

Structure sensitive nitrogen chemisorption on supported ruthenium catalysts[†]

S Khaja Masthan*, K S Rama Rao,
P S Sai Prasad & P Kanta Rao

Catalysis Section, Indian Institute of Chemical Technology,
Hyderabad 500 007, India

Received 21 October 1991; revised and accepted
10 February 1992

Nitrogen chemisorption is studied on promoted and unpromoted supported ruthenium catalysts as a function of both temperature and pressure. Ru/carbon covered alumina (CCA) catalyst does not chemisorb nitrogen at all the temperatures. Addition of promoters enhances the nitrogen chemisorption capacity of the catalysts (Cs-Ru/CCA and Cs-Ru-Ba/CCA) remarkably at and above 250°C. The chemisorption isotherms are characterized by three well defined adsorption steps. These adsorption steps are attributed to the structure sensitive chemisorption of nitrogen on the three low Miller index planes of ruthenium, (101), (100) and (001).

Ammonia synthesis over metal catalysts is shown to be highly structure sensitive by many investigators¹⁻⁴. It is well known that dissociative nitrogen chemisorption is the rate determining step in ammonia synthesis. On conventional Fe catalysts it has been shown that the synthesis gas mixture with a H₂/N₂ mole ratio of 2.5 instead of the reaction stoichiometric mole ratio of 3.0, would produce higher yields of ammonia over the catalyst^{5,6}. This is attributed to the higher concentration of chemisorbed nitrogen as a result of lower concentration of chemisorbed hydrogen. Promoted ruthenium catalysts exhibit much higher activity than the conventional Fe catalysts⁷. The ammonia synthesis activity of ruthenium catalysts is found to be influenced by the support and also by the promoter⁸⁻¹⁰. Recently carbon covered aluminas (CCA) are proved to be much superior supports for ruthenium than the conventional supports like active carbon and alumina¹¹. In the present communication the results of a study of nitrogen chemisorption on Ru/CCA (wt. ratio 10:100), Cs-Ru/CCA (51:7.7:100) and Cs-Ru-Ba/CCA (51:7.7:5:100) catalysts as a function of both temperature and pressure are presented. Inspired

by the fact that dissociative nitrogen chemisorption is the rate determining step in ammonia synthesis, these studies are carried out with a view to get information on the influence of temperature and the morphological structure of ruthenium on the nature of chemisorption on these catalysts.

Experimental

Three catalysts Ru/CCA (Catalyst 1), Cs-Ru/CCA (Catalyst 2), and Cs-Ru-Ba/CCA (Catalyst 3) were prepared by the stepwise impregnation and reduction method. CsNO₃ (Fluka Chemie) and RuCl₃.3H₂O (Aldrich, USA) were used as precursors for Cs and Ru respectively. The details of the method of preparation of the catalysts were given in a previous publication¹¹. Carbon covered alumina (CCA) support was prepared by the pyrolysis of ethylene (Matheson, USA) in N₂ (IOLAR-1, India) at 600°C over commercial γ -Al₂O₃ (Harshaw, Al-3996 R, 18/25 BSS mesh)¹¹. The flow rates of ethylene and nitrogen were 2 ml min⁻¹ and 15 ml min⁻¹ respectively per gram of alumina. The procedure followed was similar to that of Vissers *et al.*¹².

3-4 g of each catalyst were taken for nitrogen chemisorption and hydrogen chemisorption studies. The catalysts were reduced at 400°C in H₂ at a flow rate of 10 l h⁻¹ till they were free from chloride or nitrate (as judged by testing the exit gases with AgNO₃ or with Nessler's reagent), thoroughly degassed at 10⁻⁶ torr pressure and hydrogen chemisorption was studied on the reduced catalysts at 25°C in a conventional gas adsorption unit. The catalysts were again treated with H₂ at 400°C for 20 h and degassed at 10⁻⁶ torr pressure. Nitrogen chemisorption was studied on these catalysts in the temperature range from 250°C to 400°C in the same way as hydrogen chemisorption as a function of pressure upto one atmosphere. An equilibration period of one hour was found to be sufficient to attain equilibrium for each adsorption point. Two nitrogen chemisorption experiments were intercepted by hydrogen treatment at 400°C and degassing at 10⁻⁶ torr pressure in order to remove nitrogen chemisorbed strongly on the catalyst surface.

