

Cyclopropane Adsorption on Zeolites Studied by IR Spectroscopy: II. Adsorption and Conversion of Cyclopropane on Na- and Ca-Exchanged Zeolite Y

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Abstract—The adsorption and isomerization of cyclopropane on the calcium- and sodium-exchanged zeolite Y are studied by IR spectroscopy. Cyclopropane is adsorbed on CaY in two different forms. Weaker adsorption is related to residual sodium ions, which were not completely removed from the zeolite by ion exchange. This form can be removed from the surface after evacuation of the samples at room temperature. Stronger adsorption is attributed to the Ca ions. It is stable up to 100°C. The corresponding diffuse-reflectance spectrum indicates the C_{2v} symmetry of the cyclopropane complex with Ca ions. At 200°C cyclopropane adsorbed on the calcium-exchanged zeolite converts to propylene. On the sodium-exchanged zeolite, this reaction only occurs at 400°C. The reaction coordinate of cyclopropane isomerization on CaY is related to the simultaneous cleavage of the C–C bond in the cyclopropane ring and hydrogen atom transfer from one of the CH_2 fragments to another. The reaction coordinate corresponds to a combination of the stretching vibration of the C–C bond with the fan vibration of the CH_2 group and the stretching vibration of the CH bond. These composite vibrations result in the strong polarization of the C–C and C–H bonds and, hence, exhibit anomalously high molar absorption coefficients in the IR spectrum.

INTRODUCTION

In our previous papers [1, 2] devoted to IR spectroscopic study of ethylene polymerization on the hydrogen-exchanged mordenite and cyclopropane isomerization on the hydrogen-exchanged zeolite Y, we showed that the coordinates of these heterogeneous acid-catalyzed reactions correspond to the complex composite vibrations of adsorbed molecules with anomalously high molar absorption coefficients in the IR spectra. In other words, the intensities of absorption bands in IR spectra of adsorbed molecules are maximal for the composite vibrations involving several strongly polarized chemical bonds, which contribute mainly to the reaction coordinate of an elementary step. This work continues previous studies for the isomerization of cyclopropane to propylene on the sodium- and calcium-exchanged zeolite Y.

Cyclopropane isomerization is used as a model reaction because it forms only propylene as a product. The reaction has been studied on the cationic forms of zeolites in many works [3–14]. It has been shown that the isomerization of cyclopropane during its adsorption on zeolite NaCaY occurs at temperatures higher than 200°C [4], whereas on zeolite CaA [5] it occurs at room temperature. A comparison of the activities of cyclopropane conversion on NaCaY and various cationic (Ca, Co, Mg, Li) forms of zeolites A shows [6] that the

reaction rates are an order of magnitude lower on zeolite NaCaY.

In this work, we used diffuse scattering spectroscopy to study both the region of fundamental stretching vibrations of the CH bonds of adsorbed cyclopropane and its various composite vibrations. Published papers on the IR spectroscopic study of cyclopropane adsorption and conversion on the Ca- and Na-exchanged zeolite Y are scarce. The bands observed in the IR and Raman spectra of cyclopropane in the gaseous, liquid, and solid states in a wide range of vibrational frequencies were assigned according to the published data [15].

EXPERIMENTAL

The sodium- and calcium-exchanged zeolite Y with $Si/Al = 2.5$ and the degree of Na/Ca exchange ~85% were used. Before a spectroscopic study, zeolite samples were placed in a quartz ampule with an appendix having a CaF_2 window and subjected to the evacuation at 450°C similar to that described in [1].

The procedure of IR diffuse reflectance measurements was described in [1]. Measurements were carried out at room temperature after heating the samples at elevated temperatures. The spectra obtained were transformed into the Kubelka–Munk units assuming that the reflectivity of the zeolite at 5000 cm^{-1} is equal to 0.9.

