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IR Spectroscopic Study of Ethylene Adsorption and Oligomerization on the Hydrogen Form of Mordenite

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Abstract—Diffuse-reflectance IR spectroscopy is used to study adsorption and oligomerization of ethylene on the hydrogen form of mordenite at room temperature. Ethylene adsorbs on bridging acid hydroxyl groups of the zeolite and forms π-complexes with a firm hydrogen bond. The interaction with hydroxyl groups most strongly excites composite vibrations in adsorbed molecules. These vibrations are a combination of the stretching vibration of a double bond and the deformational vibrations of the CH_2 group. A conjecture is drawn that these composite vibrations correspond to the reaction coordinate of ethylene transformation to the ethoxy groups. Their further reactions with weakly adsorbed molecules result in ethylene oligomerization. A linear oligomer is formed, grafted on the zeolite surface and filling the pores of zeolites.

INTRODUCTION

The catalytic oligomerization of light olefins on high-silica zeolites is interesting because of the problem of by-product gases in oil refining [1–5]. Therefore, the adsorption of C_2–C_3 olefins on zeolites was studied extensively by IR spectroscopy [3–7]. In most papers, the main attention is given to changes in IR spectra in the region of OH vibrations. The state of adsorbed olefin molecules was poorly studied. Most of the studies were carried out for cases when olefins were weakly adsorbed and escaped oligomerization or other secondary reactions.

Compared to other olefins, ethylene has the simplest vibrational IR spectrum, which is easier to interpret. Earlier, the IR spectroscopic study of ethylene adsorption was carried out using hydrogen [7] and different cation-exchanged forms of zeolites Y [6]. It was found that ethylene weakly adsorbs at room temperature and does not react further. In this work, IR spectroscopy is used to study ethylene adsorption on the hydrogen form of mordenite (HM). The strength of Brønsted acid sites of these zeolites is higher than for other zeolites. Therefore, it catalyzes ethylene oligomerization even at room temperature.

The quantitative study of ethylene adsorption on HM showed that ethylene binds to acid sites much more strongly than to Na or alkali earth metal cations [8]. At room temperature, ethylene adsorption is reversible because of oligomerization. Mordenite pores are filled with the oligomer grafted to the zeolite surface.

To study ethylene adsorption on HM, we used diffuse-reflectance IR spectroscopy and recorded the spectra of adsorbed ethylene and strongly adsorbed oligomerization products. We also attempted determining the configuration of adsorbed ethylene and its change in the course of ethylene activation on acid sites by IR spectroscopy. In contrast to previous studies, we studied different composite vibrations in addition to the main C–H vibrations of adsorbed ethylene.

EXPERIMENTAL

In this work, we used the hydrogen form of mordenite with a Si/Al ratio of 5. Before spectral measurements, zeolite samples were placed into a quartz ampule equipped with an appendix with a CaF_2 window and trained in the following regime. First, the zeolite sample was evacuated at 100°C for 2 h. Then, the temperature was increased from 100 to 450°C for 3 h and the zeolite was evacuated at this temperature for three more hours. The sample regeneration after catalytic runs was carried out in a circulation setup at 500°C in an oxygen atmosphere at 200 torr.

The diffuse-reflectance IR spectra were recorded at room temperature using a Nikolet Impact 410 spectrometer with an attachment for recording diffuse-reflectance spectra. Measurements were carried out at wavenumbers ranging from 2000 to 6500 cm^{-1}. The spectra were transformed into Kubelka–Munk units assuming that the reflecting ability of the zeolite at ν = 5000 cm^{-1} is equal to 0.9. In some cases, the zeolite background was subtracted from the overall spectrum.

Ethylene was purified by freezing in a trap cooled with liquid nitrogen, from which the medium fraction was withdrawn. Ethylene adsorption (3–7 mmol/g) on zeolite HM was carried out at –196°C. For the uniform distribution over zeolite pores, the sample was slowly heated to –50°C, cooled to –196°C, and carried to the IR cell in a Dewar vessel filled with liquid nitrogen.

