
MECHANISMS OF CATALYTIC REACTIONS

IR Absorption Intensities As a New Spectral Criterion for the Activation of Adsorbed Molecules in Heterogeneous Acid Catalysis

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Received December 21, 2006

Abstract—The criterion conventionally used to judge bond activation in molecules adsorbed on active sites of heterogeneous catalysts is the bathochromic shift of the corresponding IR absorption bands. The intensity of these bands, which characterizes bond polarizability, can be used as an additional bond activation criterion. This new spectral criterion is particularly promising for acid and acid–base catalysis, in which the activation of adsorbed molecules is due to their polarization by active sites. Examples are provided here to illustrate the fruitfulness of the new approach. These examples include judging the strength of Brønsted acid sites from the intensity of the OH stretching band and an analysis of the dissociative adsorption and dehydrogenation of light paraffins on metal cation forms of zeolites and of proton transfer from Brønsted acid sites to adsorbed paraffin molecules.

DOI: 10.1134/S0023158407040040

INTRODUCTION

The central problem of heterogeneous catalysis theory is to learn to check the chemical activation of reacting molecules on the atomic/molecular level by spectroscopic means. It is universally accepted that the interaction between adsorbed molecules and active sites weakens the bonds to be involved in the catalytic reaction. This effect may arise from the positive or negative charging of the reactants, the formation of donor–acceptor bonds upon adsorption, the coordination of adsorbed molecules to active sites, the polarization of adsorbed molecules by cations or acid–base pairs, or other processes. In all of these cases, the activation of the adsorbed molecules is judged from the adsorption-induced bathochromic shifts of the IR absorption bands due to stretching or bending vibrations. At the same time, although these bathochromic shifts correctly reflect bond weakening due to a decrease in force constants, they do not clarify the causes and mechanism of the activation of adsorbed molecules.

However, there is a wide class of catalytic reactions for which the chemical activation of the reactants and the adsorption-induced changes in their spectroscopic properties are directly correlated. This class is acid and acid–base catalysis, in which the reactant molecules are activated through polarization. In the interaction between a reactant and a Brønsted acid site, bond polarization is due to the addition of a proton to the reactant. Another possibility is the interaction between adsorbed molecules and Lewis acid sites (cations with a small coordination number). The polarization of adsorbed

molecules by acid–base pairs involves both positively charged ions and neighboring basic oxygen atoms. As compared to unpolarized molecules, polarized molecules are more reactive and, accordingly, are more readily convertible to intermediate or ultimate products of the catalytic reaction. For all of the above cases, IR absorption intensity was demonstrated to be a spectral criterion directly related to the polarizability and polarization of adsorbed molecules and bond activation [1–12].

Indeed, the IR extinction coefficient ϵ is proportional to the squared derivative of the normal vibration-induced changes in the dipole moment with respect to the normal coordinates [13]:

$$\epsilon \sim [d\mu/dq]^2. \quad (1)$$

In other words, the changes in bond lengths or bond angles induced by molecular vibrations cause changes in the dipole moment through charge separation or through electron density shifting to more electronegative atoms. As a result, stretching or bending vibrations generate oscillating dipole moments, whose interaction with electromagnetic radiation causes absorption of this radiation, giving rise to an IR spectrum. The intensities of the resulting absorption bands reflect the polarizability of the chemical bonds associated with their extension and contraction and with the bending-induced variations in bond angles. The same parameters appear as coordinates of catalytic reactions. Therefore, if the bathochromic shift of the IR absorption band

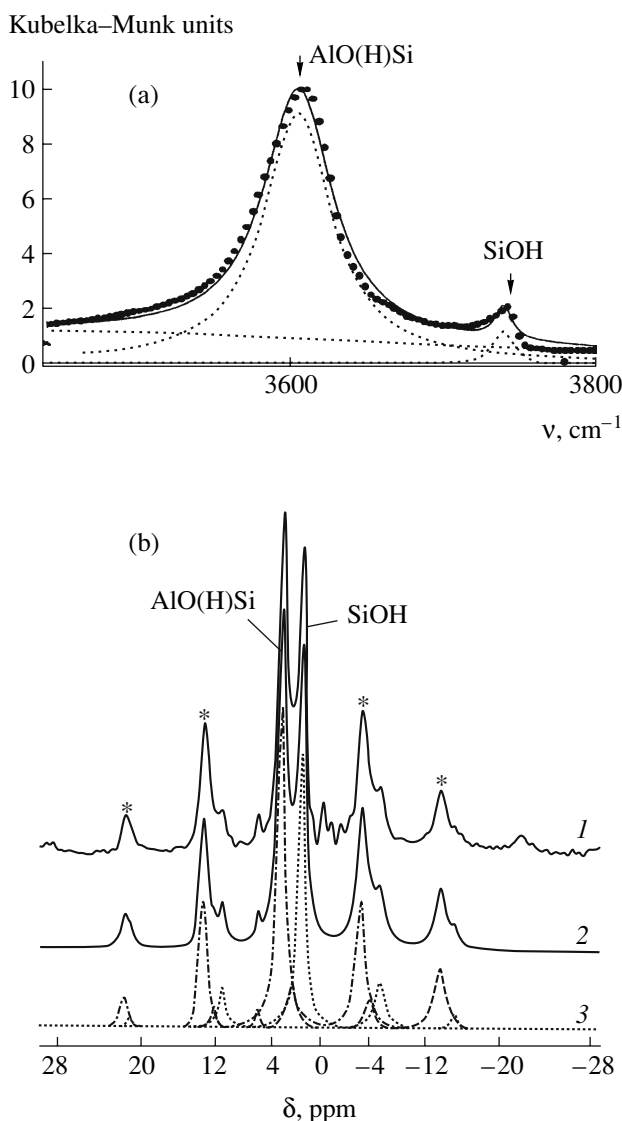


Fig. 1. (a) Diffuse reflectance IR and (b) ^1H NMR spectra of the same mordenite sample: (1) experimental data and (2, 3) simulated data.

of an adsorbed molecule is accompanied by a strengthening of this band, then the weakening of the corresponding bond is due to polarization.

