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Intensities of combination IR bands as an indication of the concerted mechanism of proton transfer from acidic hydroxyl groups in zeolites to the ethylene hydrogen-bonded by protons

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Abstract

Adsorption of ethylene by sodium forms of mordenite and Y zeolite is reversible and results in no chemical activation of olefin. Therefore, diffuse reflectance infrared Fourier transform spectra of ethylene adsorbed by these zeolites do not differ much from those of liquefied or frozen C_2H_4. In contrast, adsorption of ethylene by HY and HMOR results in strong hydrogen bonding with acidic hydroxyl groups and subsequent oligomerization of ethylene at room temperature. The hydrogen bonding strongly perturbs OH frequencies but exerts only a weak influence on the frequencies and intensities of the fundamental C–H stretching vibrations of ethylene. In contrast, intensities of the infrared (IR) bands from combinations of the double-bond stretching vibrations with the bending vibrations of CH_2 groups increase significantly. According to previously published quantum chemical calculations, these combinations contribute most significantly to the reaction coordinates of protons added to adsorbed ethylene. Therefore, the results obtained allow formulation of a new spectral criterion of the reactivity index for concerted proton transfer to adsorbed ethylene; the IR bands corresponding to combination frequencies of most strongly polarized chemical bonds involved in this elementary step have unusually high intensities. It is also suggested that this criterion is of more general significance and also can be applied to other elementary steps of acid or acid–base catalytic reactions when chemical activation of adsorbed molecules results from simultaneous polarization of several chemical bonds.

Keywords: Reactivity index; Reaction coordinate; Combinations of stretching and bending vibrations; Acid catalysis; Zeolites; IR spectra

1. Introduction

Infrared (IR) spectroscopy is most frequently used in studying the mechanisms of acid-heterogeneous catalysis. It allows both observation of the perturbation of acidic hydroxyl groups via their hydrogen bonding with adsorbed molecules and detection of the stable protonated active intermediates. The low-frequency shifts of IR stretching bands of hydroxyl groups or adsorbed molecules are also frequently used as a measure of their perturbation and chemical activation. However, for adsorbed hydrocarbons, in most cases such shifts do not exceed only a few wave numbers [1]. This finding can be explained by the covalent nature of the ground states of C–H chemical bonds. Thus, the frequencies of their fundamental stretching vibrations are rather insensitive to the polarization of chemical bonds, which is the main source of chemical activation of adsorbed hydrocarbons in heterogeneous acid catalysis.

Bearing this in mind, in previous work [2,3] we proposed using intensities of C–H IR stretching bands as measures of the polarization of adsorbed light paraffins by the low-coordinated cations in zeolites. The obvious advantage of this new spectral approach lies in the closer connection of the intensities of IR bands with the polarization of C–H chemical bonds on stretching via vibrational excitation. Indeed, it is well known from the fundamentals of IR spectroscopy that intensities of the stretching bands of different molecules are proportional to the squares of the first derivatives of additional dipole moments,

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$d\mu$, created by the stretching of chemical bonds over normal coordinates, q, of the corresponding vibrations:

$$I_{\text{fund}} \sim [d\mu/dq]^2. \tag{1}$$

In other words, the intensities of IR stretching bands allow much better tracing of polarization of adsorbed molecules by the active sites of heterogeneous catalysts than do the low-frequency shifts of these vibrations. For the acid and acid–base catalysis, when chemical activation of adsorbed molecules arises mainly from their polarization, additional application of this approach seems promising.

In the present study, we attempted to apply this new spectral criterion to another kind of acid-catalyzed reaction: to ethylene oligomerization over hydrogen forms of mordenite and Y zeolite. To do this, we compared IR spectra of ethylene adsorbed by the hydrogen and sodium forms of these zeolites.

