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IR Spectroscopic Study of Cyclopropane Adsorption on Zeolite Y: I. Cyclopropane Adsorption and Transformation on Sodium- and Hydrogen-Exchanged Zeolite Y

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Abstract—IR spectroscopy is used to study the adsorption of cyclopropane on hydrogen- and sodium-exchanged zeolite Y. It is shown that cyclohexane weakly adsorbs on the sodium-exchanged zeolite, whereas it is grafted on the surface of the hydrogen-exchanged zeolite in the form of propyl groups. A possible scheme of cyclopropane transformation into propyl groups and the configuration of the corresponding transition state are considered. It is shown that the coordinate of this reaction corresponds to the complex composite vibrations of the C–C bond with the deformational vibrations of the CH_2 groups, which have the highest extinction coefficients in the IR spectrum of the adsorbed molecule.

INTRODUCTION

IR spectroscopy is one of the most frequently used methods for mechanistic studies in heterogeneous catalysis [1]. It makes it possible to observe the protonation of intermediate species and judge the activation of adsorbed molecules. Low-frequency shifts of absorption bands in the vibrational IR spectra are usually used as reactivity indices. The value of this shift is usually smaller than 10–20 cm^{-1} compared to the frequencies of the corresponding vibrations in free molecules.

In contrast, we recently published a paper [2] devoted to the IR spectroscopic study of ethylene adsorption on H-mordenite. It was shown that the higher intensities of absorption bands in the vibrational IR spectra are more sensitive parameters making it possible to judge the activation of chemical bonds in acid catalysis. It was found that this effect reveals itself most strongly in complex composite vibrations, in which several chemical bonds that contribute to the reaction coordinate of the corresponding elementary step participate.

In this work, we checked this conclusion using cyclopropane for the adsorption and transformations. The method of IR spectroscopy was used to study cyclopropane adsorption on hydrogen- and sodium-exchanged zeolites Y and the effect of chemical activation of propane on the intensity of vibrational absorption bands.

Many papers have been devoted to cyclopropane adsorption on zeolites [3–13]. They largely concern the structural study of adsorbed cyclopropane complex with ion-exchange cations of zeolites by X-ray structure analysis [11–13] or quantum chemical calculations [9–10]. IR spectroscopy was used to study cyclopropane adsorption on zeolites Y in few papers. Thus, Tam *et al.* [4] showed that cyclopropane isomerization to propylene with the participation of zeolite OH groups occurs on HY at 200°C. Cyclopropane adsorption on sodium-exchanged zeolite Y was also studied by Zakharieva-Pencheva *et al.* [10]. The main goal of that work was quantum-chemical calculations of vibration frequencies of adsorbed cyclopropane molecules, whereas the experimental values of observed frequencies was only used for comparison with calculations without considering intensities of the corresponding absorption bands.

A cyclopropane molecule, as well as an ethylene molecule, has rather simple vibrational IR spectrum, which is easy to interpret [14–16]. The assignment of observed bands in the IR spectra and Raman spectra for gaseous, liquid, and solid cyclopropane over wide ranges was reported in [15]. In this work, we used diffuse-reflectance IR spectroscopy to study the region of main stretching vibrations of C–H bonds of adsorbed cyclopropane and the composite frequencies of various deformational vibrations of C–H bonds and C–C bond vibrations.

EXPERIMENTAL

The hydrogen-exchanged zeolite Y with Si/Al = 2.5 was prepared from the sodium-exchanged zeolite Y using a standard ion-exchange procedure to substitute NH_4^+ for Na^+ using an aqueous solution of ammonium chloride as a source of ammonium ions. The extent of ion exchange was ~95% according to the data of emission spectral analysis. Before spectral measurements, the zeolite samples were put in a quartz ampule with a CaF_2 window and treated in a vacuum in the following

