

Infrared Absorption Spectra of Adsorbed Dinitrogen on Ru-Al₂O₃-K below 2000 cm⁻¹

MOTOMU OH-KITA, HIDEO MIDORIKAWA, KEN-ICHI AIKA, AND ATSUMU OZAKI

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

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A new dinitrogen species is found by ir absorption at 1935 cm⁻¹ (Type B) when a dinitrogen species at 2020 cm⁻¹ (Type A) prepared from N₂ on Ru-Al₂O₃-K is treated with H₂ above 170°C or with NH₃ at 25°C, or when H₂-treated catalyst is treated with N₂ at 250°C. The Type B species is more reactive to H₂ or O₂ than the Type A species. Another ir band is found at around 1870 cm⁻¹ (Type C) when Type B species is evacuated at 200°C. Both species, B and C, are likely located on the surface, while the Type A species is in an adsorbed state. The Type C species is removed rapidly on introduction of H₂ or NH₃ at 25°C, probably by displacement. The very low wavenumber, the high sensitivity to gases, and the high stability to evacuation disclose the unique character of the Type C species.

INTRODUCTION

It has been shown that ruthenium is remarkably promoted by addition of potassium for catalytic activation of dinitrogen such as ammonia synthesis or isotopic equilibration (1, 2). A fairly large amount of nitrogen uptake by the Ru-K system has been found (3). In the case of Ru-Al₂O₃-K a strong ir absorption band ascribable to dinitrogen was observed at ca. 2020 cm⁻¹ (Type A) (4, 5). Although the adsorbed dinitrogen species can be hydrogenated to give ammonia (5), the rate of ammonia formation is much slower than that in the ammonia synthesis on the same catalyst (6), indicating that the ir-active dinitrogen species is not an intermediate of the ammonia synthesis. Thus the ir study was extended to throw light on the adsorbed species under the reaction condition. In this way two new ir bands ascribable to dinitrogen were found below the 2000-cm⁻¹ region. The present paper deals with the nature of the ir bands.

EXPERIMENTAL SECTION

Catalyst samples were 1.0, 2.0, and 5.0 wt% Ru on Al₂O₃ (Alon C). Catalyst prepara-

tion, hydrogen reduction, potassium addition, and nitrogen absorption as well as the ir absorption measurements were carried out using a previously described method (5). Treatment with gas was made by circulation through the *in situ* ir cell and liquid nitrogen trap. Infrared spectra were recorded using a [JASCO-A3] spectrometer at room temperature unless otherwise noted. When the ir measurements were made at elevated temperatures, the emission spectra were observable above 130°C. The reference beam was adjusted depending on the thickness of the wafer to give clear spectra. The thinner the wafer of Ru-Al₂O₃ (100 to 200 mg, 20 mm diameter) the stronger the ir absorption peak. The amount of potassium added was much larger than that of Ru resulting in potassium contents of the wafer in the range of 10 to 20 mg/wafer as reported previously (3). Atomic concentration of ¹⁵N in the samples used here was 92.8 or 99.3% for ¹⁵N₂, and 99.2% for ¹⁵NH₃. Figure 1 shows typical background spectra for Ru-Al₂O₃ after H₂ reduction (a) and Ru-Al₂O₃-K prepared in He atmosphere (b). Although a broad peak around 1900 cm⁻¹ was observed in (b), it disappeared after N₂ treatment at 300 to