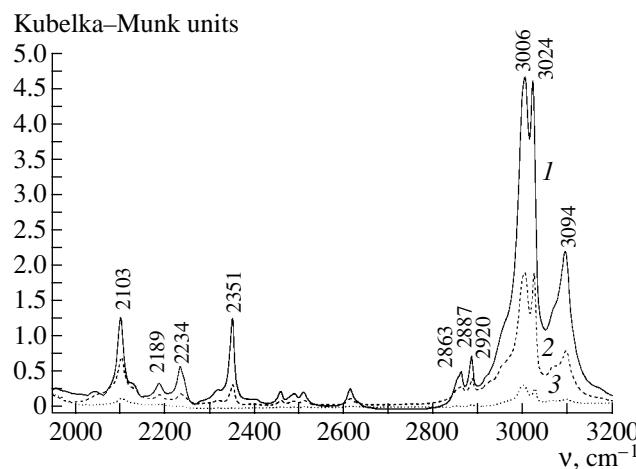


Fig. 1. IR spectrum of NaY after cyclopropane adsorption at room temperature at pressures (1) 6, (2) 1.5, and (3) 0.1 Torr in the region of stretching C–H and composite vibrations.

Then, the background of the zeolite was subtracted from the overall spectrum.

Cyclopropane was purified by freezing into a trap cooled with liquid nitrogen and collecting a medium fraction. Cyclopropane was adsorbed on the sodium-exchanged (NaY) and calcium-exchanged (CaY) zeolite Y at room temperature at an equilibrium cyclopropane pressure of 0.1–10 Torr.

RESULTS

(a) Cyclopropane Adsorption on NaY

The results on cyclopropane adsorption on zeolite NaY have already been considered in part in our previous paper [1]. In this work, cyclopropane adsorption is studied in more detail.

The IR spectrum of cyclopropane adsorbed on NaY at different equilibrium pressures is presented in Fig. 1. Two spectral regions can be distinguished: the region of stretching C–H vibrations from 3000 to 3100 cm⁻¹ and the region from 2000 to 2500 cm⁻¹ characteristic of combinations of the bending vibrations of the CH₂ groups with the vibrations of the C–C bond. The positions of the corresponding bands in the IR spectra of gaseous, liquefied, frozen, and adsorbed on NaY cyclopropane are compared in Table 1.

As can be seen from Fig. 1 and Table 1, the region of the stretching C–H vibrations for cyclopropane adsorbed on NaY exhibits three of four possible absorption bands with maxima at 3094, 3024, and 3006 cm⁻¹, including the v₈ symmetric vibration forbidden in IR spectra. The latter is explained by the effect of symmetry lowering during adsorption [16]. The region of the composite vibrations from 2000 to 2500 cm⁻¹ contains two moderately intense absorption bands with maxima at 2103 and 2351 cm⁻¹ and bands with lower intensity at 2189 and 2234 cm⁻¹.

When the equilibrium cyclopropane pressure decreases, the intensities of all absorption bands

Table 1. Positions of absorption bands (v, cm⁻¹) in the IR spectra of gaseous, liquid, and frozen cyclopropane and cyclopropane adsorbed on the sodium- and calcium-exchanged zeolite Y

Band assignment*	Gas*	Liquid at -125°C*	Solid at -190°C*	Adsorbed on NaY	Adsorbed on CaY
v ₆	3101	3081	3073	3094	3106
v ₁₂	3082 (R)	3075 (R)	3073	—	—
v ₁	3038 (R)	3027 (R)	—	3024	3036
v ₈	3025	3013	3004	3006	2985, 2958
v ₆ + 2v ₁₄	2921	2928	2934	—	—
v ₂ + v ₉	2875	2870	2877	2887	28886
2v ₉	2862	2859	2855	2863	2848
2v ₁₃	—	2372	2370	2351	2363
v ₁₀ + v ₁₃	—	—	2217	2234	2247
v ₃ + v ₁₀	—	2209	2196	2189	—
v ₉ + v ₁₄	2183	2169	2172	“	—
v ₅ + v ₁₀	2083	2082	2083	2103	2118

Note: R indicates that the bands are observed only in the Raman spectra.

* According to the data in [15].

