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Infrared-Active Nitrogen Adsorbed on Alumina, Magnesia, or Calcium Oxide both with and without Ruthenium

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Infrared-active surface nitrogen species were formed at around 2200 and/or 2040 cm^{-1} on 2% Ru–Al_2O_3, 5% Ru–MgO, MgO, or CaO following NH_3 decomposition at 200 or 350°C. The ^{15}N isotope wavenumber shifts (10 to 40 cm^{-1}) were much smaller than those (ca. 70 cm^{-1}) for weakly adsorbed dinitrogen on surfaces such as Ni–SiO_2 (R. P. Eischens and J. Jacknow, *in* "Proceedings, 3rd International Congress on Catalysis, Amsterdam, 1964" (W. M. H. Sachtler *et al.*, Eds.), p. 627, North-Holland, Amsterdam, 1965; R. V. Hardevelde and A. V. Montfoort, *Surf. Sci.* **4,** 396 (1966), **17,** 90 (1969)) or Rh–SiO_2 (Yu. G. Borodko and V. S. Lyutov, *Kinet. Katal.* **12,** 238 (1971)). NH_3 had to be decomposed in order to obtain the surface nitrogen species. However, the condition for obtaining these species was not dependent on the degree of NH_3 adsorption, the existence of surface carbonates, the extent of surface hydroxides, or the presence of Ru metal. It is suggested that these observed surface nitrogen species are dinitrogen strongly adsorbed on oxides (Al_2O_3, MgO, or CaO) even in the presence of Ru metal.

INTRODUCTION

Few reports have been written concerning infrared-active dinitrogen on a surface. Most of the ir-active dinitrogen described hitherto has been on supported metals such as Ni–SiO_2 (*1–3*), Rh–SiO_2 (*4*), Pd–Al_2O_3 (*2*), and Pt–SiO_2 (*2, 5*), which are not active catalysts for NH_3 synthesis. Infrared studies of adsorbed nitrogen on effective ammonia catalysts are intrinsically more interesting. Isotopic and adsorption techniques have suggested that both the dissociated form (N) and the molecular form (N_2) are formed on an iron catalyst at working temperatures of 100 to 450°C (*6, 7*). Although ir-active dinitrogen has been reported on Fe–Al_2O_3 or Fe–MgO following NH_3 decomposition (*8*), the relation to NH_3 synthesis has not been investigated fully.

A novel Ru–Al_2O_3–K catalyst has been shown to adsorb ir-active N_2 species which react with H_2 to give NH_3 (*9*). The relation of the ir-active dinitrogen species to NH_3 synthesis on this catalyst has been studied in detail (*10*). Among the three dinitrogen species observed, 2020–2030 cm^{-1} (Type A), 1935–1950 cm^{-1} (Type B), and 1865–1890 cm^{-1} (Type C), the reactivity to H_2 varies in magnitude with the wavenumber ($A < B \ll C$). It has been suggested that species A and B are not dynamic intermediates of the NH_3 synthesis reaction (*10*). Furthermore it was found that these stable species did not bind to Ru but formed a novel dinitrogen surface complex with K on Al_2O_3 (*11*). On the other hand, dinitrogen binding to Ru has been suggested for the Ru–K system (*12, 13*). Thus it is of interest to investigate ir-active nitrogen species on Ru–Al_2O_3 in the absence of K as a basis for studies of the Ru–Al_2O_3–K system.

In this paper, we describe new ir-active nitrogen species formed on Ru–Al_2O_3 or Ru–MgO during ammonia decomposition and discuss whether or not these species bind to Ru. We also describe nitrogen species formed on MgO or CaO in the absence of Ru which were discovered in this study.

