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Integral Absorption Coefficients of C−H Stretching Bands in IR Spectra of Ethane Adsorbed by Cationic Forms of Y Zeolite

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An attempt to measure absolute intensities of IR C−H stretching bands of ethane specifically adsorbed by Na^+, Ca^{2+}, or Mg^{2+} cations in Y zeolite was carried out via simultaneous transmission IR and volumetric measurements at very low pressures using self-supporting wafers. For wafers with a thickness of 7−9 mg/cm^2 quantitative measurements of absorption coefficients of C−H stretching bands were possible. More pronounced shifts of C−H bands toward lower frequencies indicated that the perturbation of the corresponding bonds in ethane upon adsorption by the bivalent Ca^{2+} or Mg^{2+} ions was much stronger than by the monovalent Na^+ ions. In addition, the integral extinction coefficient of the C−H stretching bands of ethane adsorbed by Na^+ ions was only about 53% of that of gas-phase ethane. For adsorption on the bivalent Ca^{2+} or Mg^{2+} ions the coefficients exceeded those of the free ethane molecule, indicating strong polarization of the C−H bonds during the vibration. Bands representing the fully symmetric C−H stretching vibrations, which are IR inactive for free ethane, were perturbed most strongly upon adsorption. Their intensities reached up to 60% of the total intensity in the C−H stretching region. In contrast, the intensities of the other C−H bands were several times lower than for free ethane. These trends indicate anisotropy in the polarizability of the adsorbed molecules. In addition, the absorption coefficients indicate a weaker adsorption and polarization of ethane by Mg^{2+} than by Ca^{2+} ions in Y zeolite. Because of their smaller ionic radius, the Mg^{2+} cations are more strongly shielded by the surrounding oxygen atoms of the zeolite framework than the Ca^{2+} cations, and therefore, their polarizing ability is decreased.

Introduction

In the IR spectroscopic investigation of hydrocarbons not only the positions of IR bands have attracted attention but also the intensities.[1−3] In combination with the band positions, consideration of the intensity allows evaluation of the polarization of chemical bonds induced by stretching or bending and assessment of various influences on the polarization, such as chemical bonds to neighboring electronegative atoms, hyperconjugation of CH_2 or CH_3 groups with adjacent double or triple bonds, or other factors (for a review devoted to intensities of C−H stretching bands of a variety of organic molecules see ref 4). Only a few papers discuss the band intensity of vibrations of adsorbed hydrocarbon molecules.[5−10] The absolute intensities of absorption bands were measured for weak CO adsorption at low coverage on titania[11] or for pyridine adsorption by acidic adsorbents.[12−17] The lack of interpretable data is mainly explained by the inhomogeneity of adsorbed species, which could be either specifically adsorbed by particular adsorption sites or physically adsorbed in the internal pores of an adsorbent. In addition, as was shown for methanol adsorption on SiO_2,[18] the intensities of IR bands may also depend on the scattering ability of an adsorbent, which in turn depends on its specific surface area or the sample thickness. Therefore, the proper measurement of intensities of IR bands of adsorbed molecules is a rather difficult task. However, the idea of gaining such information is quite intriguing, because the intensity of IR bands reflects the dynamic dipole moment, which in turn is closely related to the extent of polarization of chemical bonds in adsorbed species by the surface sites.

In a previous DRIFTS investigation of the specific adsorption of light hydrocarbons by different cationic forms of zeolites at very low pressures, we analyzed the relative intensities of C−H stretching bands.[8] The results indicated that adsorption results in a redistribution of the intensity of the C−H stretching bands. The most striking observation was the appearance of the bands of the initially (i.e., before adsorption) fully symmetric IR-inactive C−H stretching vibrations, and their intensities were much higher than those of the other C−H stretching vibrations. However, these experiments could not give any information about the influence of adsorption on the absolute intensities of IR bands.