The reason that we chose these zeolites and ethylene oligomerization as a test reaction is that ethylene is one of the simplest molecules, and thus its IR spectrum can be analyzed in detail rather easily. In addition, although ethylene adsorption on both sodium and hydrogen forms of the zeolites starts with formation of similar π-complexes, for the sodium forms it does not result in subsequent chemical activation and oligomerization. In contrast, ethylene π-bonded to acidic protons is initially transformed into surface ethoxy groups and then involved in subsequent oligomerization with formation of the growing polyethylene chains anchored to the surface of the zeolites [4,5]. Therefore, such differing ethylene activation by the hydrogen and sodium forms could be also expected to affect the IR spectra of the π-bonded species.

Another argument in favor of acid-catalyzed ethylene oligomerization as a test reaction was provided by our earlier quantum chemical calculations [6–8]. These calculations described the mechanism of proton transfer to the π-bonded olefins reasonably well; therefore, we expected that comparing the results of quantum chemical calculations with those of the present spectral study could provide insight into the role of the polarization of π-bonded olefins in the reaction mechanism of proton transfer.

Our measurements of IR spectra of adsorbed ethylene were done by the highly sensitive diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) method. The spectral range studied included the frequencies of C–H stretching vibrations and combinations of double-bond stretching with bending vibrations of CH_2 groups. Hydrogen forms of Y zeolite and mordenite with Brønsted acid sites of varying strengths were selected as the solid catalysts. The dimensions of the micropores in these zeolites also varied somewhat. However, in the present study we did not explore the role of shape selectivity in the process of ethylene oligomerization, but rather concentrated on the primary key reaction of the addition of protons to ethylene.

2. Experimental

The Y zeolites (obtained from Akzo Chemical) used in the present study had a Si/Al ratio of 2.5; for mordenite, this ratio was 5. Five-fold ion exchange of sodium forms was carried out with an ammonium nitrate aqueous solution. After ion exchange, the catalysts were washed with distilled water and dried for 5 h at 300 K. The hydrogen forms of both zeolites were prepared by decomposition of the corresponding ammonium forms in oxygen flow at 700 K. The extent of sodium substitution as detected by atomic adsorption spectroscopy analysis was as high as 90–95%.

For preparation of the deuterated mordenite, the hydrogen form was kept in vapors of heavy water for 30 min at 600 K. As follows from the DRIFTS spectrum of the deuterated sample, the extent of hydrogen substitution by deuterium was close to 100%.

For the spectral measurements, the granulated samples of both zeolites with particle size of 0.5–1 mm were placed in a quartz vacuum cell equipped with a side arm with a CaF_2 window transparent for IR irradiation. Vacuum pretreatment of the zeolites was carried out in the quartz part of the cell. Initially, the samples were heated in vacuum at 100 °C for 2 h. Then the temperature was gradually increased from 373 to 723 K, and the samples were maintained at this temperature under vacuum for 3 h or longer.

DRIFTS spectra were recorded at room temperature in the spectral range of 2000–4000 cm^{-1} with a Nicolet Impact 410 spectrophotometer equipped with a home-made DRIFTS chamber. For this purpose, the granulated powders of the zeolites were transferred to the side arm of the optical vacuum cell with a CaF_2 window. The technique used for these measurements was described in more detail previously [9]. The spectra thus obtained were converted into Kubelka–Munk units using a standard program under the assumption that the reflective ability of the zeolites at 5000 cm^{-1} was equal to 0.9. The backgrounds created by the zeolites were then subtracted from the total spectra.

Before adsorption, ethylene was purified by freezing in a trap cooled with liquid nitrogen, followed by selection of the middle fraction that was evaporated on gradually increasing temperature. To avoid rapid oligomerization over hydrogen form of mordenite (HMOR), 3–7 mmol/g of ethylene was initially adsorbed on this zeolite at 77 K. To make distribution of ethylene inside the micropores of the zeolite more homogeneous, the closed vacuum cell with samples was slowly warmed to 220 K, then cooled again to 77 K and brought to the IR spectrophotometer in a Dewar flask under liquid nitrogen. After the cell was warmed to room temperature, the zeolite granules were rapidly transferred to its side arm with a CaF_2 window, and DRIFTS measurements were started with intervals of several minutes between subsequent recordings. Ethylene adsorption on hydrogen and sodium forms of Y zeolite and on the sodium form of mordenite was carried out in the same optical vacuum cell directly at room temperature at a pressure of 8–10 Torr.

