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An Infrared Study of Surface Properties of Metal Oxides

I. The Interaction of Ammonia with the Surface of Cr_2O_3

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Infrared spectra of Cr_2O_3 taken before and after adsorption of NH_3 and $^{15}ND_3$ at 20°C are reported, as well as those registered on desorption at 20°C and higher temperatures. It has been found that ammonia is chemisorbed on electron-acceptor centers both reversibly and irreversibly. Alongside this process, ammonia interacts with oxygen of the Cr_2O_3 surface to give surface compounds involving the NO group. The formation of an NH_4^+ ion has not been detected.

INTRODUCTION

In recent years some papers have been published dealing with the influence of the acidity of oxide catalysts on their selectivity in the oxidation of organic substances, in particular, propylene and acrolein (*1–4*). The metal oxides used displayed both high and low selectivity, and accordingly it was of interest to study the nature of their acid centers. The ammonia molecule is useful for this as the variation in its ir spectra in the course of adsorption permits one to elucidate the nature of the acid centers (Lewis or Brønsted types).

The experiments reported here were carried out on Cr_2O_2 as a catalyst which displayed a high activity in complete oxidation and a low activity in partial oxidation. It is a part of extensive research on the surface properties of metal oxides.

EXPERIMENTAL

Infrared spectra were recorded by a UR-20 spectrophotometer. Powdered Cr_2O_3 was obtained by decomposition of ammonium bichromate and pressed into plates (8 × 27 mm, 10 mg) at a pressure of 5000–7000 kg/cm². The Cr_2O_3 particles were 1–10 μm in size. Before measurements took place, Cr_2O_3 was evacuated for 6 hr at 450°C and at a pressure of $3 \cdot 10^{-3}$ Torr and then activated in O_2 for 3 hr at the same temperature and $P = 100$ Torr followed by outgassing for 0.5 hr and cooling to room temperature.

Sample treatment and ammonia adsorption were performed in a quartz vacuum cell fitted with an NaCl window which had no grease connections in the used part for measurements. Spectra were taken (a) before ammonia was introduced, (b) in the presence of gaseous NH_3,[1] and (c) after ammonia desorption at room and higher temperatures.

Ammonia of commercial grade was purified by fractionation *in vacuo* and was dried over metallic sodium. Its purity was checked spectroscopically. Some experiments were carried out using deuterated

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[1] The effect of absorbance due to gaseous NH_3 was eliminated by placing a cell with NH_3 in the reference beam of the spectrophotometer.

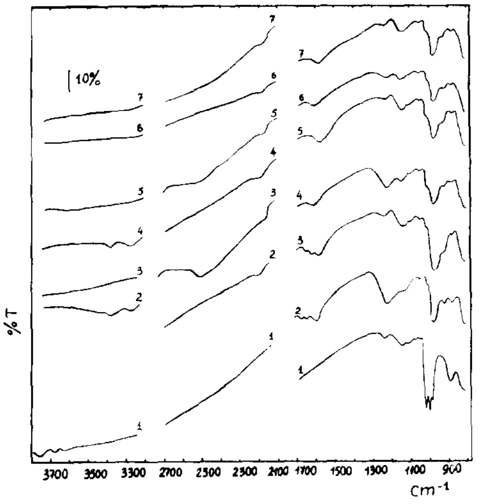

FIG. 1. Infrared spectra of Cr_2O_3 before and after adsorption of NH_3 and $^{15}ND_3$. (1), Cr_2O_3; (2), Cr_2O_3 after NH_3 adsorption at 20°C; (3), Cr_2O_3 after $^{15}ND_3$ adsorption at 20°C; (4), spectrum 2 after outgassing at 20°C; (5), spectrum 3 after outgassing at 20°C; (6), spectrum 4 after outgassing at 200°C; (7), spectrum 5 after outgassing at 200°C.

labeled ammonia $^{15}ND_3$ enriched with 97.4% ^{15}N and 99.8% deuterium.

RESULTS AND DISCUSSION

In the original Cr_2O_3 spectrum (spectrum 1 in Fig. 1), one can observe several absorption bands of different intensity at 820, 880, 985, 998, 1021, 1050, 1075, 1100, 1150, and 1235 cm^{-1}. The high frequency range of the spectrum is characterized by a smooth decrease in the transmission of a sample up to 3500 cm^{-1}. In the 3500–3800-cm^{-1} range some bands of low intensity can be seen.