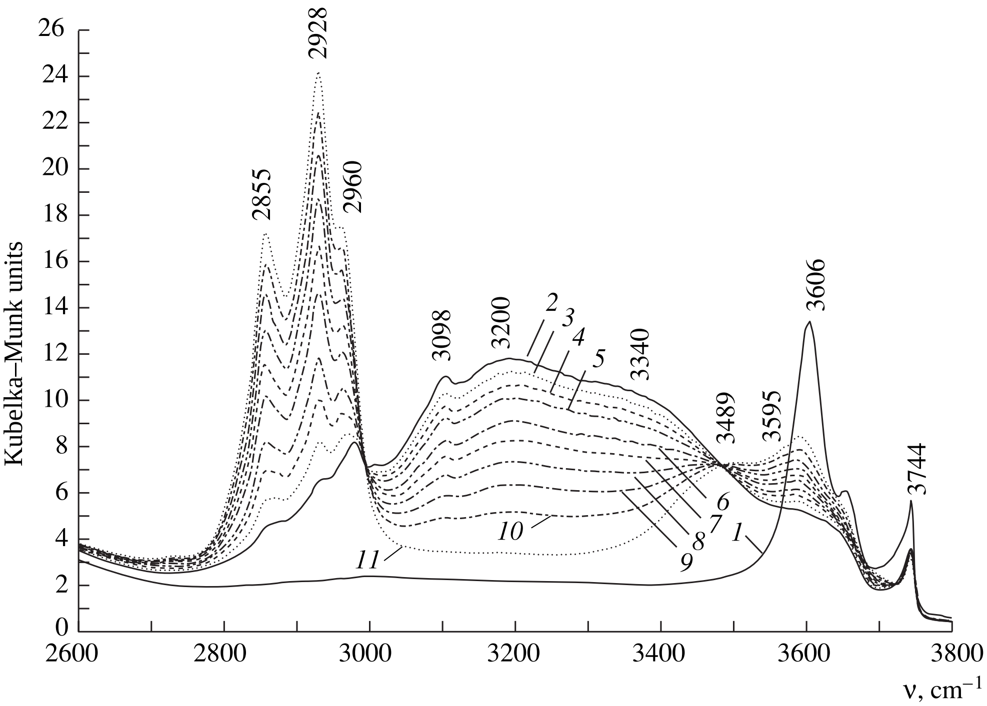


Fig. 1. IR spectra of H-mordenite measured (*1*) before and (*2–11*) after ethylene adsorption at room temperature in (*2*) 0.5, (*3*) 2.5, (*4*) 3.5, (*5*) 4.5, (*6*) 5.5, (*7*) 9, (*8*) 12, (*9*) 17, (*10*) 25, and (*11*) 48 min after the beginning of a run.

Then, the sample was heated to room temperature, rapidly poured into an appendix with a CaF_2 window, and recorded IR spectra at intervals lasting from 1 to 10 min.

RESULTS

Figure 1 shows the IR spectrum of HM recorded before ethylene adsorption (the amount of adsorbed ethylene was ~7 mmol/g).

As can be seen from the figure, after heating the sample with adsorbed ethylene to room temperature, a band at ~3200 cm^{-1} is initially observed in the spectrum pointing to the existence of OH groups strongly excited by a hydrogen bond. Weak bands are also observed in the region of C–H stretches. In ~50 min, the band at 3200 cm^{-1} disappears and more intense bands appear that are characteristic of $–CH_2–$ and $–CH_3$ group stretching. This fact points to ethylene oligomerization at room temperature.

Let us consider separately the results obtained for the region of stretching vibrations of O–H and C–H groups.