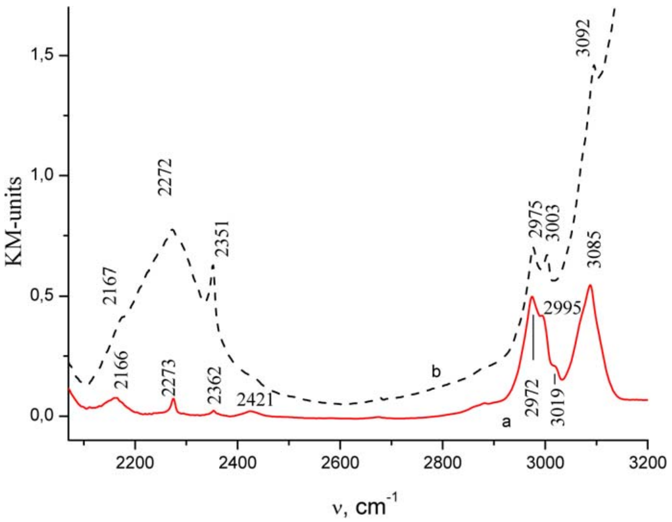


Fig. 1. DRIFT spectra of ethylene adsorbed by NaY (a) and HY(b) zeolites at room temperature at the pressure of 8 and 10 Torr respectively.

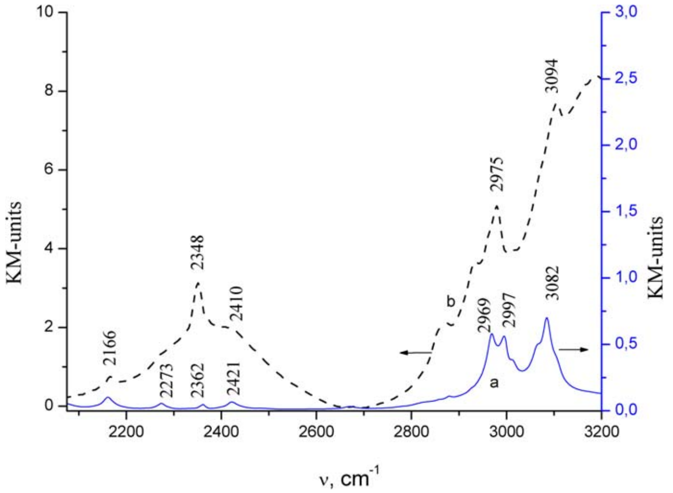


Fig. 2. (a) DRIFT spectra of ethylene adsorbed by NaMOR at room temperature at the pressure of 10 Torr. (b) DRIFT spectrum of HMOR, recorded at room temperature in 0.5 min after adsorption of ethylene in amount of 7 mmol/g.

3. Results

3.1. Adsorption of ethylene by sodium forms of NaY and NaMOR

Adsorption of ethylene at room temperature by NaMOR and NaY zeolites is reversible and results in no chemical reaction. The corresponding DRIFTS spectra are shown in Figs. 1a and 2a. In addition, the wave numbers of the bands of adsorbed species with those for gaseous or frozen ethylene are compared in Table 1.

For ethylene adsorbed by both sodium forms, the frequencies of ν_9 and ν_{11} asymmetric C–H stretching bands are very close to each other and also to those in the spectra of gaseous, liquid, or frozen ethylene. In addition, we also observe the symmetry-forbidden ν_1 and ν_5 C–H stretching bands absent in the spectrum of gaseous ethylene. This well-known effect is connected with the decreased symmetry of adsorbed molecules due to their interaction with the adsorption sites of zeolites or other adsorbents [1].

As follows from Table 1, for both sodium forms, the positions of the combination IR bands of different bending vibrations with the stretching vibrations of the double bond in the spectral range of 2100–2500 cm^{-1} are very close to each other and also very close to those in the spectra of liquid or frozen ethylene. As may be expected, the intensities of these bands are about one order of magnitude lower than those of the C–H stretching bands. Thus, the interaction of ethylene with sodium forms of both zeolites results in neither chemical activation nor large low-frequency shifts of the IR absorption bands.

