JOURNAL OF CATALYSIS 50, 441-446 (1977)

The Mechanism of the Reaction between NO_X and NH_3 on V_2O_5 in the Presence of Oxygen

MAKI TAKAGI, TOMOJI KAWAI, MITSUYUKI SOMA, TAKAHARU ONISHI, AND KENZI TAMARU

Department of Chemistry, The University of Tokyo, Bunkyo-ku, Tokyo, 113 Japan

Received June 28, 1976; revised August 5, 1977

In order to elucidate the mechanism of the reaction between nitric oxide and ammonia on a V_2O_5 catalyst, the elementary steps of the reaction were separately studied, and the reactivities of the adsorbates were examined by means of ir, XPS, mass spectrometry, and kinetic studies under reaction conditions. The role of oxygen, whose presence is essential for the reaction to occur, was examined. Nitric oxide was not adsorbed on the V_2O_5 surface in the absence of oxygen but was adsorbed as NO_2(ad) in the presence of ambient oxygen. Ammonia was adsorbed on V_2O_5 in the form of NH_4^+(ad), which gives a band at 1413 cm^{-1} in the ir spectrum. These two adsorbates, NO_2(ad) and NH_4^+(ad), reacted readily to form N_2. Accordingly, a new mechanism was proposed for the role of oxygen in the reaction; namely, that the reaction proceeds via the two adsorbates, NO_2(ad) and NH_4^+(ad), which react on the catalyst surface through a Langmuir–Hinshelwood mechanism to form N_2 and H_2O.

INTRODUCTION

From the environmental point of view, the catalytic reduction of NO is a very important reaction for removal of NO from exhaust gases. Much work has been done on this reaction over various solid catalysts using hydrogen, carbon monoxide, ammonia, and other gases as reducing agents. In the presence of oxygen, however, most of the reducing gases, except ammonia, are oxidized by oxygen in preference to NO, and ammonia is, accordingly, almost the only reducing gas for NO which may be used in practice. V_2O_5 is known as one of the best catalysts for this reaction, because it exhibits high activity and selectivity to form nitrogen and is not easily poisoned by reactant gas containing SO_2.

It is generally accepted that the rate of reduction of NO by NH_3 over some catalysts, such as Pt and V_2O_5, is accelerated by the presence of oxygen. To explain this fact, Markvart and Pour (*1*) assumed that oxygen accelerates the dissociation of adsorbed ammonia. However, the mechanism of this reaction, including the role of oxygen, has not yet been elucidated.

In order to elucidate the mechanism of the reduction of NO by NH_3 over a V_2O_5 catalyst, the nature of the adsorbates, their dynamic behaviors, and the elementary steps which constitute the overall reaction were separately studied. In particular, the effect of oxygen on the rate of the reaction and the mechanism through which oxygen accelerates the reaction were examined.

EXPERIMENTAL

Two types of catalysts, a commercial V_2O_5 (Nakarai Chemicals, special grade; BET surface area, 23 m^2/g) and an alumina-supported V_2O_5 (V_2O_5/Al_2O_3), were used for both spectroscopic and kinetic studies. Al_2O_3-supported catalyst was prepared as follows: Al_2O_3 was impregnated with a V_2O_5-saturated solution of oxalic acid,

ISSN 0021-9517

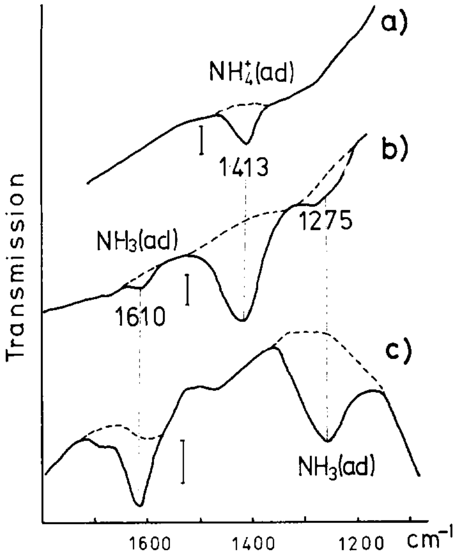


FIG. 1. The spectra of ammonia adsorbed at room temperature on (a) V_2O_5, (b) alumina-supported V_2O_5, and (c) Al_2O_3. Bars show the transmission range of 10%.

dried at 120°C for 2–3 hr, and heated at 500°C for 4–5 hr in air. The γ-Al_2O_3 used for the catalyst support and for adsorption experiments was obtained from Degussa Co., Ltd.