The Region of O–H Stretching Vibrations

As can be seen from Fig. 1, the initial HM sample contains bridging hydroxyl groups with a stretching frequency of 3606 cm^{-1} and silanol groups SiOH with a stretching frequency of 3744 cm^{-1}. In the zeolite subjected to multiple regeneration, a small band with a maximum of absorbance at 3655 cm^{-1} appears in addition to the above bands. The latter belongs to the OH groups bound to extra-framework Al atoms formed due to the partial dealumination of the zeolite.

Immediately after ethylene adsorption, the IR spectrum starts to show a broad intense band of OH groups bound to ethylene via a hydrogen bond. This band has a maximum at 3200 cm^{-1} and a small shoulder against its background at 3340 cm^{-1}. The intensity of the band with a maximum at 3606 cm^{-1} strongly decreases.

An increase in the contact time of ethylene with the zeolite results in a gradual decrease in the intensity of the broad band from the OH groups, which completely disappears in 50 min. The initial band at 3606 cm^{-1} does not appear again. Instead, two new bands appear: one is broad with a maximum at 3489 cm^{-1} and the other is a narrower band with a maximum at 3595 cm^{-1}. When ethylene contacts HM, these bands become more intense. According to [9], the first of these bands belongs to the region of OH group stretches excited by the hydrogen bond with adsorbed paraffin molecules. This fact suggests that the hydroxyl groups form hydrogen bonds with growing oligomer chains.

The evacuation of the sample at room temperature after ethylene contacted with HM for a short period of 5–10 min results in the disappearance of the broad band at 3200 cm^{-1}. As this takes place, the narrow band at

3606 cm^{-1} is restored, but its intensity is lower than in the initial zeolite sample. The intensity of the band at 3489 cm^{-1} does not change.

The Region of C–H Stretching Vibrations of Adsorbed Ethylene

As can be seen from Fig. 1, there are several bands in the region of C–H stretches of adsorbed ethylene. In the overall spectrum, we see two regions: the region of C–H stretches of ethylene (3100–2980 cm^{-1}) and the region of C–H stretches of reaction products (2970–2850 cm^{-1}).

The figure shows that the intensity of bands from adsorbed ethylene is the highest. As it was reported earlier [6, 7], ethylene adsorption on zeolite HY leads to the formation of less intense bands of stretching vibrations and more intense bands of deformational vibrations of C–H bonds compared to gaseous ethylene. Nevertheless, despite the low intensity of the bands of C–H stretching vibrations, the spectrum of ethylene contains two well-resolved bands with maxima at 3098 and 2977 cm^{-1} and with poorly resolved shoulders at 3065 and 3004 cm^{-1} (see Fig. 2, where the zero line was corrected for convenience and the spectrum of OH groups excited due to the formation of hydrogen bonds is subtracted).

The Region of Composite Vibration Frequencies of Adsorbed Ethylene

In the IR spectrum of adsorbed ethylene in the region of composite frequencies of stretching and deformational vibrations of the C–H bond and the composite vibrations of C–H and C=C bonds, we see several relatively weak bands. Comparison of these bands with those obtained for gas-phase ethylene showed that there is no substantial change in the region of composite frequencies of stretching and deformational vibrations of the C–H bond as ethylene is adsorbed. The main changes in the spectra are seen in the regon of the composite vibrations of ethylene at 2100–2600 cm^{-1}. These are the combinations of different deformational vibrations of the C–H bond and their combinations with the vibrations of the C=C bond. Indeed, immediately after ethylene adsorption, a very intense band is observed in this region. Against its background, we see relatively narrow bands with maxima at 2164 and 2348 cm^{-1} and a broad band at ~2410 cm^{-1} (Fig. 3). Undoubtedly, these bands are associated with the composite vibrations of adsorbed ethylene because they disappeared from the spectrum after sample evacuation at room temperature together with the bands of C–H stretches of adsorbed ethylene. In the course of ethylene oligomerization, the intensities of these bands decreased together with the intensities of other bands of adsorbed ethylene and the bands excited by OH groups. Table 1 lists the frequencies of composite bands observed in the IR spectrum for gaseous and liquid ethylene and their assignment according to [10]. The forms of vibrations corresponding to these frequencies are shown in Fig. 4.