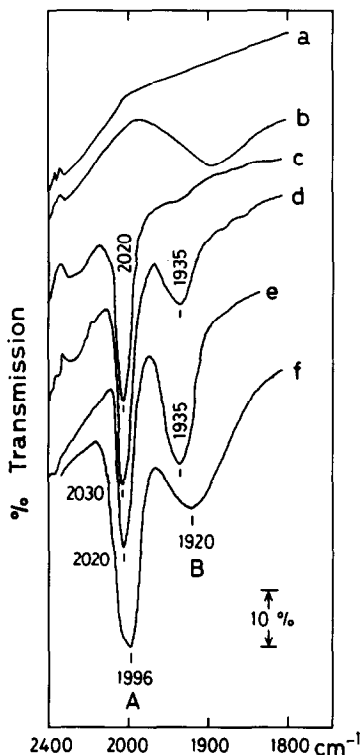


FIG. 1. Infrared spectra of 5% Ru-Al₂O₃ (a) and spectra of 5% Ru-Al₂O₃-K treated with gases at 300 to 350°C: (b) He (200 Torr); (c) N₂ (200 Torr); (d) N₂ + 3H₂ (200 Torr); (e) N₂ + 3D₂ (200 Torr); (f) ³⁰N₂ + 3H₂ (200 Torr).

350°C (c). A small band was occasionally observed at around 2350 cm⁻¹, caused by carbon dioxide in the atmosphere.

RESULTS

1. Appearance of 1935-cm⁻¹ Band (Type B)

After the 5% Ru-Al₂O₃-K was treated with N₂ at 310°C for 4 hr, one strong peak only (Fig. 1c) was observed at 2020 cm⁻¹, as reported previously. This band will be called Type A. When the catalyst wafer was treated with a N₂-3H₂ (or N₂-3D₂) mixture at 300°C giving ammonia, the ir measurement at room temperature gave a new band at 1935 cm⁻¹ irrespective of N₂-H₂ or N₂-D₂ (Figs. 1d,e) in addition to two bands at 3320 and 1563 cm⁻¹ (for N₂-H₂) ascribable to adsorbed ammonia. The 1935-

cm⁻¹ band will be called Type B. Those bands were observable even during the ammonia synthesis at 200°C, as is shown partly in Fig. 3a.

The identity of 1935-cm⁻¹ band was examined by using a ¹⁵N₂-3H₂ mixture. An isotope shift was observed (Fig. 1f) confirming that the absorption is due to a nitrogen-containing species. The wavenumber range indicates a dinitrogen species. The lower frequency suggests that the N≡N bond is more loosened in the Type B species than in the Type A species. An analogous treatment of 2% Ru-Al₂O₃-Na (instead of K) with a N₂-3H₂ mixture at 300°C resulted in the similar bands at 2030-2050 and 1950-1965 cm⁻¹.

2. Formation of the Type B Band by Hydrogen Treatment of Type A Species

Even when the catalyst was treated with N₂ only, a small band corresponding to Type B was occasionally observed as is shown in Fig. 2a. This might be caused by the presence of a small amount of hydrogen produced by reduction of surface hydroxyl with metallic potassium. Indeed a trace amount of ammonia was detected after the treatment with dinitrogen. When the Type A species was treated with a small amount

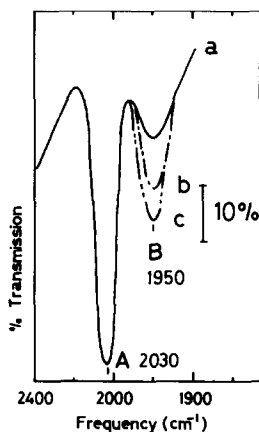


FIG. 2. Infrared spectra of 2% Ru-Al₂O₃-K: (a) treated with N₂ (200 Torr) at 350°C; (b) subsequently treated with H₂ (0.39 Torr) at 200°C for 3 hr; (c) further treated with H₂ (100 Torr) at 200°C for 1 hr.

