtered and the residue was again digested in 20 ml conc. HCl and 5 ml conc. HNO₃ for 2 hours. It was completely evaporated to obtain a dry residue, which was further stirred with 50 ml distilled water. The slurry so obtained was filtered again.

This procedure of obtaining residue, its acid digestion, complete evaporation and stirring with distilled water was repeated four times, twice with cold water and remaining with hot water. All the solutions obtained from each acid treatment and residue washing were collected and were eventually evaporated to 100 ml. This solution was used to analyse copper and nickel while the residue was used for tungsten analysis.

(a) Analysis of Copper:

The above solution was acidified slightly by few drops of dilute HCl. 25 ml of freshly prepared ammonium bisulfite solution (prepared by diluting 10 ml of ammonium
bisulfite with 100 ml distilled water) was added to this to reduce Cu(II) to Cu(I) as per following reaction.

\[
2\text{Cu}^{2+} + \text{HSO}_3^- + \text{H}_2\text{O} \rightarrow 2\text{Cu}^+ + \text{HSO}_4^- + 2\text{H}^+ \quad (6.1)
\]

The resulting solution was diluted with 150-200 ml distilled water and was heated nearly to boiling. 10 ml of 10% freshly prepared ammonium thiocyanate solution (prepared by dissolving its 10 gm in 100 ml distilled water) was then slowly added under constant stirring. The excess of ammonium thiocyanate reagent should be avoided since a large excess increases the solubility of Cu(I) thiocyanate due to formation of a complex thiocyanate ion.

\[
\text{Cu}^+ + \text{SCN}^- \rightarrow \text{CuSCN} \quad (6.2)
\]

At this stage, copper was precipitated in the form of copper thiocyanate (CuSCN). The precipitate was white and mother liquor was colourless and was smelling slightly ammonical. The precipitate was allowed to stand for 2-3 hours, preferably over night. It was then filtered in a weighed gooch crucible G-4 and washed 10-15 times with a cold solution, prepared by mixing 1 ml of 10% solution of ammonium thiocyanate and 5-6 drops of ammonium - bisulfite solution in every 100 ml distilled water, to prevent any oxidation of Cu(I) salt. Finally the precipitate was washed with 20% alcohol to remove ammonium thiocyanate and then dried at 110°-120° to constant weight.

(b) Analysis of Nickel:

After analysing copper, all the filtrates and washings were collected in a beaker and were heated to reduce the volume
to about 100-150 ml. This was allowed to cool before 20 ml. of conc. HNO₃ and 15 ml conc. HCl were added under stirring. The acidified solution was evaporated slowly and cautiously to avoid bumping. Thus destroying the excess of ammonium thiocyanate, used in copper analysis. After reduction of volume to 25 ml, 1 ml conc. H₂SO₄ is added slowly and the contents were heated until white fumes ceased to be formed. This destroys all HNO₃.

The residual portion was now allowed to cool down and mixed with 5 ml dilute HCl and 150 ml distilled water. The solution was then rendered faintly ammonical before adding 50 ml solution of 1% dimethyl glyoxime reagent, prepared by dissolving 1 gm. of the reagent in 100 ml absolute alcohol. At this stage red precipitate of nickel complex [Ni(C₄H₇O₂N₂)₂] was formed as per reaction (6.3).

\[
\text{Ni}^{2+} + \text{CH}_3 - \text{C} = \text{NOH} \quad \rightarrow \quad \text{CH}_3 - \text{C} = \text{NOH}
\]

or \( \text{Ni} (\text{C}_4\text{H}_7\text{O}_2\text{N}_2)_2 \)

Nickel dimethyl glyoximate (brick red ppt.)
The precipitate was filtered under vacuum in a weighed G-4 gooch crucible, washed with excess cold water until the filtrate was free from Ni$^{2+}$ particles and then dried at 100-105°C to constant weight. Amount of nickel was calculated by considering nickel equivalent to that of nickel complex.

(c) **Analysis of Tungsten**

The precipitate collected after the acid digestion of catalyst, was taken in a beaker. Sodium hydroxide solution was added to it and pH was maintained between 7-8 using dilute acetic acid or dilute sodium hydroxide. The volume was made to 250 ml with distilled water. The solution was then heated nearly to boiling, and a saturated solution of crystalline barium chloride in 10 ml distilled water was added dropwise with constant stirring. The white suspension formed, was allowed to cool down to room temperature. After 3 hours, white suspension was filtered using a porcelain filtering crucible under vacuum. It was washed with cold water to remove chloride ions completely and dried at about 750 to 800°C to a constant weight. The dried white precipitate was weighed as Barium tungstate (BaWO$_4$).

(ii) **Gravimetric analysis of the filtrate collected after catalyst washing**

Total volume of the filtrate and washings, collected after catalyst preparation was measured. Its 50 ml was used to analyse copper and nickel by acidifying and adding freshly prepared ammonium bisulfite solution and following the procedure
described above for the catalyst. After the analysis of copper and nickel, filtrates and washings were collected in a beaker and their pH was adjusted between 7-8 with the help of dilute acetic acid and dilute sodium hydroxide. The volume was then increased to 250 ml by adding distilled water and tungsten was analysed as Barium tungstate, following the same procedure as discussed above for the catalyst.

