

ADSORPTION OF NITROGEN OXIDE ON A V_2O_5/Al_2O_3 CATALYST

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The adsorption and desorption of nitrogen oxide on oxidized and reduced V_2O_5/Al_2O_3 catalysts (14.7% (m/m) V_2O_5) were studied by gravimetry, infrared spectroscopy, and temperature programmed desorption measurements. On the reduced catalyst, NO is adsorbed giving rise to mono- and dinitrosyls which exhibit infrared bands at 1 690, 1 760, 1 820, and 1 895 cm^{-1} . A band also appears at 1 220 cm^{-1} corresponding to nitrite structures. The ratio between the nitrosyl and nitrite structures is approximately 4 : 1. Desorption at elevated temperatures is associated with the evolution of NO and N_2O in a volume ratio of 10 : 1. On the oxidized catalyst the adsorption occurs to an extent at least two orders of magnitude lower and no nitrosyls are formed.

The selective catalytic reduction of oxides of nitrogen with ammonia and catalysts for this reaction, particularly those based on V_2O_5/Al_2O_3 , have recently been studied extensively in connection with the application of this approach to the removal of oxides of nitrogen from gas emissions¹⁻⁴. However, often inconsistent data have been obtained concerning the formation of the adsorbed surface complexes and their nature, state of vanadium and the kinetics, and different reaction mechanism concepts have been suggested. It is commonly assumed that the first step is either adsorption of ammonia on Brønsted acid centres²⁻⁴, or its dissociative adsorption giving rise to the NH_2 fragment^{1,5,6}. The problem of the adsorption of ammonia in dependence on the catalyst pretreatment has been dealt with by us previously⁷. Nitrogen oxide is usually assumed to react with the adsorbed ammonia from the gas phase. This is in agreement with the results of study of the adsorption of NO on oxidized, and also on slightly reduced, V_2O_5/Al_2O_3 catalysts which do not indicate any measurable adsorption. Tagaki⁴, on the other hand, believes that adsorbed ammonia reacts with adsorbed $NO_2(ad)$ species forming only after the oxidation of nitrogen oxide by oxygen from the gaseous phase. This mechanism, however, has raised serious objections⁸.

During the reaction of nitrogen oxide with ammonia in the absence of oxygen, however, a deeper surface reduction takes place at higher temperatures; and as evi-

denced by measurements of Sokolova⁹ on samples reduced with hydrogen at 500°C, nitrogen oxide can adsorb on this surface to an appreciable extent.

The aim of the present work was to examine the effect of the oxidation–reduction state of the catalyst on the adsorption of nitrogen oxide, and to elucidate the nature of the structures formed.

EXPERIMENTAL

Catalyst was prepared as reported previously⁷; its V₂O₅ content was 14.7% (m/m). The catalyst was calcinated in air at 575°C. The reduced samples were obtained either by heating at 500°C for 1 h in a hydrogen atmosphere under a pressure of 13 kPa, followed by heating in vacuum for 3 h, or by heating at 500°C in a stream of a hydrogen–nitrogen mixture containing 10% (V/V) hydrogen, followed by heating in a stream of pure nitrogen at the same temperature.

Nitrogen oxide was prepared by reacting a NaNO₂ solution with an H₂SO₄ + FeSO₄ solution, dried by passing it through a solid KOH trap, and purified by repeated condensation in liquid nitrogen until a colourless condensate was obtained.

GTA measurements. The degree of catalyst reduction and the extent of oxygen and nitrogen oxide adsorption were determined gravimetrically on a quartz coil balance with automatic weight recording. The carrier gas was pure nitrogen freed from oxygen over a reduced BTS catalyst (Merck) and dried with liquid nitrogen in a freezing trap. The weight changes were corrected for physical sorption, established from the weight loss after flushing with nitrogen at the temperature of measurement.

Temperature programmed desorption (TPD) curves were measured with an apparatus equipped with a katharometric detector⁹. Helium served as the carrier gas at a flow rate of 100 ml min⁻¹ for 300 mg of sample. The temperature rise rate was 30°C min⁻¹. The apparatus enabled the composition of the gas phase after the adsorption to be determined chromatographically and the gas products to be analyzed during the desorption. The modification consisted in the insertion of a pair of freezing traps, where oxides of nitrogen and nitrogen (and oxygen if present) could be successively condensed from the gas stream. The two coil freezing traps, the second of which contained silica gel, were cooled in a liquid nitrogen bath. The gases were desorbed by increasing the temperature and analyzed on a molecular sieve column (N₂, O₂) and on a Polysorb I column (NO, N₂O).

