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N_2 and CO As Probe Molecules for Determining the Properties of Acid Sites on the Surface of Zeolites

M. E. Malyshev, E. A. Paukshtis, L. V. Malysheva, A. V. Toktarev, and L. A. Vostrikova

Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia

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Abstract—The applicability of molecular nitrogen as a probe for the Brønsted and Lewis acid sites of HNaY and HZSM-5 zeolites was studied by Fourier transform IR spectroscopy. The integrated absorption coefficients of bands due to N–N vibrations in complexes with Brønsted and Lewis acid sites were determined. The correlation between the integrated absorption coefficients and the positions of bands due to N–N vibrations in nitrogen interacting with the acid sites of test samples is discussed. We propose using the low-temperature adsorption of nitrogen for express determination of the concentrations of strong Lewis and Brønsted acid sites in zeolites.

INTRODUCTION

In recent years, the IR spectroscopy of adsorbed molecules has gained widespread acceptance for studying the acid and base sites of catalyst surfaces. Molecules interacting in various ways with acid sites are commonly used as probes [1]. CO is considered to be one of the most convenient probe molecules. However, in a number of publications [2–13], use of homonuclear diatomic molecules, such as hydrogen, nitrogen, and oxygen, as probes was proposed. In these works, the adsorption of O_2, N_2, and H_2 on A, X, Y, and ZSM-5 zeolites and mordenite in hydrogen and cation-exchanged (Li^+, Na^+, K^+, Rb^+, and Cs^+) forms was studied. With the use of these weakly basic and small molecules as probes for acid sites, additional information on site-strength distribution within the cavities and channels of zeolites was obtained [3–13]. An analysis of these published data suggests that nitrogen is of great interest in studying surface acid properties by the method of adsorbed molecules. The absorption bands of adsorbed nitrogen are sufficiently intense and occur in a region that is not overlapped by the absorption bands of the zeolite framework.

It was found that O_2, N_2, and H_2 interact with both very strong acid sites (for example, the bridging OH groups of HY and HZSM-5 zeolites [3–7]) and weak proton sites (Si–OH groups [14]) to give 1 : 1 hydrogen-bonded complexes. The formation of donor–acceptor complexes between these molecules and Lewis sites was also observed.

The aim of this work is to elucidate the specific features of the nitrogen-probe method for quantitative measurement of zeolite acid sites.

EXPERIMENTAL

Materials. Zeolite Y ($SiO_2/Al_2O_3 = 5.5$) and ZSM-5 ($SiO_2/Al_2O_3 = 100$) samples prepared by hydrothermal synthesis with the use of the sol–gel method [15, 16] were used in this study. Zeolite Y samples with various degrees of exchange and the H form of ZSM-5 zeolite were prepared by ion exchange with intermediate calcination. At each stage, the sample was calcined at 400°C and then kept in a sevenfold volume of an ammonia buffer solution with pH 8–8.5 for 2 h; thereafter, it was washed to the absence of nitrate ions. The degree of exchange was determined form chemical analysis data. Samples HY(1) and HY(2) with 70 and 93% exchange, respectively, were used.

High-purity N_2 and CO were used for adsorption. The nitrogen was additionally purified on a Ni/Cr catalyst and dried with CaA zeolite. The carbon monoxide was additionally dried as well.

Experiments were performed as described below: Initially, a sample pellet was pretreated; next, nitrogen was adsorbed onto the pellet at –196°C and then desorbed by pumping under the same conditions. Next, CO was adsorbed onto the same pellet.

Sample pretreatment. The sample as a pellet (10–20 mg/cm^2) was calcined in air in an IR cell for 1 h before adsorption. HNaY zeolite with a low degree of exchange (HY(1)) was heated at 400 and 500°C, whereas the sample with a high degree of exchange (HY(2)) was heated at 600 and 700°C. HZSM-5 zeolite was calcined at 500°C. Thereafter, the sample was pumped at a pressure of $<10^{-4}$ Torr and 400°C for 1 h; next, the sample temperature was decreased to –196°C with the use of liquid nitrogen.

Nitrogen adsorption. The spectrum of an initial sample was measured at –196°C before the adsorption of N_2. Next, nitrogen was added to the cell in portions of 0.1, 1.0, 2.0, 4.0, 8.0, 16.0, and 32.0 Torr from an intermediate space. After addition of each particular portion and the establishment of adsorption equilibrium, the residual pressure in the cell was measured and the spectrum of the sample with adsorbed nitrogen was recorded.