The ir measurements were carried out as described previously (*2*). The disks of V_2O_5 and V_2O_5/Al_2O_3 for the infrared measurements were 20 mm in diameter, containing approximately 50 mg of catalyst. These catalysts were heated in the ir cell under a vacuum at 400°C for 2 hr and then oxidized by 100 Torr of oxygen at 400°C for 1 hr before use.

The XPS spectra of these catalysts after the pretreatments were obtained with a McPherson ESCA 36 instrument, which revealed that except for a small amount of carbon, no other contaminants that would influence the catalytic activity were detected on the surface. The binding energies of V ($2p_{3/2}$ = 516.8 eV) and O (1s = 529.8 eV) of V_2O_5 indicated that the surface atomic species after the pretreatments are V^{5+} and O^{2-}.

The reaction products were analyzed by a Hitachi mass spectrometer. Chemically pure NO (Takachiho Chemical Co., Ltd.) was used without further purification. NO_2 was prepared by oxidizing NO with oxygen, then purified by distillation under a vacuum until colorless crystals at liquid-nitrogen temperature were obtained.

RESULTS AND DISCUSSION

I. Adsorption of NH_3 and NO_X on V_2O_5, V_2O_5/Al_2O_3, and Al_2O_3

I-1-1. Adsorption of NH_3. The infrared spectra of adsorbed ammonia on V_2O_5, V_2O_5/Al_2O_3, and also on Al_2O_3 alone are shown in Fig. 1. The ammonia adsorbed on V_2O_5 gave only a single broad band at 1413 cm^{-1} (a), whereas three bands at 1610, 1410, and 1275 cm^{-1} on V_2O_5/Al_2O_3 (b), and two bands at 1610 and 1275 cm^{-1} on Al_2O_3 (c) were observed. The broad band at 1410 cm^{-1} disappeared when the sample was heated up to 150°C, but the other two bands at 1610 and 1275 cm^{-1}, on the other hand, stayed unchanged below 300°C. The spectrum of ammonia adsorbed on γ-Al_2O_3 has been reported by Eischens and Pliskin (*3*) to give two bands at 1620 and 1260 cm^{-1}. Therefore, these two bands at 1610 and 1275 cm^{-1} are reasonably assigned to NH_3 adsorbed on γ-Al_2O_3.

In order to determine the state of ammonia adsorbed on V_2O_5, its infrared

TABLE 1

The Binding Energy of Vanadium, Nitrogen, and Oxygen Obtained by X-ray Photoelectron Spectroscopy[a]

	Binding energy (eV)			
	V		N	O
	$2p_{3/2}$	$2p_{1/2}$	1s	1s
V_2O_5-NH_3	516.9	524.6	400.9	529.8
NH_4VO_3	516.7	524.2	400.9	529.8

[a] The binding energy of the electrons was determined by taking Au $4f_{7/2}$ = 83.7 eV as an internal standard.

spectrum was compared with that of ammonium meta vanadate (NH_4VO_3). The ir spectrum of NH_4VO_3 showed a strong band at about 1410 cm^{-1} due to NH_4^+. The data of the X-ray photoelectron spectra of NH_4VO_3 and V_2O_5 with adsorbed ammonia are listed in Table 1. The binding energies of vanadium ($2p_{3/2}$, and $2p_{1/2}$), oxygen (1s), and nitrogen (1s) had exactly the same values in both spectra. The binding energy of N (1s) of the ammonia adsorbed on V_2O_5 is 2 eV higher than that of solid ammonia (*4*), which suggests that the former is more positively charged than the latter to an extent which corresponds to 0.2 electron of net charge. It is accordingly concluded that ammonia is adsorbed on the V_2O_5 surface as NH_4^+ in a state similar to that in NH_4VO_3. Similarly the ammonia adsorbed on the reduced catalysts exhibited exactly the same ir and XPS spectra.