Infrared spectra were measured on a UR 10 spectrophotometer (Carl Zeiss, Jena). The finely ground sample was pressed at 30 MPa into 50 mg plates 30 × 10 mm. In the upper, preparatory part of the cell for measuring the spectra during the adsorption, the sample could be thermally pretreated at temperatures up to 520°C. Because of the low sample transmission, the measurements were confined to the 1 000–2 300 cm⁻¹ region. The spectra were run at ambient temperature 30 min after admitting NO.

The maximum concentration of NO for the GTA measurements was 2% (V/V), the maximum pressure of NO was 40 kPa for the infrared spectra measurements and 101 kPa for the TPD measurements.

RESULTS

GTA Measurements

The weight loss observed after a 3 hours' reduction of the calcinated sample in the nitrogen-hydrogen stream at 450°C was 18.0 mg per g of calcinated sample which corresponds to 0.563 mmol O_2 , or $3.39 \cdot 10^{20}$ molecules of O_2 per g of calcinated sample. By adsorption of oxygen at room temperature in a nitrogen stream containing 2% O_2 the weight increased by 6.5 mg per g which corresponds to the adsorption of $1.22 \cdot 10^{20}$ molecules of O_2 per g. After an hour, the adsorbed amount remained virtually constant at room temperature. If the temperature is increased, additional adsorption of oxygen takes place and at 450°C the initial weight of the oxidized sample is attained.

No measurable adsorption of NO was observed on the oxidized sample, whereas on the reduced sample the adsorption led to a weight increase of 5.7 mg, corresponding to the adsorption of $1.14 \cdot 10^{20}$ molecules of NO on 1 g calcinated sample.

The weight increase accompanying the adsorption of NO on reduced catalyst with pre-adsorbed oxygen corresponded to the bonding of only $2.3 \cdot 10^{19}$ molecules per g of catalyst.

Slow heating to 230°C in a nitrogen stream led in both cases to a weight decrease down to nearly the initial value before the adsorption.

TPD Measurements

Two series of measurements were performed; before the adsorption, the sample was heated in a helium stream at 530°C in one series (Procedure I) and at 800°C in the other series (Procedure II). The higher temperature of sample pretreatment enabled the TPD curves to be followed up to the temperature indicated. For samples pretreated by Procedure I the TPD curves were distorted at temperatures above 530°C by a high background. However, as the total surface area measurements showed, prolonged heating at 800°C resulted in a partial surface sintering and in changes in the nature of the adsorption centres. The results are shown in Fig. 1. The TPD curves for Procedure I exhibit a single maximum, shifting from $T_{max} = 180^\circ C$ for the adsorption at 22°C to $T_{max} = 230^\circ C$ for the adsorption at 300°C. The height of the maximum lowers appreciably with increasing temperature of adsorption. With samples pretreated by Procedure II, additional desorption was observed above 500°C.

The analysis of the gaseous phase above the samples showed that during the adsorption of NO at temperatures above 100°C, a partial decomposition of NO takes place and a small amount of nitrogen is evolved.

In the desorbed products liberated during the TPD in the first maximum range, NO and N_2O were invariably present, their ratio being constant, approximately 10 : 1, irrespective of the temperature of adsorption. For samples treated at the

higher temperature (Procedure II) only NO was found in the desorption products of the first maximum under similar conditions.

The TPD trace after the adsorption of NO on the oxidized samples treated by Procedure I showed a hint of a maximum at approximately 500°C. The amount of the desorbed oxides of nitrogen, however, was at least two orders of magnitude lower than that for the reduced samples.