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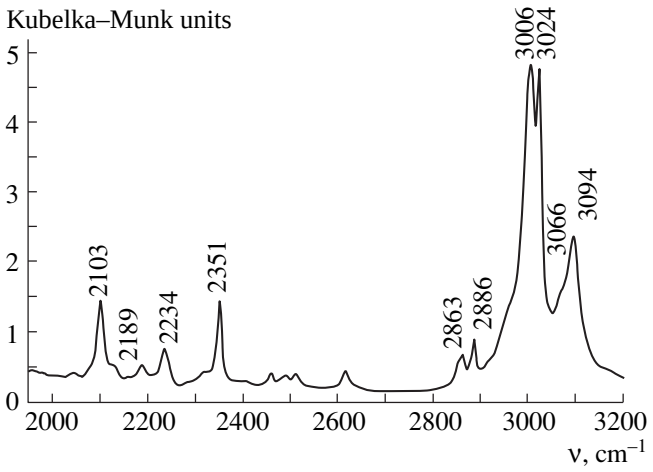


Fig. 1. IR spectrum of NaY after cyclopropane at 6 torr in the region of stretching and composite vibrations.

regime. First, the zeolite was evacuated at 100°C for 2 h. Second, the temperature was increased from 100 to 450°C for 3 h. Then, the zeolite was kept at this temperature 3 h with continuous evacuation. The samples were regenerated after catalytic runs in the circulation setup at 500°C in an oxygen atmosphere at a pressure of 200 torr.

The diffuse-reflectance IR spectra at 2000–6500 cm^{-1} were recorded at room temperature using an Impact 410 Nikolet spectrometer equipped with an attachment for measuring the diffuse reflectance spectra. The obtained spectra were transformed into the Kubelka–Munk units assuming that the reflecting ability of the zeolite at 5000 cm^{-1} is 0.9. Unless otherwise stated in the text, zeolite background was subtracted from the overall spectrum.

Cyclopropane was purified by multiple freezing into a trap cooled with liquid nitrogen and withdrawing the medium fraction. Cyclopropane adsorption on the sodium-exchanged zeolite NaY and hydrogen-exchanged zeolite HY was carried out at room temperature until the equilibrium pressure of cyclopropane (3–6 torr) was reached.

RESULTS

Cyclopropane Adsorption on NaY

Cyclopropane adsorption on NaY at room temperature is reversible and is not accompanied by any chemical transformations. Cyclopropane can completely be removed from NaY by evacuation even at room temperature. Figure 1 shows the IR spectrum of adsorbed cyclopropane. The table compares the positions of bands in the IR spectra of gaseous, liquefied, frozen, and adsorbed cyclopropane.

As can be seen from the table and Fig. 1, the IR spectra of adsorbed cyclopropane contain all the four bands of C–H stretching vibrations, including symmetric ν_8 and ν_{12} vibrations, which were observed for gaseous and liquefied cyclopropane only in Raman spectra. This fact is explained well by lowering the symmetry of molecules upon their adsorption [17]. As follows from the table, the positions of bands in the region of C–H vibrations of adsorbed, liquefied, or frozen cyclopropane differ insignificantly from the positions of the respective bands in the gas phase.

In the region 2000–2500 cm^{-1}, which is characteristic of the combinations of various deformational vibrations of CH_2 groups as well as the combinations of the deformational vibrations of CH_2 groups and C–C bond vibrations, two medium-intensity bands are observed at 2103 and 2351 cm^{-1} and the bands with a lower intensity at 2189 and 2234 cm^{-1}. All absorption bands shown in Fig. 1 decrease in a cymbate manner with a decrease in the equilibrium pressure of cyclopropane and disappear when the sample is evacuated at room temperature together with the bands in the region of C–H vibrations. This fact is evidence for the reversibility of adsorption. Note that, in the spectra of gaseous, liquefied, or frozen cyclopropane, the intensity of bands in the cited region of composite frequencies is much lower than in the region of CH vibrations [15].

