Superbase Supported Ruthenium as a Superior Catalyst for the Isotopic Equilibration Reaction of Dinitrogen

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Turnover numbers for the isotopic equilibration reaction of dinitrogen over Ru–BeO–K, Ru–MgO–K, and Ru–CaO–K catalysts have been shown to be the highest so far reported.

The catalytic activity of the isotopic equilibration reaction of dinitrogen ($^{14}N_2 + {}^{15}N_2 = 2{}^{14}N^{15}N$) is fundamental to ammonia synthesis. It has been reported that both ammonia synthesis[1,2] and the isotopic equilibration of dinitrogen[3,4] over Ru are promoted by the addition of an alkali metal. It has been suggested that this is due to electron donation from the alkali metal to ruthenium.

An alkaline earth metal oxide with alkali metal, referred to as a superbase,[5] is considered to be richer in surface electrons than the system consisting of an acidic support [such as active carbon (AC) or alumina] with alkali metal. Thus a Ru–superbase catalyst is worthy of attention for the isotopic equilibration of dinitrogen.

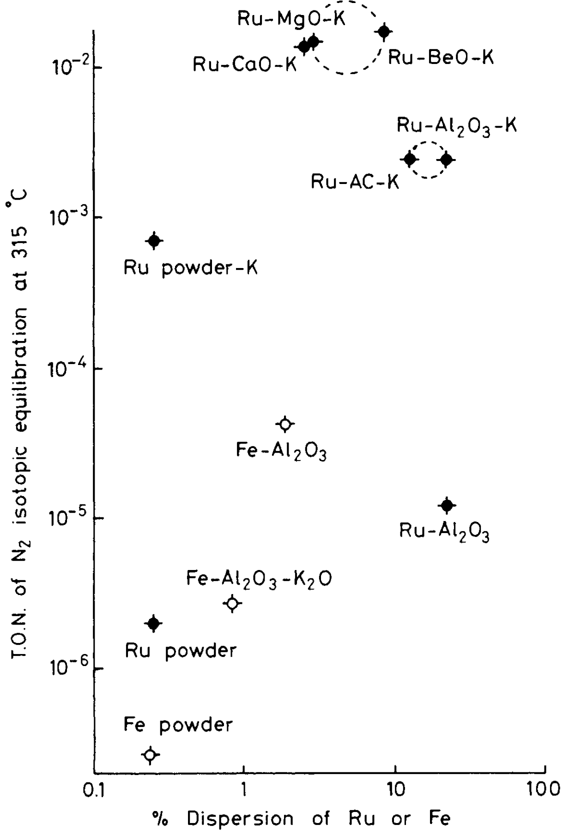

Figure 1. Turnover number (N_2 molecule/surface Ru atom/s) of N_2 isotopic equilibration at 315 °C under an N_2 pressure of 150 Torr as a function of the percentage dispersion of metal. Catalysts: 5.0 wt% Ru–BeO–K, 4.6 wt% Ru–MgO–K, 4.2 wt% Ru–CaO–K (this work); 0.50 wt% Ru–Al_2O_3, 0.50 wt% Ru–Al_2O_3–K (ref. 4); 5.0 wt% Ru–AC–K (ref. 3); Ru powder, Ru powder–K (ref. 4); Fe powder (ref. 6); Fe–2.3 wt% Al_2O_3 (ref. 7); Fe–4.9 wt% Al_2O_3–0.7 wt% K_2O (ref. 8).

2.00 g of *ca.* 5 wt% Ru–alkaline earth metal oxide were reduced and added to potassium metal as previously reported.[2,3] The reaction rate of the isotopic equilibration at a nitrogen pressure of 150 Torr (1 Torr = 133.3 N m^{-2}) over Ru–BeO–K, Ru–MgO–K, and Ru–CaO–K was measured and normalized as turnover number (T.O.N.) based on hydrogen chemisorption measurements at 25 °C. The results obtained at 315 °C are given as a function of the metal dispersion in Figure 1, together with reported data on Ru catalysts.[3,4] The activation energy was found to be 24, 26, and 25 kcal/mol† for Ru–BeO–K, Ru–MgO–K, and Ru–CaO–K, respectively. The T.O.N. of a superbase supported Ru catalyst is about one order higher than that of the best catalyst so far reported (Ru–AC–K, Ru–Al_2O_3–K). This superiority is thought to be due to effective electron donation by the superbase.

Figure 1 also gives data for iron catalysts which are active for ammonia synthesis.[6—8] It is interesting to note that the T.O.N. for this reaction on iron catalysts is quite low, although the activity for ammonia synthesis is comparable with Ru catalysts at lower temperatures.[1] This is probably because the reaction orders with respect to hydrogen pressure are negative in ammonia synthesis with Ru catalysts,[9] while those with iron catalysts are positive.[10] This demonstrates the activity of Ru for N–N bond rupture without the presence of hydrogen.

The superiority of Ru catalysts for ammonia synthesis[11] and the dinitrogen equilibration reaction[12] has already been shown, however, here we have demonstrated that a superbase as a support promotes N–N bond rupture considerably.

Received, 5th December 1983; Com. 1578

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† 1 kcal = 4.184 kJ.