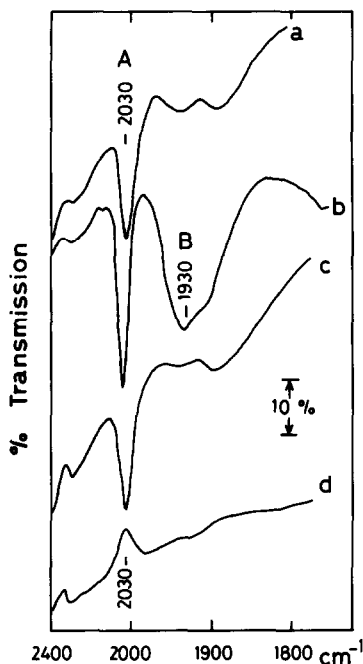


FIG. 3. Infrared spectra of 5% Ru-Al₂O₃-K: (a) during NH₃ synthesis from N₂ + 3H₂ (200 Torr) at 200°C; (b) when trapped NH₃ was released over the cooled catalyst at 25°C; (c) returned to the same condition as (a). Spectra (a), (c), and (d) were taken at 200°C. (d) is the emission spectra for (c) at 200°C.

of hydrogen (0.39 Torr) at 200°C for 3 hr, the Type B band observed at room temperature increased its intensity as is shown in Fig. 2b. A hydrogen pressure of 0.4 Torr was almost enough to give a maximum of the Type B band. (See Fig. 2c.)

There was another case to give the Type B band. After 5% Ru-Al₂O₃-K was treated with a circulating N₂-3H₂ mixture at 200°C to give ammonia trapped by liquid N₂, the spectra taken at 200°C gave two small bands at 1935 and 1895 cm⁻¹ in addition to the Type A band at 2030 cm⁻¹ as shown in Fig. 3a. When the catalyst was cooled to room temperature with the trapped ammonia released, an intense absorption at 1930 cm⁻¹ was found at room temperature (Fig. 3b).

3. Formation of a New Band below 1900 cm⁻¹ (Type C)

Two types of bands A and B were pre-

pared by N₂ treatment of 2% Ru-Al₂O₃-K at 350°C followed by H₂ treatment at 200°C, as shown in Fig. 4a. The catalyst was then evacuated at increasing temperature to examine the stability of two bands, although the temperature of evacuation was limited to 200°C above which evaporation of potassium caused trouble. A new band below 1900 cm⁻¹ was found after the evacuation with its intensity increasing with increase in the evacuation temperature from 25 to 100 and to 200°C. The relative intensity of the Type B band changed little up to 100°C and

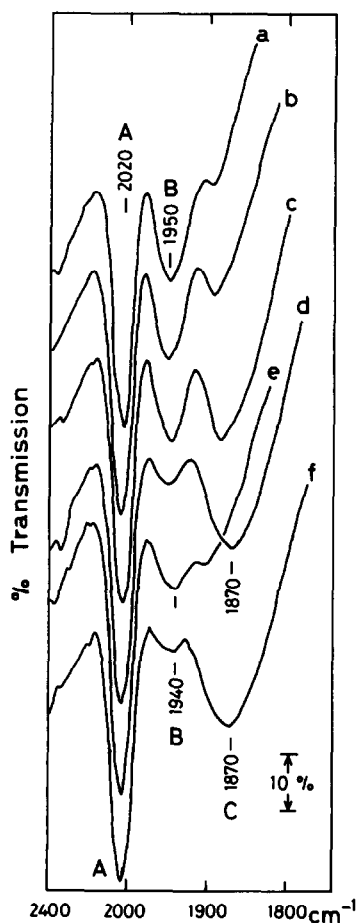


FIG. 4. Infrared spectra of 2% Ru-Al₂O₃-K treated with N₂ (200 Torr) at 350°C followed by H₂ treatment (200 Torr) at 200°C (a), and subsequent spectra after evacuation for 1 hr at 25°C (b), 100°C (c), and 200°C (d). (e) gives the spectra after introduction of 2.2 Torr of D₂ at 25°C, which was changed to (f) after evacuation at 200°C for 1 hr.

the evacuation at 200°C resulted in a substantial decrease in the Type B band accompanied by formation of a new broad band at 1870 cm⁻¹ as shown in Figs. 4b,c, and d. This new band will be called Type C.