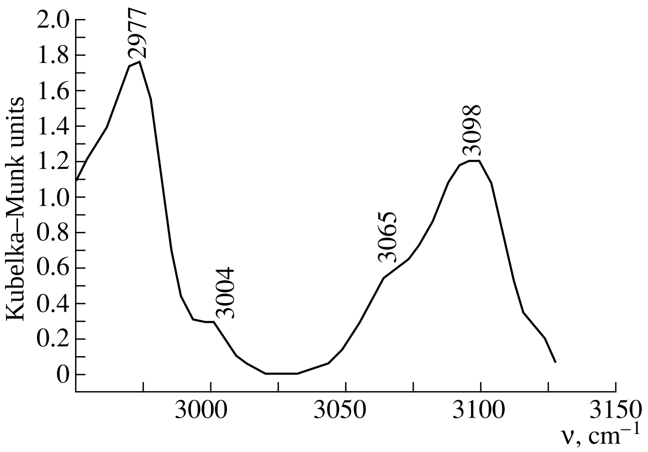


Fig. 2. IR spectrum of ethylene (with corrected zero line) in the region of CH stretching vibrations, measured after 0.5 min after ethylene adsorption on H-mordenite at room temperature.

Table 1 shows that the spectrum of adsorbed ethylene has bands that are not seen in the spectrum of gaseous ethylene. These are composite vibrations of the double bond with the deformational vibrations of CH_2 groups. Their relative intensities are comparable to the intensity of the bands of C–H stretching vibrations. This is not characteristic of gaseous and liquid ethylene.

The Region of $–CH_2–$ and $–CH_3$ Stretching Vibrations in Growing Polymer Chains

With an increase in the time of ethylene contact with HM, the intensity of bands with maxima at 2960, 2928, and 2855 cm^{-1} substantially increases. These bands are usually assigned to the asymmetric and symmetric vibrations of CH_2 and CH_3 groups in a growing polymer chain with the following frequencies $\nu_{as}(–CH_2–) = 2928$ cm^{-1}, $\nu_{as}(–CH_3) = 2960$ cm^{-1}, and $\nu_s(–CH_2–) = 2855$ cm^{-1}. An increase in the intensity of these bands with time points to the occurrence of ethylene oligomerization even at room temperature [12]. Analysis of the spectrum recorded immediately after ethylene contact with the zeolite shows that the intensities of bands of $–CH_2–$ and $–CH_3$ groups are close, suggesting the