In the present investigation we measure the integral molar absorption coefficients of C−H stretching bands of ethane adsorbed by different cationic forms of Y zeolite by transmission IR spectroscopy at room temperature, when ethane is reversibly adsorbed in molecular form. To exclude spectral contributions of physically adsorbed moieties or of species adsorbed on Na^+ ions in partially exchanged zeolites, our experiments are carried out at very low pressures, and the equivalency of the spectra at various low pressures is considered as an indication of specific adsorption of ethane by a single type of cation. Combination of the spectral information with adsorption isotherm measurements allows us to compare the polarizing power of various modifying cations in Y zeolite.

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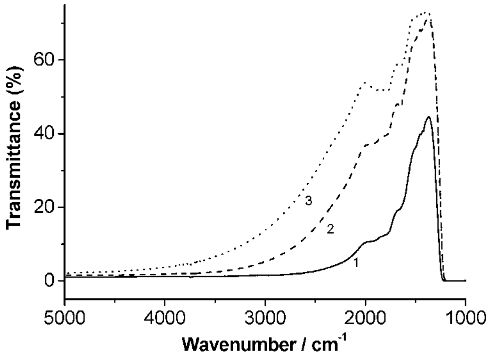

Figure 1. Transmission IR spectra of NaY zeolite with variation of the wafer thickness: (1) $w/S = 17.6$ mg/cm^2, (2) $w/S = 9.31$ mg/cm^2, (3) $w/S = 7.96$ mg/cm^2.

Experimental Procedure and Data Analysis

Experimental Procedure. Our starting material was the sodium form of Y zeolite with Si/Al = 2.5. Calcium (42% ion exchange) and magnesium (35% ion exchange) forms were prepared by multiple ion exchange of the sodium form in aqueous solution. The extent of ion exchange in all cases was determined by atomic absorption spectroscopy.

Transmission IR spectroscopic and volumetric adsorption measurements were carried out simultaneously. IR spectra were recorded using a Nicolet Protégé 460 FTIR spectrometer with a resolution of 4 cm^{-1}. The number of scans was equal to 64. The vacuum and gas-dosing apparatus, including the section with the IR-transparent windows, but excluding the pumping unit, was placed in a temperature controlled box to ensure isothermal conditions.[19] The box temperature was 308 K; however, the actual sample temperature was slightly higher because of heating by the IR beam as discussed elsewhere.[19] The calibrated volume was equal to 373 cm^3.

The zeolite powders were pressed into wafers of different thicknesses for the IR measurements. The wafer mass varied in the range of 0.01−0.03 g, corresponding to area masses of 7−17 mg/cm^2. Before the adsorption measurements, attenuation of the IR beam by scattering in the wafers of the different cationic forms of Y zeolite was investigated, as earlier investigations had shown that strong scattering can falsify the values obtained for the absorption coefficient measurement,[19] as has been supposed by other authors.[18] Broad-range IR transmission spectra of the sodium form of zeolite Y are shown for different wafer thicknesses in Figure 1. Wafers with a thickness of 7−10 mg/cm^2 transmit about 15% of the IR radiation in the region of the C−H stretching vibrations, which is sufficient for quantitative measurement of the absorption coefficients of these vibrations.

For activation the wafers were placed into a heatable section of a combined vacuum and gas-dosing apparatus. Initially the temperature was gradually increased from 293 to 423 K with a heating rate of 2 K/min, and the samples were kept at this temperature under vacuum for 2 h. Then, still under vacuum, the temperature was raised to 770 K with a heating rate of 4 K/min, and the samples were kept at this temperature for an additional 2 h. Afterward, the wafers were lowered into the spectroscopy cell, which is part of the vacuum apparatus and is equipped with KBr windows.

The adsorption experiment was conducted by stepwise dosing of ethane (99.95% purity from Air Liquide/Messer-Griesheim). The adsorbed amount was determined through the pressure measurement, and for each equilibrium pressure a spectrum was recorded. The transmittance of the cell filled with the corresponding pressure of ethane (but without the wafer in the beam) was recorded as the background. Spectra were processed with OMNIC software and converted into decadic absorbance. The spectra of the activated zeolites were subtracted from the spectra after adsorption of ethane to obtain solely the intensity contribution of the bands of the C−H vibrations.