Cyclopropane Adsorption and Transformations on HY

Cyclopropane adsorption on HY at room temperature leads to a low-frequency shift and substantial broadening of the band of OH stretching vibrations of bridging hydroxy groups. The maximum of this band shifts from 3641 to 3280 cm^{-1} (Figs. 2 and 3). Moreover, adsorption leads to the appearance of three bands with maxima at 3095, 3023, and 3010 cm^{-1} against the background of the low-frequency part of the spectrum. These bands belong to the stretching C–H vibrations in cyclopropane (Fig. 3). As can be seen from the comparison of Fig. 3 and the table, the positions of these bands differ only slightly from the positions of the corresponding bands in the spectra of liquefied cyclopropane and cyclopropane adsorbed on NaY. Thus, cyclopropane adsorption on HY only results in very short low-frequency shifts of the frequencies of C–H stretching vibrations.

In the region of combinations of deformational vibrations of CH groups and C–C bond vibrations (2000–2500 cm^{-1}, Fig. 3), the difference between the spectrum of cyclopropane adsorbed on NaY and HY is the most pronounced. In the case of NaY, only well-resolved narrow bands are observed, whereas after cyclopropane adsorption on HY, a very broad unresolved band with a maximum at 2265 cm^{-1} is observed in addition to the bands at 2103 and 2352 cm^{-1}. The integral intensity of this broad band increases compared to cyclopropane adsorption on NaY by approximately 1.5–2 orders of magnitude.

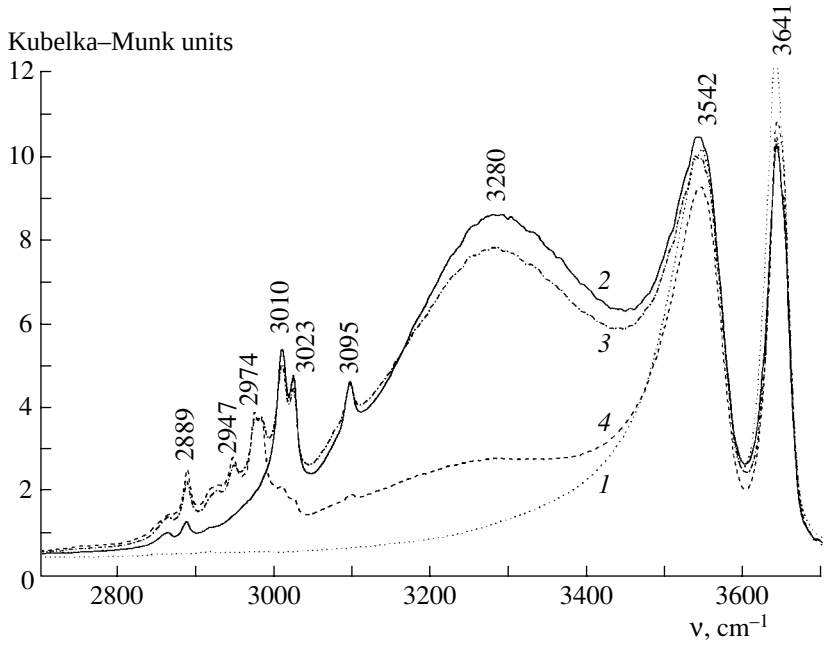


Fig. 2. IR spectrum of HY (*1*) before cyclopropane adsorption at 5 torr at room temperature after (*2*) 0.25, (*3*) 18, and (*4*) 48 h. Spectrum subtraction procedure was not carried out.

Indeed, in cyclopropane adsorption in NaY, the amplitude of the only band available in this region with a maximum at 2235 cm^{-1} is at least ten times lower than the amplitude of the adsorption band corresponding to C–H bond stretching. In cyclopropane adsorption on HY, the intensities of absorption bands at 2235 and 2265 cm^{-1} increase but remain ~2 times lower than for the C–H vibrations. The width of the band at 2265 cm^{-1} increases to 200 cm^{-1} compared to 30 cm^{-1} for the band of stretching C–H vibrations. This fact suggests that the intensity of this band drastically increases.

