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An Infrared Study of the Surface Properties of Metal Oxides

2. The Interaction of Ammonia with the Surface of Fe_2O_3, ZnO, MoO_3, and V_2O_5

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The infrared spectra of Fe_2O_3, ZnO, MoO_3, and V_2O_5 were investigated before and after the adsorption of ammonia at 20°C and after its desorption at room and higher temperatures. A general feature of all the oxides was the presence on their surfaces of Lewis acid centers capable of adsorbing ammonia by the formation of a coordination bond. In addition, MoO_3 and V_2O_5 adsorbed ammonia to yield NH_4^+ ions, indicating the presence of Brønsted centers on their surfaces which may be due to the hydrogen of OH groups. The ability of OH groups to release protons was assumed to be greatly affected by the electron-acceptor capacity of the cation of the oxide. The adsorption of ammonia on Fe_2O_3 and ZnO is also accompanied by interaction with the surface oxygen to give surface amines or oxides of nitrogen.

Previously (*1*) we studied the interaction of ammonia with the surface of Cr_2O_3, a catalyst which displays a high activity in the complete oxidation, and a low selectivity in the partial oxidation, of organic compounds. It was considered of interest to carry out an analogous study on a number of catalysts having different properties in the processes of oxidation.

EXPERIMENTAL METHODS

Fe_2O_3 and MoO_3 were prepared by decomposition of ferric hydroxide and ammonium paramolybdate (*2*); ZnO and V_2O_5 were commercial products of analytically pure grade. The characteristics of the oxide samples and the conditions of their preparation and treatment before recording ir spectra are presented in Table 1. The crystalline phases of the samples were studied by X-ray analysis and their surface areas were determined by a chromatographic method based on the desorption of nitrogen.

Ammonia adsorption was performed at room temperature.

Infrared spectra of pressed samples (20 mg, as an 8 × 27-mm plate) were recorded with a UR-20 spectrophotometer in the range 800 to 4000 cm^{-1}. Unfortunately, the samples of Fe_2O_3, MoO_3, and V_2O_5 were opaque above 1800 cm^{-1}.

RESULTS AND DISCUSSION

Fe_2O_3

In the original spectrum of Fe_2O_3 some absorption bands at 790, 925, 980, and 1050 cm^{-1} can be seen (Fig. 1, spectrum 1). It differs from the spectrum obtained in Ref. (*3*) by a smaller number of absorption bands (one band at 790 cm^{-1} instead of

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TABLE 1

The Characteristics of the Investigated Oxide Sample and Conditions of Their Treatment before Recording ir Spectra

Initial substance	Temperature of calcination (°C)	Oxide phase[a]	Specific surface area (m^2/g)	Conditions of pretreatment
$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	500	MoO_3	1.2	Evacuation for 6 hr, then heating in oxygen at 450°C for 3 hr (100 Torr) with subsequent cooling in oxygen to 20°C
$Fe(OH)_3$[b]	500	α-Fe_2O_3	9.3	As above
V_2O_5	500	V_2O_5	3.0	As above
ZnO	500	ZnO	3.0	As above

[a] The oxide phase remained unchanged after the ammonia adsprption experiments.

[b] $Fe(OH)_3$ was prepared by precipitation with ammonia from a solution of $Fe(NO_3)_2\cdot 9H_2O$.

three bands at 797, 835, and 890 cm^{-1}), a shift of the absorption bands at 918 and 965 cm^{-1} to 925 and 980 cm^{-1}, and the appearance of a new absorption band at 1050 cm^{-1}. These discrepancies can be attributed to a different temperature of sample treatment in oxygen (450°C in our tests and 250°C in Ref. (*3*)). It should be noted that the absorption band at 1050 cm^{-1} was also registered in the Fe_2O_3 spectrum of Amerikov and Kasatkina (*4*). The above absorption bands observed in the Fe_2O_3 spectrum we assign, according to previous authors (*3*, *5*), to the vibrations of the metal–oxygen bond of different orders. The intensity of these bands remains unaffected in ammonia adsorption and thermodesorption (Fig. 1, spectra 2–6).

