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Infrared Active Adsorbed Nitrogen on Alkali Metal-Promoted Transition Metal–Alumina Catalyst

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An infrared band of chemisorbed nitrogen is observed at 2020 cm^{-1} on $Ru–Al_2O_3$-K catalyst which is active for the ammonia synthesis. Similar bands are observed on analogous catalysts with Rh and Re, and also with Na. This species is formed by the adsorption at above 200°C and disappears gradually on hydrogenation at above 260°C, resulting in the formation of ammonia, while the infrared band is ascribed to an undissociated form of adsorbed nitrogen. The large extinction coefficient observed suggests that the mode of adsorption is of end-on type. The heterogeneity of adsorption site is suggested on the basis of peak shift observed during adsorption and subsequent hydrogenation.

INTRODUCTION

Eischens and Jacknow (*1*) found an infrared spectra of adsorbed nitrogen on Ni. Since that time a number of infrared spectra of adsorbed nitrogen have been observed over metals; Ni (*2–4*), Pd (*2*), Pt (*2, 5*), Ir (*6*), Fe (*7*), and Co (*8*). Most of them, however, were readily desorbed by evacuation or displaced by hydrogen so that no ammonia could be formed from those adsorbed species, although the frequency of adsorbed nitrogen were generally shifted lower as compared with free nitrogen molecule, suggesting a loosening of $N{\equiv}N$ bond.

Potassium-promoted transition metals have been shown to be highly effective for the activation of nitrogen and adsorb a significant amount of nitrogen during ammonia synthesis (*9, 10*). The first object of present study was to elucidate the nature of adsorbed species of nitrogen by means of infrared absorption. It was found that a strong absorption band appeared near 2000 cm^{-1} when the catalyst was treated with nitrogen at 350°C (*11*). The nature of this absorption band has been examined and is reported in the present paper.

EXPERIMENTALS

Transition metal (1 wt%)–Al_2O_3 catalysts were prepared by impregnating Al_2O_3 (Alon C)[1] with aqueous transition metal chloride solution followed by drying on water-bath. The sample powder (ca. 200 mg) was pressed into a thin layer disk (20 mm in diameter) under 600 kg/cm^2. The *in situ* cell is shown in Fig. 1. It was made of Pyrex glass and installed in a circulating system. The disk was set on a supporting frame installed at one end of a regulating rod, which was movable through an O-ring. In this way the hydrogen reduction of disk as well as the addition of alkali metal could be performed outside the infrared beam path. The reduction was carried out with 200 Torr of circulating hydrogen at increasing temperatures from

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[1] Alon "G" reported in previous communication (*11*) was wrong.

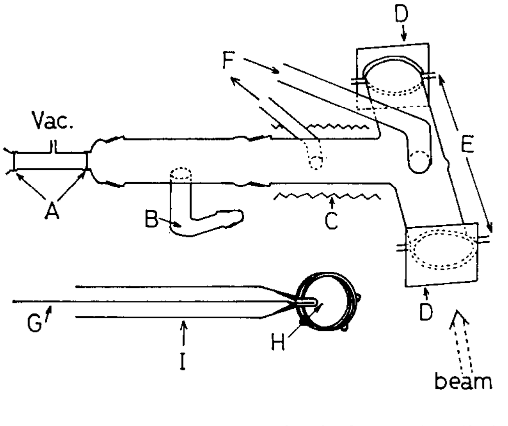

FIG. 1. Cell for infrared study. A, O-ring; B, alkali metal reservoir; C, ribbon heater; D, KBr window; E, cooling water; F, gas; G, thermocouple; H, supporting frame; I, regulating rod.

100 to 350°C. Subsequently the disk was moved to the alkali metal reservoir followed by evacuation of hydrogen. The alkali metal was evaporated *in vacuo* onto the disk followed by circulation of helium (200 Torr) at 350°C for 3~5 hr. Nitrogen was then introduced at room temperature and the disk was heated to desired temperature in the atmosphere of nitrogen of 200 Torr. The adsorption of nitrogen was carried out normally at 350°C for 3 hr. The infrared spectrum was then recorded at room temperature using a [JASCO A2] spectrometer. The amount of added potassium was determined by HCl titration of water extract of the disk.

