Infrared Spectra of Adsorbed Dinitrogen on Ruthenium Metal Supported on Alumina and Magnesium Oxide

Jun Kubota and Ken-ichi Aika*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta 4259, Midori-ku, Yokohama 227, Japan

Infrared spectra of adsorbed dinitrogen on Ru metal supported on Al_2O_3 and MgO are observed for the first time at 2214 cm^{-1} for Ru/Al_2O_3, at 2168 cm^{-1} for Ru/MgO and at 1910 cm^{-1} for Ru–CsOH/MgO.

Ruthenium is known to be the most active metal for activation of dinitrogen, when it is promoted by electron-donating compounds.[1,2] Ruthenium catalysts, thus, are considered as second generation ammonia synthesis catalysts after the iron catalysts.[3] It is generally accepted that the rate-determining step of ammonia synthesis is the dissociative adsorption of dinitrogen.[1] An adsorbed dinitrogen, if observable, might possibly be a precursor in the rate-determining step. Therefore, it is important to identify spectroscopically dinitrogen species coming from N_2 molecules on a Ru metal surface. There have been many infrared studies on dinitrogen adsorbed on various metals supported on oxides, for example Pt/SiO_2 (2230 cm^{-1}),[4] Rh/Al_2O_3 (2256 cm^{-1}),[5] Fe/MgO (2200 cm^{-1}),[6] Ni/SiO_2 (2202 cm^{-1})[7] and Co/Al_2O_3 (2214 cm^{-1}).[8] In these investigations, adsorbed dinitrogen on metals was obtained from gaseous N_2 directly[4,5,7,8] or through a decomposition of adsorbed NH_3.[6] We have recorded the infrared spectra of nitrogen species through N_2 that was activated on various Ru catalysts.[9–11] However, those bands assigned to adsorbed nitrogen species gave much smaller isotope shifts than the theoretical value, and those species were concluded to be adsorbed nitrogen species interacting strongly with alkali metals[10] or support oxides.[11] Thus, dinitrogen directly adsorbed on supported Ru metal has not yet been observed spectroscopically, although many Ru–dinitrogen complexes such as $[Ru(N_2)(NH_3)_5]Br_2$ (2118 cm^{-1})[12] and electron energy loss spectra of adsorbed N_2 on a Ru (001) single crystal[13] have been reported. Here, we report the first observation of the infrared absorption bands assigned to adsorbed N_2 on supported Ru metal by using Fourier transform infrared (FTIR) instruments and Cl-free Ru catalysts.

Cl-free Ru catalysts were prepared by impregnating γ-Al_2O_3 or MgO with $Ru_3(CO)_{12}$ in tetrahydrofuran solution followed by decomposition under vacuum at 673 K. Cs promoted catalysts were prepared by impregnating the supported Ru catalysts with $CsNO_3$ in aqueous solution. The pressed sample disk (20 mm diameter, *ca.* 40 mg) put in a quartz IR cell can be treated at temperatures between 140 and 1000 K. The cell is connected to a closed circulation vacuum system. Ru samples were pretreated at 673–873 K under 200 Torr H_2 for 12 h and evacuated at the same temperature for 1 h. For spectral measurements an FTIR spectrometer (Japan Spectroscopic Co. Ltd. model FT/IR-5300) was used with a triglycine sulphate detector with resolution of 2 cm^{-1} and the spectra were obtained by integration of 32–64 scans.

When 50 Torr of N_2 was introduced on 2 wt% Ru/Al_2O_3 and 2 wt% Ru/MgO at 300 K, broad peaks were observed around 2200 cm^{-1} as shown in Fig. 1. Corresponding peaks due to $^{15}N_2$ were observed in a lower frequency region as shown in Fig. 1. The isotope shifts of 71 cm^{-1} between $^{14}N_2$ and $^{15}N_2$ indicated that these bands were due to adsorbed N_2 [2200 $cm^{-1} \times (28/30)^{\frac{1}{2}} = 2125$ cm^{-1}]. No absorption was observed on Ru free Al_2O_3 or MgO samples and stronger absorption was observed on samples with higher Ru loading (*i.e.* 10 wt%). These facts suggest that the species which give the infrared peaks are chemisorbed N_2 on the Ru metal surface. Generally infrared absorption due to N_2 adsorbed on a metal surface has been observed at around 2200 cm^{-1} [4–8] Consequently, the absorption peak (2214 cm^{-1}) and the shoulder (2268 cm^{-1}) for Ru/Al_2O_3 and those (2168 cm^{-1}, 2150–2050 cm^{-1}) for Ru/MgO were assigned to N–N stretching of adsorbed N_2 on Ru surfaces with an on-top configuration.

Each spectrum is composed of two peaks, which might correspond to two kinds of adsorbed species of N_2 on the Ru atoms under different circumstances. The details will be published elsewhere. When CsOH promoter was applied to Ru/MgO, the main peak at 2168 cm^{-1} was decreased due to CsOH contamination, however, a new peak was observed at 1910 cm^{-1}, as shown in Fig. 1. The new peak was strongest when Cs/Ru mole ratio was 0.1 to 0.2. It is to be noted that the activity of nitrogen activation (NH_3 synthesis and isotopic equilibration of N_2) is higher on Ru–CsOH/MgO than Ru/MgO, and the least on Ru/Al_2O_3.[1,14] It has been suggested that a basic oxide donates more electrons to the Ru surface which causes a weakening of the N–N bond. The observed frequencies, 1910 cm^{-1} on Ru–CsOH/MgO, 2168 cm^{-1} and the shoulder at 2150–2050 cm^{-1} on Ru/MgO, 2214 cm^{-1} on Ru/Al_2O_3, correspond to the activity of NH_3 synthesis.