A Bruker IFS-113V Fourier transform IR spectrometer was used for recording spectra. The spectra were measured in the region 1000–6000 cm^{-1} with a resolution of 4 cm^{-1}. Averaging over 32 scans was usually done.

After performing an experiment, the cell was pumped at a pressure of $<10^{-4}$ Torr and –196°C for 1 h in order to remove the adsorbed nitrogen.

CO adsorption. CO was adsorbed in portions of 0.01, 0.04, 0.07, 0.1, and 3.0 Torr until the surface sites were completely saturated. The spectra of adsorbed CO were recorded after addition of each portion.

RESULTS AND DISCUSSION

It is well known that two types of acid sites occur on the surface of zeolites. Brønsted acid sites are bridging Al(OH)Si groups and terminal Si–OH groups. Lewis acid sites are due to aluminum ions coming out of the crystal lattice.

Figures 1a and 1b (curves *1*) show the IR spectra of the initial OH groups of a zeolite Y sample calcined at 400°C (henceforth designated as HY(1)400). The spectra exhibited two absorption bands at 3540 and 3640 cm^{-1} that are characteristic of zeolite Y; these bands are due to the vibrations of bridging OH groups localized in small and large cavities, respectively. A weak band due to Si–OH groups was also observed at 3740 cm^{-1}.

CO forms H complexes by interaction with OH groups in sample HY(1)400 (Fig. 1b, curve *2*); in this case, the intensity of the band at 3640 cm^{-1} in the IR spectrum decreased and a band at 3320 cm^{-1} simultaneously appeared at a lower frequency. The band intensity at 3540 cm^{-1} remained practically unchanged.

Nitrogen adsorbed on the surface of HY(1)400 (Fig. 1a, curve *2*) also reacted with OH groups to form H complexes. In this case, the intensity of the band at 3640 cm^{-1} decreased, bands at 3500 and 3575 cm^{-1} appeared, and the band at 3540 cm^{-1} weakened. This behavior can be explained either by the shift of the bands at 3640 and 3540 cm^{-1} to 3575 and 3500 cm^{-1}, respectively, or by the shift of the band at 3640 cm^{-1} to 3500 cm^{-1} and the shift of the band at 3540 cm^{-1} to higher frequencies up to 3575 cm^{-1}. Note that the band at 3640 cm^{-1} was shifted to 3520 cm^{-1} upon the adsorption of nitrogen onto the surface of HY(2)600. Since it is difficult to believe that the strength of acid sites is considerably changed upon calcination, we may conclude that the band at 3640 cm^{-1} for HY(1)400 is shifted to 3500 cm^{-1}. We therefore suggest that the band at 3540 cm^{-1} could indeed shift toward the higher frequency region. We cannot yet understand what causes the unusual behavior of this band.

It is well known that, at high calcination temperatures and high degrees of sodium exchange, the zeolite crystal lattice undergoes partial destruction to release aluminum from the framework. Figures 1c and 1d (curves *1*) demonstrate the IR spectra of the initial OH groups of a zeolite Y sample with a degree of sodium exchange equal to 93% calcined at 600°C (HY(2)600). These spectra exhibit much weaker absorption bands at 3540 and 3640 cm^{-1} than the spectrum of HY(1)400. Simultaneously, the intensity of the bands at 3740 cm^{-1} are increased; this is indicative of an increase in the concentration of Si–OH groups.

Figure 1d (curve *2*) shows the IR spectrum of CO adsorbed on HY(2)600. It can be seen in Fig. 1d that the intensities of the absorption bands at 3640 and 3740 cm^{-1} due to initial OH groups decreased, while absorption bands at 3350 and 3650 cm^{-1} appeared simultaneously in a lower frequency region.

Upon the adsorption of N_2 on the surface of HY(2)600, the intensities of the bands at 3640 and 3740 cm^{-1} due to initial OH groups in the IR spectrum (Fig. 1c, curve *2*) decreased with simultaneous appearance of absorption bands at 3520 and 3700 cm^{-1}. It is difficult to judge the changes in the band at 3540 cm^{-1} because it is masked with a more intense band at 3520 cm^{-1}.

