Physical Chemistry

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1962

SovietRxiv

Abstract

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Infrared Spectra of Nitric Oxide Adsorbed on Synthetic Zeolites

Several works have recently been devoted to the infrared spectra of water adsorbed by synthetic zeolites— “molecular sieves” (^{1,2}). The results are in some respects similar to those obtained earlier for the adsorption of water vapor under vacuum conditions on ordinary silicate and aluminosilicate gels ($^{3-6}$).

In the present work we studied IR spectra obtained upon adsorption of NO on a number of synthetic zeolites. In previous studies carried out in our laboratory it was shown (^{7}) that the IR band of gaseous NO (1876 cm^{-1}) undergoes considerable shifts upon adsorption, characteristic of the formation of different types of bonds of this molecule with specific surface centers. The task was to determine whether similar centers exist in crystalline aluminosilicates—zeolites—and to identify the intermediate compounds formed by NO upon adsorption on them. At our disposal were zeolites of type A and type X in Na and Ca forms, with “window” diameters on the order of 4 Å and 5 Å (^{8}). In addition to some difference in the molar ratio SiO_2/Al_2O_3, types A and X differ in the sizes of the windows leading into the large cavities.*

In addition, natural zeolites were also investigated: natrolite [$Na_2Al_2 \cdot Si_3O_{10} \cdot H_2O$] and desmine [$H_4(Na_2, Ca)Al_2Si_6O_{18} \cdot 4H_2O$], on which adsorbed NO molecules could not be detected spectrally. They were likewise not found on zeolite NaX13 of composition $0.966\ Na_2O \cdot Al_2O_3 \cdot 2.916\ SiO_2 \cdot 4.74\ H_2O$, synthesized by S. P. Zhdanov.

Zeolite powders (crystal size from 1 to 5 μm) were placed between fluorite plates with an aluminum-foil spacer** and subjected to preliminary vacuum treatment (4-8 h) at 400°. Adsorption of NO was carried out in portions through a dosing volume. The final gas pressure in the cell was usually 40 mm Hg; at such a pressure and with the gaps in the cell, which had a thickness of 8 mm, the spectrum of gaseous NO does not appear.*** The spectrum was recorded on IKS-12 and IKS-14 spectrometers (NaCl prism) in the frequency range from 2400 to 1200 cm^{-1} (the transparency limit of the zeolites). Each of the samples was recorded 2–3 times with good reproducibility. The spectral slit width did not exceed 30 cm^{-1}. In measurements on the single-beam IKS-12 spectrometer, two curves of the adsorbent were recorded: before and after gas adsorption, and, as usual, the transmittance curve of the adsorbed gas was constructed.

In the course of the work, measurements were also made of the IR spectra of adsorbed N_2O and NO_2 molecules.

Figure 1 presents the spectra of the zeolites themselves under vacuum conditions, obtained on the double-beam IKS-14 spectrometer.

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* We express our deep gratitude to Academician M. M. Dubinin, S. P. Zhdanov, and Ya. V. Mirsky for providing the zeolite samples.
** The thickness of the samples by weight was 3-15 mg/cm^2.
*** To obtain the IR spectrum of gaseous NO, a pressure of 100 mm Hg is required with a layer thickness on the order of 10 cm.

The curves correspond to the following samples*: 1 –NaA, 4 Å ($Na_2O \cdot Al_2O_3 \cdot 2.1\ SiO_2$) (M); 2 –NaA, 4 Å (Zhd.); 3 –NaA (M) (crystal diameter 2-3 μ); 4 –NaA "k" (crystal diameter 5-6 μ); 5-7 –NaX (three samples from M. M. Dubinin, differing in degree of washing, increasing from 7 to 5**); 8 –CaA, 5 Å (obtained from NaA by ion exchange) (M); 9 –CaA, 5 Å (Zhd.); 10 –CaNaX10 ($0.312\ Na_2O \cdot 0.661\ CaO \cdot Al_2O_3 \cdot 2.95\ (SiO_2 \cdot 6.93\ H_2O)$) Zhd.

As is seen from the figure, the samples have maximum transparency in the region 1300-1700 cm^{-1}. Before vacuum pretreatment all zeolites had a broad absorption band at 1600 cm^{-1} due to liquid water (shown by a dashed line on curve 1). On curves 7, 8, 9 there are two absorption bands in the region 1420-1510 cm^{-1} of unknown origin.