Data Analysis. The calculation of the integral molar absorption coefficients ε of the IR bands of ethane adsorbed by different zeolites was based on the application of the Lambert−Beer law, which was modified for adsorption by solid wafers in the following way:

$$\varepsilon = -\frac{1}{C'}\int_{\nu_1}^{\nu_2} \ln\frac{I}{I_0}\,\mathrm{d}\nu = \int_{\nu_1}^{\nu_2} \varepsilon_\nu\,\mathrm{d}\nu \qquad (1)$$

with I_0 and I the intensities of incident and transmitted radiation, C' the number of moles of adsorbed gas related to a 1 cm^2 cross section of incident radiation (mol/cm^2), ε_ν the molar absorption coefficient at frequency ν (cm^2/mol), and $\int\varepsilon_\nu\,\mathrm{d}\nu$ the integral molar absorption coefficients (cm/mol) for the frequency range from ν_1 to ν_2.

The absorbance D at frequency ν in the IR spectra is given by the following expression:

$$D_\nu = -\left(\log\frac{I}{I_0}\right) = -\frac{1}{2.303}\ln\frac{I}{I_0} \qquad (2)$$

The value of the apparent integral absorption intensity over a range of wavenumbers ν_1 to ν_2 can then be obtained by integration of the spectra:

$$\int_{\nu_1}^{\nu_2} D_\nu\mathrm{d}\nu = -\int_{\nu_1}^{\nu_2}\log\frac{I}{I_0}\,\mathrm{d}\nu = -\int_{\nu_1}^{\nu_2}\frac{1}{2.303}\ln\frac{I}{I_0}\,\mathrm{d}\nu \qquad (3)$$

After substitution of eq 3 into eq 1, the integral molar absorption coefficient is given by

$$\varepsilon = -\frac{1}{C'}\int_{\nu_1}^{\nu_2}\ln\frac{I}{I_0}\,\mathrm{d}\nu = \frac{2.303}{C'}\int_{\nu_1}^{\nu_2} D_\nu\,\mathrm{d}\nu \qquad (4)$$

Application of this equation is possible only for wafers (or spectral regions) with little loss of radiation through scattering.

The C' value corresponds to the number of molecules related to a 1 cm^2 cross section of incident radiation:

$$C' = \frac{N}{S} = n_\mathrm{w}\frac{w}{S} \qquad (5)$$

with N the number of moles of adsorbed gas (mol), w the mass of the sample (g), S the area of the sample (cm^2), and n_w the concentration of adsorbed molecules, $n_\mathrm{w} = N/w$ (mol/cm^3). Now the equation for the integral molar absorption coefficient is given by

$$\varepsilon = 2.303\frac{S}{w}\,\frac{\int_{\nu_1}^{\nu_2} D_\nu\,\mathrm{d}\nu}{n_\mathrm{w}} \qquad (6)$$

The integral ($\int D_\nu\,\mathrm{d}\nu$) is defined as the area of all bands of the C−H stretching vibrations (corresponding to a wavenumber range from 2500 to 3100 cm^{-1}) in the spectra of adsorbed ethane after subtraction of the spectrum of the activated zeolite. At low coverages (or partial pressures) a linear relationship between the integral intensity ($\int D_\nu\,\mathrm{d}\nu$) and the concentration of adsorbed ethane (n_w) was obtained for all of the investigated samples. An example of this relationship, obtained for ethane adsorption by CaY zeolite, is depicted in Figure 2. To obtain the values of the integral molar absorption coefficients of C−H stretching bands, the slopes ($\int D_\nu\,\mathrm{d}\nu$)/$n_\mathrm{w}$ received from such graphs were then substituted into eq 6. To estimate the contribution of

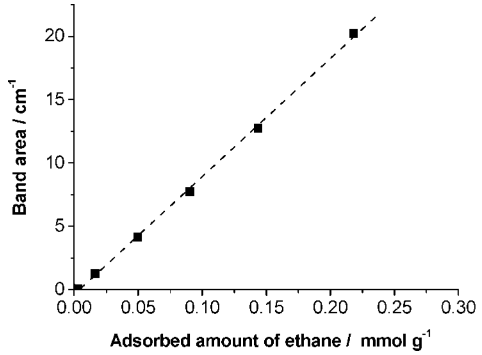

Figure 2. Band area of IR bands in the C−H stretching region (3150−2600 cm^{-1}) vs amount of ethane adsorbed by CaY.

