

## Infrared Absorption Spectra of Adsorbed Dinitrogen on Alkali-Promoted Ruthenium in the 500 $\text{cm}^{-1}$ Region

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An infrared band of chemisorbed nitrogen as well as of carbon monoxide was observed in the 500  $\text{cm}^{-1}$  region on Ru dispersed in a KBr matrix and promoted with K or Na. The band was unaffected by evacuation at room temperature, while it disappeared upon hydrogen treatment at 350°C, simultaneously forming ammonia. The band shift caused by the change from K to Na as well as the above features is in accord with the behavior of the 2020  $\text{cm}^{-1}$  band observed on Ru/Al<sub>2</sub>O<sub>3</sub>/K. Thus the band is assigned to the Ru-N stretching vibration of chemisorbed dinitrogen.

### INTRODUCTION

It is known that infrared absorption in the low-frequency region provides information concerning the metal-adsorbate bond which is important in elucidating the adsorbed state. An ir band at 2020  $\text{cm}^{-1}$  ascribable to N≡N stretching has been found on Ru/Al<sub>2</sub>O<sub>3</sub>/K (1). In view of the strong absorption at 2020  $\text{cm}^{-1}$ , a corresponding band for metal-N<sub>2</sub> can be expected in the low frequency region. Unfortunately, however, no absorption could be observed in the region below 1100  $\text{cm}^{-1}$  because of the absorption by alumina. We had to adopt some other support transparent for the low-frequency beam. After trials we found that potassium bromide could be used as a support for the dispersed ruthenium metal as will be shown in this paper.

### EXPERIMENTAL

Ruthenium metal dispersed in KBr was prepared by decomposition of a mixture of

potassium bromide and ruthenium ammine complex [Ru(NH<sub>3</sub>)<sub>5</sub>N<sub>2</sub>]Br<sub>2</sub> which was prepared after Allen *et al.* (2). The ammine complex was dissolved into a saturated aqueous solution of KBr and stirred for 1 day in a nitrogen atmosphere. The yellow solution was evaporated to dryness giving a purple material, followed by decomposition at 450°C in flowing hydrogen (3). The black powder of Ru-KBr was pressed into a disk under 600 kg/cm<sup>2</sup>. The infrared cell was the same as reported previously (1). The disk was treated with flowing hydrogen at 350°C for 10 hr, followed by evacuation at 350°C for 15 min and addition of alkali metal at 350°C. The added alkali metal was heated at 350°C for 5 hr in an atmosphere of helium to distribute it throughout the disk. The disk was then treated with nitrogen (200 Torr) at 350°C for 3 hr. The ir absorption measurements were carried out at room temperature using a JASCO A-2 spectrometer. The scanning speed was 12  $\text{cm}^{-1}/\text{min}$ .

## RESULTS

The background absorption of the sample disk shown in Fig. 1 allowed absorption measurements in the low-frequency region, while corresponding measurements in the high-frequency region were impossible because of the very small transmission. The performance of the sample disk was confirmed with adsorbed carbon monoxide on 5.4% (w/w) Ru/KBr. As shown in Fig. 2 an absorption band was found at 465 cm<sup>-1</sup>, the intensity of which increased with increase in carbon monoxide pressure and vanished upon evacuation at room temperature for 30 min. Since the band is close to the region reported on Pt (475–480 cm<sup>-1</sup>) (4–6) and Fe (500 cm<sup>-1</sup>) (7), it is reasonably assigned to the Ru–C stretching vibration.

An absorption band of nitrogen was found on 1.0% (w/w) Ru/KBr/0.5% (w/w) K at 520 cm<sup>-1</sup> with a half-width of 14 cm<sup>-1</sup> as shown in Fig. 3. The band intensity was unchanged after evacuation at room temperature for 12 hr, while the band disappeared after treatment with hydrogen (200 Torr) at 350°C for 7 hr, simultaneously giving ammonia in the liquid nitrogen trap attached to the circulating system. A separate experiment with isotopic nitrogen (<sup>15</sup>N 30%) on the same disk disclosed an isotope shift to 508–509 cm<sup>-1</sup>. When 0.3% (w/w) Na was added

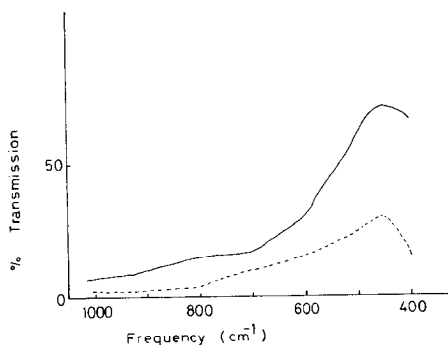


FIG. 1. Background absorption of the sample disk: (-----) 5.4% (w/w) Ru/KBr; (—) 1.0% (w/w) Ru/KBr/0.5% (w/w) K.