Below, we will illustrate the fruitfulness of this new approach and its ability to provide unique information concerning both the acid strength of surface hydroxyl groups and the activation of light hydrocarbon molecules adsorbed on low-coordinated cations of zeolites. Note that, although IR absorption intensity were used as a criterion of bond polarizability in vibrationally excited free molecules before our works on this subject (see, e.g., a review by Gussoni and Castiglioni [14]), we were the first to employ this quantity as a measure of the chemical activation of adsorbed molecules.

INTENSITY OF THE STRETCHING IR ABSORPTION BANDS OF SURFACE HYDROXYL GROUPS AS A MEASURE OF THEIR ACID STRENGTH

The conventional method of measuring the strength of Brønsted acid sites on the surface of heterogeneous catalysts is based on bathochromic shifts of OH stretching bands caused by the formation of hydrogen bonds with adsorbed molecules of weak bases [15–17]. For example, the acid strength of surface hydroxyl groups was determined using low-temperature carbon monoxide adsorption [15] as a molecular test. We suggested employing paraffins for this purpose [18]. In those studies, a correlation was established between the strength of Brønsted acid sites and the bathochromic shift of the OH stretching band caused by the adsorption of a weak base.

As compared to the bathochromic shift of the OH stretching band, the intensity of this band seems to be much more intimately related to the acid strength of the surface hydroxyl groups in hydrogen-bonded complexes. Indeed, in view of the above, the intensity of this absorption band is a measure of the stretching polarizability of the O–H bond in acid hydroxyl groups. In other words, it is directly related to proton transfer to the adsorbed molecules hydrogen-bonded to hydroxyl groups.

A good linear correlation was observed between the bathochromic shift and the intensity of the OH stretching band [19]. Furthermore, the band intensity increased several times upon the formation of a hydrogen bond with the strongest bases. By contrast, the hydroxyl stretching frequency decreased only by a few percent. Therefore, the intensity of the OH absorption band is a more sensitive indicator of the strength of acid sites than the bathochromic shift of this band.

Our earlier results [3] suggest that the strength of Brønsted acid sites can also be judged from the intensities of the absorption bands of free hydroxyl groups. This follows from a comparison of the IR and NMR spectra from free silanol OH groups with the same spectra from acid OH groups for the same samples of the H-forms of mordenite and zeolites Y and ZSM-5. In these experiments, the number of hydroxyl groups was judged from the intensities of NMR signals. By way of example, we present the data obtained for H-mordenite (Fig. 1). According to NMR data, the numbers of acid and silanol OH groups in this zeolite are similar. However, the IR absorption bands from the acid hydroxyl groups are several times more intense than the bands from the silanol OH groups. This seems to be evidence that the acid hydroxyl groups have a larger relative extinction coefficient.

A similar conclusion that the acid OH groups are more polarizable because of their positive and negative charges being more readily separable as a result of stretching vibrations was made for other zeolites (Table 1). In other words, the fact that more acidic

hydroxyl groups give rise to stronger stretching bands in the IR absorption spectrum is evidence that the higher the acidity of an OH group the stronger its tendency to heterolytic dissociation.

RELATIONSHIP BETWEEN THE POLARIZABILITY ANISOTROPY OF C–H BONDS IN LIGHT PARAFFIN MOLECULES AND THE HETEROLYTIC DISSOCIATION AND DEHYDRATION BEHAVIORS OF THESE MOLECULES

Symmetric vibrations do not change the dipole moments of free molecules and are, therefore, IR-inactive. As a consequence, the stretching bands of the diatomic symmetric molecules, such as H₂, O₂, and N₂ in the gas phase, cannot be observed. This symmetry forbiddenness is lifted by the adsorption-induced polarization of these molecules. Stretching bands from adsorbed diatomic symmetric molecules have been observed for many oxides and zeolites. This circumstance allowed us to use low-temperature dihydrogen adsorption as a molecular test to locate various cations in zeolites [20–25].

A similar situation takes place for more complex molecules. Furthermore, anisotropic polarizability is observed in this case: some absorption bands strengthen and the others weaken upon adsorption. The bands that are symmetry-forbidden for free molecules strengthen upon adsorption and sometimes outgrow the bands due to asymmetric vibrations. In some cases, the polarization of adsorbed molecules causes the opposite effect, specifically, a dramatic weakening of IR absorption bands. For example, while the IR spectrum of gaseous methane shows a single absorption band, which is from the triply degenerate C–H stretching vibrations, the IR spectrum of adsorbed methane additionally exhibits an absorption band from adsorption-perturbed symmetric vibrations.

The above can be illustrated by methane adsorption on the hydrogen and metal cation forms of zeolite Y. The diffuse reflectance spectra of methane adsorbed at a high pressure on the hydrogen and sodium forms of zeolite Y are presented in Fig. 2a. The band due to the asymmetric vibrations of gaseous methane, peaking at 3016 cm^{−1}, is seen against the background of the high- and low-frequency branches of the vibrational–rotational structure. The band peaking at 3001 cm^{−1} is due to the asymmetric vibrations of adsorbed methane, and the lower frequency band is due to the adsorption-perturbed symmetric vibrations. The intensity of the latter is one order of magnitude higher for the sodium form than for the hydrogen form because the adsorbed methane molecules are more strongly perturbed by sodium ions than by protons.

This effect is still more evident for methane adsorbed on the barium form of zeolite Y at a low pressure: the corresponding spectrum shows no bands from

Table 1. Comparison between the relative IR extinction coefficients of the acid and silanol OH groups of H-zeolites

Zeolite	Si/Al	$I_{\text{acid}}/I_{\text{SiOH}}$		Ratio of relative extinction coefficients
		NMR	diffuse reflectance spectroscopy	
HZSM-5	45	0.73	5.7	7.8
HY	11.5	1.05	8.5	16.3
H-mordenite	9.4	2.1	20.9	14.8

gaseous methane (Fig. 2b). In this case, the relative intensity of the low-frequency absorption band due to the adsorption-perturbed fully symmetric C–H vibrations is higher than the intensity of the same band for the sodium form of the zeolite. By contrast, the relative contribution from the asymmetric C–H vibrations to the observed spectrum decreases on passing from sodium to barium. Therefore, methane is more polarizable in its interaction with barium ions than in its interaction with sodium ions.