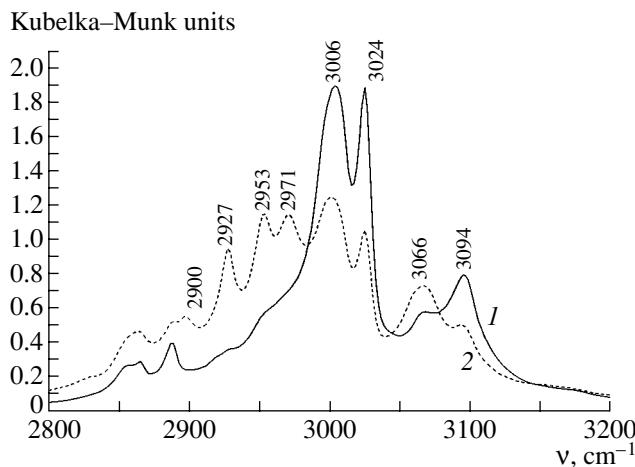


Fig. 2. IR spectrum of NaY after cyclopropane adsorption at a pressure of 1.5 Torr (1) at room temperature and (2) after heating at 400°C for 2 h.

observed in the spectrum decrease in parallel, and the bands disappear completely after evacuation at room temperature. Thus, the adsorption sites in zeolite NaY are uniform. The IR spectrum did not change upon a prolonged contact of cyclopropane with NaY for several days at room temperature, that is, the adsorption of cyclopropane on NaY at this temperature is not accompanied by any chemical transformation.

The IR spectra did not change after the NaY sample with cyclopropane adsorbed at an equilibrium pressure of 1.5 Torr was heated at 200 and 300°C for 0.5 h. However, an increase in the heating temperature to 400°C and in the heating duration to 2 h results in a strong decrease in the intensity of the absorption bands in the region of the C–H vibrations and the appearance of several new bands at 3066, 2971, 2953, and 2927 cm⁻¹ (Fig. 2). The positions of their maxima are presented in Table 2. As shown below, these bands belong to propylene formed due to cyclopropane isomerization. The absorption bands disappear completely after evacuation at room temperature.

(b) Cyclopropane Adsorption on CaY

The spectrum of cyclopropane adsorbed on CaY at a high equilibrium pressure of 3.5 Torr is presented in Fig. 3. As can be seen from these data, as for cyclopropane adsorption on NaY, the 3000–3100 cm⁻¹ region exhibits three intense absorption bands, whose maxima are at the same positions of 2985, 3006, and 3024 cm⁻¹ as those for cyclopropane adsorption on NaY.

The positions of absorption bands in the region of composite vibrations of the C–C bond with the bending vibrations of the C–H bonds at 2118, 2247, and 2363 cm⁻¹ differ from those of analogous bands in the spectrum of cyclopropane adsorbed on NaY. The intensities of two latter bands are comparable with the intensity of the absorption band in the region of the stretch-

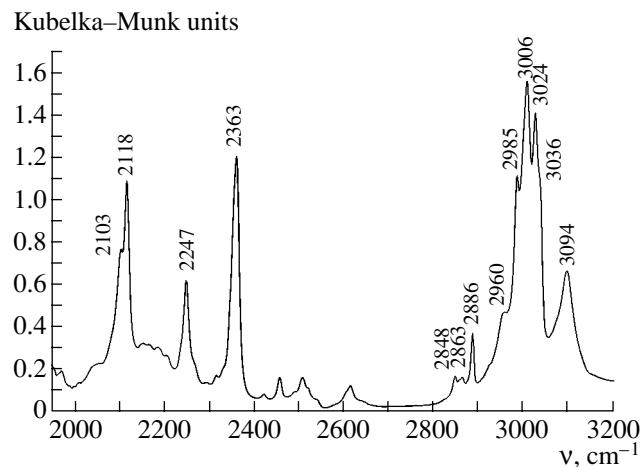


Fig. 3. IR spectrum of CaY after cyclopropane adsorption at room temperature at a pressure of 3.5 Torr in the region of stretching C–H and composite vibrations.

ing C–H vibrations. In addition, a shoulder at 2103 cm⁻¹ is observed against the background of the band at 2118 cm⁻¹. The position of this shoulder coincides with the corresponding line in the spectrum of cyclopropane adsorbed on NaY.