Infrared Spectroscopic Measurements

No new absorption bands appeared in the spectrum of the oxidized sample after admitting NO at a pressure of 40 kPa. Adsorption of NO at room temperature on the reduced sample brings about the appearance of bands at approximately 1 220, 1 690, 1 760, 1 820, and 1 895 cm^{-1} . For the band at 1 690 cm^{-1} the intensity changes with increasing pressure are different from the same dependences for the other bands of the spectra as evident from a comparison with the band at 1 760 cm^{-1} which is the most intense in the initial spectrum (Fig. 2), or from the dependence of the intensities of all the bands obtained by separation of the initial spectrum (Fig. 3).

All the adsorption forms were rather resistant to evacuation at room temperature while vanishing on increasing the temperature to 150°C. Increase in the temperature of adsorption led to a gradual intensity decrease for all the absorption bands (Fig. 4).

DISCUSSION

The formal composition of the oxide of vanadium after the reduction, as derived from the catalyst composition and the loss of oxygen during the reduction with hydrogen, can be written as $\text{V}_2\text{O}_{3.6}$, which approaches the V_4O_7 phase composition. In view of the stabilizing effect of the Al_2O_3 support on vanadium in its higher oxidation state¹⁰, however, it can be assumed that the degree of reduction will be different for the various layers of oxide of vanadium; a higher degree of reduction can be expected in the surface layer than in the inner layers, so that V^{3+} will prevail in the outer layer.

The formal composition of the oxide of vanadium after the chemisorption of oxygen at 25°C was $\text{V}_2\text{O}_{4.1}$, approaching the stoichiometric composition of V_2O_4 . The chemisorbed oxygen is bonded strongly and back-reduction only takes place on reaction with hydrogen at the initial temperature of reduction, 450°C. Thus vanadium in the oxidation state lower than 4 can be assumed to have vanished completely from the surface of the sample of the formal composition $\text{V}_2\text{O}_{4.1}$.

These assumptions concerning the oxidation state of vanadium in the surface layer form a basis for the interpretation of the interaction of nitrogen oxide as will be discussed later. V^{3+} is thus assumed to be the predominating initial state of vanadium

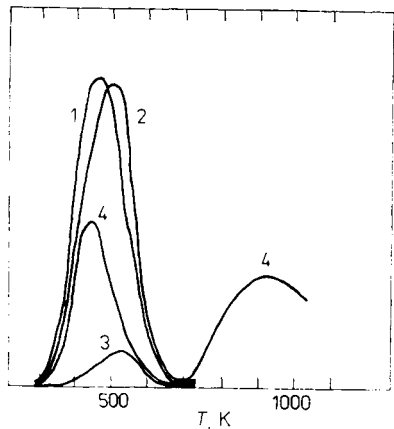


FIG. 1

TPD curves for the reduced samples pre-treated by Procedure I 1–3 and by Procedure II 4, after the adsorption of NO at 1 22°C, 2 100°C, 3 300°C, 4 22°C

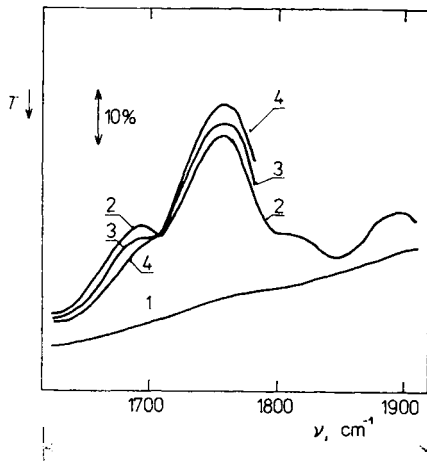


FIG. 2

Part of the infrared spectrum of reduced sample (Procedure I) after the adsorption of NO at room temperature. 1 background before the adsorption. Pressure of NO (kPa): 2 1.33, 3 6.74, 4 40

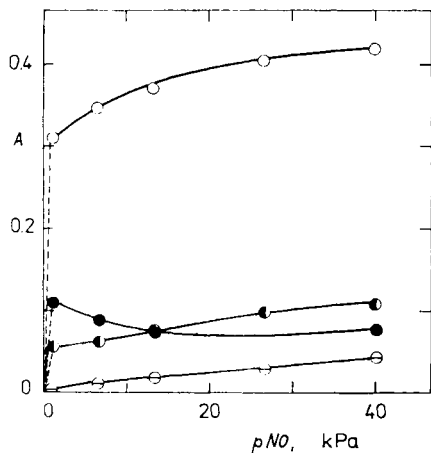


FIG. 3

Absorbances of some infrared absorption bands as a function of the pressure of NO for the reduced samples (Procedure I) at room temperature. Band position (cm^{-1}): \circ 1 220, \bullet 1 690, \circ 1 760, \bullet 1 895