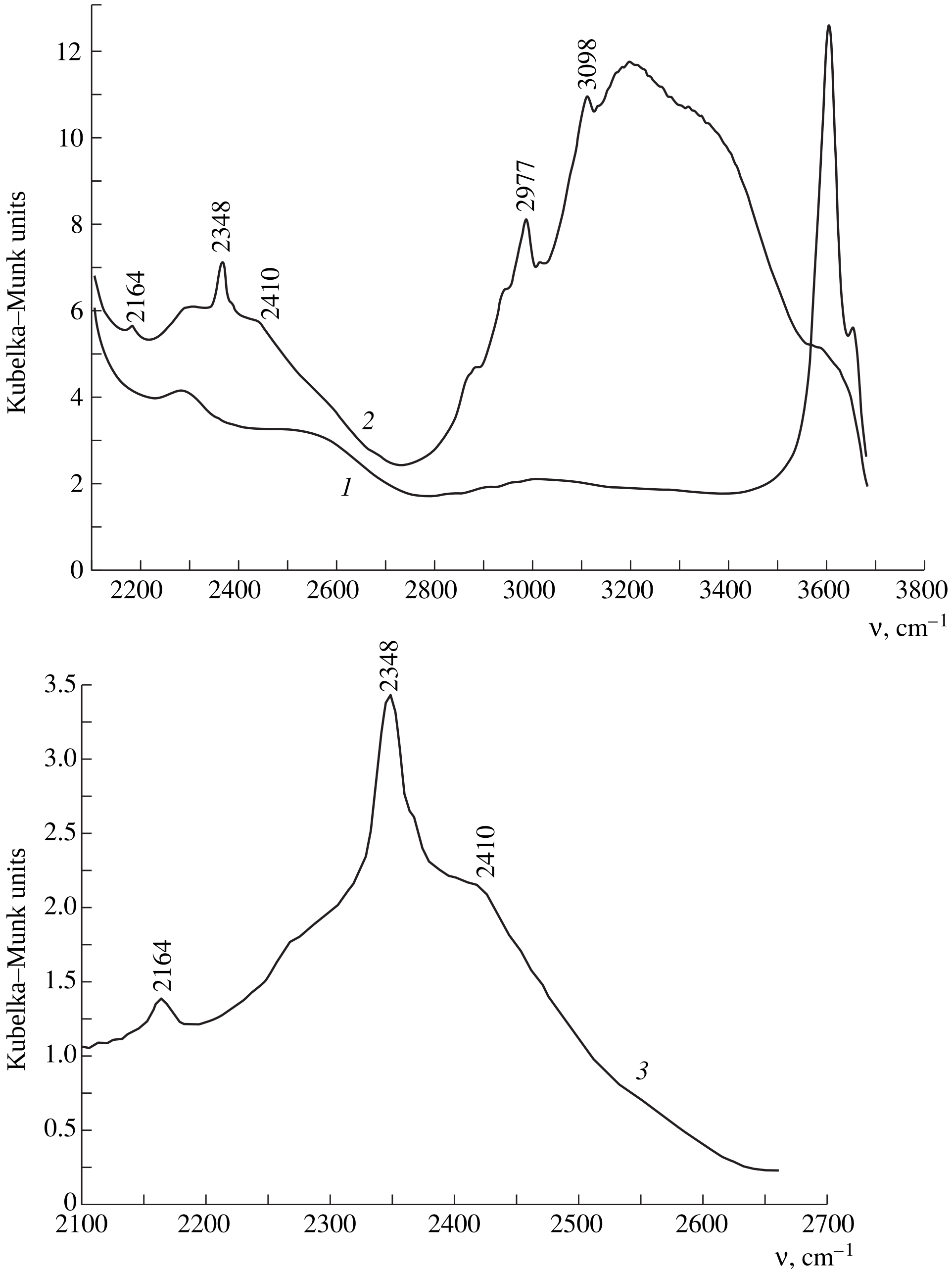


Fig. 3. IR spectra in the region of stretching and composite vibrations of ethylene for (*1*) initial mordenite, (*2*) after ethylene adsorption on H-mordenite at room temperature, and (*3*) the result of subtracting spectrum *2* from spectrum *1*.

predominant formation of ethoxy groups. With an increase in the reaction time, the relative intensities of the bands of $–CH_2–$ bond stretching increase due to the growth of a linear chain (Fig. 5).

DISCUSSION

It is known that two types of channels exist in zeolite HM [13]. Large channels are formed by 12-membered rings with a cross-section of 6.5 × 7.0 Å. Small channels are bays in the walls of large channels. They are formed by 8-membered rings with sizes of 2.6 × 5.7 Å. The entrance windows of bays from the side of large channels are also formed by 8-membered rings with a size of 3.7 × 4.8 Å. According to [9], OH groups in 12-membered rings of large channels have vibrations with a frequency of 3612 cm^{-1}, whereas those in 8-membered rings have vibrations with a frequency of 3590 cm^{-1}. As follows from Fig. 1, at the initial moment of ethylene adsorption, the vibrations of OH groups of both channels disappear virtually completely. However, with time, the intensity of bands in small-channel OH groups at 3595 cm^{-1} gradually increases.