During ammonia adsorption broad bands arise in the spectrum at 1100 to 1300 and 1620 cm^{-1} (Fig. 1, spectrum 2) which characterize symmetric and asymmetric vibrations of the N–H bond in ammonia coordinately linked with Lewis acid sites (*6*–*8*). Evacuation of the ammonia at room temperature results in practically no changes in these absorption bands. In due course (11 hr) a broad band in the spectrum range 1100 to 1300 cm^{-1} disappears and three new bands at 1090, 1320, and 1720 cm^{-1} become visible (Fig. 1, spectrum 3). These frequencies can be assigned to the vibrations of nitrogen–oxygen bonds (*9*) involving surface nitrogen oxides (*10*). We think that the above changes in the spectrum are due to a slow surface reaction

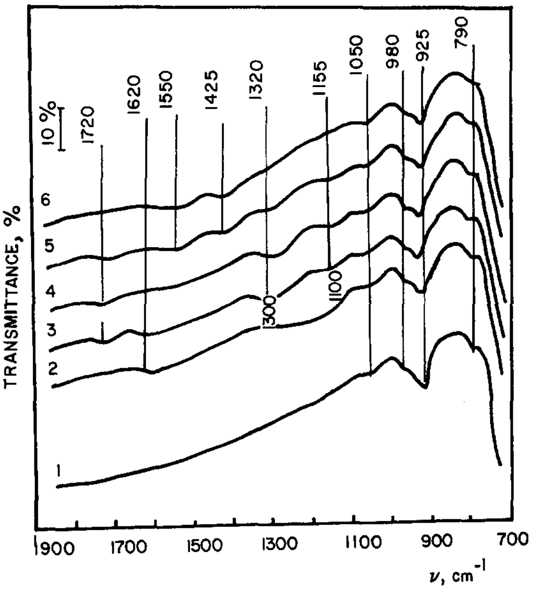

FIG. 1. Infrared spectra of Fe_2O_3 before and after adsorption–thermodesorption of NH_3. (1) Fe_2O_3; (2) after adsorption of NH_3 and outgassing at 20°C for 1 hr ($P = 5 \times 10^{-3}$ Torr); (3) spectrum 2 of NH_3 adsorbed after being left for 11 hr at 20°C and $P = 5 \times 10^{-3}$ Torr; (4) spectrum 3 after outgassing at 120°C; (5) spectrum 4 after outgassing at 165°C; (6) spectrum 5 after outgassing at 210°C.

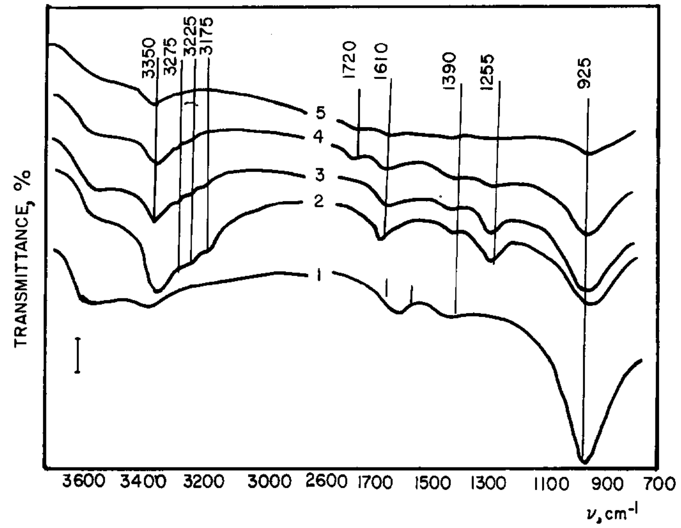

FIG. 2. Infrared spectra of ZnO before and after adsorption–thermodesorption of NH_3. (1) ZnO; (2) ZnO after adsorption of NH_3 at 20°C; (3) spectrum 2 after outgassing at 20°C; (4) spectrum 3 after outgassing at 110°C; (5) spectrum 4 after outgassing at 165°C.

between adsorbed ammonia and surface oxygen. Griffiths *et al.* (*11*) noted that a surface reaction occurred on admission of an ammonia–oxygen mixture to a cell containing heated Fe_2O_3.

Evacuation at higher temperatures reduces the intensity of the above bands until they disappear completely (Fig. 1, spectra 4–6). In this case two new absorption bands appear at 1550 and 1425 cm^{-1} (Fig. 1, spectra 5 and 6), the nature of which was not investigated in the present work. However, one can assume that the changes in the spectra observed during evacuation at elevated temperatures are due to further conversions of surface complexes.