The presence of protons on the oxidized surface of V_2O_5 in the form of OH, as is the case in various oxides, was demonstrated by the formation of H_2O when the V_2O_5 was heated to 630°C or its melting point.

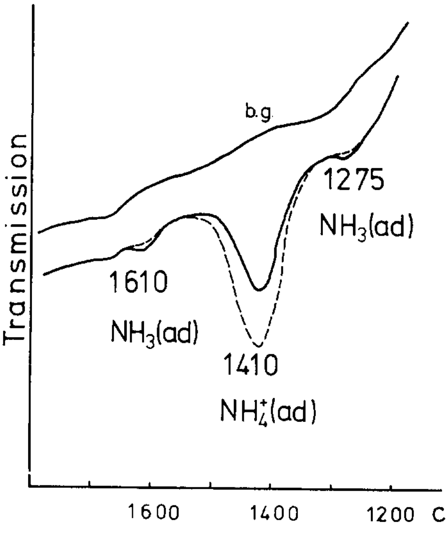


FIG. 2. Influence of oxygen on adsorbed ammonia species on V_2O_5/Al_2O_3. b.g., background spectra; solid line, adsorption of ammonia at room temperature; dashed line, after introduction of oxygen (3.1 cm Hg) at room temperature.

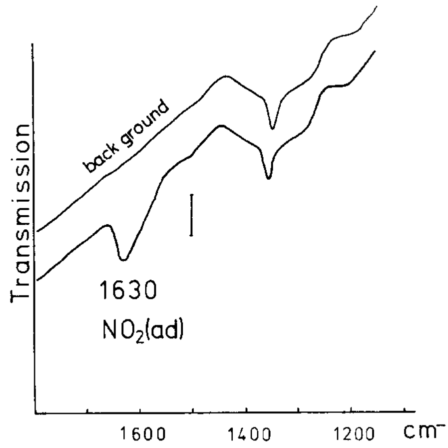


FIG. 3. The ir spectrum of adsorbed species given by NO + O_2 on V_2O_5/Al_2O_3, at room temperature.

NH_3 is consequently adsorbed on the oxidized surface to form NH_4^+. When the reduced surface of V_2O_5 was exposed to NH_3, decomposition of NH_3 to form N_2 was observed, and neither H_2 nor H_2O was detected in the gas phase.

The amount of ammonia chemically adsorbed on V_2O_5 was 3.5 ml of STP/g, when V_2O_5 was exposed to 70 Torr of ammonia followed by evacuation of the ambient gas. If we take the surface area (23.2 m^2/g by BET method) and the bond length of V–O determined by X-ray diffraction into account, the number of adsorbed ammonia molecules is estimated to be approximately of the same order of magnitude as that of the surface V atoms.

I-1-2. The influence of oxygen on adsorbed ammonia species. When oxygen was introduced after evacuation onto the V_2O_5/AlO_3 catalyst on which ammonia was preadsorbed, two bands at 1610 and 1275 cm^{-1} due to NH_3(ad) on Al_2O_3 decreased in intensity, whereas the 1410-cm^{-1} band of NH_4^+(ad) on V_2O_5 increased in intensity as shown in Fig. 2. When only V_2O_5 was used as the catalyst, the band at 1410 cm^{-1} due to NH_4^+(ad) exhibited no change with the introduction of oxygen. Consequently, it was concluded that NH_3(ad) on Al_2O_3 is expelled from Al_2O_3 and is transferred to

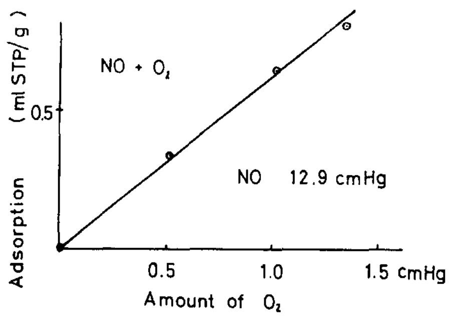


FIG. 4. Amount of NO_2(ad) vs pressure of O_2 in mixed gas of NO and O_2, at room temperature.