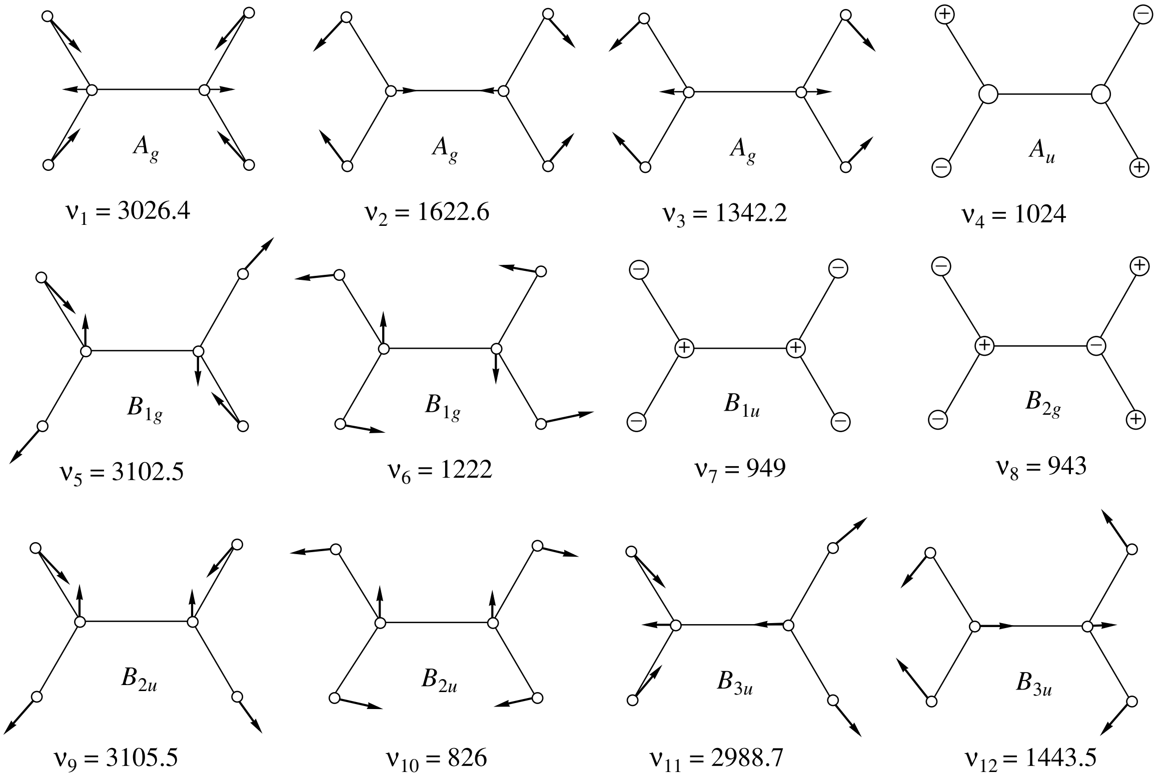


Fig. 4. Forms of vibrations of gaseous ethylene and the corresponding frequencies (in cm^{-1}) [11].

The kinetic diameter of the ethylene molecule is ~3.9 Å [14]. This enables easy ethylene penetration through the system of large zeolite channels and interaction with OH groups in them, although the contact with OH groups in small channels is hindered. Nevertheless, a change in the intensity of the band with a maximum at 3595 cm^{-1} points to the fact that this interaction does occur. This controversy can be explained if we assume that the region of 3690 cm^{-1} contains the bands of OH groups belonging to the 8-membered rings of small channels with a size of 2.6 × 5.7 Å and those positioned in the entrance windows of small channels from the size of large channels with a size of 3.7 × 4.8 Å. Then, ethylene cannot penetrate through the system of small channels but can react with the OH groups of 8-membered rings in the entrance windows of small channels. Because of steric hindrances, this interaction is weaker than the interaction with the OH groups of large channels and does not lead to the formation of the reaction product.