Since the Type A band was unaffected by the evacuation, the Type B band is less stable than the Type A band. An analogous experiment with ¹⁵N₂ gave a shift of the Type C band to lower frequency at around 1860 cm⁻¹. The Type C band may be ascribed to a more activated dinitrogen species.

In order to study the nature of Type C species, a small amount of H₂ (or D₂) was introduced over the catalyst sample at room temperature. It was found that 2.2 Torr of D₂ resulted in substantial decrease of the Type C band without regenerating the Type B band (Figs. 4e and 5b), and that reevacuation at 200°C reproduced the Type C band (Fig. 4f). Analogous experiments using H₂ showed that the pressure of hydrogen required to remove the Type C band is

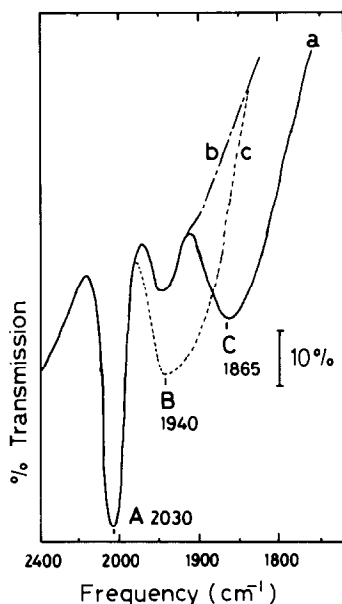


FIG. 5. Infrared spectra of 2% Ru-Al₂O₃-K treated with N₂ (200 Torr) at 350°C and H₂ (200 Torr) at 200°C followed by evacuation at 200°C (a), and subsequent spectra after introduction of either H₂ (0.5 Torr) (b) or NH₃ (1 Torr) (c) at 25°C.

TABLE 1

The Reactivity of Type C^a to Hydrogen

Run	Reactant	P (Torr)	Half-life ^b (sec)	Wavenumber Type C (cm ⁻¹)
1	H ₂	1.9	40	1880
2	H ₂	2.0	34	1880
3	D ₂	1.0	35	1870
4	D ₂	2.2	30	1890
5	D ₂	17.6	22.5	1880
6	D ₂	2.0	42.5	1880

^a Obtained on 2% Ru-Al₂O₃-K which was treated with N₂ at 350°C followed with H₂ treatment and evacuation at 200°C.

^b Half-value period of Type C exposed to H₂ at 25°C.

as small as about 0.5 Torr. The variation of Type C band intensity with time was recorded at a fixed wavenumber of 1870 to 1890 cm⁻¹ during the H₂ or D₂ treatment at 25°C. As summarized in Table 1, the half-life ranged from 22.5 to 42.5 sec, with a shorter period for higher hydrogen pressure, indicating a kinetic process associated with the disappearance. Since the Type C band was unaffected by introduction of N₂, the disappearance might be caused by a reaction of the Type C species with hydrogen to form ammonia. But no ammonia could be detected in the gas phase after the hydrogen treatment.

Since ammonia might be formed on introduction of H₂, the effect of ammonia on the Type C species was examined. NH₃, 1 Torr, was introduced on the Type C species at 25°C. As shown in Fig. 5c, ammonia also gives rise to the disappearance of the Type C band, while the Type B band appears as is the case with the ammonia treatment of the Type A species (Fig. 3).

4. Variation of A and B Bands by Hydrogen Treatment

In view of the high sensitivity of the Type C species to H₂, variation of the bands, A and B, with H₂ treatment was examined at increasing temperatures starting from the Type A species prepared on 2% Ru-Al₂O₃-

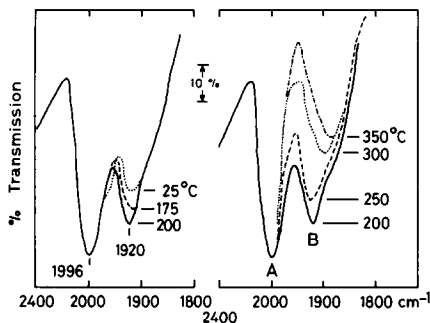


FIG. 6. Infrared spectra of 2% Ru-Al₂O₃-K treated with ³⁰N₂ (200 Torr) at 350°C followed by H₂ treatment (100 Torr) for 1 hr at 25, 175, 200, 250, 300, and 350°C.