Table 1
Wavenumbers of IR C–H stretching and combination bands for gaseous, liquefied, solid ethylene and for ethylene adsorbed by sodium and hydrogen forms of Y zeolite and mordenite

Assignment of IR absorption bands according to [10]	Gaseous C_2H_4	Liquefied C_2H_4 at −168 °C[a]	Solid C_2H_4 at −180 °C[a]	C_2H_4 adsorbed by NaY[b]	C_2H_4 adsorbed by NaMOR[b]	C_2H_4 adsorbed by HY[b]	C_2H_4 adsorbed by HMOR[b]
ν_1	3026 (R)	3016	–	2995	2997	3003	
ν_5	3103 (R)	3075 (R)	3075	3019	–	–	
ν_9	3105	3085		3085	3082	3092	3094
ν_{11}	2989	2983	2973	2972	2969	2975	2975
ν_2	1623 (R)	1620	1616				
ν_3	1342 (R)	1339	1336				
ν_6	–	1239	–				
ν_4	1027	–	1010				
ν_7	949	961	970				
ν_{10}	810	828	827				
$\nu_2 + \nu_{10}$	–	2434	2434	2421	2421	broad band at 2272	broad band at 2410
$\nu_3 + \nu_4$	–	2340	–	2362	2362	2351	2348
$\nu_3 + \nu_7$	–	–	2300	2273	2273		
$\nu_4 + \nu_6$	–	2253	2255			2167	2167
$\nu_3 + \nu_{10}$		2167	2166	2166	2166	2167	2166

[a] C. Brecher, R.S. Halford, J. Chem. Phys. 35 (1961) 1109.

[b] Present work (ν_2, ν_3, ν_6, ν_4, ν_7, ν_{10} were not recorded).

According to previous work [10], the foregoing combinations most likely arise from interaction of the ν_3 (1342 cm^{-1}) and ν_2 (1623 cm^{-1}) stretching vibrations of the double bond with the ν_4 (1027 cm^{-1}), ν_7 (949 cm^{-1}), or ν_{10} (810 cm^{-1}) twisting and CH_2 bending vibrations.

3.2. Adsorption and oligomerization of ethylene on hydrogen form of Y zeolite

As reported earlier [11], ethylene adsorption by the hydrogen forms of zeolites results in the strong broadening and low-frequency shifts of O–H stretching bands of acidic hydroxyl groups. In our case, for ethylene adsorption on HY at the equilibrium pressure of 10 Torr, the maximum of this band shifts from 3660 to 3285 cm^{-1}. In addition, the weak C–H stretching bands of adsorbed ethylene at 3092, 3003, and 2975 cm^{-1} are superimposed on the background of this broad band (Fig. 1b). Similar to the situation in adsorption by NaY, the positions of these bands differ only slightly from those for frozen or liquefied ethylene. Thus, adsorption of ethylene on HY does not significantly perturb the bands from the C–H stretching vibrations.

In contrast, comparing spectra (a) and (b) in Fig. 1 reveals a huge difference between DRIFTS spectra of ethylene adsorbed by NaY and HY zeolites in the spectral range of combinations of different bending vibrations with the stretching vibrations of the C=C double bond. Indeed, for ethylene adsorption by NaY, this part of the IR spectrum displays four well-resolved weak narrow bands [spectrum (a) in Fig. 1]. In contrast, for ethylene adsorbed by HY, only a narrow band with a maximum slightly shifted to 2351 cm^{-1} is detected. The intensity of this band strongly increases and becomes comparable with those of the C–H stretching bands. The other combination bands are transformed into a very broad unresolved line with a maximum at about 2400 cm^{-1}. The intensity of this line is more than by two orders of magnitude greater than that of the corresponding narrow bands for ethylene adsorbed by the sodium form [spectrum (b) in Fig. 1].