According to previous workers (*5*, *6*), the absorption in the 1000–800-cm^{-1} range is due to chromium–oxygen vibrations of different Cr–O bond order. It is known that, regarding the metal–oxygen bond and its order, the vibration frequency is higher, the lower the cation saturation (*6*). The absorption bands at 880, 985, 998, and 1021 cm^{-1} are in good agreement with those of Davidov *et al.* (*6*). As special experiments have shown, the appearance of new bands unregistered in Ref. (*6*) is due to a different preliminary thermal treatment of the sample in oxygen (450°C in our work and 250°C in Ref. (*6*)]. It should be noted that the absorption in the 1100–1200-cm^{-1} range is characteristic for MnO_2, Fe_2O_3, and some other oxides which have adsorbed oxygen at high temperatures (*6*, *7*).

The character of the absorption in the wavenumber (frequency) range higher than 3500 cm^{-1} indicates the presence of individual and hydrogen-bonded hydroxyls of different strength on the surface of Cr_2O_3 (*8*, *9*).

Ammonia adsorption at room temperature (spectrum 2, Fig. 1) causes the appearance of absorption bands at 1675, 1650, 1610, and 1225 cm^{-1}; the band maximum at 1150 cm^{-1} is shifted to 1140 cm^{-1}, and there is a simultaneous increase in the absorption within this range. Significant changes are also observed in the 1100–700-cm^{-1} range. Instead of the two bands at 998 and 985 cm^{-1}, one appears at 980 cm^{-1}. The intensity of the band at 1021 cm^{-1} is sharply reduced and that at 880 cm^{-1} is decreased to a lesser degree. One can observe a new band of low intensity at 920 cm^{-1}; the position and intensity of the two bands at 1050 and 820 cm^{-1} remain unchanged while those at 1100 and 1075 cm^{-1} disappear.

In the spectrum range higher than 2100 cm^{-1}, some changes have also been noticed. In the interval 2220–2180 cm^{-1} and at about 3370 and 3275 cm^{-1} some new bands have been registered while three bands at frequencies higher than 3500 cm^{-1} have disappeared.

Ammonia evacuation at room temperature (spectrum 4) resulted in the disappearance of bands at 1675 and 1650 cm^{-1}, a decrease in the intensity of bands at 3370, 1610, and 1225 cm^{-1}, and a lowering of the $\bar{\nu}$ value of the band at 1150 cm^{-1}.

The observed absorption bands and the changes in the spectra may be interpreted as follows. Using data from the literature

(*9*, *10*), the absorption bands at 1225 and 3370 cm^{-1} were attributed to symmetric and those at 1610 and 3275 cm^{-1} to asymmetric deformational and stretching vibrations in the molecule of adsorbed ammonia coordinately linked with electron-acceptor centers of the surface (Lewis acid centers). It will be shown below that the band at 1610 cm^{-1} is complex and consists of two bands corresponding to the vibration of different surface compounds.

The above assignment of bands is confirmed by data on the $^{15}ND_3$ adsorption (spectrum 3). The substitution of hydrogen by deuterium in gaseous ammonia is known to lead to a shift in vibration frequency to the low wavenumber region. In this case the ratio of frequencies in light and deuterated ammonia spectra calculated from literature data (*11*) is 1.30–1.38. Therefore, one can expect that in the $^{15}ND_3$ adsorption the above absorption bands of coordinately linked ammonia will be observed at 940, 2520, 1170, and 2360 cm^{-1}. The first two bands are in close agreement with the experimental bands at 930 and 2510 cm^{-1}; the third one occurs in the vibration region of a chromium–oxygen bond at 1150 cm^{-1}, and therefore it is shielded, while the band at 2360 cm^{-1}. does not appear, presumably because of low intensity (spectrum 3).

The position of bands assigned to coordinately linked ammonia remains unchanged after evacuation at room temperature (spectra 4 and 5) though their intensity is somewhat reduced. This is evidence for a partial ammonia desorption and, hence, for reversible and irreversible ammonia adsorption on Lewis acid centers.