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EXPERIMENTAL

A sample (50 to 120 mg) of Al_2O_3 (Alon C) obtained from Japan Aerogel, MgO and CaO(s) both obtained from Soekawa Rikagaku, or CaO(W) obtained from Wako Chemicals was pressed into a wafer with a diameter of 20 mm, and evacuated at 350°C in an *in situ* ir cell. Supported Ru catalysts made by $RuCl_3 \cdot 3H_2O$ impregnation were also pressed into wafers and reduced with H_2 at 350°C for 10 h in an *in situ* cell. NH_3 synthesis ($N_2 + 3H_2$ at 200 Torr and 350°C for 1 h), N_2 adsorption (N_2 at 200 Torr and 350°C for 1 h), or NH_3 decomposition (NH_3 at 100 Torr and 200°C for 1 h) was carried out, followed by an ir measurement done at room temperature. H_2, O_2, or He at 100 Torr was used for sample treatment in some cases. The reaction apparatus with an ir cell and the ir spectrometer were similar to those described previously (*9, 10*). Since the ir cell (130 mm long) was placed only in the sample beam side, most of the ir spectra exhibited noise at 2349 and around 1600 cm^{-1} due to atmospheric CO_2 and H_2O in the reference beam side, N_2 and H_2 were purified using copper-kieselguhr and $Pd-Al_2O_3$, respectively, and NH_3 was purified by distillation in a vacuum system. $^{15}NH_3$ with a purity of 99.3 at.% was used for the ir identification of the adsorbed species.

Volumetric measurements of NH_3 decomposition were studied in a conventional closed-circulation system using 6.42 of pelleted MgO. For this run heavy ammonia with both ^{15}N (77 at.%) and D (34 at.%) was used as a reactant in order to avoid product misidentification caused by background peaks at mass numbers 1 (H), 2 (H_2), and 28 (N_2, CO). Mass spectra of the reactant and the products were recorded by a NEVA-NAG-515 quadrupole mass spectrometer.

RESULTS

1. *Infrared Measurements of $Ru-Al_2O_3$ and Al_2O_3*

$Ru-Al_2O_3$ is an active catalyst for NH_3 synthesis and decomposition (*14, 15*). During NH_3 synthesis (350°C) or decomposition (200°C), a 2% $Ru-Al_2O_3$ wafer was cooled to room temperature. Infrared peaks corresponding to N_2 species were not found in this sample even after the most careful measurement especially between 2400 and 1800 cm^{-1}. However, when the catalyst was exposed overnight to NH_3 at 100 Torr at room temperature, and then heated to 200°C for 1 h, a weak peak was observed at 2060 cm^{-1} along with the peaks due to adsorbed NH_3 on Al_2O_3 (1280, 1465, 1620 cm^{-1}) (*16*) as is shown in Fig. 1b. The peak at 2060 cm^{-1} was shifted slightly to a

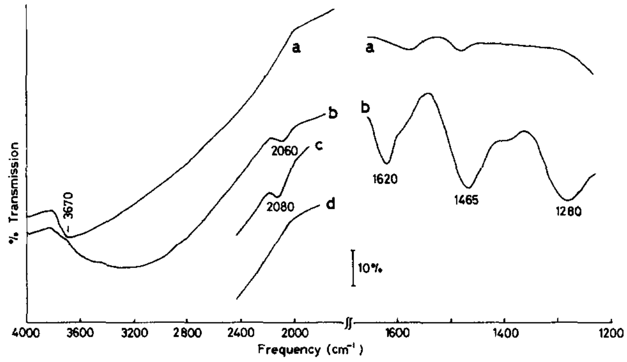


FIG. 1. Infrared absorption of 2.0% $Ru-Al_2O_3$: (a) after H_2 reduction at 350°C; (b) after ammonia treatment overnight at room temperature and for 1 h at 200°C; (c) after evacuation at 200°C for 1 h; (d) after evacuation at 350°C for 1 h.

higher-frequency position following evacuation at 200°C for 1 h (Fig. 1c) and disappeared following evacuation at 350°C for 1 h (Fig. 1d). However, the peaks due to the adsorbed NH_3 remained unchanged. Since treatment with $^{15}NH_3$ instead of NH_3 resulted in an isotopic shift to 2030 cm^{-1}, it was decided that the new peak was produced by N-containing species.

N_2 treatment of 2% Ru–Al_2O_3 at 350°C for 1 h did not produce a new ir peak. The same NH_3 treatment of 0.1% Ru–Al_2O_3 or Al_2O_3 as that of 2% Ru–Al_2O_3 did not produce a new peak around 2000 cm^{-1}. The reason is not clear but is probably related either to NH_3 decomposition efficiencies or to chlorine ion contents. NH_3 was not decomposed on Al_2O_3 at 200 or 350°C. The problem of the adsorption site will be discussed in a later section.