Indeed, for ethylene adsorbed by NaY zeolite, the amplitudes of the combination bands are about one order of magnitude lower than those for the bands from C–H stretching vibrations, whereas for hydrogen-bonded ethylene, the amplitude of the broad band is comparable with that of the C–H stretching bands. Moreover, this new combination band is more than one order of magnitude broader. Therefore, the hydrogen bonding of ethylene with acidic hydroxyl groups results in significantly higher-intensity bands due to the combination of the double-bond stretching vibration and the bending vibrations of CH_2 groups.

This effect is undoubtedly related to the chemical activation of adsorbed molecules, because maintaining HY zeolite in ethylene atmosphere at room temperature results in very slow oligomerization. In Fig. 3 this reaction is indicated by the appearance of new C–H stretching bands. Two of these bands, at 2865 and 2930 cm^{-1}, correspond to symmetric and asymmetric CH_2 stretching vibrations of the growing oligomer chains, whereas the band with the maximum at 2960 cm^{-1} belongs to the asymmetric vibration of CH_3 groups. These bands could not be removed by evacuation at room temperature.

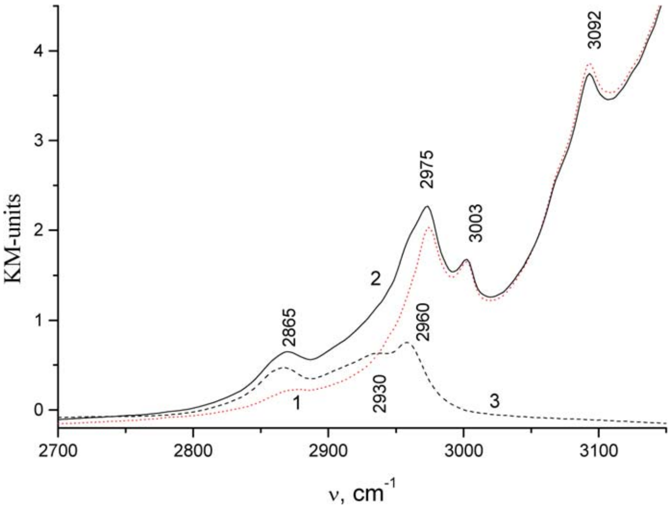


Fig. 3. DRIFT spectra of ethylene adsorbed by HY at room temperature at the pressure of 200 Torr after 1 (1) and 50 h (2) from the beginning of the reaction. Spectrum (3) was recorded after evacuation of the sample after reaction at room temperature.

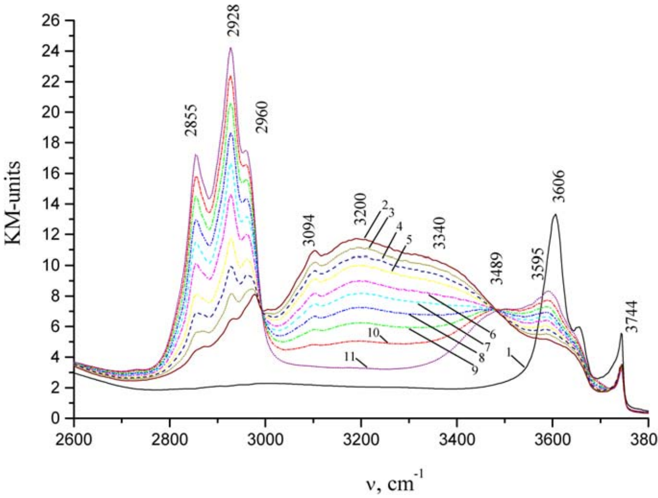


Fig. 4. DRIFT spectra of initial HMOR (1) and those recorded after adsorption of ethylene at room temperature in amount of 7 mmol/g. The spectra were recorded after 0.5 (2); 2.5 (3); 3.5 (4); 4.5 (5); 5.5 (6); 9 (7); 12 (8); 17 (9); 25 (10); and 48 min (11) after beginning of the reaction. The background created by the zeolite was not subtracted.