Polarizability anisotropy is still more pronounced in methane adsorbed on the modifying zinc cations of the

Kubelka–Munk units

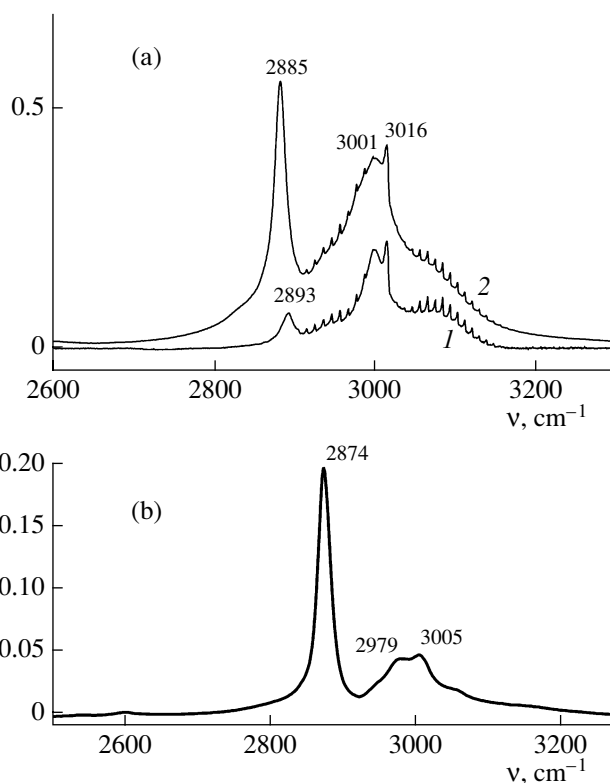


Fig. 2. Diffuse reflectance IR spectra of methane adsorbed on (a) zeolites NaY and HY at a high pressure and (b) zeolite BaY at a low pressure.

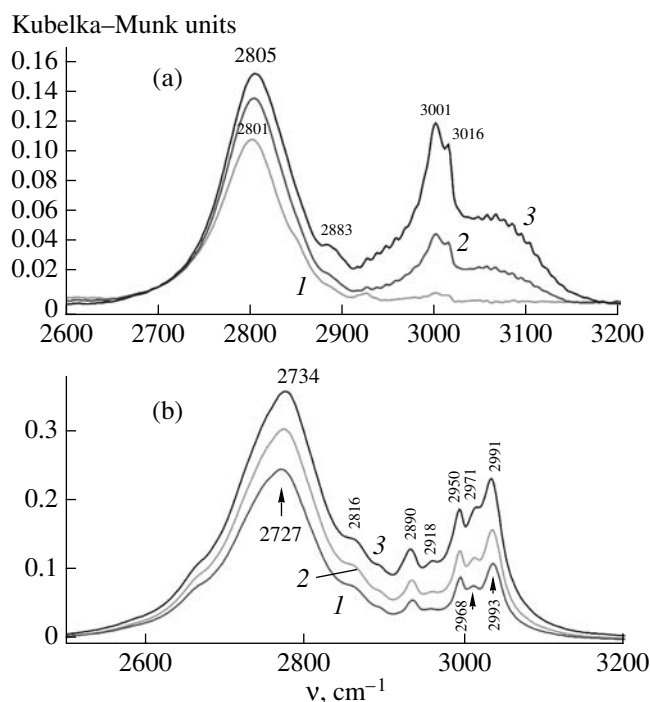


Fig. 3. Diffuse reflectance IR spectra of (a) methane and (b) ethane adsorbed on zeolite ZnZSM-5 at room temperature and various pressures (Torr): (a) (1) 1, (2) 5, (3) 15; (b) (1) 0.02, (2) 0.18, (3) 0.30.

zinc form of the high-silica zeolite ZSM-5 [5]. In this case, polarizability anisotropy is so high that, at low pressures, when the overall spectrum contains no contribution from weakly adsorbed methane, the bands due to the asymmetric C–H vibrations can hardly be seen. Instead, the diffuse reflectance IR spectrum shows a single broad adsorption band from very strongly polarized, totally symmetric C–H vibrations (Fig. 3a). A similar situation is observed for ethane adsorbed on the same zeolite [7] (Fig. 3b). In this case, the identity of the IR spectra at different low pressures is evidence that all adsorption bands are due to one strongly adsorbed molecular species. For both methane and ethane, the bands due to the highly perturbed C–H vibrations are many times stronger than the bands arising from the other stretching vibrations. This obviously indicates that the C–H bonds responsible for these broad and strong IR absorption bands are highly polarizable.

Furthermore, we established that the vibrational excitation of the adsorbed molecules of the light paraffins at elevated temperatures causes these molecules to dissociate heterolytically to release protons and to yield methyl or ethyl groups bound to zinc ions. As a consequence, high-temperature treatment of the sample in a hydrocarbon atmosphere weakens the absorption bands due to the low-frequency vibrations (2800–2900 cm^{-1}), which are most highly perturbed by zinc ions. At the same time, new absorption bands appear in the IR spectrum, namely, a band due to the hydroxyl groups