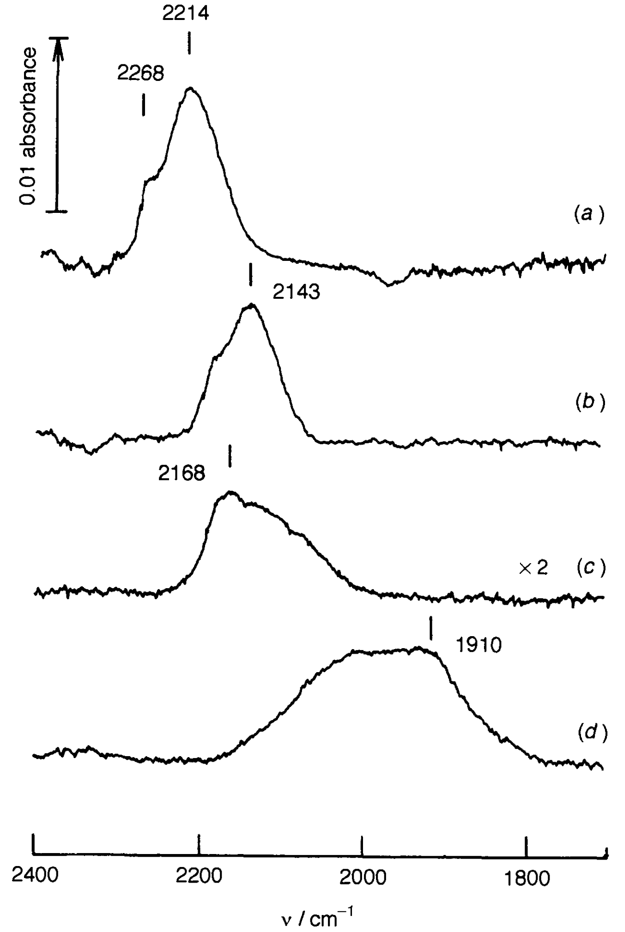

Fig. 1 FTIR spectra of adsorbed dinitrogen, on 2 wt% Ru/Al_2O_3 pretreated at 873 K; $^{14}N_2$ (*a*) and $^{15}N_2$ (*b*), and $^{14}N_2$ on 2 wt% Ru/MgO pretreated at 673 K (*c*). These spectra were obtained under 50 Torr on N_2 at 300 K. Spectrum (*d*) was obtained under 50 Torr $^{14}N_2$ at 160 K, on 2 wt% Ru–CsOH/MgO (Cs/Ru = 0.2 mole ratio) pretreated at 773 K.

In conclusion, adsorbed N_2 has been observed spectroscopically for the first time on supported Ru metal. The stretching frequency of N_2 was found to be influenced by the electronic state of Ru surface, which is closely related with the activity of NH_3 synthesis. Although the concentration and lifetime of adsorbed N_2 might be quite low and short under NH_3 synthesis conditions at higher temperatures, the species observed here could be a precursor in the rate-determining step.

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References

1 A. Ozaki and K. Aika, in *Catalysis-Science and Technology*, eds. J. R. Anderson and M. Boudart, Springer-Verlag, Berlin, 1981, vol. 1, p. 87.
2 A. Ohya, K. Aika and A. Ozaki, *J. Chem. Soc., Chem. Commun.*, 1984, 321.
3 Report article, in *Appl. Catal.*, 1991, **67**, N18.
4 T. A. Egerton and N. Sheppard, *J. Chem. Soc., Faraday Trans. 1*, 1974, **70**, 1357.
5 H. P. Wang and J. T. Yates, Jr., *J. Phys. Chem.*, 1984, **88**, 852.
6 T. Okawa, T. Onishi and K. Tamaru, *Z. Phy. Chem. N. F.*, 1977, **107**, 239.
7 R. P. Eischens and J. Jacknow, Proc. 3rd Int. Congr. Catal., Amsterdam, 1965, p. 627.
8 N. Kinoshita, K. Kido, K. Domen, K. Aika and T. Onishi, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 2269.
9 M. Oh-kita, K. Aika, K. Urabe and A. Ozaki, *J. Chem. Soc., Chem. Commun.*, 1975, 147.
10 K. Aika, H. Midorikawa and A. Ozaki, *J. Catal.*, 1982, **78**, 147.
11 K. Aika, H. Midorikawa and A. Ozaki, *J. Phys. Chem.*, 1982, **86**, 3263.
12 A. D. Allen and C. V. Senoff, *J. Chem. Soc., Chem. Commun.*, 1965, 621.
13 A. B. Axton, N. R. Avery, B. M. Toby and W. H. Weinberg, *J. Electron Spectrosc. Relat. Phenom.*, 1983, **29**, 181.
14 K. Aika, K. Shimazaki, Y. Hattori, A. Ohya, S. Ohshima, K. Shirota and A. Ozaki, *J. Catal.*, 1985, **92**, 296.