Indeed, as oligomeric chains grow and ethylene is consumed in large channels, it gradually desorbs from the bays into large channels. The OH groups are freed in the bays, and the intensity of the band at 3695 cm^{-1} grows. The contact of ethylene with these OH groups probably corresponds to the shoulder at 3340 cm^{-1}, although the stronger interaction with OH groups excited by the hydrogen bond in large channels corresponds to the band with a maximum at 3200 cm^{-1}.

We should emphasize that in the case of ethylene adsorption on HM, the excitation of OH groups is stronger than in the case of adsorption on HY [7] (a low-frequency shift of OH vibration in ethylene adsorption on mordenite is 415 cm^{-1} compared to 350 cm^{-1} for ethylene adsorption on HY [7]). This results in ethylene oligomerization on HM, although this reaction does not occur on HY at room temperature.

Let us turn to the IR spectra of ethylene adsorbed on acid hydroxyl groups. Table 2 compares the frequencies of C–H stretching vibrations of gaseous and liquid ethylene borrowed from [10] (see also Fig. 4, which shows the forms of these vibrations).

Table 1. Frequencies in the region of composite vibrations of the double C=C bond and deformational vibrations of CH_2 for the gaseous and liquid ethylene molecule and for ethylene adsorbed on HM at room temperature

$\nu_i + \nu_j$, cm^{-1}	Ethylene state		
	gas [10]	liquid [10]	adsorbed on HM
$\nu_3 + \nu_{10}$	2167	2167	2164
$\nu_3 + \nu_4$	–	2340	2348
$\nu_2 + \nu_{10}$	–	2434	~2410

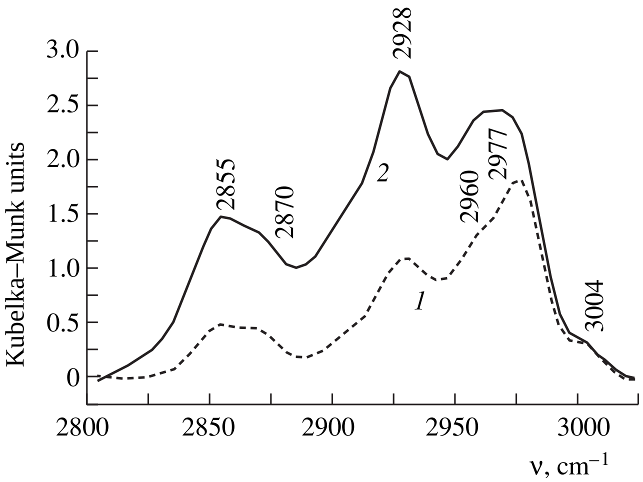
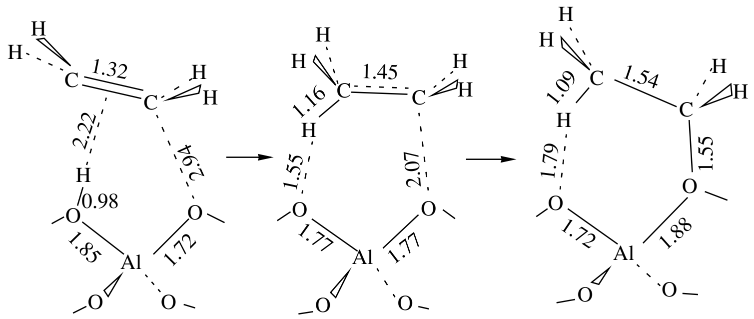


Fig. 5. IR spectra in the region of the stretching vibrations in –CH_2– and –CH_3 (with the corrected zero line) after ethylene adsorption on H-mordenite at room temperature measured (*1*) 0.5 min and (*2*) 2.5 min after the beginning of a run.