RESULTS

Infrared Spectrum of Adsorbed Nitrogen

After adsorption of nitrogen ($^{14}N_2$; 200 Torr) at 350°C for 3 hr on Ru–Al_2O_3–K, the infrared spectrum was observed at room temperature as shown in Fig. 2. A sharp peak appears at 2020 cm^{-1}. The dotted line shows the infrared spectrum of heavy nitrogen (^{15}N; 92.8%) adsorbed on the same catalyst sample at 350°C and 50 Torr for 3 hr after evacuation of gas phase $^{14}N_2$ at room temperature for several hours. The previously adsorbed $^{14}N_2$ was replaced by $^{15}N_2$ resulting in the peak shift to 1996 ~1998 cm^{-1}. The isotopic peak was reproduced by $^{15}N_2$ adsorption on a fresh sample of Ru–Al_2O_3–K at 350°C.

It was confirmed that no such spectra could be obtained on Al_2O_3, Al_2O_3–Na, or Ru–Al_2O_3, while similar spectra were obtained on Rh– and Re–Al_2O_3–K and also on Ru–Al_2O_3–Na after the nitrogen adsorption at 350°C and 200 Torr for 3 hr. The reduction of Re catalyst with hydrogen at 350°C might be incomplete (*12*), while it could be further reduced during the treatment with potassium at 350°C. The frequencies of observed peaks are shown in Table 1. The change from potassium to sodium causes a peak shift of 6~10 cm^{-1} to higher frequency, while the changes from Ru to Rh and Re result in shifts of 20 and 4 cm^{-1}, respectively, also to higher frequency. It is to be noted that the peak shift was accompanied by decrease in the intensity of infrared absorption, i.e., the intensity decreases in the order K > Na, Ru > Rh > Re, which is in accordance with the activity sequence of metals in the activation of nitrogen (*10*).

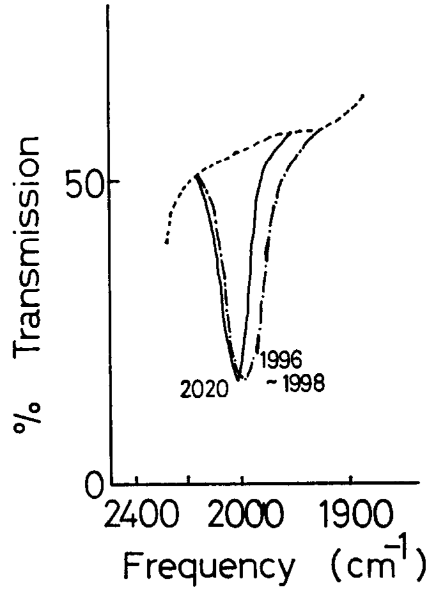

FIG. 2. Spectra of N_2 chemisorbed on Ru–Al_2O_3–K. ———, $^{14}N_2$; —·—·—, $^{15}N_2$.

TABLE 1

Infrared Frequencies of Chemisorbed N_2

Catalyst	Introduced gas	Peak of N_2 (cm^{-1})	Shift (cm^{-1})
$Ru\text{-}Al_2O_3\text{-}K$	$^{14}N_2$	2020	0
$Ru\text{-}Al_2O_3\text{-}K$	$^{15}N_2$	1996 ∼ 1998	−22 ∼ −24
$Ru\text{-}Al_2O_3\text{-}Na$	$^{14}N_2$	2026 ∼ 2030	+6 ∼ +10
$Rh\text{-}Al_2O_3\text{-}K$	$^{14}N_2$	2040	+20
$Re\text{-}Al_2O_3\text{-}K$	$^{14}N_2$	2024	+ 4

Effects of Various Treatments on the Infrared Band

(a) The intensity of the infrared band at 2020 cm^{-1} was unchanged after evacuation at room temperature for 24 hr.

(b) The gaseous nitrogen was replaced by helium at room temperature and the catalyst disk with adsorbed nitrogen was heated up to 350°C for 3 hr. The intensity of infrared band observed at room temperature decreased to about one-half the initial value, indicating the desorption of adsorbed nitrogen.

(c) When hydrogen gas (200 Torr) was introduced onto the adsorbed nitrogen replacing the gaseous nitrogen at room temperature and circulated at 350°C for 5 hr with liquid nitrogen trap, the infrared band disappeared, and ammonia was obtained in the liquid nitrogen trap. When nitrogen was readsorbed on this disk at 350°C for 3 hr, the infrared band was reproduced.