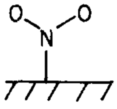
NH_4^+ by the introduction of oxygen or that water is formed to change NH_3(ad) to NH_4^+(ad).

I-2. Adsorption of NO_x on V_2O_5 surface and the influence of oxygen on the adsorption. It has been reported that NO gas is adsorbed to a considerable extent on Cr_2O_3, Fe_2O_3, and Pt catalysts in a molecular form (*5, 7*). However, no adsorption of NO was observed on the V_2O_5 catalyst.

The adsorption measurements were carried out on the V_2O_5 surfaces in the following three ways: (i) On an oxidized surface, the V_2O_5 disk was heated to 400°C in an oxygen (100 Torr) atmosphere for 2 hr (yellowish orange); (ii) on a surface reduced by H_2, the V_2O_5 was heated to 400°C under about 100 Torr of H_2 for 2 hr (dark blue); and (iii) on a surface reduced by NH_3, the sample was heated to 200°C in an NH_3 (50–70 Torr) atmosphere for 1–2 hr (green). NO gas was introduced to these surfaces at temperatures of 25, 200, and 400°C, and the gas was allowed to circulate for 1–2 hr at each temperature before it was cooled to room temperature. No adsorption of NO could be observed in any of these cases.

When the gaseous mixture of NO and O_2 was introduced onto surfaces (i), (ii), and (iii), however, adsorption was observed in all cases. The ir spectrum of the adsorbed species exhibited two bands at 1632 and 1355 cm^{-1} as shown in Fig. 3. The band at 1355 cm^{-1} stayed unchanged when the catalyst was heated to 300°C, whereas that at 1632 cm^{-1} readily disappeared on heating.[1] The band at 1632 cm^{-1}, on the other hand, decreased when the sample was heated *in vacuo*. In this case, NO_2 gas desorbed was detected in the gas phase by the ir technique. When NO_2 gas, instead of the mixture of NO and O_2, was introduced onto the V_2O_5 surface, it also gave exactly the same ir spectrum as that shown in Fig. 3.

The position of the absorption band at 1632 cm^{-1} is identical to that of the antisymmetric stretching of NO_2 gas, which is interpreted to indicate that NO_2 is adsorbed on V_2O_5 in the following configuration (*6–8*):



No absorption band of symmetric stretching of NO_2 could be observed in this case, probably because the absorption is generally weaker than that of the antisymmetric mode and, moreover, the amount of NO_2 adsorbed is small.

The relationship between the amounts of NO_2(ad) and the pressure of gaseous NO_2 was linear in this pressure range. When the amount of O_2 introduced was changed in the mixture of NO and O_2, keeping that of NO constant ([NO] > [O_2]), the amount of NO_2(ad) increased linearly with the amount of O_2 (Fig. 4).

On the basis of this evidence, it was concluded that NO is not adsorbed on the V_2O_5 surface as such, but that it is adsorbed

---

[1] The vacant ir cell without catalyst gave an absorption band of the same intensity and wavenumber (1355 cm^{-1}), and a band appears at 837 cm^{-1} after the adsorption experiment of NO + O_2. The ir spectrum of $NaNO_3$ has a strong band at 1360 cm^{-1} due to the ν_3 mode of NO_3^- and a weak band at 831 cm^{-1} due to the ν_2 mode. The band at 1355 cm^{-1} is completely irrelevant to the adsorbed species on V_2O_5 and is assigned to NO_3^- ion on the NaCl window of the ir cell.

as NO_2 being oxidized to NO_2 by the ambient oxygen. The same results were obtained on the V_2O_5/Al_2O_3 catalyst. Terenin and Roev (*8*) have reported that on the surface of degassed Al_2O_3 gel, NO is adsorbed in the form of Al–O- - -N=0. However, no adsorbed NO species was found on the V_2O_5/Al_2O_3 catalyst.