Figures 1e and 1f (curves *1*) demonstrate the spectra of the initial OH groups of HZSM-5 zeolite calcined at 500°C. The spectra exhibited two bands at 3610 and 3726 cm^{-1}, which are characteristic of HZSM-5 zeolite; these bands are assigned to the vibrations of bridging OH groups in channels and on the outer surface, respectively [1]. Bands at 3698 and 3737 cm^{-1}, which are assigned to the vibrations of Al–OH and Si–OH groups, respectively, were also observed.

Upon the adsorption of CO on HZSM-5, the IR spectrum (Fig. 1f, curve *2*) exhibited a decrease in the intensities of absorption bands at 3610, 3726, 3698, and 3737 cm^{-1} due to initial OH groups; absorption bands at 3280, 3420, 3570, and 3635 cm^{-1}, respectively, simultaneously appeared at lower frequencies.

Upon the adsorption of nitrogen on the surface of HZSM-5, the IR spectrum (Fig. 1e, curve *2*) exhibited a decrease in the intensities of bands at 3610, 3698, and 3737 cm^{-1} due to initial OH groups, and bands at 3485, 3655, and 3700 cm^{-1} appeared. The shift of the absorption band at 3726 cm^{-1} upon the adsorption of N_2 will be considered below.

It is well known that the shift of an absorption band due to the OH group upon interaction with a probe molecule depends on both the proton affinity (PA) of the acid site and the basicity of the probe [1]. Figure 2 compares the shifts of the absorption bands due to the OH groups of the test samples upon interaction with CO and nitrogen. The lower value of PA = 494 kJ/mol for