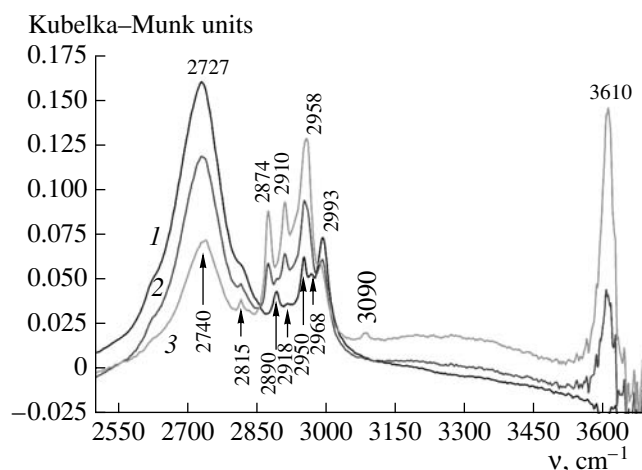
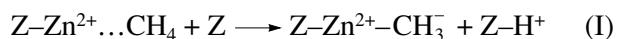
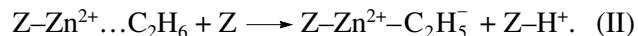


Fig. 4. Manifestation of the heterolytic dissociative adsorption of ethane on zeolite ZnZSM-5 in the diffuse reflectance IR spectrum. The spectra were recorded at room temperature (1) before and (2, 3) after heat-treatment of the sample at (2) 423 and (3) 463 K.

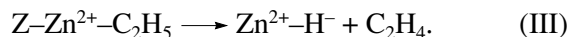
(3610 cm^{-1}) and C–H stretching bands from the alkyl groups bound to zinc ions (2900–3000 cm^{-1}) (Fig. 4). This is evidence of the heterolytic dissociative adsorption of the light paraffins:



or



Subsequent high-temperature treatment of the sample causes the decomposition of the ethyl fragments, yielding ethylene and zinc hydrides (which give rise to a band peaking at 1934 cm^{-1}):



Thus, the high intensity of the low-frequency IR absorption bands is another index of the reactivity of light paraffins. This index is more intimately related to the heterolytic dissociation reaction coordinate than the bathochromic shift of the corresponding C–H vibrations.

Indeed, the above data indicate that the activation of adsorbed light paraffins upon their interaction with acid–base pairs is a complicated, concerted process. Heterolytic dissociative adsorption begins with comparatively weak interaction between the reacting molecules and the zinc cations. The dissociative adsorption coordinate in this case is the vibrational excitation of the adsorbed molecules at an elevated temperature. The polarizability and polarization of the most strongly cation-perturbed C–H vibrations increase, resulting in stronger adsorption and stronger perturbation of the reacting molecules. In turn, this increases the polarizability and polarization of the most strongly perturbed C–H bonds. Further progress of this concerted process causes C–H bond breaking and, after a comparatively

low activation barrier is surmounted, results in the heterolytic dissociative adsorption of the light paraffin. Therefore, the polarizability and polarization of adsorbed molecules play the key role in acid-base catalysis and the abnormally high intensities of the IR absorption bands due to the C–H stretching vibrations are the best indicator of the polarization-induced chemical activation of the adsorbed molecules.

QUANTUM CHEMICAL ANALYSIS OF THE ANOMALOUS IR SPECTRA OF LIGHT PARAFFINS ADSORBED ON LOW-COORDINATED CATIONS

For a more detailed analysis of the observed anomalous IR spectra of adsorbed paraffins, we performed quantum chemical calculations of the structure of the adsorption complexes and of the positions and intensities of the corresponding IR absorption bands [6, 9, 11]. The calculations were carried out by DFT methods with full optimization of the geometry of the surface structures.

For ethane adsorption on the zinc-modified zeolite ZSM-5, an adsorption site was modeled as a cluster consisting of two condensed five-membered rings each containing one aluminum atom (Fig. 5a) [9]. The results of these calculations are displayed in Fig. 5b as a comparison between the calculated IR spectrum of the free ethane molecule and that of the ethane molecule adsorbed on a zinc ion. Applying the correction factor 0.964 to take into account the anharmonicity effect brings the band positions in the calculated spectra into good agreement with the corresponding experimental data. Furthermore, the results of these calculations reflect the fact that the low-frequency absorption band due to ethane adsorbed on zinc ions is many times stronger than the other absorption bands present in the spectrum. These calculations also suggest that this band should be assigned to the totally symmetric mode ν_1 perturbed by adsorption.

A similar cluster was used as the adsorption site model in the simulation of the IR spectrum of methane adsorbed on zinc ions [6]. It was proved that the strong and broad low-frequency absorption band is due to the totally symmetric C–H stretching vibrations perturbed by the interaction between the adsorbed molecules and the zinc ions.

The unusual spectrum of adsorbed ethane was also successfully simulated for gallium oxide as the adsorbent [11]. The spectrum observed in this case (Fig. 6a) is very similar to the spectrum of ethane adsorbed on zinc ions in zeolite ZSM-5. It was simulated using the simplest cluster, Ga_2O_3 , as the adsorption site model. Clearly, the calculated positions and intensities of the C–H bands in the IR absorption spectrum of adsorbed ethane are in satisfactory agreement with the observed spectrum.

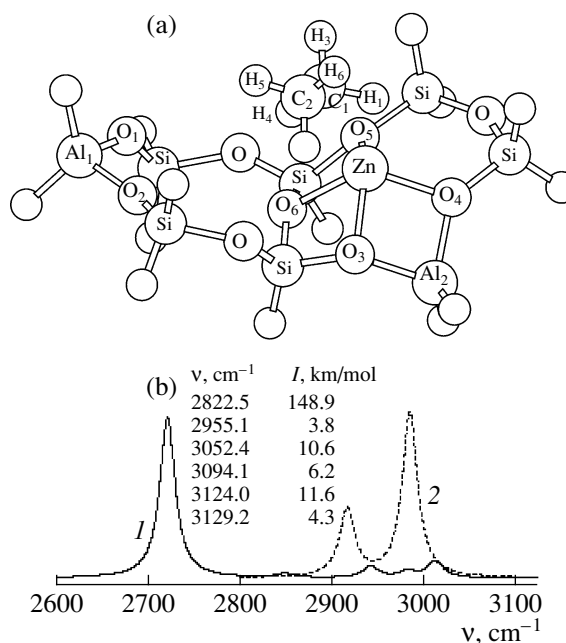


Fig. 5. Quantum chemical simulation of ethane adsorption on zeolite ZnZSM-5: (a) calculated structure of the adsorption complex and (b) calculated IR spectrum of (1) adsorbed and (2) gaseous ethane.