ZnO

In the original ZnO spectrum one can see some absorption bands at 925, 1390, and 1550 to 1600 cm^{-1} and a broad band in the high-frequency region with two maxima at 3390 and 3560 cm^{-1} (Fig. 2, spectrum 1). The first band lie in the spectral region typical of metal–oxygen bonds (*5*). During evacuation the intensity of this band decreases markedly and is reestablished completely on heating in oxygen. The absorption bands at 1390 and 1550 to 1600 cm^{-1} are commonly observed in background ZnO spectra (*12–15*) though they have been interpreted differently. These bands were not eliminated even on prolonged evacuation at high temperature. However, they do not affect the detection of new bands. The broad band with maxima at 3390 and 3560 cm^{-1} can be ascribed to the surface hydroxyls linked by hydrogen bonds (*6*, *7*).

During ammonia adsorption new adsorption bands occur in the spectrum at 1255, 1625, 3175, 3225, 3275, and 3335 cm^{-1} (Fig. 2, spectrum 2). Their intensity is reduced with increasing temperature of evacuation (spectra 3–6). Evacuation of the sample at room temperature shifts the two bands at 1625 ayd 3335 cm^{-1} to 1610 and 3350 cm^{-1}, respectively, and at 110°C causes the appearance of a new band at 1720 cm^{-1}. At 165°C the transmission of the sample is sharply decreased though one can observe the bands at 1610, 1720, and 3350 cm^{-1} (Fig. 2, spectrum 5).

The data obtained after ammonia adsorption over ZnO can be interpreted as follows. The adsorption bands at 3335 and 1625 cm^{-1} correspond to the stretching and deformation vibrations of ammonia linked with the surface OH groups by a weak H bond (*6*, *7*). The four bands at 3350, 3275, 1610, and 1255 cm^{-1} present in the spectra after evacuation are due to the asymmetric and symmetric stretching and deformation vibrations of ammonia coordinately linked to the surface Lewis centers (*6*, *7*).

The bands at 3225 and 3175 cm^{-1} we assign to the asymmetric and symmetric stretching vibrations of the surface NH_2 groups resulting from the oxidation of ammonia by catalyst oxygen. Such an assignment is based on the empirical relationship for the frequencies of the above vibrations established for a great number of primary amines, (*16*):

$$\nu_{sNH} = 345.8 \quad \text{(a lower frequency band)} \quad + \quad 0.876\,\nu_{as} \quad \text{(a higher frequency band)}$$

It should be noted here that the stretching vibration for free NH_2 groups is observed at higher frequencies (3500–3400 cm^{-1}) and the corresponding deformation vibration within the frequency range 1560 to 1640 cm^{-1} (*15*, *17*). However, in the case of N–H groups involved in a H bond, the stretching vibration is shifted to lower frequencies and the deformation vibration to higher frequencies (*16*, *17*). The above relationship holds if both hydrogen atoms in the NH_2 groups participate in the formation of the H bond. Thus the absorption bands at 3225 and 3175 cm^{-1} may be attributed to vibrations of the NH_2 group in which the two hydrogen atoms are bound to adjacent oxygen atoms of the catalyst by a H bond. The deformation vibration band seems to be overlapped by the bands at 1610 and 1600 cm^{-1} observed in the spectrum and, therefore, is not resolved separately.

The absorption band at 1720 cm^{-1} which appears in the spectrum after evacuation of the sample at 110°C (Fig. 2, spectrum 3) may be assigned to the vibrations of the surface nitrogen oxide, Me–N=O (*18*).