TABLE 2

Variation of Infrared Band with the Amount of Potassium Added

Frequency (cm^{-1})	log (I_0/I)	Half width of the bands (cm^{-1})	Amount of K (mg/disk)
—	—	—	2.4
2050	0.041	50	3.9
2040	0.278	100	7.9 ∼ 8.3
2020	0.425	110	11.2
2020	0.425	110	18.2

(d) When ammonia gas (60 Torr) was introduced and circulated at 350°C for 3 hr on a $Ru\text{–}Al_2O_3\text{–}K$ (K content was not determined), a broad infrared band appeared at around 2040 cm^{-1}, with an intensity of log $(I_0/I) = 0.04$.

To sum up the foregoing results, it may be concluded that the adsorbed nitrogen is stable at room temperature while it desorbs at 350°C and can be hydrogenated to ammonia.

Change of the Infrared Band with the Amount of Potassium

The infrared spectra of adsorbed nitrogen were obtained on $Ru\text{–}Al_2O_3$ with varied amounts of potassium. The amount of adsorbed nitrogen was determined by hydrogenating it to ammonia at 350°C for 7 hr. The results are summarized in Table 2. In the range of small amount of potassium, the infrared peak shifts from higher frequency to lower one, as the amount of potassium increases, while no more shift is observed with larger amounts of potassium. Both the optical density of the infrared band and the amount of adsorbed nitrogen increases with the amount of added potassium as illustrated in Fig. 3.

Change of the Infrared Band with the Extent of Adsorption

Since the frequency scale of Fig. 2 is different below and above 2000 cm^{-1}, the

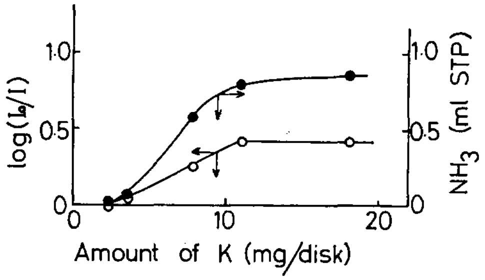

FIG. 3. Optical density of infrared band and amount of NH_3 formed on hydrogenation as a function of amount of potassium added.

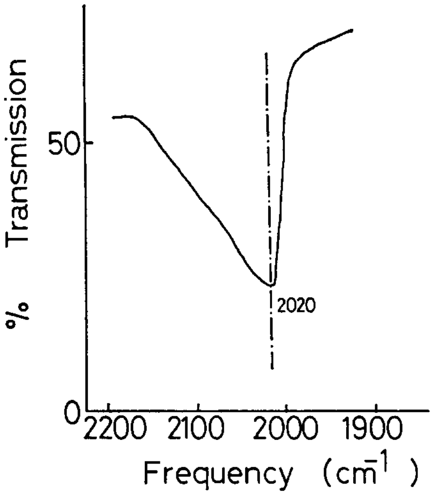

Fig. 4. Asymmetry in the infrared band at 2020 cm^{-1}.

real peak is unsymmetrical and broad with a half width of 100~110 cm^{-1}, as illustrated in Fig. 4, which is much larger than obtained by Eischens and Jacknow (*1*) over Ni at 30°C (a half width of 21 cm^{-1}). The nature of the infrared band was examined in terms of the extent of adsorption in the courses of adsorption and removal by hydrogenation made on a Ru–Al_2O_3–K (K 5.5 wt%).

Adsorption of nitrogen. After the addition of potassium, the catalyst disk was cooled in helium which was replaced by nitrogen (200 Torr) at room temperature. The temperature was raised stepwise, with nitrogen being in contact with the disk at each temperature for 3 hr. The infrared measurements were made at room temperature after each heat treatment.

Hydrogenation of adsorbed nitrogen. After the series of adsorption experiments made at increasing temperature up to 350°C, the gas phase nitrogen was replaced by hydrogen (200 Torr) at room temperature and the temperature was again raised stepwise (about 1 hr at each temperature) in circulating hydrogen with liquid nitrogen trap. The infrared spectrum was again recorded at room temperature.