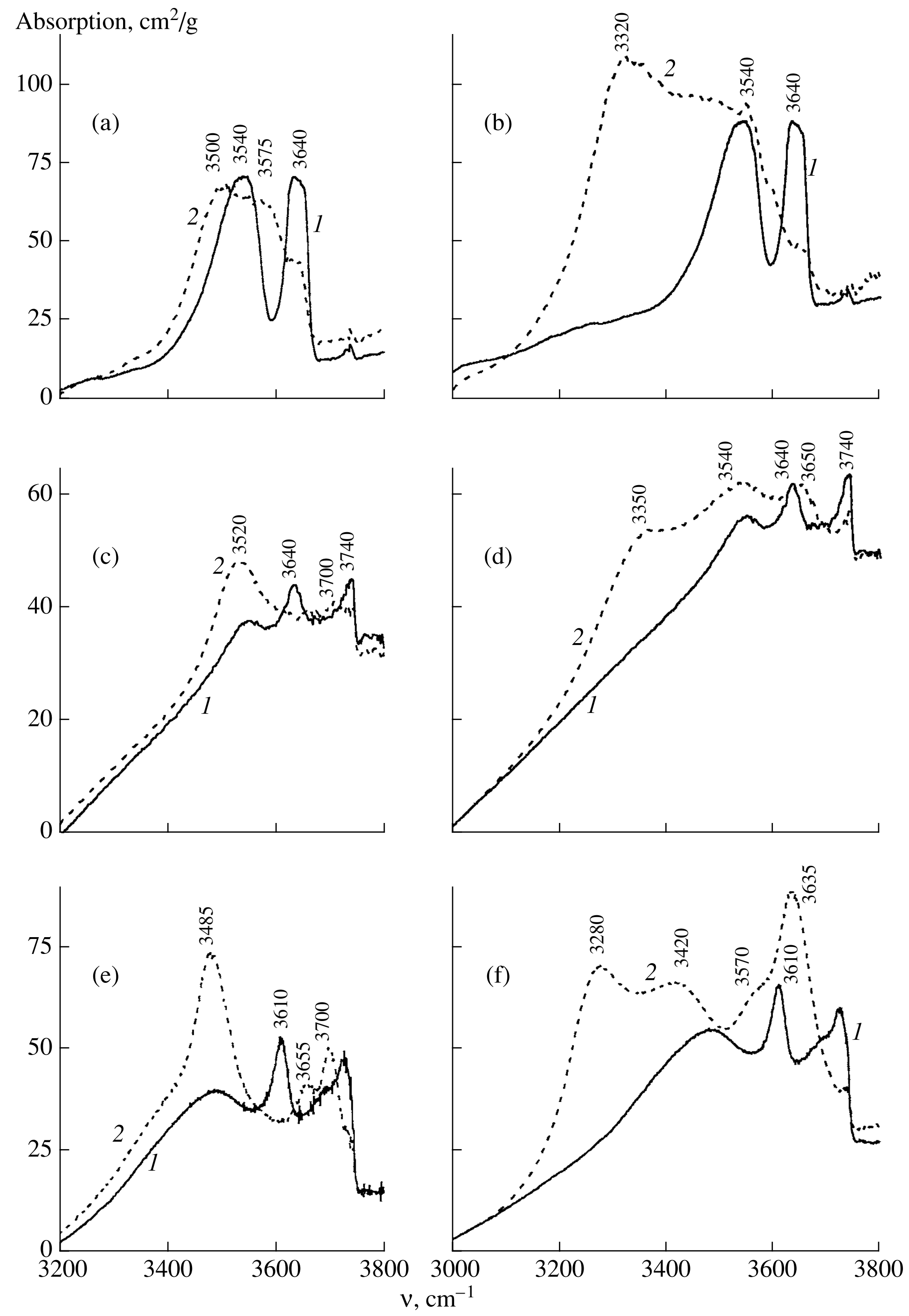

Fig. 1. IR spectra of OH groups in samples (a, b) HY(1)400, (c, d) HY(2)600, and (e, f) HZSM-5 500: (*1*) initial samples and (*2*) samples after the adsorption of (a, c, e) N_2 (32 Torr) or (b, d, f) CO (3 Torr).

nitrogen, as compared with PA = 594 kJ/mol for CO, resulted in a smaller (by a factor of 2.3) shift of OH groups upon the formation of H complexes.

The discovered relationship allowed us to determine the position of the band due to bridging OH groups in H complexes with nitrogen. The spectrum (Fig. 1e, curve *2*) indicates that the intensity of the band at 3726 cm^{-1} decreased upon interaction with nitrogen. Since the $\Delta\nu(\text{OH})_{\text{CO}}/\Delta\nu(\text{OH})_{\text{N}_2}$ ratio is equal to 2.3, the corresponding band due to H-bonded OH groups would be expected to appear at 3610 cm^{-1}. However, this band is difficult to distinguish against the background of the growing band at 3485 cm^{-1} and the decreasing band due to bridging OH groups in channels (3610 cm^{-1}).

Figure 3 shows the IR spectra of nitrogen and CO adsorbed on the test zeolites. The band at 2134 cm^{-1}, which corresponds to physically adsorbed CO species, was observed for all samples with adsorbed CO. In the case of HY(1)400 and HY(1)500 (Figs. 3b, 3d), a band was observed at 2170 cm^{-1}, which was attributed to the vibrations of CO in H complexes with bridging OH groups. The shift of this band to 2165 cm^{-1} with increasing CO pressure is indicative of nonuniformity of the strength of Brønsted acid sites that correspond to these bridging OH groups. Moreover, the weak absorption band at 2154 cm^{-1}, which was assigned to the vibrations of CO adsorbed at Si–OH groups, was also observed in the spectrum recorded after addition of CO (3 Torr).

A narrow band at 2329 cm^{-1} was observed in the spectra of nitrogen adsorbed on HY(1)400 and HY(1)500 (Figs. 3a, 3c). It can be attributed to the N–N vibrations of nitrogen adsorbed on bridging OH groups.

Figures 3f and 3h show the spectra of CO adsorbed on HY(2)600 and HY(2)700. It can be seen that the absorption bands at 2170, 2200, and 2225 cm^{-1} increased with pressure. The band due to the vibrations of CO in H complexes with bridging OH groups at 2170 cm^{-1} shifted to 2160 cm^{-1} as the pressure of CO was increased. As in the case of samples HY(1)400 and HY(1)500, this suggests the nonuniformity of the bridging OH groups. The bands at 2200 and 2225 cm^{-1} are due to the vibrations of CO in complexes with Lewis acid sites.

Upon the adsorption of nitrogen on the similar samples HY(2)600 and HY(2)700 (Figs. 3e, 3g), the spectra exhibited absorption bands at 2330 and 2350 cm^{-1}. As well as in the case of HY(1)400 and HY(1)500, the band at 2330 cm^{-1} was assigned to N_2 adsorbed at OH groups. It is believed that the band at 2350 cm^{-1} corresponds to the vibrations of nitrogen bound to Lewis sites or, most likely, to the strongest Lewis sites. This is evidenced by the fact that the band intensity at 2350 cm^{-1} reached a maximum even at minimum pressures of N_2 and then remained virtually unchanged.