A decrease in the equilibrium pressure of cyclopropane qualitatively changes the spectrum shape in the region of the CH vibrations (Fig. 4). The intensities of absorption bands at 3006 and 3024 cm⁻¹ decrease and they almost completely disappear at a pressure of 0.1 Torr in the gas phase. The maximum of the band at 3097 cm⁻¹ shifts toward 3106 cm⁻¹. As a result, the absorption bands with maxima at 2985 and 3036 cm⁻¹ become most intense in this spectral region. The further

Table 2. Positions of absorption bands (ν, cm⁻¹) in the IR spectra of gaseous and adsorbed propylene and the products of cyclopropane conversion on NaY and CaY

assignment of bands*	Propylene		Product of cyclopropane conversion	
	gas*	adsorption on CaY	CaY	NaY
ν ₁	3081	3059	3054	3066
ν ₂	3012	2990	2990	–
ν ₃	2979	2971	2972	2971
ν ₁₅	2960	2958	2958	2953
2ν ₁₆	2942	2929	2930	2927
ν ₄	2916	2900	2898	2900
ν ₅	2852	2866	2865	–
ν ₆	1647	1624	1624	–

* According to the data in [17].

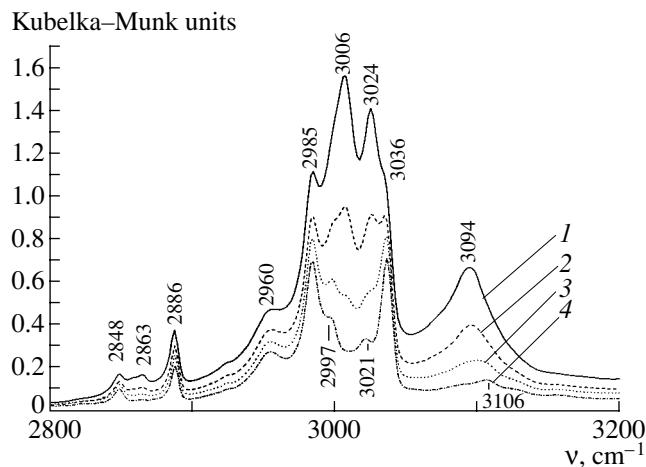


Fig. 4. IR spectrum of CaY after cyclopropane adsorption at room temperature at pressures (1) 3.5, (2) 1.5, (3) 0.5, and (4) 0.1 Torr in the region of stretching C-H vibrations.

evacuation of the sample at room temperature does not remove these absorption bands, which disappear only after evacuation at 100°C.

Unlike the bands of the stretching C-H vibrations, the intensities of the bands of the composite vibrations with maxima at 2118 and 2363 cm^{-1} practically do not decrease with a decrease in the equilibrium cyclopropane pressure to 0.1 Torr and become more intense than the bands of the C-H vibrations (Fig. 5). The shoulder at 2130 cm^{-1} at the band with a maximum at 2118 cm^{-1} disappears. These results indicate that zeolite CaY contains two different sites of cyclopropane adsorption: weaker adsorption sites related to the sodium ions and stronger adsorption sites related to the calcium ions.

The further evacuation of the sample in combination with heating at 100°C results in the disappearance of the

bands in the regions of both composite and C-H vibrations. The absorption bands, which are not removed by evacuation at room temperature, are assigned to adsorption on the calcium cations. The positions of their maxima are presented in Table 1.

The following changes are observed in the spectrum after heating the sample with cyclopropane adsorbed at an equilibrium pressure of 0.1 Torr at 200°C for 10 min. In the region of the stretching C-H vibrations (Fig. 6), the intensities of the absorption bands with maxima at 2985 and 3036 cm^{-1} decrease, and new absorption bands appear at 2958, 2930, and 3054 cm^{-1} . The intensities of the bands in the range 2000–2500 cm^{-1} also decrease. A further increase in the heating temperature to 300°C completely changes the spectrum shape (Fig. 7): the absorption bands of the C-H vibrations at 2985, 3036, and 3106 cm^{-1} and the bands of the composite vibrations at 2118 and 2363 cm^{-1} disappear. Instead of them, the absorption bands at 3054, 2958, and 2930 cm^{-1} become the main in the IR spectrum. A new band with a maximum at 1624 cm^{-1} appears after heating the sample in the low-frequency 1000–1800 cm^{-1} region, which is not presented in Fig. 7. The position of this line is characteristic of vibrations of the double C=C bond.

