Infrared Spectra of Adsorbed Dinitrogen on Alkali Metal-promoted Transition Metal–Alumina Catalyst

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Summary I.r. absorption peaks of dinitrogen on Ru–, Rh–, and Re–Al_2O_3 catalysts promoted by Na or K, in which form N_2 can readily react with H_2 to form NH_3, are observed at 2020—2040 cm^{-1}.

DINITROGEN can combine with some metallic surface or metal complexes to give adducts, most of which can be observed by i.r. methods. A large number of these have been reported since the earlier work by Eischens *et al.*[1] on metallic surfaces and Yamamoto *et al.*[2] on metal complexes. However, it has not been reported that i.r.-observable dinitrogen reacts with 'dihydrogen' to form ammonia, although the reaction of N_2, combined in a metal complex, with protons of HCl to form NH_3 or N_2H_4 has been reported.[3]

We have reported that the addition of alkali metal to a transition-metal surface activates N_2 as shown by synthesis of ammonia and the isotopic equilibration of N_2.[4] We report the observation of the i.r. spectrum of N_2 adsorbed on the catalyst system at moderate temperatures (170—350 °C), and that subsequent reaction with H_2 at above 230 °C gives ammonia.

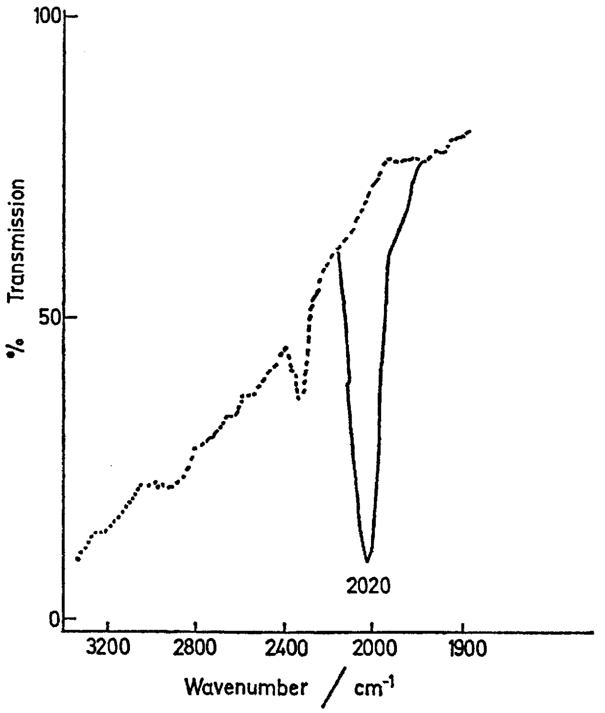

FIGURE. I.r. spectra of adsorbed dinitrogen on Ru–Al_2O_3–K at 25 °C: – – – background; ———, N_2 adsorbed.

The catalyst sample was prepared by impregnating 200 mg of alumina (Alon G) with aqueous transition-metal chloride, and then drying the product, which was pressed and reduced with H_2 with the temperatures increasing from 100 to 350 °C to give the transition-metal (1% w/w)–Al_2O_3 catalyst. (Reduction of Re catalyst might be incomplete at 350 °C). *Ca.* 20 mg of K or Na was then adsorbed ***in vacuo*** on to the catalyst, which was treated with He at 350 °C for 3 h, and finally with N_2 (200 Torr) at 350 °C for 3 h. The i.r. spectrum was then recorded at room temperature using a JASCO A2 spectrometer.

After reaction between N_2 and the catalyst, new broad and intense absorption peaks appeared at 2020 cm^{-1} for Ru–Al_2O_3–K, 2026—2030 cm^{-1} for Ru–Al_2O_3–Na, 2040 cm^{-1} for Rh–Al_2O_3–K, and 2024 cm^{-1} for Re–Al_2O_3–K (see Figure for the N_2–Ru–Al_2O_3–K system). Neither N_2 adsorption nor a new i.r. peak was observed for any of the transition-metal–alumina or alkali metal–alumina systems. On increasing the temperature of the reaction of N_2 with the Ru–Al_2O_3–K catalyst from 100 °C, the new i.r. peak appeared after reaction at 170 °C for 3 h, and its intensity increased with temperature up to 350 °C.

While the peak for N_2–Ru–Al_2O_3–K is close to the KN_3 absorption (2041 cm^{-1}),[5] the peak for N_2–Ru–Al_2O_3–Na is quite different from that for NaN_3 (2128 cm^{-1}). Thus the adsorbed nitrogen active in the i.r. does not seem to be the alkali metal azide, but rather dinitrogen itself.

The N_2 is so stable as to be unaffected by evacuation for 1 day or by introduction of air at room temperature. At *ca.* 100 °C the i.r. absorption is almost the same as that at room temperature. However, the i.r. absorption decreases after treatment with He at 350 °C for 1 h, possibly because of N_2 desorption. After the introduction of H_2 at 350 °C for 5 h, the i.r. peak almost disappears and NH_3 is formed simultaneously (mass spectrometry). Ammonia reacts with Ru–Al_2O_3–K to yield a similar peak (2040 cm^{-1}).

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