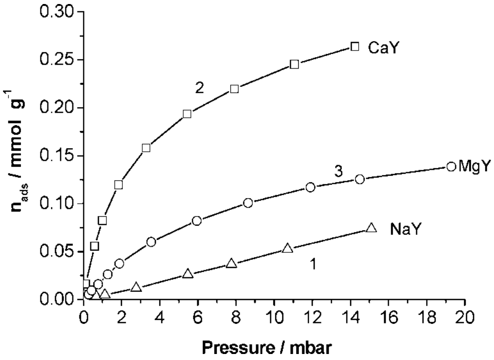

Figure 3. Ethane adsorption isotherms at room temperature on different cationic forms of Y zeolite.

individual C−H stretching bands to the total intensity, the bands were decomposed by a fitting procedure using ORIGIN software and Lorentzian band shapes.

Results and Discussion

Adsorption Isotherms. The isotherms of ethane adsorption by different cationic forms of Y zeolite are shown in Figure 3. In the pressure range of 0−20 mbar the saturation of zeolites with adsorbed molecules was not achieved. Assuming that, in NaY, 70% of the cations are located in the supercages, a cation: alkane ratio of 1:1 is reached at 38 adsorbed molecules per unit cell, which corresponds to approximately 3 mmol of alkane g^{-1}. Literature data show that for NaY saturation with ethane is not achieved at 323 K and 120 kbar of ethane;[20] hence, our conditions are far from saturation, and indeed, a linear isotherm, which is typical of low coverages, is observed for NaY. As expected, ethane is more strongly adsorbed by MgY and CaY zeolites than by NaY, as indicated by higher adsorbate concentrations at equal equilibrium pressure. This result also ensures that, at low coverages, solely the bivalent cation sites in these partially exchanged zeolites are populated. However, the stronger adsorption of ethane by Ca^{2+} ions in comparison with Mg^{2+} ions is an unexpected result, because the Mg^{2+} ions are smaller in radius than the Ca^{2+} ions and the higher effective field strength should lead to stronger polarization and bonding of the adsorbate. A simple electrostatic interaction with the cation alone may not adequately describe the adsorbate complex.

This result could not be explained by significant contributions of weaker adsorption of ethane on MgOH^{+} sites, which can be generated via hydrolysis during ion exchange in aqueous solution or by activation at high temperature. Indeed, the IR spectra of MgY in the OH region indicated only a very weak intensity of MgOH bands. In addition, toward low equilibrium pressures all bands in the C−H stretching region for ethane adsorbed on MgY decrease in intensity without any changes of position or intensity distribution. This behavior indicates homogeneity of the desorption sites. Thus, ethane adsorption takes place specifically on Mg^{2+} cations, and there is no additional contribution through adsorption on Mg(OH)$^{+}$ ions. Therefore, the weaker adsorption of ethane by Mg^{2+} ions in comparison with Ca^{2+} cations requires some other explanation (vide infra).