Taking into account that, according to published data, cyclopropane transforms into propylene on the cationic forms of the zeolite, we recorded the IR spectrum of propylene adsorbed in CaY, which is presented in Fig. 7 (curve 2). In both cases, the positions of the bands practically coincide, indicating the formation of propylene as a product of cyclopropane conversion.

The frequencies of vibrations of gaseous propylene [17] with the vibrational frequencies of the product of cyclopropane conversion formed in our experiments are compared in Table 2, which shows that, according to published data, propylene is a single product of

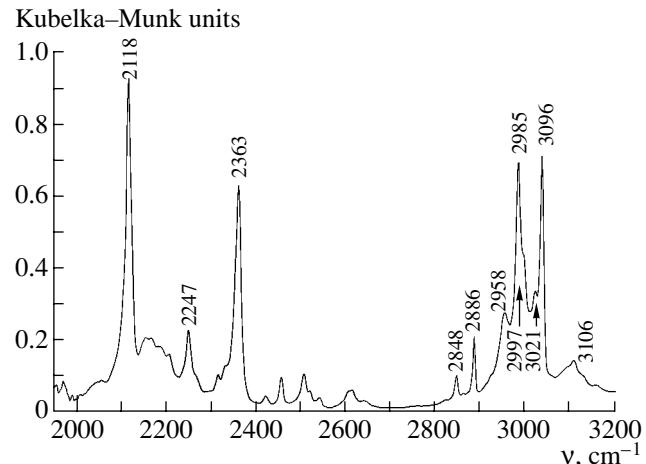


Fig. 5. IR spectrum of CaY after cyclopropane adsorption at room temperature at a pressure of 0.1 Torr in the region of stretching C-H and composite vibrations.

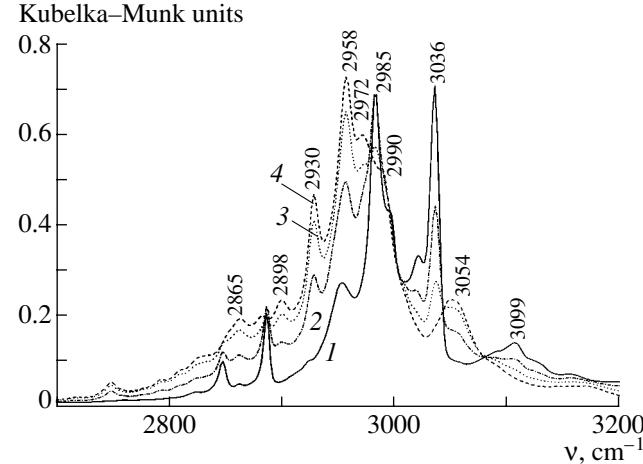


Fig. 6. IR spectrum of CaY after cyclopropane adsorption at a pressure of 0.1 Torr (1) at room temperature and after heating for 10 min at (2) 200, (3) 250, and (4) 300°C.

cyclopropane conversion on the cation-exchanged zeolite Y.

DISCUSSION

Our experimental results show that the adsorption of cyclopropane on CaY is stronger than on NaY. Cyclopropane can completely be removed from zeolite CaY only at temperatures higher than 100°C. This can be explained by a high effective charge of the Ca cation and, therefore, a stronger interaction of cyclopropane with the adsorption sites. The calcium-exchanged zeolite also manifests a higher reactivity of cyclopropane, which is converted to propylene at temperatures as low as 200°C, whereas on NaY this reaction only occurs at 400°C. The IR spectra of cyclopropane adsorbed on NaY and CaY also differ in the positions of absorption bands and the ratio of their intensities.

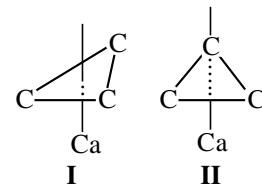
As mentioned above, the weaker form of cyclopropane adsorption, which decomposed after evacuation at room temperature, is related to the Na cations that were not completely removed by ion exchange. This form predominates at high cyclopropane pressures, which is indicated by the coincidence of the positions of band maxima for cyclopropane adsorbed at a high pressure on the sodium and calcium forms.