Results and discussion

It was observed that catalyst 1 (Ru/CCA) without promoter did not adsorb any measurable quantity of

nitrogen at all the temperatures. This catalyst exhibited very low activity in this temperature range¹¹. The catalysts 2 and 3 (with promoters) did not chemisorb nitrogen and did not exhibit ammonia synthesis activity at lower temperatures upto 200°C. Addition of the promoters Cs and Ba to catalyst 1 was observed to enhance the adsorption capacity and activity of the catalysts only at and above 250°C. The results indicate the importance of electron donation by the promoter to the metal and the back donation of Ru *d* electrons to the antibonding orbital of nitrogen molecule. Aika *et al.*⁸ have attributed the inertness of Ru/AC (or Ru/CCA) to the drift of Ru *d* electrons to the electron deficient graphite lattice of the support. The nitrogen chemisorption isotherms of the promoted catalysts 2 and 3 are presented in Figs 1 and 2. The results of the ammonia synthesis activity studies of these catalysts have been published elsewhere^{13,14}. It is clear from Figs 1 and 2 that the N₂ chemisorption isotherms of these catalysts contain three well defined adsorption steps in them. The three steps in nitrogen chemisorption do not show up at 400°C because of the small amount of nitrogen chemisorption on both the catalysts.

The highest N₂ uptake of 43 $\mu\text{mol g}^{-1}$ was measured on Cs-Ru/CCA catalyst at 350°C and at a pressure of 740 torr (Fig.1). Nitrogen chemisorption was found to increase with rise in temperature upto 350°C and decrease on further rise in temperature. The increase in nitrogen chemisorption with rise in temperature should be attributed to the promotional effect of temperature on the electron donation by the promoter to the metal and also on the electron donation by the metal to nitrogen molecule. Maximum electron transition seems to occur at 350°C. It is clear that temperature has a detrimental effect on the adsorption of nitrogen above 350°C.

Nitrogen chemisorption isotherms are not reported on Fe and Ru catalysts in the literature. Isotopic nitrogen exchange transient response studies on Ru catalysts^{15,16} have clearly shown that a major part of adsorbed nitrogen is in the form of activated nitrogen atoms under reaction conditions. Aika and Ozaki¹⁷ have studied nitrogen adsorption as a function of time on K-Ru/AC catalysts and have carried out IR studies of nitrogen adsorbed on these catalysts^{18,19}. They found that the equilibrium nitrogen chemisorption increased proportionately with K loading on the catalyst. It was observed that potassium decreased the vibrational frequency of N $\equiv$ N bond on the catalyst surface.

The three steps in the N₂ chemisorption iso-

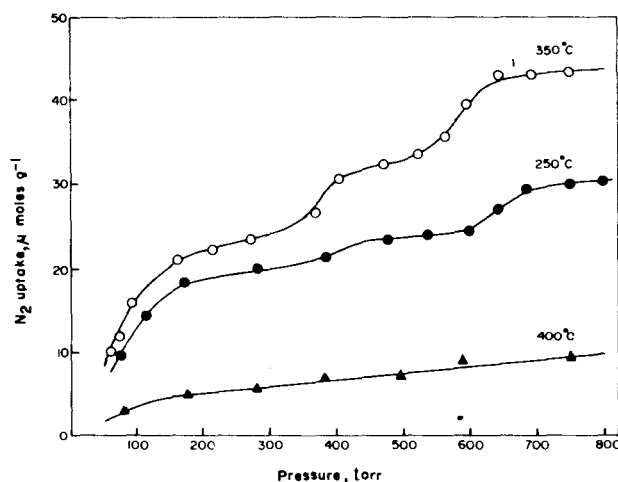


Fig. 1—Nitrogen chemisorption isotherms of Cs-Ru/CCA catalyst at different temperatures ● 250°C; ○ 350°C; ▲ 400°C

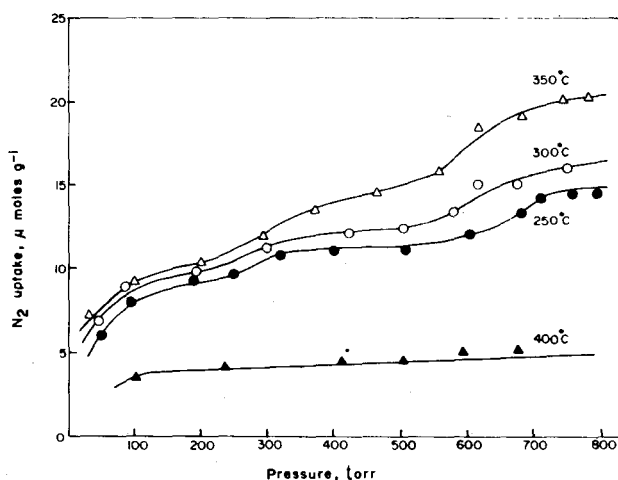


Fig. 2—Nitrogen chemisorption isotherms of Cs-Ru-Ba/CCA catalyst at different temperatures ● 250°C; ○ 300°C; △ 350°C; ▲ 400°C

therms would certainly indicate the heterogeneity of ruthenium surface in the catalysts. Structure sensitivity of nitrogen chemisorption and ammonia synthesis was very well demonstrated on Fe single crystal surfaces. N₂ chemisorption rates and NH₃ synthesis rates were found to decrease in the order: (111) > (110) > (100) for the three low Miller index planes of iron^{1,20}. The Fe(111) crystal plane has a less dense and more open structure than the other two crystal planes. Very recently Strongin and Somorjai³ have demonstrated that on mild treatment with NH₃ at 400°C the less active crystal faces (110) and (100) get transformed into the more active crystal plane (111).

