

Hysteresis during ammonia synthesis over promoted ruthenium catalysts supported on carbon-covered alumina*



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Dissociative chemisorption of nitrogen is the rate-determining step in the synthesis of ammonia. The nitrogen molecule donates a pair of electrons to the empty d-orbitals of the metal catalyst, which in turn donates the d-electrons to the antibonding orbitals of the nitrogen [1, 2]. The strength of adsorption and the extent of dissociation of nitrogen depend presumably on the extent of back-donation of the electrons from metal to nitrogen. Aika *et al.* [3-8] and various other investigators [9-12] have carried out extensive work on Ru catalysts using various supports and promoters in order to obtain better ammonia synthesis activity at atmospheric pressure. Very recently, it has been found that the addition of alkali ionic promoters, Cs and K, and some alkaline earth metals such as Ba [8], to the Ru supported on active carbon form effective catalysts.

There has been renewed interest in identifying novel promoters and supports which increase the electron density on the metal. As a part of this process, the authors have recently studied the synthesis reaction on Cs-Ru and Cs-Ru-Ba catalysts supported on carbon-covered alumina and have reported the influence of the support and the Ba addition to it on the steady state activity [12, 15]. In the present study the activity of the catalysts with increasing and decreasing reaction temperature has been determined. During these temperature cycles, a rate hysteresis is observed on these catalysts, just as Richard and Vanderspurt [13] observed on their triply-promoted Fe catalyst at 30 and 90 atm.

Carbon-covered alumina (CCA) 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). 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.* [14]. The carbon

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content (17 wt.%) of this support was determined on a CHN-600 carbon analyser (Leco Corp., USA).

Unpromoted Ru/CCA catalyst was prepared by impregnating the support (CCA) with aqueous $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (Aldrich Chemicals, USA) solution followed by evaporation of excess water and drying at 110 °C in an oven overnight. For preparation of the cesium-promoted catalyst (Cs-Ru/CCA, Catalyst-1), the above catalyst was reduced in a stream of hydrogen at 400 °C, which was attained over a period of 3 h, until such time as it was free from chloride, as judged by testing the vent gas with AgNO_3 solution. The reduced catalyst was impregnated in aqueous CsNO_3 (Fluka Chemie) solution followed by drying at 110 °C. For preparing the Ba added catalyst (Cs-Ru-Ba/CCA, Catalyst-2), the CCA support was first impregnated with aqueous $\text{Ba}(\text{NO}_3)_2$ (Rechem Pvt.Ltd., India) solution followed by drying at 110 °C and reduction at 400 °C. The other components Ru and Cs were deposited following the procedure described above. The weight ratio of the components was fixed at Cs:Ru:CCA = 51:7.7:100 for Catalyst-1 and at Cs:Ru:Ba:CCA = 51:7.7:5:100 for Catalyst-2.

Ru dispersion on these catalysts was determined from the irreversible hydrogen uptakes measured at 25 °C on reduced catalysts in a conventional volumetric adsorption apparatus. The details of the procedure are described elsewhere [16]. Ammonia synthesis activities of these catalysts were evaluated in a glass microreactor operating at atmospheric pressure at different temperatures in the range 225–400 °C.

Prior to the activity measurements, the catalysts were reduced in a H_2 stream at a flow rate of 10 l h^{-1} at 400 °C which was attained gradually over a period of 3 h. The complete reduction of the catalyst was confirmed by testing the vent gas with Nessler's reagent for NH_3 originating from NO_3^- ion. The synthesis gas ($\text{N}_2 + 3\text{H}_2$, IOLAR-1, India) was further purified through deoxo and molecular sieve towers to ensure that the oxygen concentration in the inlet stream was less than 2 ppm. Its flow rate was maintained at 10 l h^{-1} . The weight of the catalyst ($\sim 4 \text{ g}$) was fixed such that it gave a Ru content of 0.195 g.

Estimation of the NH_3 concentration was carried out by bubbling the vent gas through a known volume of a standard H_2SO_4 (0.01 N) solution till the methyl orange indicator changed colour from red to yellow. The excess NH_3 dissolved was determined by back-titration with the same acid solution. The NH_3 concentration was determined initially at 2-min intervals. After confirming that the catalyst had attained the steady state, the reaction was further continued for 2 h, continuing the NH_3 analysis at 10-min intervals. Then the temperature was slowly raised to the next higher temperature over a period of 30 min and the procedure continued as described above. The steady state was attained within 5-10 min, depending on the reaction temperature. No change in the steady-state rate was observed after this period. After determining the rate at 400 °C, the catalyst was cooled to the next lower temperature within a period of 30 minutes and the outlet concentration of NH_3 was determined again. Steady-state activities of the catalysts during

the decreasing temperature regime were noted at the corresponding temperatures of the increasing temperature regime.