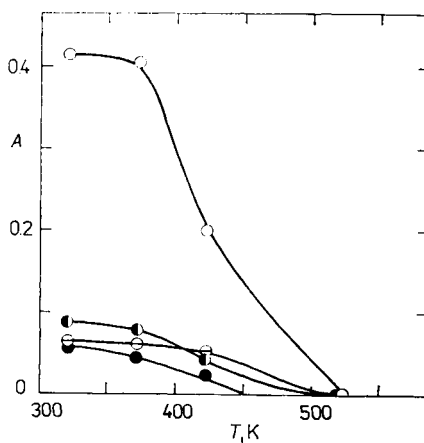


FIG. 4

Absorbances of infrared absorption bands after the adsorption of NO at 13.3 kPa on the reduced samples (Procedure I) as a function of the temperature of adsorption. Band position (cm^{-1}): \circ 1 220, \bullet 1 690, \circ 1 760, \bullet 1 895

on the reduced sample surface. After the chemisorption of oxygen at 25°C, the possibility of interaction predominantly with V⁴⁺ is considered.


A number of surface complexes can arise from the interaction of NO with transition metals in different oxidation states and with their oxides. In addition to nitrite and nitrate complexes, linear and nonlinear mononitrosyls, dinitrosyls and or polynitrosyls, and dimers which usually make up mixtures¹¹⁻¹³, can also be formed.

In addition to the bonding arising from the electron transfer from the σ orbital of ligand to a free d -orbital of transition metal, the electron back-transfer to the antibonding π^* orbital of ligand¹⁴ also participates in the NO bonding to transition metals, and the bond strength in the N—O grouping after the adsorption is affected considerably by the extent of this back-transfer. As a consequence, the ν_{NO} vibration can be observed over a wide wavenumber range, its band position reflecting sensitively the changing nature of the adsorption. Hence, interpretation of the infrared spectra can be of assistance in the elucidation of the nature of the complexes sorbed.

As mentioned above, the bands can be divided into two groups with respect to the properties observed. One group comprises the bands above 1 600 cm⁻¹, the other group contains the band at approximately 1 220 cm⁻¹. The bands in the first group can be characterized according to their position and behaviour as follows.

1) The band at 1 690 cm⁻¹ is the only one to decrease in intensity with increasing pressure of NO and time of adsorption.

2) The band at 1 895 cm⁻¹ is shifted to higher wavenumbers as compared with that of gaseous NO, indicating the occurrence of a different adsorption centre with an enhanced electroaffinity and a lowered extent of electron back-transfer, giving rise to a species that can be written as NO ^{δ^+} .

3) The remaining bands at 1 760 and 1 820 cm⁻¹, of which that at the lower wavenumber is considerably more intense, appear in an intensity ratio which is virtually constant under various conditions. This suggests that the two bands are due to the asymmetric and symmetric vibrations of NO in the surface M  complex (dinitrosyl). The $A_{\text{sym}}/A_{\text{asym}}$ absorbance ratio is approximately 0.16 which inserted into the equation¹²

$$A_{\text{sym}}/A_{\text{asym}} = \cot^2 \theta \quad (1)$$

gives an estimate of 135–140° for the angle θ between the two M–NO bonds; this value approaches the values found for dinitrosyl¹². With regard to this great θ value the adsorption to the vanadium cation can be assumed to be subject to no appreciable steric hindrance and the adsorption centre on the surface to be well accessible. Hence the band at 1 690 cm⁻¹ can be attributed to mononitrosyl, and its

intensity decrease at higher pressures of NO can be explained in terms of its conversion to dinitrosyl. A similar reaction has been reported, *e.g.* in ref.¹². The fact that the band at $1\ 690\text{ cm}^{-1}$ does not vanish completely at high pressures appears to indicate that at least part of the adsorption centres are not readily accessible for the bonding of the second group.