The stronger form, which is only decomposed after heating at 100°C, is related to cyclopropane adsorption on the calcium cations. In this case, two factors should be considered: the number of cations is halved upon the replacement of sodium by calcium and, according to the X-ray diffraction data, a considerable portion of calcium is localized inside the hexagonal prisms and inaccessible to adsorbed cyclopropane molecules. Therefore, the intensity of the spectrum of cyclopropane adsorbed at a high pressure on the calcium form is almost twofold lower than that for the sodium form. In this connection, measurements at different pressures are very important. For example, Forester and Seebode [5] studied the IR spectra of cyclopropane adsorbed on different cation-exchanged zeolites A and found that the positions of maxima of the absorption bands were almost identical for all cations. This result is probably due to the fact that adsorption was carried out only at high pressures.

Based on the IR spectra of cyclopropane adsorbed on CaY, we considered possible structures of adsorbed cyclopropane complexes. Two adsorbed cyclopropane structures can probably exist: one is formed via the interaction with a calcium ion through three equivalent σ bonds of the carbon ring (structure I) and the other is formed when only one of three C–C bonds interacts with the calcium cation (structure II). The first of these structures is characterized by C_{3v} symmetry, and the second structure has C_{2v} symmetry.

Forester and Seebode [5] attempted to determine the symmetry of the cyclopropane molecule adsorbed on

the cation-exchanged (Ca, Mg, Zn, and Co) zeolites A using the IR spectra. It was concluded that complex I



was formed in the course of adsorption. However, as noted above, in this work the IR spectra were only measured at a high cyclopropane pressure (~10 Torr), ignoring absorption bands from the weak and strong forms of adsorbed cyclopropane. Thus, this conclusion may be incorrect. Indeed, according to data in the more recent work [10] of the same authors using quantum chemical calculations, structure II is formed in the cyclopropane complex with the Ca cation localized in the six-membered ring. We also believe that complex II is formed by the adsorption of cyclopropane on CaY. This is confirmed by the appearance of a new band at 2958 cm⁻¹, which is absent from the spectrum of gaseous and liquefied cyclopropane, most likely because one of the methylene groups of the cyclopropane ring in structure II is not equivalent to the other two (elimination of degeneracy for the doubly degenerate v_8 vibration of the cyclopropane ring is due to symmetry lowering from C_{3v} to C_{2v} for the cyclopropane molecule).

Two different opinions concerning the mechanism and the nature of active sites in cyclopropane isomerization on the cationic forms of zeolites were expressed in the literature. In the first opinion this reaction is assumed to occur via the carbenium ion mechanism involving Brønsted acid sites formed in the alkaline-earth forms of zeolites by the hydrolysis of bivalent cations [19, 20, 22]. The isomerization of cyclopropane according to this mechanism, which indeed occurs on the hydrogen form of zeolite Y, has been studied in our

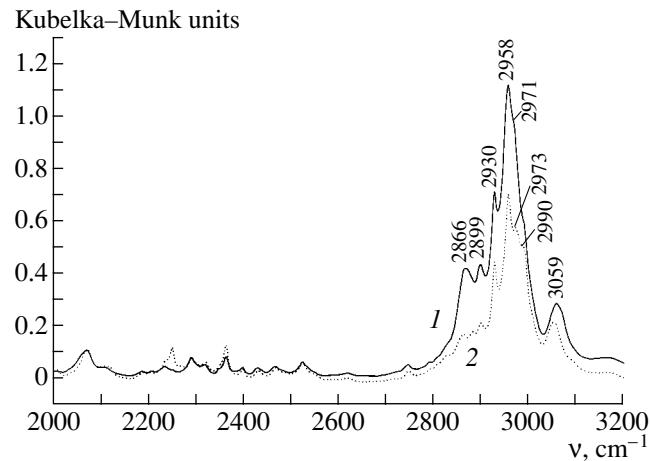


Fig. 7. IR spectra of (1) propylene adsorbed at room temperature on CaY and (2) the product of cyclopropane conversion at 300°C on CaY in the region of stretching C–H vibrations and in the composite 3800–4500 cm⁻¹ region.