Table 2 shows that the IR spectrum of gaseous ethylene has only two bands for C–H stretches with frequencies ν_9 and ν_{11}, and two additional bands with frequencies ν_1 and ν_5 are observed in Raman spectra. On the other hand, Sheppard and Yates [15] showed that vibrations that are inactive in the IR spectra of gaseous molecules can reveal themselves in the case of adsorbed molecules due to changes in their symmetry and the appearance of induced dipole momentum. Thus, in ethylene adsorption on porous silicate glass, three IR bands are observed at room temperature: ν_1 = 3010, ν_9 = 3100, and ν_{11} = 2980 cm^{-1} [15]. In adsorption on Vycor glass at –194°C, four bands are observed: ν_1 = 3007, ν_5 = 3070, ν_9 = 3093, and ν_{11} = 2977 cm^{-1} [16]. These data led us to assign the bands observed in our spectra to the stretching vibrations of adsorbed ethylene.

Earlier, we carried out a quantum chemical study of the reaction coordinate of proton transfer from acid hydroxyl groups of high-silica zeolite to adsorbed ethylene [17]. We found that the reaction coordinate of proton transfer is complex. It corresponds to the simultaneous stretch of the O–H bond in acid OH group and the double bond in the ethylene molecule, while the double bond transforms into a single C–C bond. The valence angles in one of the CH_2 groups change when this group transforms into CH_3. As a result, the transition state is formed whose geometry and high positive charge resemble those in adsorbed ethyl carbenium ion that transforms further into the ethoxy group bound to a neighboring oxygen atom of the zeolite lattice via a covalent bond (bond lengths are shown in angstroms):



As follows from the forms of ethylene vibrations shown in Fig. 4, a change in the double bond length corresponds to the stretching vibrations ν_2 and ν_3. Ethylene molecules also change valence angles in methylene groups and the hybridization of carbon atom orbitals. The vibration with frequency ν_4, which moves hydrogen atoms out of the plane of a double bond, also leads to a change in the orbital hybridization of carbon atoms in methylene groups from sp^2 to sp^3.

According to ideas devised in our previous work [18], the combinations of these vibrations should make the main contribution to proton transfer. The corresponding composite frequencies should be highly inharmonic; that is, the intensities of the corresponding bands of composite vibrations should be abnormally high, and their frequency should be much lower than the arithmetic sum of the frequencies of constituent vibrations. This agrees with our results. Indeed, as follows from Table 1, which shows composite vibrations of the double C=C bond with deformational vibrations of CH_2, and Fig. 3, the composite vibration $\nu_2 + \nu_{10}$ has anharmonism since its frequency is noticeably lower than the arithmetic sum of constituent vibration frequencies. Also, the intensity of bands corresponding to this and other composite vibration frequencies are abnormally high. This also points to a high anharmonism.

Thus, the results of this work support an earlier conclusion that the composite frequencies in the IR spectra of adsorbed molecules are a better index of their activation than the shifts of their stretching vibrations. Note also that, in our additional runs on ethylene adsorption on HY and the alkali-earth forms of mordenite, the composite frequencies of stretching vibrations and deformational vibrations of the CH_2 group found for

Table 2. The frequencies of C–H stretching vibrations of gaseous and liquid ethylene and ethylene adsorbed on HM at room temperature observed in IR and Raman spectra

ν_i, cm^{-1}	Ethylene state				
	gas [10]		liquid [10]		adsorbed on HM
	Raman	IR	Raman	IR	IR
ν_1	3026	–	3019	3016	3004
ν_5	3103	–	3075	–	3065
ν_9	–	3105	–	3085	3098
ν_{11}	–	2989	–	2983	2977

HM are not observed or have very low intensity. On these zeolites, ethylene adsorption is weaker than on mordenite, and oligomerization does not occur.

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