II. Reaction between Two Adsorbates

NO or NO_2 gas was introduced over the catalysts where ammonia was preadsorbed (Fig. 5), and the reaction was studied by the ir technique. As shown in Fig. 5a, when the mixed gas of NO and O_2 was introduced at room temperature, the absorption band of NH_4^+(ad) on V_2O_5 gradually decreased, whereas no changes were observable when NO gas alone was introduced even at temperatures as high as 90°C. The NH_4^+(ad) was not decreased by evacuation in this temperature range (room temperature to 90°C). N_2 and H_2O were detected as the reaction products between NO_2 gas and NH_4^+(ad) on V_2O_5 by mass spectrometry.

When NH_3 gas, on the other hand, was introduced onto the V_2O_5 where NO_2(ad) was preadsorbed (Fig. 5b), the band of adsorbed NO_2 at 1630 cm^{-1} rapidly disappeared, the absorption band of NH_4^+(ad) appeared at 1410 cm^{-1}, and mass spectrometry exhibited the formation of N_2 as a reaction product.

It was consequently demonstrated that both NO_2(ad) formed from gaseous NO and oxygen, and NH_4^+(ad) from NH_3 are reactive surface species on the V_2O_5 catalysts forming N_2 and H_2O.

By controlling the pressure of NO, O_2, and NH_3, two adsorbates, NO_2(ad) and NH_4^+(ad), were observable concurrently at 1630 and 1410 cm^{-1}, respectively (Fig. 5C). When the gas phase was evacuated, both absorption bands gradually decreased and almost disappeared in 30 min at room temperature, while the band at 1355 cm^{-1} due to NO_3^- on the window of the ir cell remained unchanged. This indicates that NO_2(ad) reacted readily with NH_4^+(ad) on V_2O_5 at room temperature. The reaction between NO_2 and NH_3 to form N_2 is very slow without the catalyst.

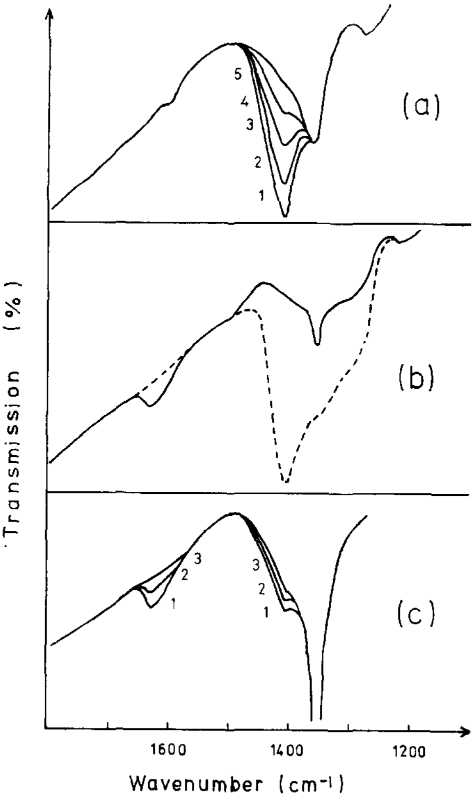
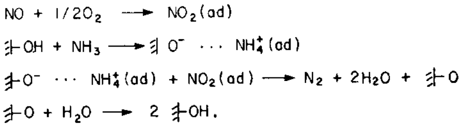


FIG. 5. (a) Reaction of NH_4^+ (ad) with NO + O_2 gas. The decrease of the absorption band was measured every 20 min [1 to 5]. (b) Reaction of NO_2(ad) with NH_3 gas. Broken line shows the spectrum after the introduction of NH_3. (c) Reaction between NO_2(ad) and NH_4^+(ad) on V_2O_5/Al_2O_5 catalyst [1 to 3].