K by ¹⁵N₂ treatment at 350°C. H₂, 100 Torr, was circulated for 1 hr at each temperature through the ir cell with a liquid nitrogen trap included in the circulation loop to confirm the ammonia formation. The rather high hydrogen pressure was adopted because of the known less reactivity of the Type A species. The ir measurements were made exclusively at room temperature after the treatments.

The variation of bands with the treatment temperature is shown in Fig. 6. The Type B band appears at around 1920 cm⁻¹ after the treatment even at 25°C and increases its intensity with increase in the treatment temperature up to 200°C, while decreases after treatments at higher temperature. Little change in the intensity of the Type A band is observed during the H₂ treatments, although it is decreased during a prolonged treatment at 350°C. It is clear that the Type B species formed by the interaction with H₂ is less stable than the Type A species. Although the peak top of the B band (for ³⁰N₂) shifts to below 1900 cm⁻¹ after the H₂ treatment at 350°C, the remaining band must be different from the Type C band which is readily removed by H₂ treatment at room temperature.

5. Relative Reactivities of Three Species against O₂

The two species A and B (Fig. 7a) were prepared by treatment of 5% Ru-Al₂O₃-K

with a N₂-3D₂ mixture at 350°C and subjected to a treatment with 20 Torr of O₂ at and above 25°C for ½ hr.

The Type B band was decreased significantly even at 25°C (Fig. 7b) and disappeared substantially at 65°C (Fig. 7c) and completely at 116°C (Fig. 7e). The Type A band was also decreased by the O₂ treatment, although the extent of decrease was much less than that of the Type B band at each treatment temperature. The higher reactivity of Type B species is again demonstrated. It was found that the decreases in A and B bands were accompanied by formation of a new band at 2160 cm⁻¹ that can be ascribed to adsorbed N₂O as seen in Fig. 7, while the details of N₂O formation will be reported separately (7).

On the other hand the Type C band was found to be removed rapidly on introduction of air at room temperature. Thus the reactivity sequence of the three species can

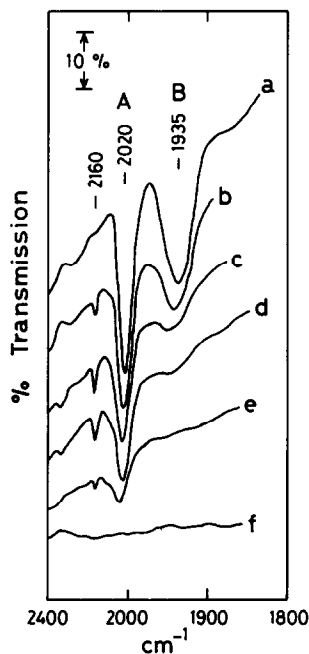


FIG. 7. Infrared spectra of 5% Ru-Al₂O₃-K treated with N₂ + 3D₂ (200 Torr) (a) and subsequent spectra after replacing N₂ + 3D₂ by 20 Torr of O₂ for 0.5 to 1 hr at 25°C (b), 65°C (c), 100°C (d), 116°C (e), and 190°C (f).

be assessed as

$$A < B \ll C$$

irrespective of the reacting gas H₂ or O₂.