The changes due to the adsorption both of NH_3 and $^{15}ND_3$ in the 1100–700-cm^{-1} range are of an analogous character. We consider that the appearance of one absorption band at 980 cm^{-1} instead of the two bands at 998 and 985 cm^{-1}, the sharp decrease in intensity of the absorption band at 1021 cm^{-1} and the disappearance of bands at 1100 and 1075 cm^{-1} are due to both the ammonia adsorption on Lewis centers [which result in an increase in the saturation of a chromium cation in electron-donor interaction with ammonia (*6*)] and the oxidation of ammonia by surface oxygen.

The absorption in the 2220–2180-cm^{-1} range and the bands at 1675, 1650, and 1140 cm^{-1} which occurred in the spectrum after NH_3 adsorption (spectrum 2) and the absorption in the 2175–2155-cm^{-1} range and at 1650, 1580, and 1115 cm^{-1} which appeared in the spectrum after $^{15}ND_3$ adsorption (spectrum 3) testify to the oxidation of ammonia alongside its adsorption.

A small difference (25–45 cm^{-1}) in the position of the corresponding bands in the spectrum after NH_3 and $^{15}ND_3$ adsorption indicates that these bands are determined by the ^{14}NO and ^{15}NO bond vibration. This is confirmed by data on absorption of different nitrogen oxides involving ^{14}N and ^{15}N for which the difference in frequencies is of the same order (*11*).

It should be noted that the absorption band at 1610 cm^{-1} is likely to consist of two overlapping bands corresponding to the δ_{as} NH_3 vibration, as mentioned above, and to the NO bond vibration. Evidence in favor of the latter is the appearance of the band at 1580 cm^{-1} in the Cr_2O_3 spectrum after adsorption of $^{15}ND_3$.

The absorption bands at 1675–1650 and 1140 cm^{-1} after NH_3 adsorption and those at 1650–1625 and 1115 cm^{-1} after $^{15}ND_3$ adsorption appear and disappear under analogous conditions, i.e., after adsorption and outgassing at room temperature. These bands we assign to the vibration of a surface compound involving the NO bond weakly linked with Cr_2O_3. The absorption bands at 1610 and 2220–2180 cm^{-1} (spectrum 2) and at 1580 and 2175–2155 cm^{-1} (spectrum 3) are also assigned to the vibration of a surface compound involving the NO bond chemisorbed, however, in an irreversible form.

It is impossible, judging from the data

obtained, to assign the above bands to surface compounds of any definite structure. By analogy with the surface compounds formed in NO and NO_2 adsorption on metal oxides (*8*, *12*, *13*), we assume that they are due to valence vibrations of the bonds in both neutral NO and NO^+ groups. The formation of surface compounds involving the NO group was observed by Griffiths *et al.* in ammonia adsorption on Fe_2O_3 (*14*).

The surface oxidation of ammonia together with the formation of surface compounds involving the NO group is inevitably accompanied by the formation of OH groups. The disappearance of the absorption bands in the Cr_2O_3 spectra in the range higher than 3500 cm^{-1} and the occurrence of a weak broad band at 3600–3400 cm^{-1} after adsorption of NH_3 and a more intensive band at 3690–2400 cm^{-1} after $^{15}ND_3$ adsorption can be attributed to the formation by hydrogen bonds between OH groups on the surface and those originated by the ammonia oxidation.

Evacuation at higher temperatures results in a decrease in the absorption band intensities of ammonia irreversibly chemisorbed at room temperature and also those of its oxidation products (spectra 6 and 7 at an evacuation temperature of 200°C). These changes can be accounted for by a partial desorption of ammonia from electron-acceptor centers, the interaction of the latter with oxide oxygen, and the desorption of ammonia oxidation products. The absorption bands corresponding to adsorbed ammonia completely disappear at an evacuation temperature of 250°C while the remaining bands disappear only when the temperature is increased as high as 400°C.

Considering *in toto* the data obtained, it should be noted that on the chromium oxide surface in contact with ammonia one can observe two types of interaction, namely, ammonia adsorption on electron-acceptor centers (Lewis acid centers) and the surface reaction between ammonia and surface oxygen. NH_4^+ ion formation at the expense of a proton of the OH groups remaining on the catalyst surface after the treatment and those formed in partial ammonia oxidation have not been detected by ir techniques.

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