Bands at 2154 and 2170 cm^{-1} were observed in the spectrum of CO adsorbed on HZSM-5 (Fig. 3j). The bands in the region 2150–2160 cm^{-1} can be ascribed to CO vibrations in H complexes with Al–OH and Si–OH groups. The fact that the CO pressure had no effect on the position of the band at 2170 cm^{-1} (which is associated with CO vibrations in H complexes with bridging OH groups) suggests uniformity of OH groups.

The adsorption of nitrogen on HZSM-5 (Fig. 3i) resulted in appearance of a single band at 2328 cm^{-1}, which corresponds to the N–N vibrations in H complexes with OH groups. A weak shoulder at 2321 cm^{-1} can also be seen, which is likely due to the vibrations of nitrogen in H complexes with Al–OH and/or Si–OH groups.

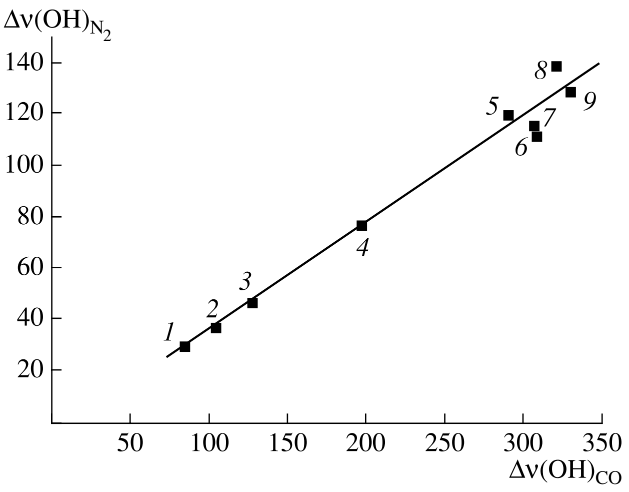

Fig. 2. Comparison of the shifts of absorption bands due to the vibrations of OH groups upon the formation of H complexes with CO and N_2: (*1*) 3740 cm^{-1}, HY(2)600; (*2*) 3740 cm^{-1}, HZSM-5 500; (*3*) 3700 cm^{-1}, HZSM-5 500; (*4*) 3677 cm^{-1}, SAPO 31 [17]; (*5*) HY(2)600; (*6*) 3621 cm^{-1}, HZSM-5 [7]; (*7*) 3726 cm^{-1}, HZSM-5 500; (*8*) 3640 cm^{-1}, HY(1)400; and (*9*) 3610 cm^{-1}, HZSM-5 500.

Based on the above experimental data, we conclude that nitrogen complexes with Lewis and Brønsted sites give rise to absorption bands in the regions 2340–2360 and 2320–2330 cm^{-1}, respectively, in agreement with published data [2–13].

A comparison between the spectra of adsorbed CO in the region of C–O vibrations and nitrogen in the region of N–N vibrations demonstrates that the spectrum of adsorbed nitrogen is simpler; it is not complicated by absorption bands due to the vibrations of nitrogen in the gas phase or a physically adsorbed species. The bands of adsorbed nitrogen were narrower than those in the case of CO by a factor of almost 1.5. The intensities of the bands due to the zeolite structural OH groups decreased in proportion to the increase in the corresponding bands due to adsorbed nitrogen in the region of N–N vibrations.

The integrated absorption coefficient $A_{0(N-N)}$ of the band due to the N–N vibrations of nitrogen was determined from the ratio between the integrated intensity of the band of adsorbed nitrogen and the concentration of OH groups in complexes with nitrogen:

$$A_{0(N-N)} = A_{(N-N)}/N_{(OH\ldots N-N)}.$$

The concentration of OH groups in complexes with nitrogen was determined from the decrease in the concentration of bridging OH groups, whereas the concentration of structural OH groups was determined from the integrated intensity of bands due to OH groups with