2. *Infrared Measurements of MgO and Ru–MgO*

A MgO wafer evacuated at 350°C for 12 h was measured using an ir spectrometer (Fig. 2a). Bands at 1424 and/or 1420 and 1120 cm^{-1} were assigned to carbonate ions (CO_3^{2-}) on MgO by reference to bands at 1460 and 1096 cm^{-1} produced by magnesite ($MgCO_3$) (*17*). Bands at 1424 and/or 1420 and 985 cm^{-1} were assigned to HCO_3^- ions on MgO (*18*). Following exposure to NH_3 (100 Torr) at 350°C for 1 h, twin peaks were observed at 2170 and 2150 cm^{-1} while a very weak peak due to adsorbed NH_3 was observed at 1190 cm^{-1} (Fig. 2b). Since ^{15}N isotopic shifts were observed (2150 and 2135 cm^{-1}, respectively), it was decided that these peaks were also due to N-containing species. Heights of these peaks were decreased but they remained at a trace level after 12 h evacuation at 350°C (Fig. 2c). It was proved that NH_3 was decomposed by MgO at 350°C. The detailed mechanism will be described later.

After H_2 (100 Torr) reduction at 350°C for 15 h, the MgO sample with 5% Ru showed a simple ir spectrum with only surface OH groups at around 3600 cm^{-1} (Fig. 2d). Carbonate bands disappeared because of the hydrogenation by H_2 which was activated on reduced Ru. Upon the introduction of NH_3 (100 Torr) at 185°C, new peaks appeared at 2225, 2035, 3385, 3270, 1608, and 1195 cm^{-1}. The first two peaks are assigned to N-containing species because a ^{15}N iso-

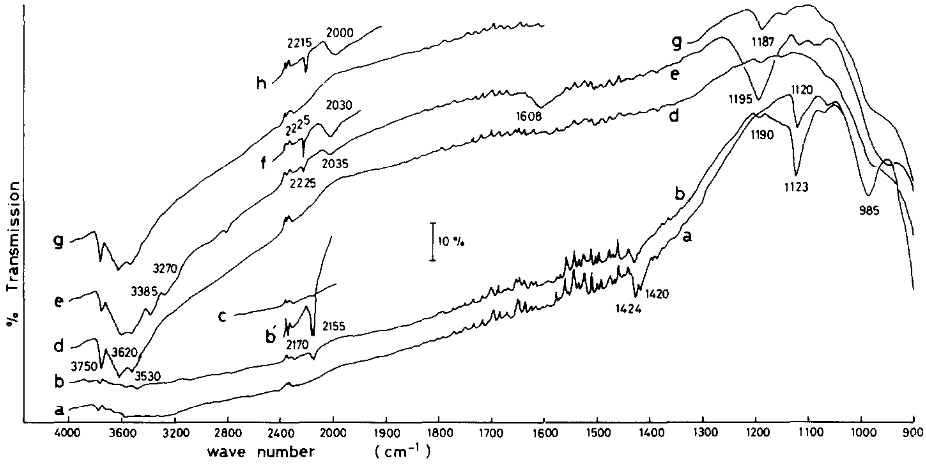
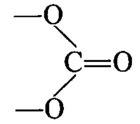


FIG. 2. Infrared absorption of MgO (a–c) and 5% Ru–MgO (d–h). MgO: (a) after evacuation at 350°C for 12 h; (b) after NH_3 treatment at 350°C for 1 h; (b′) the same sample as (b) measured with reduced reference beam; (c) after evacuation at 350°C for 12 h. 5% Ru–MgO: (d) after H_2 treatment at 350°C for 15 h; (e) after NH_3 treatment at 185°C for 1 h; (f) after NH_3 treatment at 204°C for 1 h; (g) after H_2 treatment at 350°C for 10 h; (h) after $^{15}NH_3$ treatment at 209°C for 1 h.

tope shift was observed (2215 and 2000 cm^{-1}; see Fig. 2h). The following four peaks are assigned to adsorbed NH_3 on MgO by reference to the spectra of adsorbed NH_3 on γ-Al_2O_3 (3380, 3260, 1660, and 1280 cm^{-1}) (*16*). When the sample was heated to 204°C for 1 h under an NH_3 atmosphere, the peaks due to N-containing species increased in magnitude while those due to NH_3(a) diminished. Both species disappeared following H_2 treatment at 350°C for 10 h. The N-containing species were reproduced by $^{15}NH_3$ treatment as is shown in Fig. 2h.