MECHANISM OF PROTON TRANSFER FROM ACID HYDROXYL GROUPS TO HYDROGEN-BONDED ETHYLENE MOLECULES

Ethylene adsorption on zeolite NaY is reversible, does not lead to the chemical activation of ethylene, and is not accompanied by any chemical reactions. By contrast, the hydrogen forms of mordenite and zeolite Y are olefin oligomerization catalysts. In view of this, it was expected that the acid OH groups of this zeolite would perturb the adsorbed ethylene molecules to a greater extent than the sodium ions and this difference would be manifested in the IR spectrum of adsorbed ethylene. However, no relevant data have been found in the literature. At the same time, it was reliably demonstrated by numerous earlier studies that olefins form stable π -complexes with acid hydroxyl groups. This causes a bathochromic shift of the O–H stretching band and the chemical activation of the adsorbed molecules.

In order to reveal the manifestations of the chemical activation of ethylene adsorbed on acid hydroxyl groups, we carried out a comparative study of ethylene adsorption on the sodium and hydrogen forms of mordenite and zeolite Y [10]. As in the above examples, IR measurements were performed using the diffuse reflectance technique at room temperature in the spectral region accommodating the C–H stretching vibrations and the combinations between the double bond vibrations and the bending and twisting vibrations of the CH_2 group. The results of these experiments are

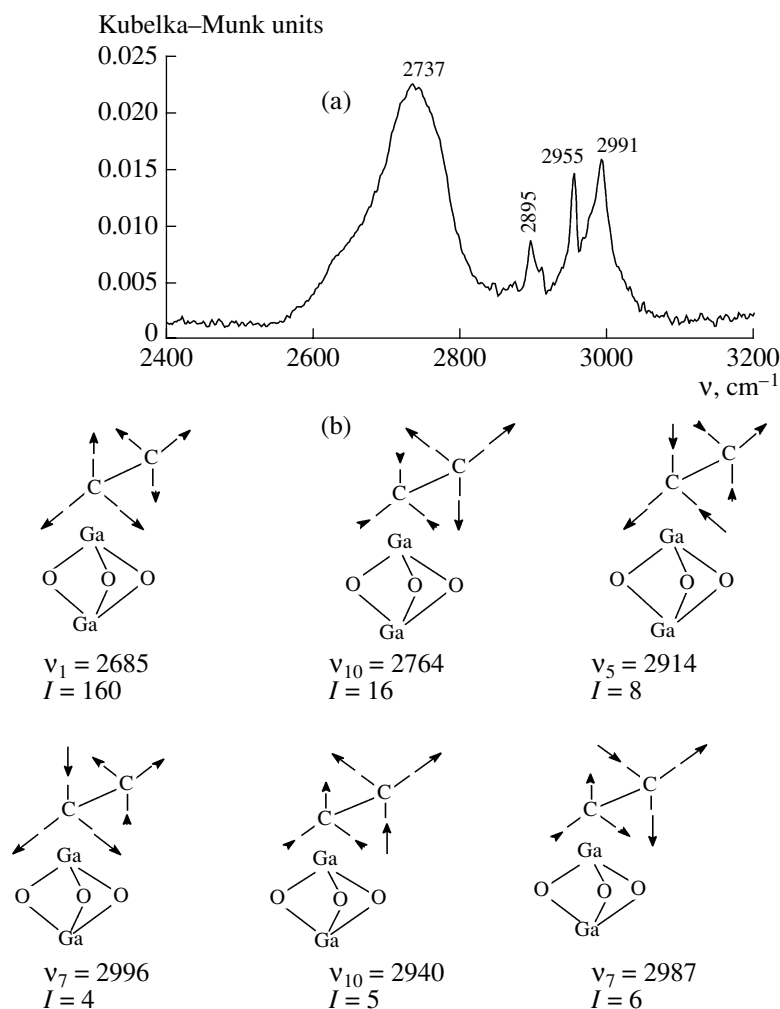


Fig. 6. Quantum chemical simulation of ethane adsorption on gallium oxide: (a) observed diffuse reflectance IR spectrum and (b) results of the quantum chemical simulation of this spectrum (ν_i —frequency, cm^{-1} ; I —band intensity, Kubelka–Munk units).

presented in Fig. 7. A comparison between the observed absorption band positions and the corresponding data from the literature for gaseous, liquefied, and frozen ethylene is presented in Table 2.

It follows from these data that, in the region characteristic of the C–H stretching vibrations ($2900\text{--}3100\text{ cm}^{-1}$), the bands from liquefied, frozen, gaseous, and adsorbed ethylene occur at similar frequencies. The main differ-

Table 2. Band positions in the IR absorption spectra of gaseous, liquid, and frozen ethylene [37, 38] and ethylene adsorbed on the sodium and hydrogen forms of mordenite and zeolite Y

Band assignment	Gas	Liquid at -168°C	Solid at -180°C	NaY	NaM	HY	HM
ν_9	3105	3085	3075	3085	3082	3002	3094
ν_5	3102(R)	—	—	3019	—	—	3065
ν_1	—	3016	—	2995	2997	3003	3003
ν_{11}	2989	2983	2973	2972	2969	2975	2975
$\nu_2 + \nu_{10}$	—	2434	2434	2427	2421		
$\nu_3 + \nu_4$	—	2340	—	2353	2362	2351	2353
$\nu_4 + \nu_6$	—	2253	2255	2277	2273	2272	2267
$\nu_3 + \nu_{10}$	—	2167	2166	2163	2166	2167	2167

ence here is that all of the four possible C–H stretching bands are observed for adsorbed ethylene, including the symmetry-forbidden vibrations ν_1 and ν_5 (Fig. 7a). As was noted above, this well-known effect is due to symmetry reduction in the adsorbed molecules.