3.3. Adsorption and oligomerization of ethylene on the hydrogen form of mordenite

The results obtained for ethylene adsorption by the hydrogen form of mordenite are very similar to those for adsorption by HY, as illustrated by the DRIFTS spectra in Fig. 4. They indicate that due to the hydrogen bonding, ethylene adsorption at room temperature also results in strong perturbation of O–H stretching vibrations. In this case the low-frequency shift of the OH band to 3200 cm^{-1} is somewhat larger than that for ethylene adsorption by HY. This is consistent with the higher acidity of mordenite compared with HY.

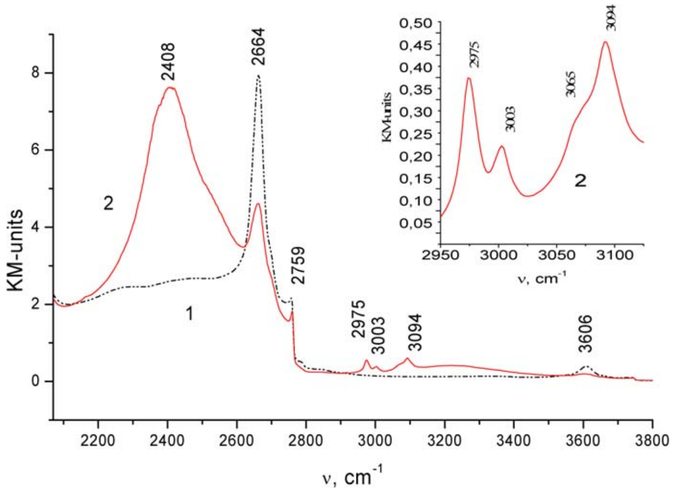


Fig. 5. DRIFT spectra of DMOR, recorded before (1) and after (2) adsorption of ethylene in amount of 5 mmol/g at room temperature. The background created by the zeolite was not subtracted.

Similar to HY, at the beginning of reaction, much weaker narrow bands from adsorbed ethylene are also clearly seen on the background of the broad band from the hydrogen-bonded hydroxyl groups. However, in accordance with the higher acidity of HMOR, ethylene oligomerization catalyzed by this zeolite is much faster than that catalyzed by HY. Therefore, the DRIFTS spectrum of π-bonded ethylene was observed only at the very first stage of oligomerization, when the π-complexes was not yet transformed into ethoxy groups.

At room temperature, the broad band from the hydrogen-bonded OH groups disappears within about 50 min from the start of the reaction. In contrast, the intensities of the bands from the growing chains of the oligomer increase significantly. The intensities of the bands at 2855 and 2928 cm^{-1} increase with time more rapidly than that of the band from the asymmetric vibrations of CH_3 groups at 2960 cm^{-1}. This indicates a linear structure of the growing oligomer chains.

To avoid the background created by the hydrogen-bonded OH groups, we studied ethylene adsorption on the deuterated sample. The corresponding DRIFT spectrum is shown in Fig. 5. As one could expect, the low-frequency shift of the band from the hydrogen bonded OD groups is considerably smaller than that for OH groups. Therefore, for the deuterated sample, the C–H stretching bands from adsorbed ethylene are not superimposed on the broad band from the hydrogen-bonded OD groups, and the positions of the C–H bands can be detected more precisely. They also differ only slightly from those for ethylene adsorption by HY or by the sodium forms of both zeolites.

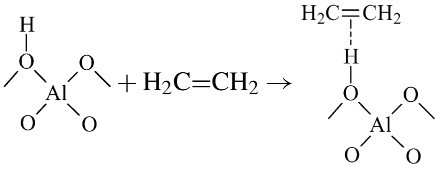
In contrast, similar to ethylene adsorption on HY, the intensities of the combinations of the CH_2 bending and twisting vibrations with the double-bond stretching vibrations in IR spectrum of HMOR also increase significantly; compare spectra (a) and (b) in Fig. 2. Despite the fact that positions and shapes of the combination bands for HY and HMOR are slightly different, these results indicate that chemical activation of π-bonded ethylene in mordenite also results in unusually high intensity of the combination band from double-bond stretching and CH_2 bending and twisting vibrations.