3. *Infrared Measurements of CaO and Ru–CaO*

Infrared measurements of CaO(w) were carried out after evacuation at 350°C for 16 h. The results are shown in Fig. 3a. Various carbonates were identified as follows. The strong bands at 1490, 1430, 1082, 876, and 710 cm^{-1} are due to surface carbonate on CaO by reference to calcite ($CaCO_3$) bands at 1492, 1429, 1087, 876, and 706 cm^{-1} (*17*). Bands at 2520, 1025, and 846 cm^{-1} are due to HCO_3^- ions (*18*), and bands at 1798, 1185, ca. 1000, and ca. 800 cm^{-1} are probably due to bridged carbonate similar to organic carbonate:



(*16*). Since all of these bands shifted following the addition of metallic K in a final run (Fig. 3j), they are believed to be surface anionic species like the carbonates mentioned above. Bands appearing at 1415, 1045, 882, and 684 cm^{-1} following the K addition (Fig. 3j) correspond well to free carbonate ions (1415, 1063, 879, and 680 cm^{-1}) (*18*). This sample did not produce any new ir bands following N_2 treatment at 350°C (Fig. 3b). However, new peaks were observed at 2180–2190 and 2025–2040 cm^{-1} following NH_3 (100 Torr) treatment at 350°C for 1 h. Since a ^{15}N isotope shift was observed as shown in Fig. 3h (2170 and 2000 cm^{-1}), it was decided that these peaks were due to N-containing species on CaO. These peaks decreased slightly following evacuation at 350°C (Fig. 3e) or H_2 (100 Torr) treatment at 350°C for 1 h (Fig. 3f),

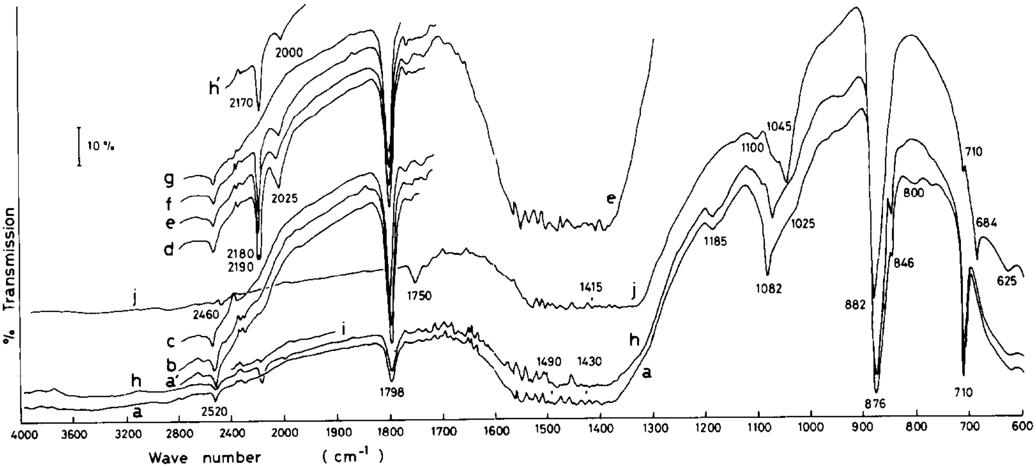


FIG. 3. Infrared absorption of CaO(w): (a and a') after evacuation at 350°C for 16 h; (b) after N_2 treatment at 350°C for 1 h; (c) after evacuation at 350°C for 16 h; (d) after NH_3 treatment at 350°C for 16 h; (e) after evacuation at 350°C for 16 h; (f) after H_2 treatment at 350°C for 1 h; (g) after O_2 treatment at 350°C for 2 h; (h and h') after evacuation at 350°C for 5 h, then $^{15}NH_3$ treatment at 350°C for 1 h; (i) after evacuation at 350°C for 16 h; (j) after K addition in He at 350°C for 1 h. Spectra of (a') and (h') are measured with reduced reference beam.

but disappeared after O_2 (400 Torr) treatment at 350°C for 2 h (Fig. 3g). Peaks due to adsorbed NH_3 were not observed following NH_3 treatment at 350°C (see Fig. 3h).