Two pairs of curves A and B in Fig. 1 give the steady state NH_3 concentrations over Catalyst-1 and Catalyst-2 respectively during the upward and downward temperature changes. It can be observed from this figure that the steady-state rate is higher during the decreasing temperature regime compared to that of the increasing temperature regime. After completing one cycle, if the catalyst was not allowed to cool below 225 °C and a second cycle with increasing temperature followed, the activity followed the upper curve (Fig. 1A, curve b; Fig. 1B, curve d). However, if the catalyst was cooled to room temperature, kept for 24 h and the activity measured with the increasing temperature, the activity followed the lower curve (Fig. 1A, curve a; Fig. 1B, curve c). The same observations were made for a number of cycles. The data are not included in the figures for the sake of clarity.

An important observation, however, is a shift in the temperature of maximum activity (300 °C to 275 °C) with the addition of Ba to Catalyst-1. The turnover frequencies of ammonia synthesis over the two catalysts were calculated based on the irreversible hydrogen uptakes. At the temperature of maximum activity (300 °C), the TOF values of Catalyst-1 were 9.56×10^{-4}

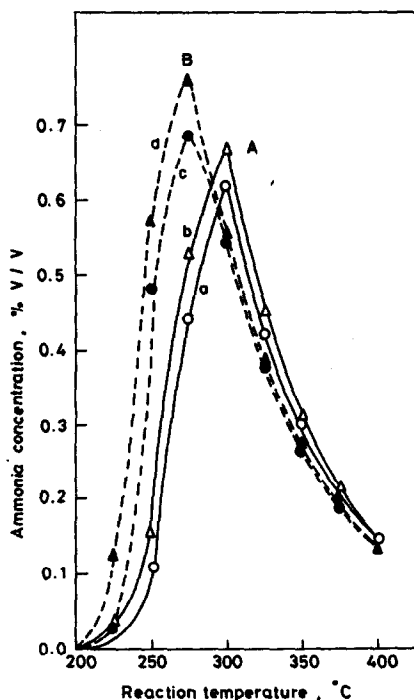


Fig. 1. Hysteresis during ammonia synthesis over promoted Ru/CCA catalysts. (A) Cs-Ru/CCA (—): (○) increasing temperature, (△) decreasing temperature; (B) Cs-Ru-Ba/CCA (---): (●) increasing temperature, (▲) decreasing temperature; (a)–(d) see text.

S^{-1} and $10.27 \times 10^{-4} S^{-1}$ during increasing and decreasing temperature regimes respectively. The TOF values for Catalyst-2 obtained at 275 °C were $8.98 \times 10^{-4} S^{-1}$ and $9.98 \times 10^{-4} S^{-1}$ respectively. However, the TOF values of Ba-added catalyst are higher up to 275 °C, the temperature of its maximum activity, compared to those of Catalyst-1. A decrease in TOF was observed beyond this temperature. Further details have been discussed in our earlier communication [15].

An explanation for the hysteresis behaviour of the ruthenium catalysts at atmospheric pressure could be deduced from the information available on Fe catalysts, based on the similarity of structure of the crystal faces of Fe and Ru. Ammonia synthesis activity of a pure iron catalyst varies with the exposed crystallographic planes. Surface reconstruction to a more open structure [17, 18] or transformation of the less active face to a more active face [13, 19] have been the reasons proposed. In the case of Ru, it may also be presumed that similar structural transformations or a change in the exposed crystallographic planes such as that of Fe are possible. The more dense and less active Ru(100) and Ru(001) crystal faces might be transformed into the more favourable open structure of Ru(101) during ammonia synthesis. Since the solid phase transformations take longer times compared to the gas phase, the transformed active phase may still exist during the decreasing temperature regime, thus giving higher activity. If the system was left for more than 24 h at room temperature, such that the solid regained its original form, the catalyst showed low activity following the lower curves of hysteresis. It was observed that neither catalyst showed any measurable activity even at 200 °C. From this it could be inferred that to retain the higher activity, after the hysteresis cycle, it is essential that the catalyst should be held at a temperature at which it exhibits its minimum activity.

The presence of O_2 or moisture as a cause of the hysteresis is ruled out, because there was no decrease in the steady-state activity over a period of 2-4 h. Further study on these catalysts is in progress which could possibly lead to a detailed explanation for the phenomenon of hysteresis.

Thus, the hysteresis phenomenon exhibited by the Ru surface under mild synthesis conditions clearly demonstrates the highly pronounced structure sensitivity of promoted Ru catalysts, in contrast to Fe catalysts which are active only under severe synthesis conditions.

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