

INFRARED STUDY OF THE ADSORPTION AND REACTIONS OF  
NITRIC OXIDE ON CuY ZEOLITES

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The adsorption and the reactions of nitric oxide on CuY zeolites with copper ions in various states have been studied by IR-spectroscopy. Forms of NO adsorbed on individual  $\text{Cu}^{2+}$  ions, on weak and strong magnetic formations, and on  $\text{Cu}^+$  ions have been observed. Processes of oxidation and reduction of NO to  $\text{NO}_2$ ,  $\text{N}_2\text{O}$  and  $\text{N}_2$  occurring on CuY zeolites are discussed. Adsorption of nitrogen on coordinatively unsaturated copper ions has been observed.

Методом ИК-спектроскопии изучены адсорбция и превращения окиси азота на CuY цеолитах с катионами меди в различных состояниях.

Обнаружены комплексы NO с изолированными ионами  $\text{Cu}^{2+}$ , слабыми и сильными магнитными ассоциатами и ионами  $\text{Cu}^{1+}$ . Обсуждаются процессы окисления-восстановления, протекающие на CuY цеолитах с образованием  $\text{NO}_2$ ,  $\text{N}_2\text{O}$  и  $\text{N}_2$ . Наблюдалась адсорбция азота на координационно-ненасыщенных ионах меди.

The adsorption of NO on CuY zeolites has been studied by several authors /1-3/. The admission of NO leads to a decrease in the ESR signal of  $\text{Cu}^{2+}$  and to the appearance of an adsorption band at  $1918\text{ cm}^{-1}$ , assigned to the  $\text{NO}^+$  stretching vibration in the  $\text{Cu}^+-\text{NO}^+$  complex. According to Refs. /4-6/, depending on the ion exchange conditions, the copper content and the treatment of CuY zeolites, samples may be obtained which contain metal ions fixed in the zeolite framework

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with structures corresponding to different degrees of association (individual ions, weak magnetic formations, strong magnetic formations involving oxygen which does not belong to the framework, oxide phase) and to ions in different charge states. The cations in these states differ in their interaction with the CO molecule /6/. In this connection it is of interest to study the interaction of NO with copper ions, taking into account their state in the zeolites.

The CuY samples used in this work were obtained from NaY zeolites by ion exchange under conditions of partial hydrolysis of the exchanging salt (CuY-A, copper content 0.9%), or without hydrolysis (CuY-I, copper content 1%, 1.5%, 6.3%) /5/. It has been shown /4/ for CuY-I zeolites that at small copper contents the cations are present mainly as isolated ions. However, weak magnetic formations prevail as the copper concentration is increased. In CuY-A zeolites a large fraction of the cations exists in strong magnetic formations.

The relative amount of  $\text{Cu}^{2+}$  in the form of individual ions, weak magnetic formations and  $\text{Cu}^+$  ions was varied by treating the samples under special conditions (I, II or III).

- I. Evacuation for 3 hrs at  $450^{\circ}\text{C}$ ,
- II. Evacuation at  $250^{\circ}\text{C}$ , then repeated heating in  $\text{O}_2$  at  $450^{\circ}\text{C}$ , with subsequent evacuation for 2.5 hrs at  $20^{\circ}\text{C}$ ,
- III. Same as II, using CO instead of  $\text{O}_2$ , with final evacuation for 3 hrs at  $450^{\circ}\text{C}$ .

The IR spectra were recorded at room temperature on a UR-20 spectrophotometer. The slit width was  $13\text{ cm}^{-1}$  at  $2000\text{ cm}^{-1}$ .

No absorption bands attributable to surface complexes were detected after NO adsorption on HY and CuY (1% Cu) at 50 Torr in the temperature range  $20-200^{\circ}\text{C}$ . Apparently, the absence of a specific interaction between NO and copper ions is

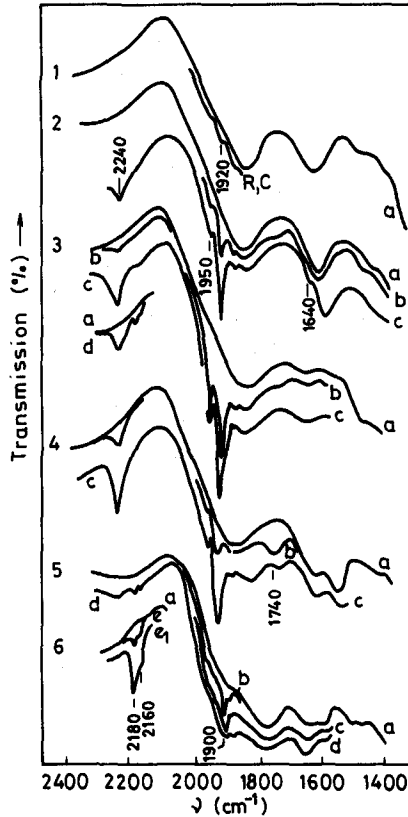
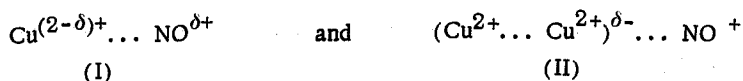