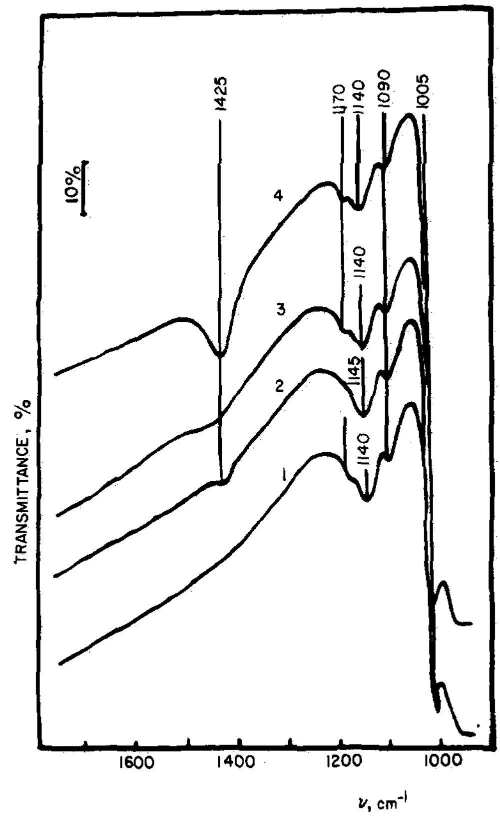

FIG. 3. Infrared spectra of MoO_3 before and after adsorption–thermodesorption of NH_3. (1) MoO_3; (2) MoO_3 after NH_3 adsorption at 20°C; (3) spectrum 2 after outgassing at 20°C; (4) spectrum of ammonia adsorbed after adsorption of H_2O.

MoO_3

The original MoO_3 spectra (Fig. 3, spectrum 1) taken of both ammonium paramolybdate and molybdenic acid after after their appropriate treatment were similar and displayed absorption bands at 1005, 1090, and 1140 cm^{-1} with a shoulder at 1170 cm^{-1} (in the lower frequency range complete absorption was observed). There is no information on infrared spectra of MoO_3 in the frequency range higher than 1000 cm^{-1}; the available literature data deal with the frequency range 700 to

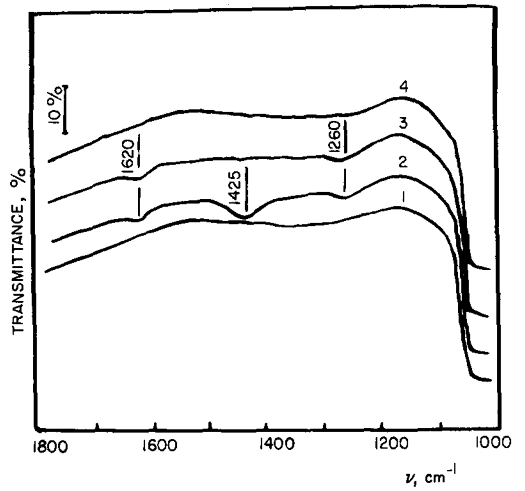

FIG. 4. Infrared spectra of V_2O_5 before and after adsorption–thermodesorption of NH_3. (1) V_2O_5; (2) V_2O_5 after adsorption of NH_3 at 20°C; (3) spectrum 2 after outgassing at 120°C; (4) spectrum 3 after outgassing at 250°C.

1000 cm^{-1} (*5, 19, 20*). In the spectrum of MoO_3 pressed with KBr some absorption bands can be observed at 710, 825, 890, and 995 cm^{-1} which are roughly in agreement with literature data (*19, 20*) and there is also an absorption band of low intensity at 1140 cm^{-1}. The low intensity of the latter is evidently due to reaction with KBr. The absorption bands observed in the frequency range higher than 1000 cm^{-1} we assign to the Mo=O vibration by analogy with some other oxides (*3, 4*).

After ammonia adsorption the shoulder at 1170 cm^{-1} disappears, the absorption band at 1140 cm^{-1} shifts to 1145 cm^{-1}, and a low-intensity band appears at 1425 cm^{-1} (Fig. 3, spectrum 2).

Outgassing at 20°C reestablished the spectrum in the frequency range 1170 to 1190 cm^{-1}. The absorption band at 1425 cm^{-1} remained in the spectrum (Fig. 3, spectrum 3) and disappeared only after evacuation at temperatures, higher than 200°C.

Some experiments were carried out on ammonia adsorption on MoO_3 on which water vapor had been preadsorbed. In this case an intense absorption band appeared at 1425 cm^{-1} and the band did not disappear on evacuation of the sample at room temperature (Fig. 3, spectrum 4).

The reversible changes in the range 1170 to 1090 cm^{-1} observed during the introduction and evacuation of ammonia are due, in our opinion, to ammonia adsorption on Lewis centers, accompanied by appearance of the absorption band at 1145 cm^{-1}. The disappearance of the band at 1170 cm^{-1} may be attributed to the overlapping of the coordinately linked ammonia absorption band and the absorption bands of the original metal oxide. The bond between ammonia and surface Lewis centers is unstable as the original MoO_3 spectrum reappeared during outgassing at 20°C.