The sample of CaO(s) from a different source was less transparent ir spectrometrically than the CaO(w) sample. However, this sample also produced the same new peaks at 2180 and 2040 cm^{-1} following NH_3 treatment at 350°C for 1 h. In addition, this species was slightly more stable against O_2 treatment at 350°C than CaO(w). It was proved that NH_3 was decomposed by CaO(s) or CaO(w) at 350°C.

4.2% Ru–CaO(s) gave an ir spectrum similar to that of CaO(w). Peaks due to carbonate ions still remained even after H_2 reduction at 350°C. Although Ru–CaO is an active ammonia catalyst (*15*), no new ir peak was observed after N_2 (100 Torr) or NH_3 (100 Torr) treatment for 1 h at any temperature below 350°C.

4.2% Ru–CaO(w) which was prepared by an impregnation of $RuCl_3 \cdot 3H_2O$ in acetone solution only produced peaks due to OH groups and there were no peaks due to carbonate ions following H_2 treatment at 350°C. This sample did not produce any new peaks following NH_3 treatment at 350°C. Most of the ir results are summarized in Table 1.

4. NH_3 Decomposition by MgO

It was known from previous work that a supported Ru catalyst (Ru–Al_2O_3, Ru–MgO, Ru–CaO) would catalyze the NH_3 decomposition reaction. However, none of the oxides of Group II or III elements were known to catalyze ammonia decomposition at moderate temperatures such as 350°C. Hence, since the ir study revealed that MgO and CaO decomposed NH_3 at 350°C producing N-containing species on the catalyst surface, the MgO-catalyzed decomposition reaction was studied volumetrically. Heavy ammonia (containing 77 at.% of ^{15}N and 35 at.% of D) at a pressure of 71 Torr was introduced to 6.42 g of MgO(s) at 350°C. The resultant variation with time of the pressure (ammonia and hydrogen) and D content is shown in Fig. 4. Following a sharp decrease in the ammonia pressure due to adsorption, a steady decrease was observed in accordance with hydrogen evolution. However, almost no dinitrogen (below 2% of hydrogen level

TABLE 1

Infrared Data of Samples[a]

	Sample							
	Al_2O_3	2% Ru–Al_2O_3	MgO	5% Ru–MgO	CaO(w)	CaO(s)	4.2% Ru–CaO(w)	4.2% Ru–CaO(s)
Carbonate ion band								
Before H_2 treatment	–	–	+	+	++	++	++	+
After H_2 treatment	–	–	+	–	++	++	+	–
NH_3(a)	+	++	±	++	–	–	–	–
NH_3 decomposition reaction	–	++	+	++	+	+	++	++
New band (N_2)	–	+	+	+	+	+	–	–
Wavenumber[b]			2170	2225	2190	2180		
		2060	2150	2030	2040	2040		
Wavenumber from $^{15}NH_3$			2150	2215	2170			
		2030	2135	2000	2000			
NH_3 treatment condition	25 to 350°C	25°C, 16+ h; 200°C, 1 h	350°C, 1 h	200°C, 1 h	350°C, 1 h	350°C, 1 h	25 to 350°C	25 to 350°C
Reactivity to H_2		+	–	+	–	–		

[a] ++, strong; +, weak; ±, very weak; –, not observed.

[b] Wavenumbers are measured in inverse centimeters.

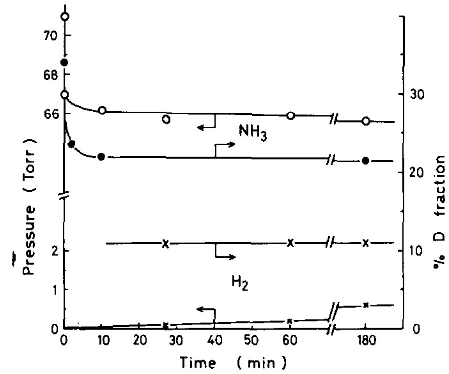


FIG. 4. Pressure and D fraction changes of ammonia and hydrogen during heavy-ammonia (77% ^{15}N, 34% D) decomposition on 6.42 g of MgO at 350°C.