This effect is undoubtedly associated with the chemical activation of adsorbed molecules, because the intensities of absorption bands of adsorbed cyclopropane in the region 2000–2500 cm^{-1} decrease when the sample is allowed to stay with adsorbed cyclopropane at room temperature for 18 h. As this takes place, a number of new bands appear in the region 2970–2850 cm^{-1}. We did

Positions of adsorption bands (ν, cm^{-1}) in the IR spectra of gaseous, liquid, and frozen cyclopropane and cyclopropane adsorbed on NaY and HY

Band assignment*	Gas*	Liquid at –125°C*	Solid at –190°C*	Adsorbed cyclopropane	
				NaY	HY
ν_6	3101	3081	3073	3094	3095
ν_{12}	3082(R)**	3075(R)	3073	3066	–
ν_1	3038(R)	3027(R)	–	3024	3023
ν_8	3025	3013	3004	3006	3009
$2\nu_{13}$	–	2372	2370	2351	2350
$\nu_9 + \nu_{11}$	2314	2304	2294	–	2265
$\nu_{10} + \nu_{13}$	–	–	2217	2234	2235
$\nu_3 + \nu_{10}$	–	2209	2196	2189	2190
$\nu_9 + \nu_{14}$	2183	2169	2172	″	″
$\nu_5 + \nu_{10}$	2083	2082	2083	2103	2100

* According to [15].

** R means that the band was detected only in Raman spectra.

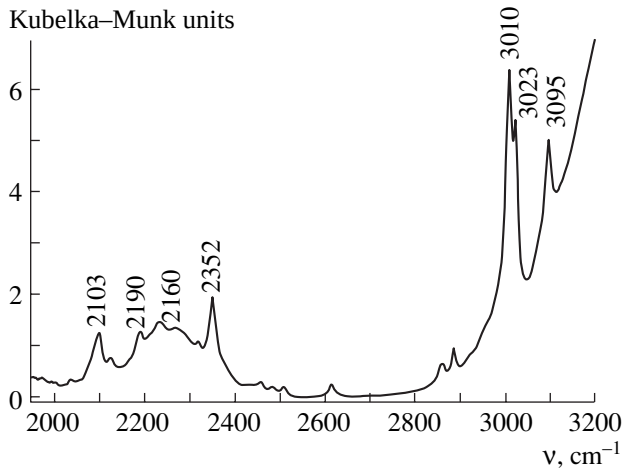


Fig. 3. IR spectrum of HY after cyclopropane adsorption at 5 torr at room temperature in the region of stretching and composite vibrations.

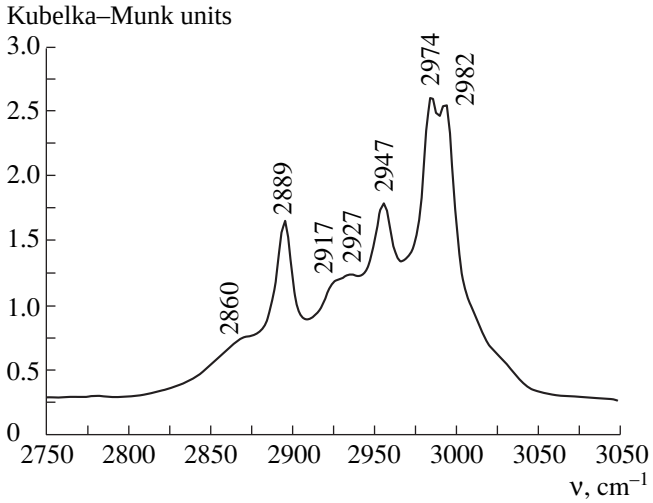


Fig. 4. IR spectrum of HY in the region of CH vibrations after the contact with cyclopropane (5 torr) at room temperature for 48 h and further evacuation at this temperature.

not find any new absorption bands above 3000 cm^{-1} belonging to the C–H stretching vibrations at a double bond. Thus, at room temperature, propylene is not formed when cyclopropane contacts with HY. With an increase in the time of cyclopropane contact with the zeolite to 48 h, further changes occur in the spectrum: virtually all bands from perturbed OH groups and adsorbed cyclopropane disappear, while the intensities of the bands from C–H stretching vibrations in the region 2950–2850 cm^{-1} further increase (Fig. 2).

