A direct correlation between nitrogen chemisorption and ammonia synthesis activity of ruthenium catalysts supported on carbon covered alumina (CCA)\textsuperscript{1}

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Nitrogen chemisorption uptakes determined at atmospheric pressure (740 torr) at various temperatures on singly (Cs) and doubly (Cs + Ba) promoted Ru catalysts supported on carbon covered alumina (CCA) have been found to correlate well with the ammonia synthesis activities at atmospheric pressure at the corresponding temperatures.

Aika \textsuperscript{1} et al., have done pioneering work on the preparation of highly active supported and promoted ruthenium catalysts. Rao \textsuperscript{5} et al. have shown that carbon covered alumina (CCA) acts as a better support than active carbon for ruthenium catalysts. Choice of a support and promoters is aimed at increasing the dispersion of ruthenium on the support\textsuperscript{6} and the dissociative chemisorption of nitrogen on ruthenium which is the rate determining step in ammonia synthesis. Rao \textsuperscript{6} et al. have shown that addition of Ba prior to the addition of Ru and Cs to CCA improves Ru dispersion over that of Cs promoted catalyst and brings down the temperature of maximum activity of the catalyst. Addition of Ba is thought to create a more favourable surface structure of Ru for the chemisorption of nitrogen compared to Cs promoted catalyst.

In the present work nitrogen chemisorption is studied on the reduced Cs-Ru/CCA and Cs-Ru-Ba/CCA catalysts in the temperature range from 250°C to 400°C. It is shown that nitrogen chemisorption uptakes at 740 torr pressure correlate very well with the ammonia synthesis activities of these catalysts determined at the same temperatures.

\textbf{Experimental}

Two catalysts, Cs Ru/CCA (catalyst-1) and Cs-Ru-Ba/CCA (catalyst-2) were prepared by the stepwise impregnation method\textsuperscript{6}. The support, CCA was prepared by the pyrolysis of ethylene on a commercial $\gamma$-Al$_2$O$_3$ (Harshaw, Al-3996, BET, S.A. 204 m$^2$ g$^{-1}$) following a procedure reported by Vissers \textit{et al.}\textsuperscript{8}. The weight ratios of the components of the catalysts were maintained at 8.0:51:100 (Ru:Cs:CCA) and 8.0:51:5:100 (Ru:Cs:Ba:CCA).

The Ru dispersions of the two catalysts were calculated from the irreversible hydrogen uptakes measured at 25°C on reduced catalysts in a conventional adsorption unit\textsuperscript{8}. Steady state ammonia synthesis activities of these catalysts were determined in a glass micro-reactor with the synthesis gas ($3H_2+N_2$) under atmospheric pressure in the temperature range 250-400°C. Further details of the method of preparation of the catalysts and their evaluation are given elsewhere\textsuperscript{5}.

The high vacuum system employed for hydrogen chemisorption measurements was also used to generate nitrogen chemisorption isotherms on these catalysts at different temperatures. Prior to \textit{N}_2 adsorption measurement each sample (4g) was reduced at 400°C in \textit{H}_2 at a flow rate of 101 h$^{-1}$ till it was free of chloride or nitrate as judged by testing the vent gases with AgNO$_3$ solution or Nessler’s reagent. The sample was then evacuated at 10$^{-6}$ torr pressure at 400°C for 2 h. Then \textit{N}_2 chemisorption was studied on the catalyst at different temperatures. An equilibration period of one hour was found to be sufficient for achieving equilibrium in \textit{N}_2 adsorption at each point.

\textbf{Results and discussion}

The \textit{N}_2 chemisorption isotherms of catalyst-1 and catalyst-2 resembled those reported earlier for similar catalysts\textsuperscript{10}. These isotherms are flat at pressures above 600 torr at all the temperatures, indicating that the catalysts are saturated with nitrogen at high pressures. The \textit{N}_2 uptakes taken from \textit{N}_2 chemisorption isotherms at 740 torr pressure, \textit{NH}_3 synthesis activities (% v/v), Ru dispersions, metal areas and crystallite sizes for the two catalysts are given in Table 1. Catalysts-1 and 2 have exhibited the highest ammonia synthesis activities at 300°C and 275°C respectively. They have also adsorbed maximum amounts of nitrogen at 740 torr at these temperatures. Their \textit{N}_2 uptakes at 740 torr are plotted against their ammonia synthesis activities at the corresponding temperatures in Fig. 1.
Table 1—Ru dispersions, crystallite sizes, N2 uptakes and NH3 synthesis activities of Ru catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% Ru dispersion</th>
<th>Crystallite size, Å</th>
<th>N2 uptakes (μmoles g⁻¹) at</th>
<th>NH3 synthesis activities (%) v/v</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>area, m² g⁻¹</td>
<td></td>
<td>250°C</td>
<td>275°C</td>
</tr>
<tr>
<td>Catalyst-1 (Cs-Ru/CCA)</td>
<td>41.0</td>
<td>11.2</td>
<td>b 10.50</td>
<td>27.00</td>
</tr>
<tr>
<td>Catalyst-2 (Cs-Ru-Ba/CCA)</td>
<td>51.2</td>
<td>13.5</td>
<td>c 0.12</td>
<td>0.45</td>
</tr>
</tbody>
</table>

* Determined according to ref. 8.

Fig. 1—Correlation between N2 uptakes at 740 torr and NH3 synthesis activities of ruthenium catalysts [O, catalyst-1 (Cs-Ru/CCA); Δ, catalyst-2 (Cs-Ru-Ba/CCA); a, 250°C; b, 275°C; c, 300°C; d, 350°C; e, 400°C]

The linear plots in Fig. 1 show that the ammonia synthesis activities of the two catalysts vary proportionately with N2 uptakes required to saturate the ruthenium surface of the catalysts. This gives the inference that the fraction of the total N2 uptake responsible for the activity of the catalyst changes proportionately with the total N2 uptake at different temperatures of adsorption.

It is also clear from the data in Table 1 that though the activity values of catalyst-2 are higher up to its temperature of maximum activity compared to those of catalyst-1, the N2 uptake values are not as large as those of catalyst-1 though Ru dispersion has increased from 41.0% to 51.2%. This leads one to the logical conclusion that Ba addition enhances the intrinsic activity of Ru sites to create more number of activated nitrogen atoms on Cs-Ru-Ba/CCA catalyst. Lowering down the temperature of maximum activity from 300°C [Cs-Ru (CCA)] to 275°C should be attributed to the formation of highly active surface structure of ruthenium by deposition of barium on the acidic carbon coated alumina. Aika et al.11 have found that Ba is the most efficient promoter among the alkaline earth metals for Ru/active carbon catalysts for ammonia synthesis.

Yet another example of formation of highly active ruthenium surface is provided by Aika et al.4. They have found that the deposition of rare earth oxides La2O3, Ce2O3 and Sm2O3 reduces Ru dispersion whereas Cs2O does not reduce the same on Ru/Al2O3 catalyst. Inspite of decrease in Ru dispersion only 1-3 rare earth atoms per Ru atom are found to be enough to promote ammonia synthesis activity of Ru catalyst to the same extent as 10 atoms of Cs per Ru atoms. It is clearly established that electron donation to Ru surface from a support or a promoter is generally the most important factor for activation of N2 over Ru surface. In the case of rare earth oxide promoted catalysts, it is probably the interface between the promoter particles and the Ru surface that adsorbs large number of nitrogen molecules and activates them for ammonia synthesis.

References