In Fig. 2 are shown the bands arising upon adsorption of NO on various zeolite samples. These bands (with the exception of the bands 1940 and 2110 cm^{-1} on curve 8) disappear under pumping at 20° over the course of 1-2.5 hr. The numbering of the curves is the same as in Fig. 1.

The observed bands are shifted by more than 300 cm^{-1} to the high-frequency and low-frequency sides from the position of the absorption band of gaseous nitric oxide (1876 cm^{-1}). It was suggested that these bands are due to the formation of other nitrogen oxides as a result of reaction of adsorbed NO molecules with one another. To verify this, infrared spectra of adsorbed N_2O and NO_2 molecules on CaA zeolite (M) were also obtained (Fig. 3).

From comparison of the spectral curves of this figure it follows that the bands 2250, 1300 cm^{-1} and all the other low-frequency bands appearing upon adsorption of NO undoubtedly belong to N_2O molecules. A certain high-frequency shift of the bands in comparison with the gaseous phase (^{9}) (2230 and 1285 cm^{-1}) is evidently caused by interaction with the adsorbent.

The formation of N_2O molecules may proceed according to the following mechanism:

$$2NO_{ads} \rightarrow N_2O_{ads} + O_{ads}.$$

Fig. 1. Infrared spectra of zeolites. (For numbering of curves see the text)

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Fig. 2. Spectra arising upon adsorption of NO on various zeolites.

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Fig. 1. Infrared spectra of zeolites. (For numbering of curves see the text)

The above-mentioned bands arise upon adsorption of N_2O and NO on all the zeolites investigated. The remaining bands (1940 and 2100 cm^{-1}) arise upon adsorption of NO and NO_2 only on the indicated zeolite, which has a somewhat larger diameter of the entrance "windows" (5 Å) than the others. The smallest cross-section of the linear molecule N_2O is 3.14 Å, as also for NO and N_2. For the triangular molecule NO_2 with an angle of 140° this cross-section is larger (3.36 Å) (the largest cross-section of the molecule is 4.95 Å).

Upon adsorption of NO_2 alone, strong absorption is observed in the region 1350-1490 cm^{-1} and bands at 1940 and 2110 cm^{-1}, sharply different from the bands of the gaseous molecule: 1616 and 1322 cm^{-1} (^{10}). Absorption at 1350-1490 cm^{-1} can be explained by the formation on the zeolite surface of NO_3^- groups, having a vibrational frequency in the region 1340-1410 cm^{-1} (^{11}). The appearance of bands at 1940 and 2110 cm^{-1} is apparently due to the fact that the NO_2 molecule decomposes during adsorption with the formation of a chemisorbed NO molecule, to which the high-frequency band at 2110 cm^{-1} belongs.

Fig. 2. Spectra arising upon adsorption of NO on various zeolites.

Indeed, in the work already cited (^{7}) it was established that, for molecules adsorbed on metal cations with unfilled $3-d$ orbitals, a frequency of this magnitude appears, indicating the formation of the ionic form NO^+, for which frequencies in the range 2100-2400 cm^{-1} are characteristic (^{7,11}). Strong electron-acceptor centers on the surface of aluminosilicates, ionizing molecules of aromatic amines and acenes, are detected from the visible absorption spectra of these compounds that arise upon adsorption ($^{12-14}$).

Fig. 3. Spectra of molecules adsorbed on zeolite.
1 $-NO$; 2 $-N_2O$; 3 $-NO_2$

[*] Samples obtained from Ya. V. Mirskii are marked with the letter M in parentheses; from S. P. Zhdanov, with the letters Zhd.; the others are from Academician M. M. Dubinin. The sizes of the windows in the zeolite structure are given in angstroms.

[**] Probably in these zeolites an exchange of Na^+ ions for H^+ occurred owing to the presence of carbonic acid in the distilled water.

Fig. 3. Spectra of molecules adsorbed on zeolite. 1 –NO; 2 –N2O; 3 –NO2

Figure 3: Fig. 3. Spectra of molecules adsorbed on zeolite. 1 –NO; 2 –N2O; 3 –NO2

The frequency 1940 cm^{-1} is characteristic of a coordination bond of the NO molecule with electrophilic centers in nitroso complexes with various salts ([7,11]). Thus, it may be supposed that in zeolites there are also electrophilic and electron-acceptor centers on the surface (presumably uncompensated positive Al cations). Bands of NO weakly perturbed by adsorption were not found.

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Received
30 VII 1962

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