The present experimental results and the information on Fe crystal planes in the literature suggest that the three low Miller index planes of Ru, (101),

(100) and (001) also play a prominent role in chemisorption of nitrogen and ammonia synthesis. Therefore, the three adsorption steps in N_2 chemisorption isotherms on these catalysts can certainly be attributed to the structure sensitive nitrogen chemisorption on the three Ru crystal planes.

Transmission electron microscopic studies of ruthenium catalysts derived from $RuCl_3$ and supported on SiO_2 and MgO carried out by Datye *et al.*²¹ provide an indirect support to the results of nitrogen chemisorption studies on ruthenium catalysts. They have observed that Ru particles in the catalysts with Ru loadings below 1 wt% are small and spherical in shape. Ru particles in the catalysts with Ru loadings above 1 wt% assume ellipsoidal shapes with diameters above 2 nm. These hexagonal platelets have well developed facets of ruthenium (101), (100) and (001).

Buglass *et al.*²² have carried out transition electron microscopic studies and ammonia synthesis over active carbon supported Ru catalysts with constant loading of the promoter KNO_3 . They have observed that tiny Ru crystallites with well defined faces are surrounded by small islands of the promoter and the turnover frequency of ammonia synthesis increased with Ru loading. This leads to the conclusion that TOF of ammonia synthesis increases with increase in Ru crystallite size and hence that Ru crystal faces play a prominent role in ammonia synthesis. Very recently Masthan *et al.*¹⁴ have invoked the structure sensitivity of Ru crystal planes to explain the hysteresis phenomenon observed during ammonia synthesis over these catalysts. They have suggested that the more dense and presumably less active crystal planes (100) and (001) get transformed into less dense and more active crystal plane (101) which has open structure like that of Fe(111)

under the influence of nitrogen and ammonia under reaction conditions. So it can be concluded that the three nitrogen adsorption steps undoubtedly demonstrate the structure sensitivity of nitrogen chemisorption on the three dominant crystal faces of ruthenium on supported ruthenium catalysts.

References

- 1 Spencer N D, Schoonmaker K C & Somorjai G A, *J Catal*, 74 (1982) 129.
- 2 Dumesic J A, Topsoe H, Khammouma S & Boudart M, *J Catal*, 37 (1975) 503.
- 3 Richard M A & Vanderspur T H, *J Catal*, 94 (1985) 563.
- 4 Strongin D R & Somorjai G A, *J Catal*, 118 (1989) 99.
- 5 Nielsen A, *Advances in catalysis*, Vol.5 (Academic Press, New York) 1953, p 30.
- 6 Reddy K V & Hussain A, *Ind Eng Chem Process Des Dev*, 21 (1982) 359.
- 7 Aika K & Kakegawa T, *Catalysis Today*, 10 (1991) 73.
- 8 Aika K, Hori H & Ozaki A, *J Catal*, 27 (1972) 424.
- 9 Aika K, Shimazaki K, Hattori Y, Ohya A, Ohshima S, Shirota K & Ozaki A, *J Catal*, 92 (1985) 296.
- 10 Aika K, Ohya A, Ozaki A, Inoue Y & Yasumori I, *J Catal*, 92 (1985) 305.
- 11 Rama Rao K S, Kanta Rao P, Masthan S K, Kaluschnaya L & Shur V B, *Appl Catal*, 62 (1990) L19.
- 12 Vissers J P R, Mercx F P M, Bouwens S M A M, de Beer V H J & Prins R, *J Catal*, 114 (1988) 291.
- 13 Rama Rao K S, Khaja Masthan S, Sai Prasad P S & Kanta Rao P, *Appl Catal*, 73 (1991) L1.
- 14 Khaja Masthan S, Sai Prasad P S, Rama Rao K S & Kanta Rao P, *J mol Catal*, 67 (1991) L1.
- 15 Urabe K, Aika K & Ozaki A, *J Catal*, 32 (1974) 108.
- 16 Urabe K, Aika K & Ozaki A, *J Catal*, 42 (1976) 197.
- 17 Aika K & Ozaki A, *J Catal*, 35 (1974) 61.
- 18 Oh-Kita M, Midorikawa H, Aika K & Ozaki A, *J Catal*, 70 (1981) 384.
- 19 Oh-Kita M, Aika K, Urabe K & Ozaki A, *J Catal*, 44 (1976) 460.
- 20 Bozso F, Ertl G & Weiss M, *J Catal*, 50 (1977) 519.
- 21 Datye A K, Logan A D & Long N J, *J Catal*, 109 (1988) 76.
- 22 Buglass J G, Tennison S R & Parkinson G M, *Catal Today*, 7 (1990) 209.