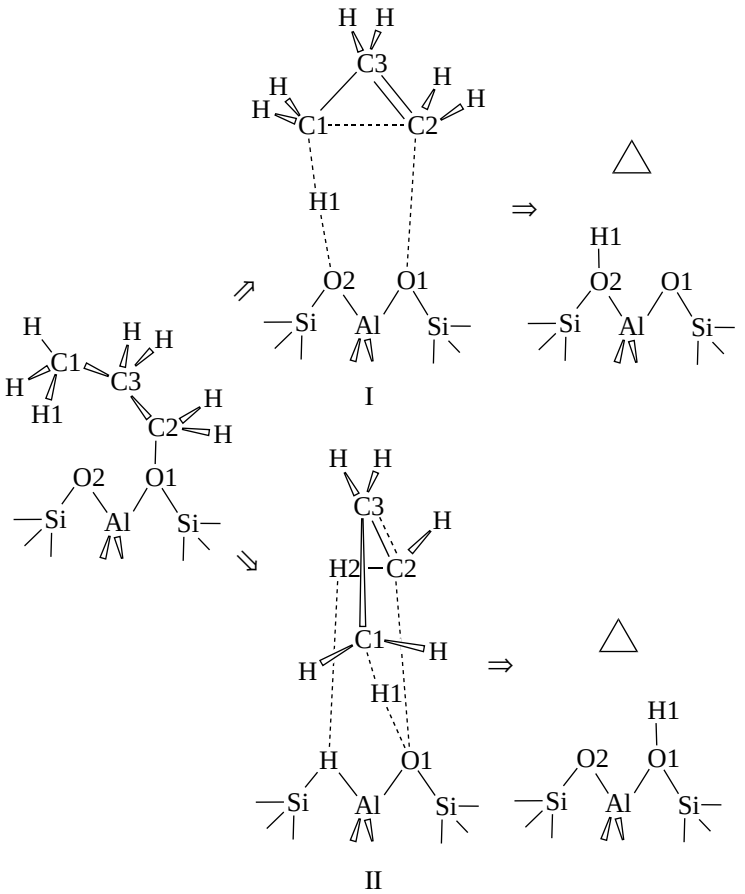
HY evacuation at room temperature after prolonged contact with cyclopropane leads to the disappearance of the bands from cyclopropane C–H stretching vibrations and the bands in the region 2000–2500 cm^{-1}. At the same time, the bands belonging to the product of cyclopropane transformation remain in the spectrum: two unresolved absorption bands with close maxima at 2982 and 2974 cm^{-1}, the bands at 2946 and 2889 cm^{-1} and weak bands at 2926 and 2860 cm^{-1} (Fig. 4). The bands belonging to this region are characteristic of the C–H stretching vibrations in saturated hydrocarbons. With an increase in the cyclopropane–HY contact time, the overall intensity of all bands in the spectrum of the product increases, while the positions of maxima and the intensity ratios are preserved.