(iii) Sample Calculations:

In one of the analysis following results were obtained:

(a) Analysis of Cu, Ni, and W from catalyst

Weight of catalyst taken for analysis = 1.0 gm.

Copper

wt. of empty gooch crucible = 22.2671 gm.
wt. of gooch crucible + Cu complex = 22.2902 gm.

Thus,

wt. of Cu complex (CuSCN) = 0.0231 gm.

And

0.0231 gm CuSCN is equivalent to 0.0121 gm copper.

Nickel

wt. of empty gooch crucible = 31.5568 gm.
wt. of gooch crucible + Ni Complex = 33.1058 gm.

Thus,

wt. of Ni Complex \([\text{Ni(C}_4\text{H}_7\text{O}_2\text{N}_2]_2\) = 1.5490 gm.

And

1.5490 gm \([\text{Ni(C}_4\text{H}_7\text{O}_2\text{N}_2]_2\) is equivalent to 0.3147 gm nickel.
Tungsten

wt. of empty gooch crucible = 32.8430 gm.
wt. of silica crucible + BaWO$_4$ = 33.0778 gm.

Thus,

wt. of BaWO$_4$ = 0.2348 gm

And

0.2348 gm BaWO$_4$ is equivalent to 0.1121 gm tungsten.

Thus in 1 gm catalyst,

Copper = 0.0121 gm
Nickel = 0.3147 gm.
Tungsten = 0.1121 gm

Hence % composition of the catalyst is,

Copper = 1.2%
Nickel = 31.5%
Tungsten = 11.2%

As total catalyst formed = 70 gm

Thus Total 70 gm catalyst contains-

Copper = 0.8449 gm
Nickel = 22.0290 gm.
Tungsten = 7.8470 gm.

(b) Analysis of Cu, Ni and W from filtrate

Volume of filtrate taken for analysis = 50 ml.

Copper -

wt. of empty gooch crucible = 31.3362 gm.
wt. of gooch crucible + CuSCN = 31.3426 gm.
Thus,

wt. of CuSCN = 0.0064 gm.

And

0.0064 gm CuSCN is equivalent to 0.0034 gm copper.

Nickel

wt. of empty gooch crucible = 31.1225 gm.
wt. of gooch crucible Ni(C\textsubscript{4}H\textsubscript{7}O\textsubscript{2}N\textsubscript{2})\textsubscript{2} = 32.6104 gm.

Thus,

wt. of Ni(C\textsubscript{4}H\textsubscript{7}O\textsubscript{2}N\textsubscript{2})\textsubscript{2} = 1.4879 gm.

And

1.4879 gm Ni(C\textsubscript{4}H\textsubscript{7}O\textsubscript{2}N\textsubscript{2})\textsubscript{2} is equivalent to 0.3022 gm nickel.

Tungsten

wt. of empty silica crucible = 37.4164 gm.
wt. of silica crucible + BaWO\textsubscript{4} = 37.4929 gm.

Thus,

wt. of BaWO\textsubscript{4} = 0.0765 gm.

And

0.0765 gm BaWO\textsubscript{4} is equivalent 0.0365 gm tungsten

Thus in 50 ml filtrate.

Copper = 0.0034 gm
Nickel = 0.3022 gm
Tungsten = 0.0365 gm.

As total volume of filtrate = 2315 ml.

Thus,

total wt. of Cu in filtrate = 0.1549 gm,
total wt. of Ni in filtrate = 13.9919 gm,
total wt. of W in filtrate = 1.68995 gm.
Analysed amounts of Cu, Ni, and W may be counter checked as-

\[ \text{total Cu used} = \text{Cu in the catalyst} + \text{Cu in the washings}. \]
\[ \text{total Ni used} = \text{Ni in the catalyst} + \text{Ni in the washings}. \]
\[ \text{total W used} = \text{W in the catalyst} + \text{W in the washings}. \]

178.4 gm nickel nitrate, 3.82 gm cupric nitrate and 13 gm tungstic acid contain 36.0286 gm nickel, 1.0051 gm copper and 9.5659 gm tungsten respectively.

Now by analysis -

- Copper in the catalyst = 0.8449 gm.
- Copper in the filtrate = 0.1549 gm.
- Total copper analysed = 0.9998 gm.
- Copper taken for catalyst preparation = 1.0051 gm
- % error = 0.53

And,

- Nickel in the catalyst = 22.0290 gm.
- Nickel in the filtrate = 13.9919 gm.
- Total nickel analysed = 36.0209 gm.
- Nickel taken for catalyst preparation = 36.0286 gm.
- % error = 0.02

Similarly,

- Tungsten in the catalyst = 7.8470 gm.
- Tungsten in the filtrate = 1.68995 gm.
- Total tungsten analysed = 9.5369 gm.
- Tungsten taken for catalyst preparation = 9.5659 gm.
- % error = 0.3

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