TABLE 3

Variation of Infrared Spectra with Temperature of Adsorption

Temperature (°C)	160	200	230	250	350
Frequency (cm^{-1})	—	2020	2020	2020	2020
log (I_0/I)	—	0.024	0.088	0.150	0.358
Ratio	—	1	3.7	6.3	15.0

The change of infrared band with the increase in adsorption temperature is shown in Table 3 and Fig. 5. The infrared band did not appear after the nitrogen adsorption at room temperature for 24 hr. But it first appeared after the heat treatment at 200°C and increased its intensity with the adsorption temperature. It is to be noted that the infrared band first appeared on the low frequency side and then expanded and shifted to higher frequency as the temperature of adsorption was increased. The change of infrared band in the course of hydrogenation is shown in Table 4 and Fig. 6. The nitrogen adsorption band was unchanged with hydrogen treatment (from 26.5 to 218.5 Torr) at room temperature. But it began to decrease at around 260°C again on the low frequency side and decreased its intensity with increase in the hydrogenation temperature.

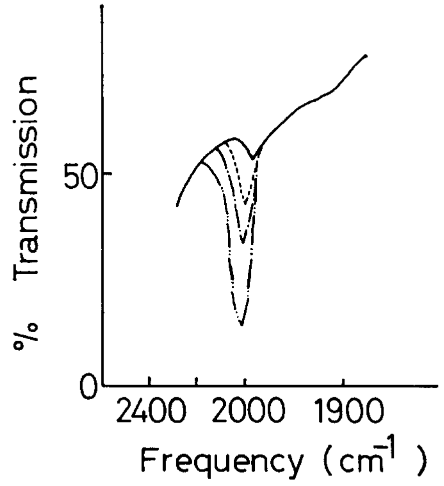

Fig. 5. Variation of infrared spectra with temperature of N_2 adsorption. ———, 200°C; - - - -, 230°C; —·—·—, 250°C; —··—··—, 350°C.

TABLE 4

Variation of Infrared Spectra with Temperature of Hydrogenation

Temperature (°C)	160	260	280	330	350	350	350
Time (hr)	2.5	1.5	0.8	1.0	0.5	1.5	4.5
Frequency (cm^{-1})	2020	2028–2032	2036	2044	2044–2092	2060–2108	—
$\log(I_0/I)$	0.358	0.339	0.284	0.091	0.052	0.041	—
Ratio	1	0.947	0.793	0.254	0.145	0.115	—

In view of the time given for the hydrogenation at each temperature, the hydrogenation appeared to proceed slowly requiring a high energy of activation. Thus, 4.5 hr were required at 350°C for the complete disappearance of the infrared band, suggesting that a structural rearrangement of ruthenium metal is required for the adsorption as well as the hydrogenation.

DISCUSSION

Assignment of the Infrared Band

The infrared band observed at 2020 cm^{-1} seems to be attributed to the adsorbed nitrogen since an isotopic shift was observed. There are two possibilities for the adsorbed species which give infrared band at near 2000 cm^{-1}: (i) undissociated nitrogen; (ii) azide. Gray and Waddington (*13*) reported the infrared band of alkali azides as follows:

KN_3	sym. str.	1344 cm^{-1}
	def.	645 cm^{-1}
	asym. str.	2041 cm^{-1}
NaN_3	sym. str.	1358 cm^{-1}
	def.	639 cm^{-1}
	asym. str.	2128 cm^{-1}

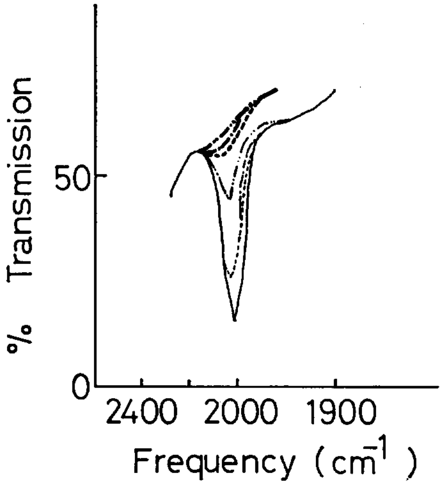

FIG. 6. Variation of infrared spectra with temperature of hydrogenation. ———, 160°C (2.5 hr); - - - -, 260°C (1.5 hr); —·—·—, 280°C (0.8 hr); —··—, 330°C (1.0 hr); ----, 350°C (0.5 hr); —•—•—, 350°C (1.5 hr); —••—••—, 350°C (4.5 hr).