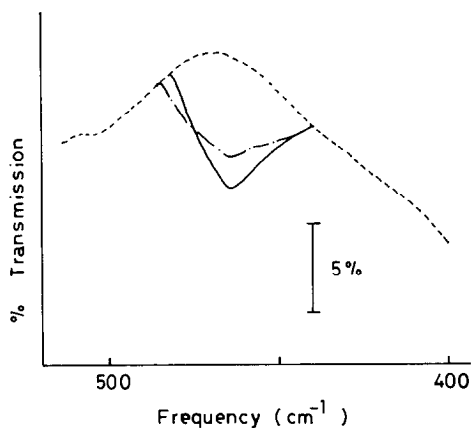


FIG. 2. Infrared spectra of carbon monoxide on 5.4% (w/w) Ru/KBr: (---) 3 Torr of CO; (—) 16 Torr of CO.

instead of K to 1.0% (w/w) Ru/KBr, the band was found at 505–510 cm<sup>-1</sup>.

## DISCUSSION

Since no hydrogen was present during the nitrogen treatment at 350°C, the band must be ascribed to a nitrogen species. The high stability of the band observed upon evacuation, as well as the formation of ammonia upon hydrogen treatment at 350°C, is in agreement with the behavior of the 2020 cm<sup>-1</sup> band observed on Ru/Al<sub>2</sub>O<sub>3</sub>/K, suggesting that both bands are assigned

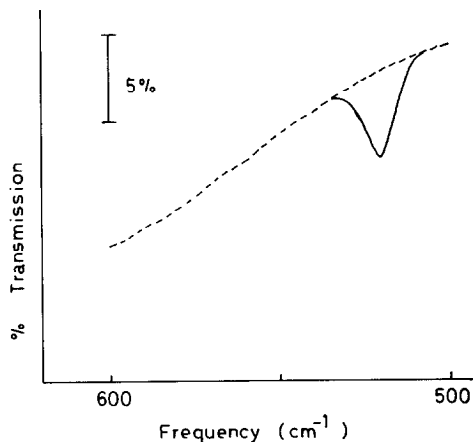


FIG. 3. Infrared spectra of dinitrogen chemisorbed on 1.0% (w/w) Ru/KBr/0.5% (w/w) K.

to the same species. Indeed a band at  $520\text{ cm}^{-1}$  is reasonable as the stretching frequency of Ru-N<sub>2</sub> (8). Analogous bands have been observed with Ru-N<sub>2</sub>L<sub>5</sub> ( $490\text{--}510\text{ cm}^{-1}$ ) (9) and [RuN<sub>2</sub>(NH<sub>3</sub>)<sub>5</sub>]<sup>2+</sup> ( $507\text{ cm}^{-1}$ ) (10). If nitrogen is dissociated to give a nitride, the band should appear near  $1000\text{ cm}^{-1}$  (11). Hence the band at  $520\text{ cm}^{-1}$  is assigned to the Ru-N stretching vibration of adsorbed dinitrogen. The observed isotope shift,  $11\text{--}12\text{ cm}^{-1}$ , is in fairly good agreement with the calculated value of  $15\text{ cm}^{-1}$  for Ru-<sup>15</sup>N.

Important information about the nature of adsorbed species arises from the band shift caused by the change of promotor from potassium to sodium, which suggests that the Ru-N<sub>2</sub> bond is weakened by the change. It is recalled that the  $2020\text{ cm}^{-1}$  band on Ru/Al<sub>2</sub>O<sub>3</sub>/K shifts to  $2026\text{--}2030\text{ cm}^{-1}$  on Ru/Al<sub>2</sub>O<sub>3</sub>/Na, indicating that the N≡N bond is strengthened by the change. Since the weakening of the Ru-N<sub>2</sub> bond should be compensated for by the strengthening of the N≡N bond, the above observations are consistent each other. It is

demonstrated in both cases that potassium addition gives rise to a weakening of the N≡N bond, thus activating dinitrogen molecule.

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