mass spectrometrically) was produced at this temperature. In order to avoid confusion with the background N_2 and CO, the dinitrogen content was estimated from the mass numbers 29 and 30. These results demonstrate that ammonia reacts with MgO yielding hydrogen and leaving nitrogen on the MgO at a temperature of 350°C. An initial sharp decrease in the D content of the ammonia indicates rapid hydrogen atom exchange between the ammonia and the surface hydroxide (Eq. (2)). The difference in the D content between ammonia and hydrogen is considered to be due to the deuterium isotope effect in the equilibrium adsorption of ammonia (Eqs. (1) and (2)) which would apply if the kinetic isotope effect in hydrogen desorption (Eq. (4)) is negligible because of the high temperature. A possible decomposition mechanism is considered as follows.

Adsorption:

$$ND_3 \rightleftharpoons ND_3(a). \qquad (1)$$

Surface hydrogen exchange:

$$ND_3(a) + OH(a) \rightleftharpoons ND_2H(a) + OD(a). \qquad (2)$$

Surface decomposition:

$$2ND_3(a) \rightarrow N_2(a) + 6D(a). \qquad (3)$$

Desorption:

$$2D(a) \rightarrow D_2. \qquad (4)$$

Reaction (3) is considered to be the slowest. The possible production of $N_2(a)$ in Eq. (3) will be discussed later.

DISCUSSION

1. Adsorbed Nitrogen on MgO and CaO

Although we began this work with the intention of surveying N_2 adsorbed species on a Ru catalyst, N-containing species were detected on MgO and CaO in the absence of Ru following NH_3 decomposition. Azide and cyanamide are known to be N-containing inorganic compounds which may exhibit ir absorption around 2000 cm^{-1}. For example, KN_3 exhibits ir absorption at 2041 cm^{-1} and Na_2CN_2 similarly at 2120 cm^{-1} (*16*).

In the case of MgO or CaO for which the surfaces are partly changed to carbonates, the following reactions would occur respectively:

$$MgCO_3 + 2NH_3 = MgCN_2 + 3H_2O, \qquad (5)$$

$$CaCO_3 + 2NH_3 = CaCN_2 + 3H_2O. \qquad (6)$$

Although free-energy data are not available, the enthalpy change for reaction (5) is positive (53.4 kcal/mol) (*19*, *20*). Hydrogen evolution which occurred during the NH_3 decomposition run on MgO cannot be explained by reaction (5). Moreover, 5% Ru–MgO which has no carbonate following H_2 reduction (Fig. 2d, Table 1) gives a similar N-containing species at 2225 cm^{-1}. Hence, if the species producing ir absorption at around 2200 cm^{-1} on Ru–MgO is considered to be a species similar to that produced on MgO without Ru, then this ir absorption band cannot be due to cyanamide. Possibilities that it is due to CN^-, OCN^-, or SCN^-, which contain carbon and have wavenumbers around 2100 cm^{-1} (*18*), are excluded by similar reasoning.

The possibility that it might be due to azide was considered, because H_2 was evolved when NH_3 reacted with MgO or CaO as follows:

$$MgO + 6NH_3 = Mg(N_3)_2 + H_2O + 8H_2, \quad (7)$$

$$CaO + 6NH_3 = Ca(N_3)_2 + H_2O + 8H_2. \quad (8)$$

Although no thermodynamic data are available for these reactions, they are known to be very unstable (*21*). Though we cannot deny the possibility completely, both reactions ((7) and (8)) seem impractical under these conditions.

Most of the adsorbed dinitrogen on metals and dinitrogen complexes exhibit ir absorption in the wavenumber range 2260 to 1900 cm^{-1} apart from some multinuclear dinitrogen complexes (*15, 22*). We suggest that the N-containing species observed in this work are dinitrogen strongly adsorbed on an oxide surface. Since NH_3 decomposition is thermodynamically very favorable at higher temperatures, nitrogen can be adsorbed strongly once decomposition occurs.

The question of the active site is discussed in the following. MgO (assay 99.75%) contains Ca and Al, and both CaO(s) and CaO(w) (assay 99.99%) contain Mg, Al, Si, and Ti as major impurities as indicated by emission spectroscopy. No Group VIII transition metal is detectable as a major impurity. The addition of Ru to CaO was even found to inhibit the formation of nitrogen species. Thus the adsorption site cannot be a transition metal impurity.