In our case when the alkali metal was changed from potassium to sodium, the accompanied shift of infrared band was as small as 6 ~ 10 cm^{-1} in contrast to the azide band (ca. 100 cm^{-1}). Thus, although the infrared band observed on Ru–Al_2O_3–K was close to that of KN_3, the much smaller shift from K to Na rules out the possibility of azide species formed on alkali metal. The band at 2020 cm^{-1} seems to be attributable to the stretching vibration $\nu_{N\equiv N}$ of chemisorbed nitrogen molecule.

The Nature of Adsorbed Nitrogen

The stretching frequency of nitrogen adsorbed on Ir–SiO_2 was observed by Sheppard and co-workers (*6*) at 2185 cm^{-1}. Moskovits and Ozin (*4*) found an infrared band for adsorbed nitrogen on Ni at 2090 cm^{-1} using a matrix method. As compared with these results, the infrared band observed here occur at even lower frequency, suggesting that $N \equiv N$ bond is considerably weaker. The increase in frequency (6 ~ 10 cm^{-1}) observed when potassium was replaced by sodium suggests that the electron donation from alkali metal is responsible for the weakening of $N \equiv N$ bond.

The form of adsorbed nitrogen, end-on or side-on, may be examined on the basis of extinction coefficient, which can be estimated according to the equation:

$$k = (2.3/c) \times \log (I_0/I)_{\text{adsorption max.}},$$

where I and I_0 are the intensities of transmission beam and incident beam, respectively, and c is the concentration of nitrogen molecules per square centimeter of cross-sectional area of the disk. The amount of adsorbed nitrogen is obtained from the quantity of ammonia formed in the hydrogenation runs. The values of k estimated in this manner are shown in Table 5. They are in a range of $(0.2 \sim 0.3) \times 10^{-18}$ cm²/molecule and about one order of magnitude smaller than the value for Ni–N≡N as reported by Eischens and Jacknow (*1*) (0.2×10^{-17} cm²/molecule). Nevertheless an end-on type of adsorbed nitrogen is more likely because of the high intensity of the infrared band observed. If this is the case, an infrared band due to the stretching vibration $\nu_{\text{Ru-N}_2}$ should appear near 500 cm⁻¹ (*14, 15*), where it would be obscured by the strong absorption by Al_2O_3. However we have observed it for Ru–K dispersed in a KBr matrix at 520 cm⁻¹ (*16*), thus confirming the end-on nature of adsorbed species.

Although a number of infrared bands of adsorbed nitrogen have been observed, they are observable only at lower temperature ($-196 \sim 100$°C) and removed by evacuation. The higher stability of adsorbed nitrogen found in this study is consistent with higher heat of adsorption of nitrogen obtained from the adsorption constant during the isotopic equilibration of nitrogen over Ru–K (*17*).

On the Broadening of Infrared Band

The infrared band of adsorbed nitrogen observed here is rather broad and unsymmetrical as described. The change of infrared peak was examined during the course of adsorption and subsequent hydrogenation to ammonia, as shown in Figs. 5 and 6. In both cases, the first changes of infrared band, appearance on adsorption at ca. 200°C or disappearance on hydrogenation at 260°C, are observed in the lower frequency side. It appears that the easier the adsorption, the easier the hydrogenation, suggesting a distribution of adsorption strength on the catalyst surface. Thus, nitrogen seems to be adsorbed preferentially on a stronger and more active site at lower temperature, the adsorption on less active sites taking place at increasingly higher temperature, as indicated by the shift of infrared band towards higher frequency. On the other hand, in the hydrogenation, the adsorbed nitrogen on more active site is preferentially hydrogenated at lower temperature, the hydrogenation on less active sites taking place at increasingly higher temperature, as indicated again by the shift of infrared band. In this way the broadening of infrared band observed here can be ascribed to a distribution of Ru–N bond strengths on the catalyst surface.

TABLE 5

Extinction Coefficient for the Adsorbed Nitrogen

Frequency (cm⁻¹)	Adsorbed N_2 (ml STP)	$2.3 \times \log (I_0/I)$	k (cm²/molecule)
2040	0.27	0.45	0.2×10^{-18}
2040	0.39	0.64	0.2×10^{-18}
2020	0.43	0.98	0.3×10^{-18}

ACKNOWLEDGMENTS

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