DISCUSSION

The present results are summarized in Table 2 including previous results of the Type A band. The three species are ascribed to dinitrogen species in view of wavenumber range as well as isotope shift. The Type B band is formed in a wavenumber range of 1935 to 1950 cm⁻¹ for ¹⁴N₂ and 1915 to 1920 cm⁻¹ for ¹⁵N₂ by an interaction of sorbed dinitrogen with hydrogen, where the hydrogen atom may come from molecular hydrogen, adsorbed hydrogen, or ammonia. Since ammonia may be formed in the presence of hydrogen, it is difficult to identify the real species responsible for the formation of Type B species, whether hydrogen or ammonia. At any rate, however, in view of the higher reactivity of the type B species than that of Type A, which has been suggested to be formed in the bulk phase as an adsorbed species (8), the Type B species seems to be formed on the surface.

When the Type B species is formed on introduction of H₂ or NH₃ over the Type A species, a likely source of dinitrogen is the Type A species, because no dinitrogen is added in the experiment. Although it might be formed from an unknown species other than Type A, there is no positive indication for the other species. If Type B is formed from Type A, the little change in transmittance of the Type A band observed on the formation of Type B should be explained.

Some reasons may be given for this behavior. First, the very small transmittance at the Type A band can be hardly affected by concentration change. Second, the Type B species may have a larger extinction coefficient than the Type A species because of a more extensive polarization in the Type B species as suggested by the lower wavenumber. Third, the Type A species formed in an adsorbed phase may not be fully transparent to the ir beam reproducing the Type A species in the surface layer after the formation of Type B. Thus the Type A species can be the source of Type B.

The Type C band is formed in a wavenumber range of 1865 to 1890 cm⁻¹ for ¹⁴N₂ and 1860 to 1875 cm⁻¹ for ¹⁵N₂ by evacuation of the Type B species, accompanied by decrease in the intensity of Type B band. The Type C band is readily removed by hydrogen treatment even at 25°C without returning to the Type B species. Although a small increase in the Type B band is observed after the hydrogen treatment at 25°C (Fig. 4e), it is much weaker than that before the formation of Type C (Fig. 4a).

The disappearance of the Type C band on introduction of H₂ may be due to either displacement or reaction with H₂. It is known that the chemisorption of N₂ on the Ru-K or Ru-Al₂O₃-K is inhibited by competitive adsorption of hydrogen (9). Hydrogen may kick out the chemisorbed dinitrogen. The disappearance of the Type C band on introduction of NH₃ may be caused by hydrogen atom formed by its dissociative adsorption. It is also possible that NH₃ itself displaces the Type C species. Thus the disappearance can be accounted for by displacement. In fact no ammonia was detected after the hydrogen treatment.

Since the Type C band is formed by evacuation of Type B species at elevated temperature, it would be natural to suppose that something is removed from the Type B species resulting in the transformation of B

TABLE 2

Wavenumbers of N₂ on Ru-Al₂O₃-K (cm⁻¹)

Type	²⁸ N ₂	³⁰ N ₂	Difference
A ^a	2020-2030	1995-2000	25-30
B ^b	1935-1950	1915-1920	20-30
C ^c	1865-1890	1860-1875	5-15

^a Treated with N₂ at 350°C.

^b Treated with H₂ at 200°C.

^c Evacuated at 200°C.

to C. This suggestion is supported by the fact that the Type B species is stable in the presence of hydrogen even at 200°C. Most probably the Type B species is formed by an irreversible hydrogenolysis of an adsorbed dinitrogen species so that the adsorption site for Type B species is perturbed by a hydrogen atom. If this hydrogen atom is removed by evacuation, the Type B species should be converted to a more unstable form of dinitrogen that is consistent with the observed ready disappearance by hydrogen treatment at room temperature. The quick response to hydrogen indicates that the Type C species is formed on surface Ru. The Type C species is unique as the adsorbed dinitrogen in view of the highly activated state of dinitrogen strongly held by the surface as demonstrated by the stability at 200°C under vacuum. Such activation of dinitrogen must be associated with the effect of potassium.

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