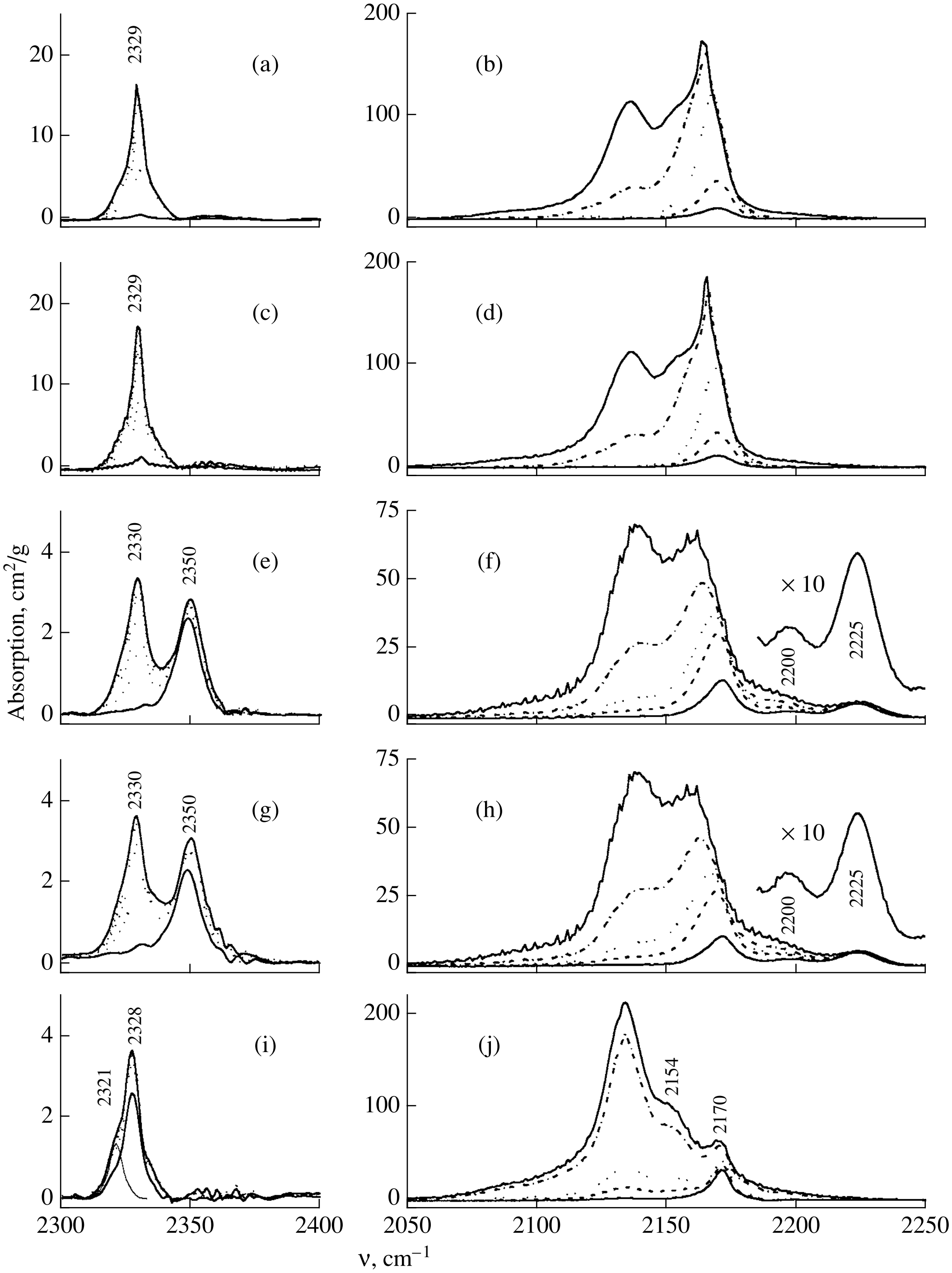

Fig. 3. IR spectra of N_2 and CO adsorbed on the samples (a, b) HY(1)400, (c, d) HY(1)500, (e, f) HY(2)600, (g, h) HY(2)700, and (i, j) HZSM-5 500. The spectra were recorded as the pressure of adsorbates was increased to 32 Torr for N_2 or 3 Torr for CO.

the use of the corresponding integrated absorption coefficients $A_{0(OH)}$.

The integrated absorption coefficients for the bands of bridging OH groups in zeolites Y (3640 cm^{-1}) and HZSM-5 (3610 cm^{-1}) are equal to 5.5 and 7.5 cm/μmol, respectively [1]. The integrated absorption coefficient for the band of Si–OH groups in HZSM-5 zeolite (3737 cm^{-1}) is equal to 3.0 cm/μmol [1]. For the samples HY(1)400 and HY(2)600, the values of $A_{0(N-N)}$ measured for the bands due to the N–N vibrations in complexes with bridging OH groups at 2328–2330 cm^{-1} were 0.21 and 0.27 cm/μmol, respectively, whereas this value for HZSM-5 zeolite was 0.16 cm/μmol. The value of $A_{0(N–N)}$ for the band at 2321 cm^{-1} due to the N–N vibrations of nitrogen in complexes with Si–OH groups in HZSM-5 zeolite was equal to 0.091 cm/μmol.