The reaction between gaseous NO and ammonia (NH_4^+) adsorbed on the oxidized or CO-reduced surface of V_2O_5 was studied kinetically. An appreciable amount of N_2 was observed as a reaction product over the oxidized surface, whereas a negligible amount was detected over the reduced one. The reaction rate was accelerated by adding oxygen to the system. As some oxygen is always adsorbed on the surface of V_2O_5 in its working state, it is strongly suggested that the presence of oxygen is essential in the reduction of NO by NH_3.

Under these circumstances the following new mechanism is proposed for the reaction between NO and NH_3 over V_2O_5 in the presence of oxygen: NO is oxidized by the ambient O_2 and is adsorbed as NO_2(ad), and NH_3 as NH_4^+(ad), on the V_2O_5 catalyst. Then both adsorbates readily react through a Langmuir–Hinshelwood mechanism. Under the reaction conditions, surface protons (OH) could be supplied from the reaction product, H_2O, to form adsorbate NH_4^+, and the reaction continues as follows:



It is generally accepted that oxygen accelerates the reaction of NO and NH_3 over various catalysts. To explain the enhancement of the reaction rate by the presence of oxygen, Markvart and Pour (*1*) presumed that oxygen would help the dissociative adsorption of NH_3 on the catalyts surface. But in our work, it was demonstrated that O_2, which is essential for the reaction to occur, enables NO to be adsorbed as NO_2(ad) on V_2O_5 and also enriches NH_4^+(ad) species from ammonia on V_2O_5/Al_2O_3. Both of these adsorbates are the intermediate species of the overall reaction.

No N_2O was detected by introduction of NO gas onto the reduced surface of V_2O_5, and also no oxidation of the reduced surface occurred during the exposure to NO. Thus we expect that the surface reaction

$$2\,NO \rightarrow N_2O + O(ad)$$

does not occur on V_2O_5 under the reaction conditions studied. This reaction is an indispensable elementary process in the so-called "redox mechanism" (*9*).

Otto and Shelef (*10*) have proposed a Langmuir–Hinshelwood-type mechanism over Pt, Fe_2O_3, and other oxide catalysts, NO(ad) and NH_2(ad) being the reaction intermediates. On the V_2O_5, however, the reactive adsorbed species are NO_2(ad) and NH_4^+(ad) and are entirely different from those over other catalysts. This is the mechanism by which the reduction of NO by NH_3 is accelerated by the presence of oxygen.

REFERENCES

1. Markvart, M., and Pour, V., *J. Catal.* **7**, 279 (1967).

2. Noto, Y., Fukuda, K., Onishi, T., and Tamaru, K., *Trans. Faraday Soc.* **63**, 2300 (1967).

3. Eischens, R. P., and Pliskin, W. A., "Advances in Catalysis," Vol. 10, p. 1. Academic Press, New York, 1958.

4. Siegbahn, K., Nordling, C., Nordberg, R., Hamrin, K., Hedman, J., Johansson, G., Bergmark, T., Karlsson, S.-E., Lindgren, I., and Lindberg, B., "ESCA Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy." Almqvist and Wiksells, Uppsala, 1967.

5. Cerruti, L., *J. Chem. Soc. Faraday I*, **70**, 729 (1974).

6. Parkyns, N. D., *in* "Proceedings Fifth International Congress on Catalysis," p. 255 (1973).

7. Little, L. H., "Infrared Spectra of Adsorbed Species." Academic Press, New York, 1966.

8. Terenin, A., and Roev, L., *Spectrochim. Acta* **14**, 192 (1957).

9. London, J. W., and Bell, A. T., *J. Catal.* **31**, 96 (1973).

10. Otto, K., and Shelef, M., *J. Phys. Chem.* **74**, 2690 (1970); **76**, 37 (1972).