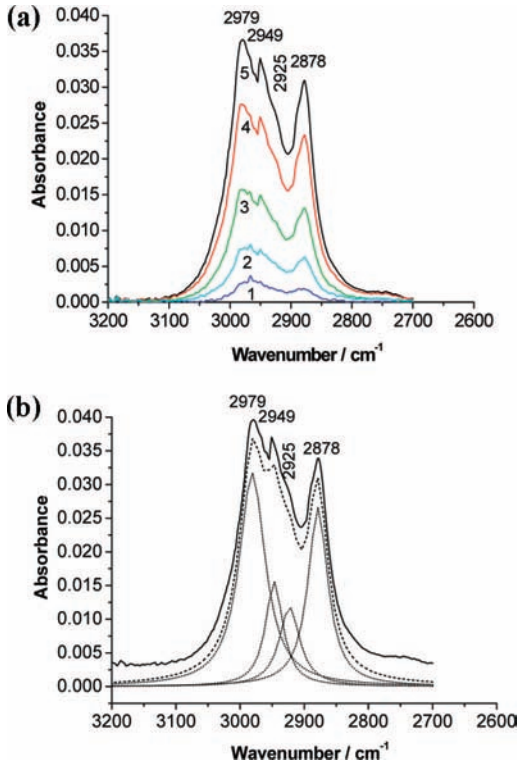

Figure 4. (a) Transmission IR spectra of ethane adsorbed by NaY zeolite at 308 K and the following equilibrium pressures: (1) 1.12, (2) 4.65, (3) 10.94, (4) 19.72, and (5) 28.2 mbar. (b) Result of fitting of the spectrum of ethane adsorbed by NaY: solid line, original spectrum; dotted lines, individual contributions according to the fit with four bands; dashed line, sum of individual contributions.

IR Spectra of Adsorbed Ethane. The transmittance IR spectra of ethane adsorbed at different pressures by the Na, Ca, and Mg forms of Y zeolite are presented in Figures 4a, 5a, and 6a. The spectra are very similar to those obtained in our previous paper[8] by DRIFTS. For ethane adsorption by NaY the spectrum contains three well-resolved and one nonresolved C−H stretching band (Figure 4a). The bands can be assigned as follows (gas-phase frequencies in parentheses):[21] 2979 cm^{-1}, ν_7 (IR 2994 cm^{-1}); 2949 cm^{-1}, ν_{10} (Raman 2963 cm^{-1}); 2925 cm^{-1}, ν_5 (IR 2954 cm^{-1}); 2878 cm^{-1}, ν_1 (Raman 2899 cm^{-1}). Neither the positions nor the relative intensities of these bands changed with variation of the equilibrium pressure; thus, the sites of specific adsorption can be considered homogeneous.

The spectra of ethane adsorbed by CaY and MgY exhibit five and six absorption bands, respectively (Figures 5a and 6a). The higher number of bands in comparison with adsorption on NaY indicates a stronger lowering of the symmetry of ethane, which is a result of the interaction with the bivalent cations in CaY and MgY. Upon raising the ethane pressure to 5 mbar, the positions of the bands and their relative intensities did not change. Hence, contributions in the IR spectra from nonspecific adsorption or adsorption on Na^{+} ions should be negligible.

Two trends can be recognized when the spectra of ethane adsorbed by Na^{+}, Ca^{2+}, or Mg^{2+} cations are compared. The

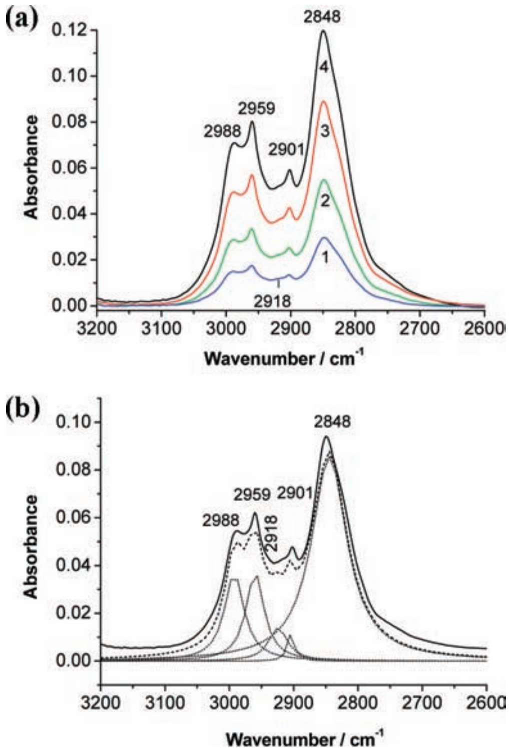

Figure 5. (a) Transmission IR spectra of ethane adsorbed by CaY zeolite at 308 K and the following equilibrium pressures: (1) 0.48, (2) 1.06, (3) 2.4, and (4) 4.85 mbar. (b) Result of fitting of the spectrum of ethane adsorbed by CaY: solid line, original spectrum; dotted lines, individual contributions according to the fit with five bands; dashed line, sum of individual contributions.