Integrated absorption coefficients for the bands due to the N–N vibrations in donor–acceptor complexes with Lewis sites are determined from the ratio between the integrated intensity of the band due to adsorbed nitrogen and the concentration of Lewis sites in complexes with CO for the same type of fully occupied sites:

$$A_{0(L...N–N)} = A_{(L...N–N)}/N_{(L...CO)}.$$

The concentration of Lewis sites in complexes with CO is determined from the integrated intensity of the band due to CO vibrations and the integrated absorption coefficient of this band. The integrated absorption coefficient $A_{0(L...CO)}$ for the band at 2225 cm^{-1} due to CO in complexes with Lewis sites, which is equal to 1.24 cm/μmol, was taken from [1]. For the bands due to the N–N vibrations in complexes with the above sites, integrated absorption coefficients were calculated to be 0.42 and 0.58 cm/μmol for samples HY(2)600 and HY(2)700, respectively; these are close to published data [1, 3–7].

Figure 4 illustrates the correlation between the integrated absorption coefficients and the positions of the bands due to the N–N vibrations of nitrogen interacting with acid sites of the test samples prepared in this work and of samples known from the literature. As can be seen in Fig. 4, points are arranged as two groups about a common straight line. Points *1–6* reflect the interaction of nitrogen with Brønsted acid sites, while points *7* and *8* reflect the formation of nitrogen complexes with Lewis acid sites. To a first approximation, it can be seen that the integrated absorption coefficient for the bands due to N–N vibrations increased with the frequency of these vibrations. We have recently performed studies of the adsorption of nitrogen on oxides, which (as is well known from studies of the spectra of adsorbed CO) have Lewis and Brønsted acid sites of another nature and strength. The data array obtained on both zeolites and oxides indicates that integrated absorption coefficients for bands due to the N–N vibrations in complexes with Lewis and Brønsted acid sites depend differently on the frequency of the N–N vibrations. Results relevant to the adsorption of nitrogen and CO on oxides will be published elsewhere [18].

Thus, we found that nitrogen interacts with both strong and weak surface OH groups to form H complexes and with Lewis acid sites to form donor–acceptor complexes. A linear correlation between the shifts of absorption bands due to OH groups upon the formation of H complexes with nitrogen and CO was found, the proportionality factor being 2.3.

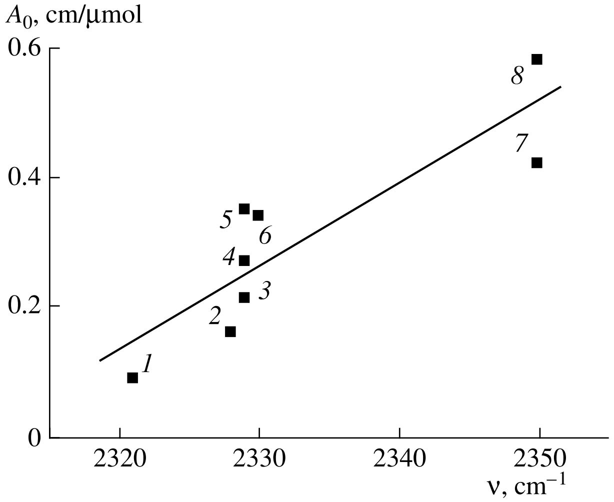

Fig. 4. Correlation between the integrated absorption coefficients and the positions of bands due to the N–N vibrations of nitrogen interacting with the acid sites of the samples: (*1*, *2*) HZSM-5 500, (*3*) HY(1)400, (*4*, *8*) HY(2)700, (*5*) HY(1)500, and (*6*, *7*) HY(2)600.

Integrated absorption coefficients were calculated for the bands due to the N–N vibrations in complexes with bridging OH groups of HY and HZSM-5 zeolite, as well as for bands due to the N–N vibrations in complexes with Lewis acid sites of HY zeolite.

We found experimentally that the interaction of nitrogen with the strongest acid sites in the region of N–N vibrations gives rise to a simple spectrum that does not require sophisticated analysis. This allows one to use the low-temperature adsorption of nitrogen for express determination of the concentrations of strong Lewis and Brønsted acid sites in zeolites.

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