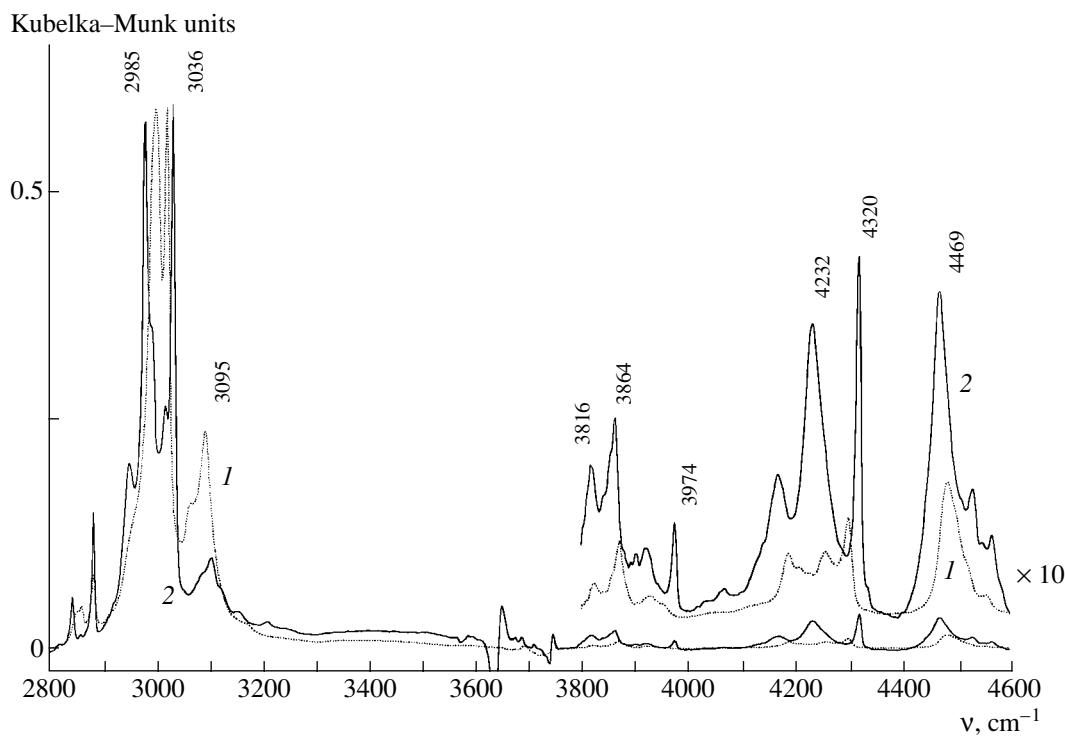
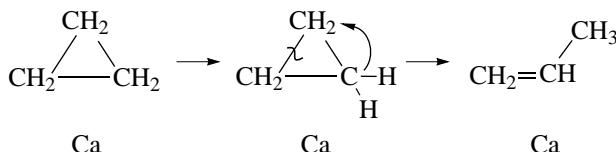


Fig. 8. IR spectra of cyclopropane adsorbed at room temperature on (1) CaY and (2) NaY in the region of stretching C–H vibrations and in the composite 3800–4500 cm^{−1} region.

previous work [1]. However, the bridging acidic hydroxy groups formed by hydrolysis were absent from the calcium-exchanged zeolite, and the IR spectrum of cyclopropane in the region of the composite vibrations of the C–C bond of the cyclopropane ring and fan bending vibrations of the methylene groups differed from the spectrum of cyclopropane adsorbed on the hydrogen-exchanged zeolite. We did not observe the formation of alkyl fragments grafted to the zeolite surface, which are formed as intermediate products in the reaction occurring via the carbenium-ion mechanism. Therefore, as in [5], we believe that the Ca²⁺ cations are themselves the active sites of isomerization on the calcium form.