4. Discussion

Adsorption of light olefins by hydrogen forms of zeolites has been thoroughly studied by Domen and coworkers [12–15] and by other authors in Refs. [16–18], who also found that π-complexes with acidic protons initially formed on adsorption are subsequently involved in the acid-catalyzed reactions of double-bond shift, skeletal isomerization, or oligomerization via formation of carbenium ion-like intermediates or transition states. Selectivity of these reactions depends on the temperature and dimensions of zeolite micropores. For instance, for ferrierite, due to the narrow micropores, the main reaction at low temperatures is the double-bond shift. For the larger pores in mordenite or ZSM-5 zeolite, the predominant reaction at higher temperature is oligomerization, whereas skeletal isomerization and other secondary reactions require even higher temperatures.

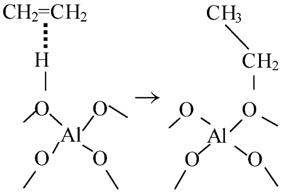
For ethylene, the only possible reaction is oligomerization, which does not depend on the pore size. According to IR [19,20] and solid-state ^{13}C-NMR studies [21] or temperature-programmed experiments [22], this begins already at room temperature. The resulting oligomer chains anchored to the surface of the zeolites gradually fill the zeolite micropores. Decomposition of oligomers occurs above 500 K, resulting in desorption of a mixture of hydrocarbons of similar composition regardless of the initial olefin. This temperature is close to that for the conventional catalytic oligomerization of ethylene on the corresponding hydrogen forms, which includes the following sequence of elementary steps:

1. Hydrogen π-bonding of adsorbed ethylene by the bridging acidic hydroxyl groups:



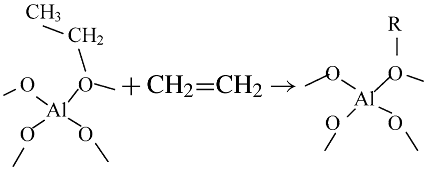
(1)

2. Proton transfer to π-bonded ethylene, resulting in formation of the surface ethoxy groups via a carbenium ion-like transition state:



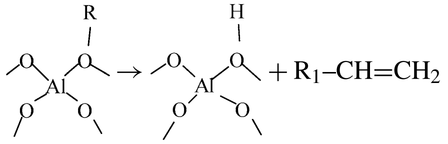
(2)

3. Growth of the chains of linear oligomer due to the subsequent reaction of the polarized ethoxy groups (of adsorbed ethyl carbenium ions) with the next ethylene molecules:



(3)

4. Desorption of olefins from the zeolite at elevated temperatures via decomposition or cracking of the linear oligomers anchored to the zeolite surface:



(4)

In the present study, steps (2) and (3) were monitored directly by DRIFTS; however, here we focus on reaction (2), which is associated with the activation of hydrogen-bonded ethylene via formation of a carbenium ion-like transition state that is subsequently converted to the surface ethoxy group.

Earlier proton transfer from acidic hydroxyl groups of the zeolites to the π-bonded ethylene was a subject of our earlier quantum chemical calculations [6,7], which indicated that the reaction coordinate of this concerted elementary step is rather complicated. As follows from Fig. 6, which shows the results of these calculations, the addition of protons to ethylene corresponds to the simultaneous stretching of the O–H bond of the acidic hydroxyl group in combination with the carbon–carbon double-bond stretching. Simultaneously, the H–C–H angles in both CH_2 fragments of the π-bonded ethylene are changing due to transformation of one of these to the methyl group and to binding of the other with the adjacent basic oxygen atom of the zeolite framework. The geometry and the high positive charge of ethyl fragment in such a transition state resemble those of adsorbed ethyl carbenium ions. The latter is then converted into the polarized ethoxy group that is covalently bonded to the adjacent oxygen atom of the zeolite framework. Later, this reaction mechanism was confirmed by the more sophisticated quantum chemical calculations performed by others [23–26].