In the 2100–2500 cm^{-1} region, which is characteristic of the combinations between the bending and twisting CH_2 vibrations and the double bond vibrations, the bands from liquefied and frozen ethylene and ethylene adsorbed on zeolite NaY again occur in close positions. These bands are ~ 10 times weaker than the C–H stretching bands. Thus, since the interaction between ethylene and sodium ions is not accompanied by the chemical activation of the former, it does not cause any significant difference between the spectra of adsorbed and free ethylene.

Room-temperature ethylene adsorption on zeolite HY causes a bathochromic shift and marked broadening of the band due to the stretching vibrations of the bridging hydroxyl groups of this zeolite (Fig. 7b), just as was reported in numerous earlier publications. For an ethylene equilibrium pressure of 10 Torr, the peak of this band is shifted from 3660 to 3285 cm^{-1} and three narrow bands from the C–H stretching vibrations of adsorbed ethylene (3092, 3003, and 2975 cm^{-1}) are seen against its background. As is clear from Table 1, the positions of these bands are close to the positions of the same bands in the spectra of liquefied and frozen ethylene. Therefore, ethylene adsorption on zeolite HY also does not cause a noticeable perturbation of the fundamental C–H stretching frequency.

A different situation is observed in the region of the combinations between the bending and twisting CH_2 vibrations and double bond vibrations: a very broad absorption band is seen in place of four well-resolved low-intensity narrow lines (Fig. 7b). As compared to the same band in the case of zeolite NaY, it is stronger by more than one order of magnitude, while its maximum is shifted only slightly. Thus, ethylene adsorption on the bridging acid hydroxyl groups of zeolite HY dramatically strengthens the band due to the combinations between the bending and twisting CH_2 vibrations and the double bond vibrations and does not significantly change the position or intensity of the C–H stretching band.

Undoubtedly, this effect is due to the chemical activation of adsorbed ethylene. Indeed, exposing a zeolite sample to an ethylene atmosphere at room temperature eliminates the band from the hydrogen-bonded acid hydroxyl groups and gives rise to bands at 2960, 2855, and 2928 cm^{-1} from ethoxyl fragments grafted to the surface and from growing polymer chains. The ethylene π -complex protonation and ethylene oligomerization kinetics on H-mordenite are illustrated in Fig. 8.

Ethylene oligomerization on H-zeolites has been the subject of a number of studies [26–30]. According to the results of these studies, this process consists of the following sequence of elementary steps:

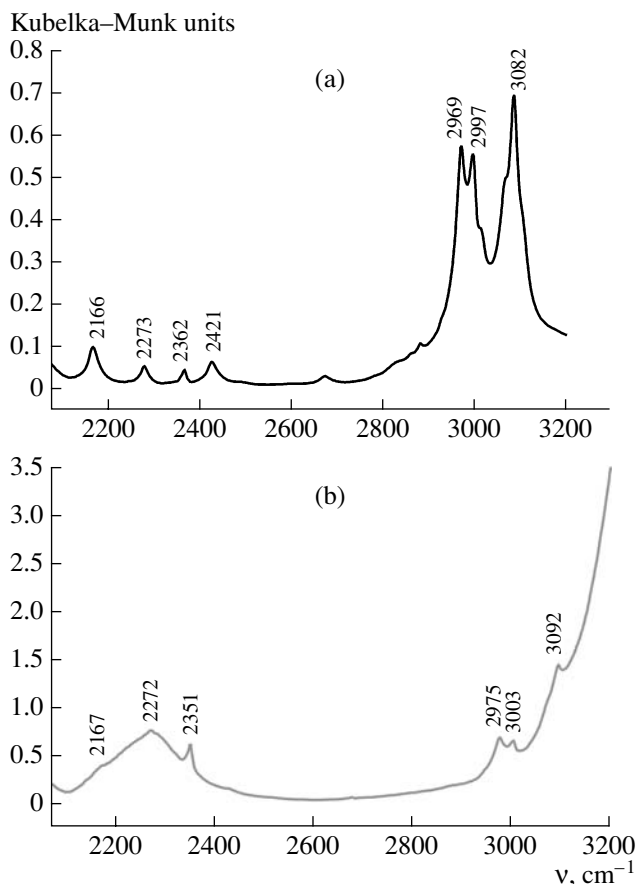
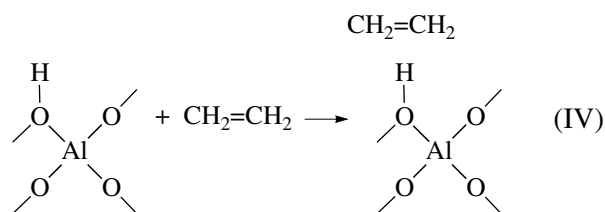
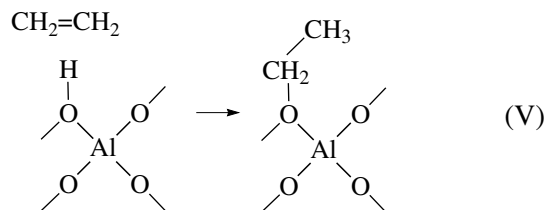


Fig. 7. Diffuse reflectance IR spectra of ethylene adsorbed on zeolites (a) NaY and (b) HY at room temperature.