DISCUSSION

The results obtained in this work suggest that, in adsorption on HY at room temperature, cyclopropane transforms chemically, whereas it only weakly adsorbs on NaY. Let us consider the nature of products formed in the interaction of cyclopropane with HY based on IR data. The result of this transformation can be ring opening with further grafting of propyl on the zeolite surface and cyclopropane isomerization to propylene or its oligomerization. It is also known that, at room temperature, propylene easily polymerizes on HY [18]. However, we did not see any bands from the C–H bond vibrations at a double bond in the IR spectrum of adsorbed cyclopropane either at the beginning or after prolonged interaction (for several days). The formation of a polymer chain was not observed either. Indeed, the C–H vibrations in alkanes are characterized by the symmetric and asymmetric vibrations of CH_2- groups (2855 and 2930 cm^{-1}) and CH_3 groups (2870 and 2960 cm^{-1}). With an increase in the oligomer chain length, some changes are usually seen in the IR spectra. These are associated with an increase in the intensities of the bands of C–H vibrations in CH_2 groups. In our experiments, there were no qualitative changes in the spectra of the product with an increase in the cyclopropane–HY contact time. This points to the fact that cyclopropane does not polymerize, and the only result of its transformation is ring opening with grafting the alkyl fragment on the zeolite surface.

Indeed, according to [19], the presence of an oxygen atom near the CH_3 group increases the frequencies of CH-vibrations in this group. Therefore, the adsorption bands at 2982 and 2974 cm^{-1} (Fig. 4) can be assigned to asymmetric vibrations and the band at 2889 cm^{-1} to symmetric C–H vibrations in this group. The presence of symmetric and asymmetric CH stretching vibrations in the CH_2 group in the product spectra with maxima at 2860 and 2927 cm^{-1} led us to conclude that an *n*-propyl fragment is formed.

Let us consider a possible scheme for cyclopropane transformation to adsorbed *n*-propyl fragment. Earlier [20], quantum-chemical calculations have shown that the formation of cyclopropane from the surface alkoxy in the zeolite occurs via a transition state (TS) similar to the protonated cyclopropane ring. Such a transition state may exist in two configurations described below.



The second of these structures is energetically more favorable. Let us consider cyclopropane transformation into the grafted propyl group taking into account that the reverse reaction passes through the same transition state. Let us assume that the second of the above configurations corresponds to the transition state.

The reaction pathway associated with the formation of such a transition state implies the simultaneous formation of the O1–C2 bond, the O–H bond stretch in the acidic hydroxy group, and the stretch of the C1–C2 bond in the cyclopropane molecule. Simultaneously, the valence angles CCH and HCH also change as the CH_2 group transforms into the CH_3 group. In the cyclopropane molecule, a change in the C–C bond length corresponds to the vibrations ν_3, ν_{10}, and ν_{11} [15–17]. The ν_3 vibration is a fully symmetric vibration of a cyclopropane ring, whereas vibrations ν_{10} and ν_{11} also include a simultaneous change in the valence angle CCH [10, 17]. A change in the HCH angle corresponds to cutter vibrations ν_9 and ν_2. Our experimental data support the discussed requirements to the formation of a transition state. It follows from the table and Fig. 3 that the most pronounced anharmonism and the highest intensity are observed for the composite $\nu_9 + \nu_{11}$ vibration. Elongation of the O–C bond in the cyclopropane ring (ν_{11}) together with the deformational cutter vibration ν_9, which decreases the HCH angle in the CH_2 group, enable the addition of proton from the acidic hydroxy group to the CH_2 group resulting in the formation of the CH_3 group.

Thus, the results of this work show that the first act of cyclopropane interaction with zeolite protons is the formation of surface-grafted propyl group, which can further isomerize to form propylene.

The reaction coordinate in cyclopropane transformation into the propyl group corresponds to complex composite vibrations of the adsorbed molecule, which have the highest extinction coefficient. The same behavior was observed earlier [2] in the transformation of ethylene to ethyl groups grafted to the mordenite surface. This effect is less pronounced in the case of cyclopropane than in the case of cyclopropane. This is reflected in the fact that the ratio of intensities of composite vibrations and C–H vibrations is higher for ethylene than for propane. This probably due to stronger polarization of the C–H bond in cyclopropane molecule and the stronger perturbance of the double bond in an ethylene molecule.

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