In this case, the reaction mechanism can be presented as follows. The adsorption of cyclopropane on the calcium ions in form **II** results in the polarization of the adsorbed molecule. The hydride ion transfer from one of the methylene groups bound to the calcium ion to the positively charged methylene fragment that is not bound to the surface combined with the cleavage of one of the C–C bonds of the cyclopropane ring results in isomerization.



This mechanism does not involve the intermediate formation of the propyl fragment grafted to the zeolite surface, which is characteristic of the carbenium ion mechanism. Cyclopropane isomerization via this mechanism is characterized by the complicated composite vibration, which is a combination of stretching vibrations of the cleaved C–C and C–H bonds with bending vibrations of the methylene groups. By analogy to the results of our previous works [1, 2], these composite vibrations of the strongly polarized activated chemical bonds should exhibit anomalously high molar absorption coefficients. Therefore, let us compare in more detail the intensities of bands in the IR spectra of cyclopropane adsorbed on CaY, where the activation of the chemical bonds involved in the isomerization of adsorbed cyclopropane should manifest itself much more strongly than for NaY.

In fact, as can be seen from Fig. 5, the composite vibrations of the C–C bond of the cyclopropane ring (v_{10}) with the bending vibration of the C–H bonds (v_5) are the most intense bands in the spectrum of cyclopropane adsorbed on CaY. Such a high intensity of this line is unusual because lines of composite vibrations are usually at least an order of magnitude weaker than those for fundamental vibrations. For cyclopropane adsorption on zeolite CaY, the ratio of intensities of the composite and stretching C–H vibrations v_8 is equal to 1.35. It is also informative that for CaY the ratio of the intensity of the composite vibration to the intensity of the stretching C–H vibration is ~5 times higher than for

cyclopropane adsorbed on NaY: $I(v_5 + v_{10})/I(v_8) = 0.27$. Thus, a certain relationship exists between the intensity of composite vibrations and the catalytic activity of these zeolites. The results of this further confirm and develop our previous concept on the maximum contribution of the complex composite vibrations with anomalously high molar absorption coefficients of the polarized chemical bonds to the coordination of acid-catalyzed reactions.

Based on this concept, let us compare the IR spectra of cyclopropane adsorbed on the Na- and Ca-exchanged zeolite Y in the 3800–4500 cm^{-1} region corresponding to the composite vibrations of the C–H bond with the vibration of the C–C bond or with the bending vibrations of the CH_2 groups. The corresponding spectra normalized to the same intensity of the bands in the region of the stretching C–H vibrations are presented in Fig. 8. As can be seen, for almost the same intensity of the bands in the main region of C–H vibrations, the intensities of the absorption bands for cyclopropane adsorbed on the Ca ions in the 3800–4500 cm^{-1} region are much higher than for Na. Thus, the qualitative comparison of the intensities of the absorption bands of the composite stretching vibrations of the C–H bond with the bending vibrations of the CH_2 group of adsorbed cyclopropane reflects the chemical transformation, which is also associated with the proton transfer.

To summarize the results comparing the IR spectra of cyclopropane adsorbed on the hydrogen and cationic forms of zeolite Y, we would like to note that the composite vibrations corresponding to transformations of the strongly polarized chemical bonds are the most intense in both cases. For the previously studied isomerization of cyclopropane on zeolite HY, these vibrations correspond to the reaction coordinate of the formation of the propyl group grafted onto the zeolite surface (composite vibration of the C–C bond with the bending scissoring vibrations, which change the HCH angle in the CH_2 group when a proton is added to this group and the latter is transformed into a methyl group). Similarly, for cyclopropane adsorbed on CaY, these are the composite vibrations of the C–C bond in the cyclopropane ring with the fan bending C–H vibrations, which take into account C–C bond cleavage and the hydrogen-atom transfer (related to the rearrangement of the cyclopropane ring) from one methylene group to another. It was also shown for this zeolite that the composite stretching vibrations of the C–H bond with the bending vibrations of the CH_2 group had the highest intensity. Thus, regarding the study of cyclopropane isomerization on the cationic forms of zeolite Y, we confirmed our previous conclusion [2] that the complex vibrations of the polarized chemical bonds

with the highest molar absorption coefficients in the IR spectra of adsorbed molecules correspond to the coordinate of heterogeneous acid-catalyzed reactions.

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