The absorption band at 1425 cm^{-1} may be assigned to the NH_4^+ vibration (*6, 7, 20*). The corrrectness of this assignment is confirmed by the increase of the intensity of this absorption band after the preadsorption of water vapor. These data indicate that H_2O is adsorbed over MoO_3 in the form of OH groups. This adsorption is irreversible because the absorption band at 1425 cm^{-1} remains in the spectrum after sample evacuation at room temperature. It is worth mentioning that physically adsorbed water can also act as a proton source which in the ammonia adsorption yields the NH_4^+ ion, as was previously observed on Fe_2O_3 by Griffiths *et al.* (*11*). However, evacuation at toom temperature causes water desorption and removal of the NH_4^+ ion from the surface.

V_2O_5

In the original V_2O_5 spectrum (Fig. 4, spectrum 1) there is a broad absorption band of low intensity in the frequency region 1180 to 1400 cm^{-1} which cannot be eliminated from the spectrum by high-temperature treatment *in vacuo*. These bands are attributed to metal–oxygen bonds of different bond orders (*5*).

TABLE 2

Absorption Bands of Ammonia Adsorbed on Metal Oxides at 20°C

Oxide	$\delta_{as}NH_3$ (cm^{-1})	δ_sNH_3 (cm^{-1})	δNH_4^+ (cm^{-1})	ν_sNH_3 (cm^{-1})	$\nu_{as}NH_3$ (cm^{-1})	νNH_2 (cm^{-1})
Cr_2O_3	1610	1255	—	3370	3275	—
Fe_2O_3	1620	1100–1300	—	No transmittance		
ZnO	1625	1255	—	3350	3275	3225, 3175
V_2O_5	1620	1260	1425	No transmittance		
MoO_3	Weak transmittance	1145	1425	No transmittance		

During ammonia adsorption three absorption bands arise at 1260, 1425, and 1620 cm^{-1} (Fig. 4, spectrum 2). The two at 1260 and 1620 cm^{-1} may be ascribed to symmetric and asymmetric bond vibrations of ammonia coordinately linked to Lewis centers.

The absorption band at 1425 cm^{-1} is characteristic of the NH_4^+ ion (*6,7*). It is eliminated from the spectrum when the outgassing temperature is 120°C (Fig. 4, spectrum 3), while the absorption bands of coordinately linked ammonia disappear only during outgassing at 250°C (spectrum 4). These data enable us to suggest that on V_2O_5 the Lewis centers display a greater acid strength than the Brønsted centers.

CONCLUSIONS

Our findings on the interaction of ammonia with the surfaces of Fe_2O_3, ZnO, MoO_3, and V_2O_5 as well as previously obtained data on ammonia adsorption on Cr_2O_3 (*1*) are presented in Table 2. These data permit some conclusions to be made.

The presence of Lewis acid centers, electron-accepting centers, capable of adsorbing ammonia by forming a coordinated bond on the surface of the oxides is common for all the oxides studied. In addition, MoO_3 and V_2O_5 are capable of adsorbing ammonia to yield the NH_4^+ ion. The presence or absence of Brønsted centers on the surface of metal oxides may be accounted for as follows. It is known from the literature that hydroxyl groups resulting from water chemisorption are observed on most metal oxides. These can be eliminated from the surface by high-temperature treatment *in vacuo*. However, not all of them can act as Brønsted acid centers. Thus, on the ZnO surface (Fig. 2) we observed the presence of OH groups, and according to the literature they can remain on the surface of Cr_2O_3 (*21*) and Fe_2O_3 (*22*). But after thermal treatment *in vacuo* these OH groups are unlikely to be a proton source in the interaction with ammonia to yield the NH_4^+ ion. Besides, the addition of water in the ammonia adsorption on Cr_2O_3 (*8*) gives no NH_4^+ ion, as was shown on Al_2O_3 (*6, 7*).

At the same time MoO_3 and V_2O_5 are capable of protonizing OH groups during water chemisorption even at high temperature.

Such a discrepancy in the surface properties of these metal oxides may be due to different electron-acceptor properties of the metal ion. A comparison of data on the interaction of ammonia, olefins, and acrolein with the surface of a series of metal oxides (*23–25*) permits the conclusion to be drawn that the electron-acceptor ability of chromium and iron ions is greater than that of molybdenum ions. We think that the ability of OH groups to release protons is mainly due to the electron-acceptor properties of the oxide ion bound to the OH group. However, an electronic mechanism for the formation of OH groups on the oxide surface with different electron-acceptor abilities has not yet been elucidated and requires further investigation.

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