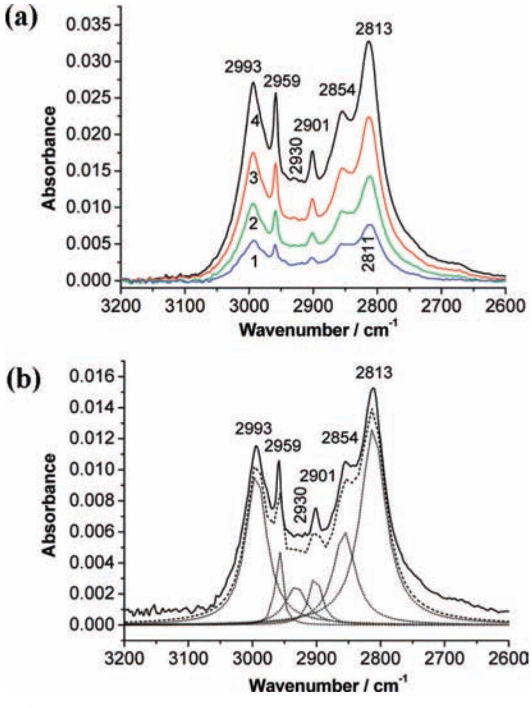

Figure 6. (a) Transmission IR spectra of ethane adsorbed by MgY zeolite at 308 K and the following equilibrium pressures: (1) 0.52, (2) 1.13, (3) 2.22, and (4) 4.46 mbar. (b) Result of fitting of the spectrum of ethane adsorbed by MgY: solid line, original spectrum; dotted lines, individual contributions according to the fit with six bands; dashed line, sum of individual contributions.

TABLE 1: Integral Molar Absorption Coefficients of IR Bands of Ethane Adsorbed by Different Cationic Forms of Y Zeolite

	w/S, mg/cm^2	ε^b (km/mol)	$\varepsilon_{hf}{}^b$ (km/mol)	$\varepsilon_s{}^b$ (km/mol)
gas[3]		169		
	7.96	92	66	26
	8.77	104	75	
ads by NaY	9.32	119	86	33
	9.32^a	100	72	28
	9.32^a	102	73	29 (2878 cm^{-1})
ads by CaY	8.23	261	95	166
	8.23^a	258	93	165 (2848 cm^{-1})
ads by MgY	9.9	185	111	74 (2813 cm^{-1})
				104 (2813+ 2854 cm^{-1})
	13.4	225		

[a] Reproducibility on the same sample. [b] ε = integral molar absorption coefficients of all C−H stretching vibrations, ε_s = integral molar absorption coefficients of the initially fully symmetric C−H stretching vibration, and ε_{hf} = integral molar absorption coefficients of high-frequency bands, $\varepsilon_{hf} = \varepsilon - \varepsilon_s$.

lowest observed C−H stretching frequency becomes lower in this sequence of cations; that is, the red shift relative to the gas-phase vibration increases. Moreover, the relative intensities of these strongly red-shifted IR bands increase in the same order. These trends indicate a stronger polarizability of the species adsorbed by bivalent cations in comparison with species adsorbed by sodium ions. According to quantum-chemical modeling,[22] the most strongly red-shifted IR band belongs to the fully symmetric C−H stretching vibration of ethane perturbed by adsorption.