Fig. 1. a - Spectra of samples treated under various conditions. I - curves 2, 6; II - curves 1, 3, 5; III - curve 4; b - after NO admission (50 Torr, 20°C); c - after keeping the sample in NO (50 Torr, 20°C) for 15 hrs; d - heating in NO (50 Torr) at 300°C for 30 min; e, e<sub>1</sub> - adsorption of N<sub>2</sub> (200 Torr) at 300 and 400°C, respectively

due to a high coordinative saturation of Cu<sup>2+</sup> ions located at the S<sub>I</sub> sites /4/. A weak maximum at 1920 cm<sup>-1</sup> is observed after a 20 hour treatment with NO (50 Torr, 20°C) of the sample containing 1.5% Cu (treatment I). However, in the case of the same sample treated with oxygen (treatment II) a maximum at 1950 cm<sup>-1</sup> appears together with the band at 1920 cm<sup>-1</sup> (Fig. 1, 1b). An increase of the NO

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pressure to 50 Torr and of the temperature to 200<sup>o</sup> C does not lead to any changes in the spectrum. Neither of these bands is observed after evacuation at room temperature. The appearance of the band at 1920 cm<sup>-1</sup> has been reported by Naccache et al. /1, 2/, whilst the band at 1950 cm<sup>-1</sup> was not observed earlier. According to accepted views, during NO adsorption on Cu<sup>2+</sup>Y, partial electron transfer from an antibonding orbital to a metal 3d orbital occurs with the formation of a  $\sigma$  bond. On the other hand, the back-donation of Cu<sup>2+</sup> d-electrons to a vacant  $\pi$  orbital of NO with the formation of a  $\pi$ -bond is also possible. As a result, the N-O bond is strengthened and the frequency shifted as compared with gaseous NO (1876 cm<sup>-1</sup>). Thus, the predominance of  $\sigma$  or  $\pi$  bonding strengthens or weakens the N-O bond and shifts the N-O stretching band. The contribution of Cu<sup>2+</sup> d-electrons to the  $\pi$  bond should decrease relative to isolated ions if an exchange interaction between cupric ions is possible (weak magnetic formations). Thus, the bands at 1920 and 1950 cm<sup>-1</sup> may be ascribed to the N-O bond in the complexes, which can be described schematically as I and II, respectively:



In this case the adsorption centers are likely to be tetracoordinate Cu<sup>2+</sup> ions which appear at S<sub>I</sub>, S<sub>II</sub> and S<sub>II</sub><sup>\*</sup> sites as the copper content in zeolites is increased. The low intensity of the 1920 and 1950 cm<sup>-1</sup> bands is due to a negligibly small amount of Cu<sup>2+</sup> ions in the sample with a copper content of 1.5%. The absence of the 1950 cm<sup>-1</sup> band after treatment I may be due to the reduction of some Cu<sup>2+</sup> to Cu<sup>+</sup> ions during the treatment.

An increase of the copper content to 6.3% increases the number of individual ions ( $S_I$ ,  $S_{II}$ ,  $S_{II}^2$ ) and weak magnetic formations, and thus the intensity of the bands at 1920 and 1950  $\text{cm}^{-1}$ . In fact, these bands are very intensive and they appear in the spectrum immediately after NO adsorption on the sample with 6.3% Cu (treatment II) (Fig. 1, 3b). A drop of the above intensities is observed after treatment I (Fig. 1, 2b) as a result of the reduction of some  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  ions. A band at 1740  $\text{cm}^{-1}$  appears owing to NO adsorption on the same sample (treatment I). The appearance of this band in the spectrum of NO adsorbed on the sample containing cuprous ions may be ascribed to the formation of a  $\text{Cu}^+ \dots \text{NO}$  (III) complex. The presence of one more electron in  $\text{Cu}^+$  as compared with  $\text{Cu}^{2+}$  must lead to the strengthening of the  $\pi$ -bond and weakening of the N—O bond, as well as to a frequency shift toward longer wavelengths. The interpretation proposed for the appearance of the band at 1740  $\text{cm}^{-1}$  is supported by the increase in its intensity after NO adsorption on a more reduced sample (treatment III) (Fig. 1, 4b). The band at 1740  $\text{cm}^{-1}$  decreases after keeping the sample in NO for 15 hrs at 20°C and disappears after heating to 100-200°C. However, on reduced samples the band intensity at 1920  $\text{cm}^{-1}$  increases with increasing NO pressure and with the exposure time (Fig. 1, 2c and 4c). The decrease of the 1740  $\text{cm}^{-1}$  band and the increase of the 1920  $\text{cm}^{-1}$  band may be due to the reoxidation of  $\text{Cu}^+$  to  $\text{Cu}^{2+}$  taking place on the surface. This results in the decrease of the amount of complex III, and in the increase of the concentration of complex I. Under the same conditions, NO disproportionation occurs, as confirmed by the appearance of the bands at 1640 and 2240  $\text{cm}^{-1}$  (Fig. 1, 2c-4c). The former band belongs to  $\text{NO}_2$  adsorbed on the framework /9/, while the latter is close to the vibration frequency of gaseous  $\text{N}_2\text{O}$  (2224  $\text{cm}^{-1}$ ) and corresponds to the absorption of weakly adsorbed nitrous oxide molecules in the zeolite cavities /9, 10/.