(1) ethylene adsorption on acid hydroxyl groups, which results in the formation of a strong hydrogen bond,



(2) proton transfer to the adsorbed ethylene molecules, which yields highly polarized ethoxyl groups,



(3) the growth of hydrocarbon oligomer chains grafted to the zeolite surface, which results from the interaction between the polarized ethoxyl groups

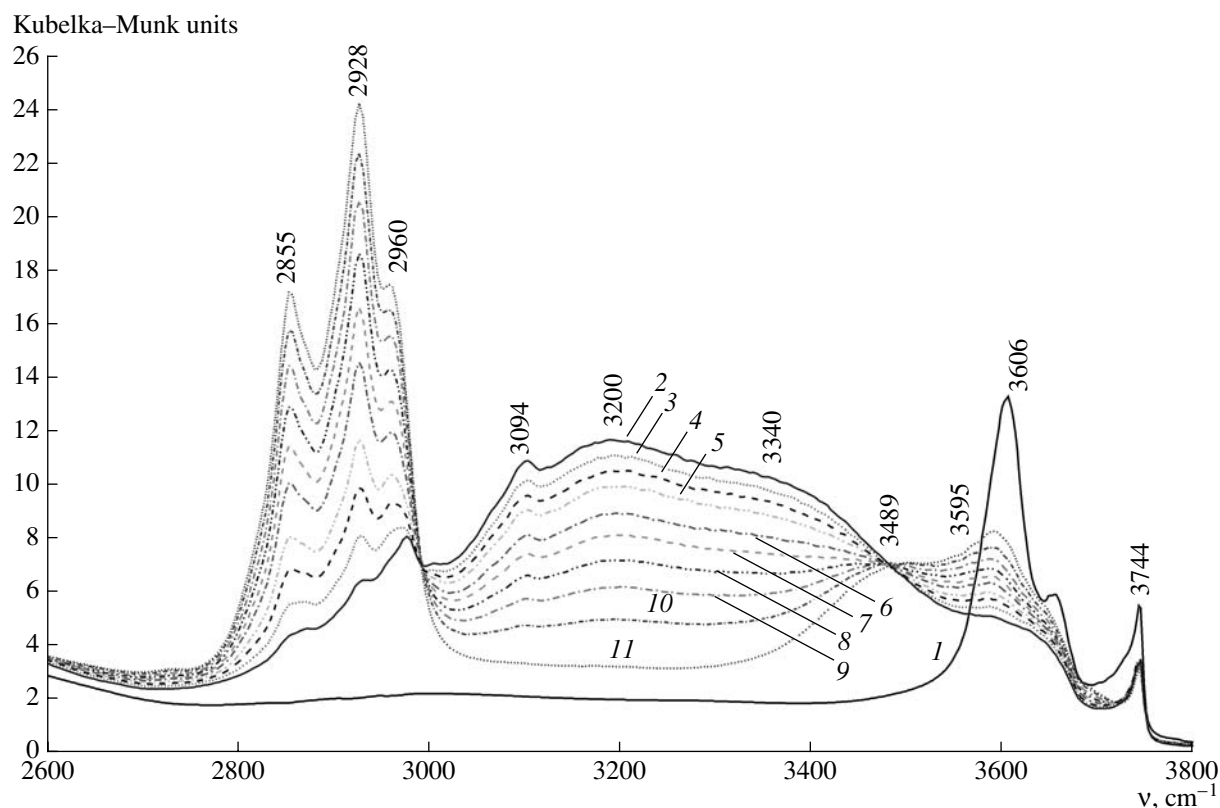
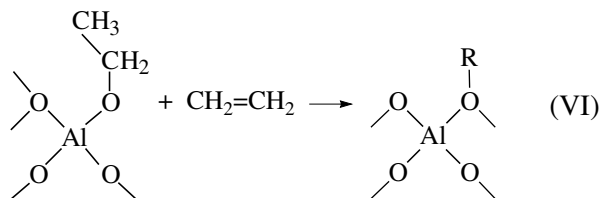
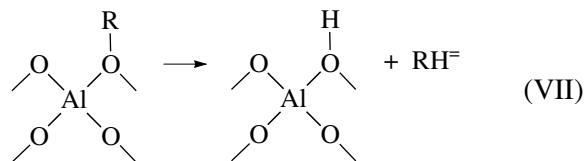


Fig. 8. Kinetics of the conversion of ethylene π -complexes adsorbed on H-mordenite into ethoxyl groups. (1) Diffuse reflectance IR spectrum of initial mordenite and (2–11) the spectra of mordenite with adsorbed ethylene (7 mmol/g) recorded (2) 0.5, (3) 2.5, (4) 3.5, (5) 4.5, (6) 5.5, (7) 9, (8) 12, (9) 17, (10) 25, and (11) 48 min after the onset of the reaction.

(adsorbed ethyl carbonium ions) and new ethylene molecules,



(4) the desorption of the oligomers or their cracking products at high temperatures,



The first two steps of this sequence were observed IR-spectroscopically in this study. Below, we will focus on the mechanism of the second step, namely, proton transfer from the acid hydroxyl groups to the adsorbed ethylene molecules.

A quantum chemical analysis of the reaction coordinate for elementary step (V) was carried out in our earlier works [31, 32]. It was deduced that the reaction coordinate involves the simultaneous lengthening of

the O–H bond in the acid hydroxyl group and of the ethylene double bond turning into an ordinary C–C bond, the change of the bond angles in the ethylene CH_2 group turning into a CH_3 group, and the change of the bond angles in the CH_2 group adding to the nearest neighbor oxygen atom of an active site (Fig. 9). These changes result in a transition state resembling an adsorbed ethyl carbenium ion in its geometry and high positive charge. The transition state turns into a highly polarized ethoxyl group bound to a neighboring oxygen atom of the zeolite lattice (Fig. 9). These inferences were confirmed by quantum chemical calculations carried out by other authors [33–36].