The stretching of the double bond in the π-bonded complex corresponds to the ν_3 and ν_2 normal vibrations. These vibrations simultaneously change the valence angles in the CH_2 groups and, hence, hybridization of the orbitals of the ethylene carbon atoms. The valence angles in both CH_2 groups are also influenced by the ν_{10} bending vibration. In addition, ν_4 and ν_7 vibrations bring the hydrogen atoms of CH_2 groups out of the plain of the ethylene double bond.

According to the aforementioned quantum chemical calculations, all of these vibrations are involved in the reaction coordinate of the addition of protons to ethylene. The compensation of the energy required for heterolytic dissociation of the bridging hydroxyl group and for the stretching of the double bond on transformation into the single bond is then supplied by the newly forming C–O and C–H bonds. Therefore, an important feature of the addition of protons to adsorbed ethylene is a simultaneous rearrangement of several chemical bonds, resulting in compensation of the energy required for activation of initial molecules by the energy of the newly forming bonds in the ethoxy fragment. The relatively low activation barrier of this elementary step is favored by the strong polarization of the corresponding combination modes in the π-bonded molecules.

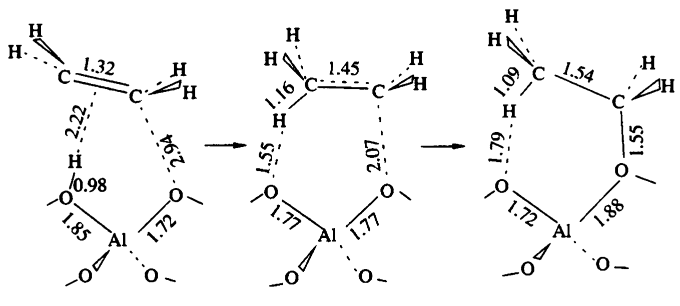


Fig. 6. The reaction coordinate of proton addition to of π-bonded ethylene according to Ref. [7].

As follows from the aforementioned DRIFTS spectra, the increasing positive charge and dipole moment of π-bonded ethylene also strongly influence the intensities of IR bands from the corresponding combination vibrations. Unlike intensities of the fundamental IR vibrational bands, which are proportional to the squares of the first derivatives of additional dipole moments created by normal vibrations over normal coordinates of these vibrations, intensities of the combination bands are proportional to the squares of the second derivatives of the combination vibrations over their normal coordinates [27]:

$$I_{\mathrm{comb}} \sim \left[\mathrm{d}^2\mu/\mathrm{d}q^2\right]^2. \tag{6}$$

Therefore, the very high intensity of the broad IR bands from the combinations of the double-bond stretching vibrations with different deformation vibrations of the CH_2 groups definitely indicate strong polarization of these combination vibrations. In contrast, unlike adsorption of light paraffins on the Lewis sites that we studied previously [2,3], formation of the π-complexes has practically no influence on the intensities of the fundamental bands from C–H stretching vibrations. This indicates the absence of polarization of C–H bonds in the π-bonded species that are not involved in the reaction coordinate of proton transfer to adsorbed ethylene.

Thus, according to results of the present study, the previously formulated new spectral criterion for polarization of adsorbed molecules can be also used as a reactivity index for the concerted acid-catalyzed oligomerization of ethylene. For this reaction, this criterion should be reformulated as follows: The strongly polarized vibrations of several chemical bonds involved in the initial stages of the concerted reaction mechanism result in the unusually high intensities of the corresponding combination IR bands.

Most likely, this criterion is of more general significance and could also be applied to other chemical reactions when the reaction coordinate involves strong polarization of initial molecules resulting from their vibrations. For acid-catalyzed concerted reactions, the intensities of the combination IR bands probably provide an even better reactivity index than the low-frequency shifts of the fundamental stretching bands commonly used for this purpose. Indeed, according to the results of the present study, the intensities of IR bands from the chemical bonds rearranging on transformation of initially adsorbed molecules into final products increase more than by one order of magnitude, while the corresponding fundamental stretching and combination frequencies decrease only by few percentage points.

Acknowledgments

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