Since all bands in the $1\ 600\text{--}1\ 900\text{ cm}^{-1}$ range vanish completely on the action of oxygen at 25°C both before and after the adsorption of NO, we suppose that all the corresponding adsorbed species are bonded to V^{3+} ; this interpretation seems to be more adequate than the alternative explanation in terms of the formation of mononitrosyl on centres in different oxidation states, where in analogy to nitrosyls with iron ions^{15,16} bands at higher wavenumbers would correspond to adsorption on ions in higher oxidation states. Within this concept, the lowest-wavenumber band at $1\ 690\text{ cm}^{-1}$ should belong to $V^{3+}\text{-NO}$ and the band pair at $1\ 760$ and $1\ 820\text{ cm}^{-1}$ to the bonding to V^{4+} . The decrease of the band at $1\ 690\text{ cm}^{-1}$ at higher pressures would then imply oxidation of V^{3+} on the action of NO even at room temperature. This, however, disagrees with the identical decrease of all of the bands on adsorption of NO at elevated temperatures when oxidation definitely takes place, and also with the same intensity decrease for all the bands above $1\ 600\text{ cm}^{-1}$ on the chemisorption of oxygen. The assignment of the bands at $1\ 760$ and $1\ 820\text{ cm}^{-1}$ to the dimer, which is usually stable at low temperatures only, does not seem appropriate either.

Proceeding from the concept of the formation of the NO^+ species and a mononitrosyl and dinitrosyl pair, adsorption on vanadium in a single oxidation state, *viz.* V^{3+} , can be assumed. This is consistent with the above discussion of the oxidation state of the surface after its reduction with hydrogen and with the observation of Davydov¹⁷ that during the adsorption of CO on the system under study, $V^{3+}\text{-CO}$ is predominantly formed.

The different dependences on the experimental conditions for the band at $1\ 220\text{ cm}^{-1}$ indicate that this band belongs to an entirely different structure. Assignment to the nitrate complex can be ruled out although the band of the latter usually appears within this range, because in our case the other characteristic absorption band near $1\ 600\text{ cm}^{-1}$ is lacking and also nitrate structures are usually considerably more stable¹⁸. A surface complex giving rise to a band at $1\ 220\text{--}1\ 240\text{ cm}^{-1}$, which decomposed, similarly as observed by us, even during the evacuation at temperatures up to 180°C , has been reported for the adsorption of NO on samples of alumina; the absorption band has been attributed to structures, where NO is in interaction with surface oxygen anions¹⁸⁻²⁰.

Regarding the fact that chemisorption of oxygen at 25°C prevents the formation of nitrosyls while no apparent interaction with a group characterized by the band at $1\ 220\text{ cm}^{-1}$ takes place, the initial fractions of the two forms of adsorption could be estimated based on the GTA measurements of the amounts of NO adsorbed before

and after the chemisorption of oxygen. In this manner, more than 80% of the total bonded NO was found to be adsorbed on the reduced catalyst in the form of a complex of nitrosyl type.

A comparison of the number of chemisorbed oxygen atoms with the corresponding number of NO molecules bonded in the form of the group of nitrosyls shows that the number of adsorbed oxygen atoms is about 2.5 times higher. If dinitrosyl formed predominantly, the ratio of the centres on which oxygen and nitrogen oxide adsorbed would additionally increase. On the other hand, adsorption on V^{3+} centres is assumed both for the adsorption of oxygen and for the formation of nitrosyls. This discrepancy can be explained so that due to the mobility of its atoms, oxygen is sorbed partly also within inner layers of the vanadium oxide bulk, whereas the formation of nitrosyls involves interaction with V^{3+} in the surface layer only.

Both infrared spectroscopy and TPD measurements showed that the stability of all the structures formed is approximately the same. Their decomposition takes place below 180°C. The analysis of the decomposition products during the TPD measurements showed that in addition to NO, N_2O is also present and the ratio of the two is approximately 10 : 1.

The TPD measurements up to 800°C on samples treated at the higher temperature (Procedure II) point to the existence of additional adsorption forms with a higher stability which, however, do not give rise to an observable absorption in the infrared spectrum. The temperature at which these structures decompose giving NO is considerably higher than, *e.g.*, that for the nitrate ion which is among the more stable with respect to the thermal decomposition in similar systems^{18,20}.

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