As follows from normal mode shape analysis for the ethylene molecule [13] (Fig. 10), the length of the double bond $\text{C}=\text{C}$ changes owing to the stretching vibrations ν_2 and ν_3 . Furthermore, these vibrations change the bond angle in the CH_2 group. Another cause of the changes in this bond angle is the vibrational mode ν_4 , which bends the hydrogen atoms out of the double bond plane. According to quantum chemical calculations, it is the combination of these vibrations that makes the main contribution to changes in the reaction coordinate in proton addition to the ethylene molecule. The increase in the positive charge of the ethylene molecule as a result of proton transfer causes polarization of the chemical bonds involved in this elementary step and an

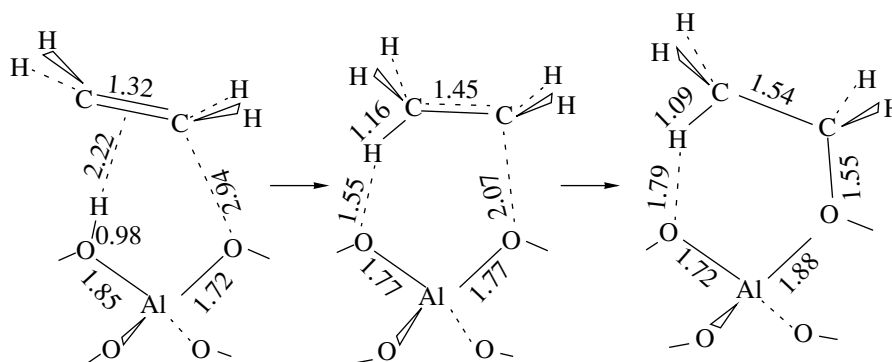


Fig. 9. Results of the quantum chemical simulation of the elementary reaction of proton transfer from an acid hydroxyl group on the surface of the hydrogen form of a high-silica zeolite to an adsorbed ethylene molecule [32, 33].

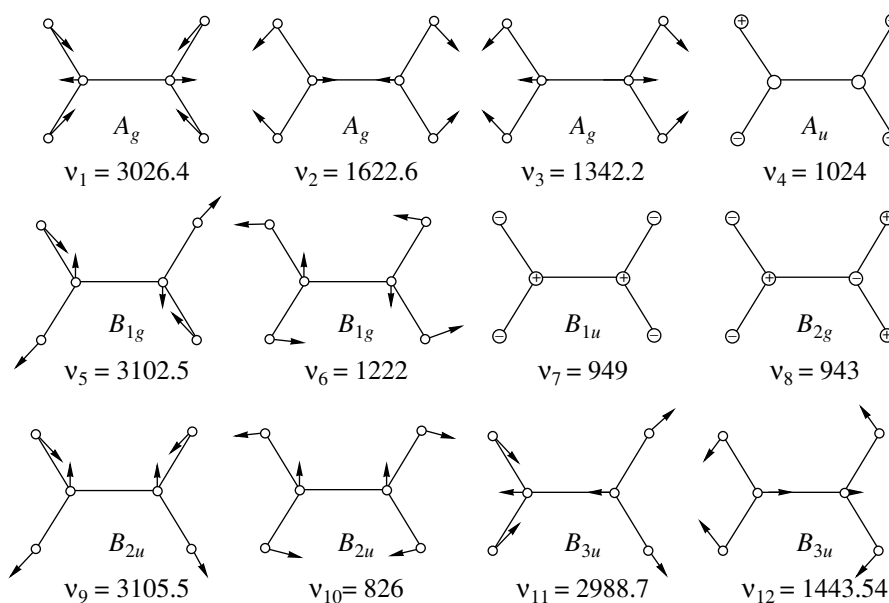


Fig. 10. Normal mode shapes for the ethylene molecule [13].

abnormal strengthening of the IR absorption band due to the combination of the above vibrations.

Indeed, it is well known that the IR extinction coefficient for composite vibrations is proportional to the squared second derivative of the dipole moment of these composite vibrations with respect to the normal coordinates of these vibrations. It is, therefore, obvious that composite vibrations characterized by abnormally large extinction coefficients must correspond to the complicated reaction coordinate of the proton transfer step.

Thus, our experimental data confirm the complicated nature of concerted proton transfer from the acid hydroxyl groups the adsorbed ethane molecules. They suggest the following new spectral criterion for the reaction coordinate of such concerted mechanisms: The complicated composite vibrations of the adsorbed mol-

ecule that are involved in such a mechanism must have abnormally large IR extinction coefficients.

In this connection, note again that the abnormally large extinction coefficients of the complicated composite vibrations are not the property of free or weakly cation-bound adsorbed ethylene molecules. They result only from proton transfer causing further polarization of the adsorbed molecules. The energy of the heterolytic dissociation of the O-H bond in the hydroxyl group is partially counterbalanced by the formation energy of the C-H bond in one of the methylene groups of ethylene and by the binding of the other methylene group to the framework oxygen of the zeolite. It is due to this fact that the activation energy of the protonation reaction is low. The conditions necessary for this energy compensation taking place are provided by the complicated composite vibrations of the adsorbed molecules. These vibrations are combinations of the bend-

ing and twisting vibrations of the methylene groups and the double bond vibrations.

Although the above criterion is formulated for the concerted reaction coordinate of the elementary reaction of proton transfer to adsorbed ethylene molecules, it is obviously applicable to other catalytic reactions involving strong vibrational polarization of adsorbed molecules. For example, abnormally high intensities of the IR bands from the combination between the C–C–C vibrations of the cyclopropane ring and the CH₂ bending vibrations are observed for the catalytic conversions of cyclopropane on the hydrogen and metal cation forms of zeolite Y and mordenite [1, 2].

CONCLUSIONS

Note again that the bathochromic shift of stretching vibrations, which is conventionally used as the index of the reactivity of adsorbed molecules, is much less sensitive to the chemical activation of these molecules than the intensity of the corresponding absorption bands. The bathochromic shift of the IR band of an adsorbed molecule is no greater than a few tens of reciprocal centimeters, while the intensities of the bands from composite vibrations change by 1–2 orders of magnitude owing to bond polarization. As was mentioned above, this deduction is quite natural because force constants characterize the fundamental homolytic terms of chemical bonds. For acid catalysis, the fundamental homolytic terms are mixed with excited, heterolytic terms and this effect manifests itself as a multifold strengthening of the fundamental and composite absorption bands in the vibrational IR spectrum.

ACKNOWLEDGMENTS

This work was supported by the President of the Russian Federation (Support to Leading Scientific Schools Program, project no. 5746.2006.3) and by the Division of Chemistry and Materials Science of the Russian Academy of Sciences (program no. 1, “Theoretical and Experimental Investigation of the Nature of the Chemical Bond and of the Most Important Chemical Reactions and Processes”).

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