The intensity of the band at  $2240\text{ cm}^{-1}$  is a maximum on the samples reduced by CO, which is due to the reduction of NO to  $\text{N}_2\text{O}$  accompanied by disproportionation when  $\text{Cu}^+$  ions are oxidized. If the temperature is raised to  $300^\circ\text{C}$ , the intensity of the band at  $1640\text{ cm}^{-1}$  and the rate of disproportionation increase for all samples containing 6.3% Cu. At the same time the maximum at  $2240\text{ cm}^{-1}$  decreases, which is accompanied by the appearance of two poorly resolved bands in the region  $2150\text{--}2180\text{ cm}^{-1}$  (Fig. 1, 3d). The drop in the band intensity at  $2240\text{ cm}^{-1}$  is likely to be due to the decomposition of  $\text{N}_2\text{O}$  ( $2\text{N}_2\text{O} \longrightarrow 2\text{N}_2 + \text{O}_2$ ). Nitrogen formed as a result of this process is adsorbed on copper ions and, correspondingly, absorption bands appear at  $2150\text{--}2180\text{ cm}^{-1}$ . This is supported by the appearance of the same bands after  $\text{N}_2$  adsorption (200 Torr,  $300^\circ\text{C}$ ) on the sample containing 6.3% copper (treatment I) (Fig. 1, 6). No absorption bands appear in the spectrum as  $\text{N}_2$  is adsorbed on the sample containing 1% Cu. This indicates that stabilization of  $\text{N}_2$  takes place only at coordinatively unsaturated sites.

When NO is adsorbed on sample CuY-A (0.9% Cu, treatment II), an absorption band at  $1900\text{ cm}^{-1}$  and weak maxima at  $1925$  and  $1945\text{ cm}^{-1}$  appear only at appreciable pressures (50 Torr) (Fig. 1, 5b). The predominant states of copper in such a sample are strong magnetic formations,  $\text{Cu} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{Cu} \end{array}$ , involving an oxygen bridge between two  $\text{Cu}^{2+}$  ions /4, 5/. However, a fraction of  $\text{Cu}^{2+}$  ions may be in the other states mentioned above. According to this, the band at  $1900\text{ cm}^{-1}$  which is close to the vibrational frequency of NO adsorbed on the CuO phase /11, 12/ can be ascribed to the stabilization of the NO molecule on strong magnetic formations (complex IV). The bands at  $1925$  and  $1945\text{ cm}^{-1}$  correspond to complexes I and II, respectively. A decrease of all band intensities and the appearance of absorptions at  $1640\text{ cm}^{-1}$  ( $\text{NO}_2$ )<sub>ads</sub> and  $2240\text{ cm}^{-1}$  ( $\text{N}_2\text{O}$ )<sub>ads</sub> are observed as the system is

heated to 100°C. The subsequent increase of temperature to 300°C leads to a decrease in the band intensities at 1900, 1925 and 1945  $\text{cm}^{-1}$ , and to the disappearance of the band at 2240  $\text{cm}^{-1}$  (Fig. 1, 5d). In addition, maxima at 2160 and 2180  $\text{cm}^{-1}$  appear and the intensity of the band at 1640  $\text{cm}^{-1}$  increases as in the case of samples with a copper content of 6.3%. The band at 1640  $\text{cm}^{-1}$  is the most intensive in this case (CuY A, 0.9% Cu, treatment II) since NO is readily oxidized by the active oxygen in the strong magnetic formations. In the spectrum of NO adsorbed on the samples treated under conditions I and II, weak bands at 1900 and 2240  $\text{cm}^{-1}$  appear only after keeping the sample in NO for 15 hrs, as a result of reduction of  $\text{Cu}^{2+}$  ions. This implies that  $\text{N}_2\text{O}_{\text{ads}}$  (2240  $\text{cm}^{-1}$ ) and complex IV are formed due to the reoxidation of the specific sites by NO molecules. After oxidation these sites can form strong magnetic associates.

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