The magnitude of the ir isotope shift for adsorbed N_2 or for a simple N_2 end-on complex which has a wavenumber of around 2000 cm^{-1} is 60 to 70 cm^{-1} (*23*). In the case of a N_2 complex with Re or Mo in which one N atom is bound to Re or Mo and the other N atom is bound to an electron-acceptor molecule, the isotope shift is not so large (ca. 40 cm^{-1}) (*24*). The small isotope shift found in this study (10 to 40 cm^{-1}) as given in Table 1 is considered to be probably due to a site with a strong electric field such as an oxide defect, where the N_2 is adsorbed.

Since the apparent pressure of dinitrogen which is in equilibrium with NH_3 at a pressure of 100 Torr at 200 or 350°C is very much higher than 200 Torr, it is not surprising that the adsorbed dinitrogen is not formed by N_2 adsorption (200 Torr) but is formed by NH_3 decomposition (100 Torr). Reported cases of N_2 species strongly adsorbed on nonmetals are very rare except in the form of a surface complex with K (*11*). The species found here are quite different from the weakly adsorbed dinitrogen species which have been observed by ir spectroscopy at lower temperatures on ZnO (2337 cm^{-1} at -195°C) (*25*) or Na–A-zeolite (2339 cm^{-1} at -88°C) (*26*) with respect to both its thermal stability and the observed wavenumber.

2. *Adsorbed Nitrogen on Ru–Al_2O_3 and Ru–MgO*

Since the peak at 2060 cm^{-1} produced by 2% Ru–Al_2O_3 and the peak at 2030 cm^{-1} produced by 5% Ru–MgO do not appear with Al_2O_3 or MgO, these peaks might be assigned to N_2 adsorbed on the Ru metal surface. In general, the adsorbed dinitrogen which is coordinated linearly with the metal atoms has the normal isotope shift magnitude corresponding to the harmonic oscillator model; e.g., 74 cm^{-1} for Ni–SiO_2 (*1, 2*) and 74 cm^{-1} for Rh–SiO_2 (*4*). In view of the smaller isotope shift (about 30 cm^{-1}) the dinitrogen species formed on Ru–Al_2O_3 or Ru–MgO are not considered to be the ordinal one which is bound linearly to the Ru atom.

If we survey all of the data in Table 1 and the figures, the peaks can be classified into two groups: sharp peaks around 2200 cm^{-1} and broad peaks around 2040 cm^{-1} irrespective of the presence of Ru. Thus we suggest that the N-containing species formed on Ru–Al_2O_3 or Ru–MgO are also dinitrogen strongly adsorbed on the oxide surface. It seems strange that Ru–CaO does not produce any ir-active nitrogen species from NH_3 despite being an active ammonia catalyst. The conditions under which N-containing species are obtained are not clear. As is summarized in Table 1, the appearance of new peaks due to nitrogen is independent of the existence of carbonate ions, the extent of the OH group, the strength of NH_3 adsorption, and the existence of Ru metal. Only NH_3 decomposition is necessary.

We do not intend to suggest that the Ru surface cannot adsorb any nitrogen. In fact it has been reported that Ru powder is covered with nitrogen which is very reactive to hydrogen even at room temperature (*27*). However, in this case nitrogen has been considered to be adsorbed on the Ru powder in the form of dissociated atoms. Even though the Ru surface of Ru–Al_2O_3, Ru–MgO, or Ru–CaO may be covered by nitrogen atoms, we could not observe them in our work because of the existence of other peaks produced by carbonates, for example, in the lower wavenumber region. The ir-active surface nitrogen species found in this work is not directly related to NH_3 synthesis.

CONCLUSIONS

Infrared-active nitrogen species were detected on Ru–Al_2O_3, Ru–MgO, MgO, or CaO. These were formed only by NH_3 decomposition in contrast to the situation with the Ru–Al_2O_3–K, Al_2O_3–K, or CaO–K systems where N_2 species are formed by N_2 adsorption as well as by NH_3 decomposition (*11*). The oxide surface (MgO and CaO) was proved to adsorb nitrogen species (probably dinitrogen) even in the absence of a transition metal (Ru) or alkali metal (K). It is suggested that nitrogen species are adsorbed on the oxide, even in the case of an oxide-supported Ru catalyst.

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