To estimate the contributions of these low-frequency bands to the entire C−H stretching region in the spectra of ethane adsorbed by NaY, CaY, or MgY zeolites, the bands were decomposed by fitting. A comparison of the individual bands as obtained by the fits with the experimental spectra is presented in Figures 4b, 5b, and 6b. In the three different cases, fitting the spectra with four, five, or six components, respectively, gave good least-squares fits with $R^2 > 0.996$. The ratios of the area of the low-frequency band obtained by a fit to the total area of all C−H stretching bands were equal to 0.28, 0.41, and 0.64 for ethane adsorbed by NaY, MgY, and CaY zeolite. Thus, the relative contribution of the low-frequency band to the intensity in the entire C−H region is larger for ethane adsorbed on bivalent cations than for ethane adsorbed on sodium ions. It follows that the initially (i.e., prior to adsorption) fully symmetric C−H stretching vibrations are more strongly perturbed by bivalent cations than by monovalent ions.

Comparison of Absolute Intensities of Individual IR Bands in the Spectra of Ethane Adsorbed by Different Cations in Y Zeolite. The results of a transmission IR spectroscopic investigation of methanol adsorption on SiO_2, previously reported in ref 18, demonstrated that the absolute intensities of C−H bands depend on the thickness of the wafers. Because of this observation, we started our experiments with the investigation of ethane adsorption on NaY wafers of different thicknesses. The results are presented in Table 1. It is evident that the values for the molar absorption coefficients increase with increasing thickness of the wafers. There should be no relation between these two quantities, and some of the values are thus not accurate. We believe that this effect is connected to the increasing light-scattering ability of thicker wafers, which is responsible for the decrease in measured transmittance (Figure

1). Multiple light scattering makes the effective optical path length longer than one accounts for through dividing by w/S. In addition, for a transmittance of less than 10%, the errors of the calculated apparent integral absorption intensity $\int D_\nu \, d\nu$ increase. Therefore, the most reliable results in Table 1 are those obtained for the thinnest wafers weighing 7−9 mg/cm^2.

To investigate the reproducibility of our results, we carried out multiple measurements of ethane adsorption on the same NaY wafer, which had a thickness of 9.32 mg/cm^2, and further adsorption measurements on two wafers with similar thicknesses of 7.96 and 8.77 mg/cm^2. These experiments confirmed the tendency toward lower apparent integral molar absorption coefficients of C−H bands for thinner wafers, and thus, the lowest measured value of about 90 km/mol, which was obtained for the thinnest wafer, should be considered the most reliable. This value corresponds to 53% of the absorption coefficient of the free ethane molecule, which is equal to 169 km/mol.[3] This result indicates that upon perturbation of ethane by interaction with sodium cations the absolute intensity of the C−H stretching bands decreases strongly.

In contrast, for ethane adsorbed by Y zeolite modified with bivalent Ca^{2+} or Mg^{2+} cations the values of the integral molar absorption coefficients of the C−H bands are larger than for gaseous ethane (Table 1). Hence, the absorption coefficients increase in the following sequence of cations: $Na^+ < Mg^{2+} < Ca^{2+}$. This order is equivalent to a stronger polarization of the adsorbed ethane by bivalent cations in comparison with the Na^+ cation.

The same trend was observed for the integral molar absorption coefficients of the most strongly red-shifted bands (which originate from the initially fully symmetric C−H stretching vibrations) obtained after a fit of the IR spectra (Table 1, last column). After subtraction of the band that is not observed in the spectrum of gaseous ethane from the group of bands in the C−H region, one can conclude that the intensities of the other C−H stretching bands of ethane adsorbed on NaY are approximately 2.5 times lower than for gas-phase ethane. Although the absorption coefficients of these bands of adsorbed ethane are higher for MgY or CaY than for NaY, they are still lower than for the gas phase. The variations in the values of the integral molar absorption coefficients of the high-frequency bands for ethane adsorbed on Na^+, Ca^{2+}, or Mg^{2+} cations did not exceed 20%. At the same time, the values of the absolute intensities of the most strongly red-shifted bands differed much more significantly when ethane adsorption by Na^+ and Ca^{2+} cations were compared. Moreover, it was found that for ethane adsorbed by Ca^{2+} cations the intensity of the low-frequency band absorption was equal to the absolute intensity of *all* C−H stretching bands of gaseous ethane. Thus, the strong perturbation of adsorbed species by bivalent cations results in a strong contribution of the low-frequency bands of the initially fully symmetric C−H stretching vibrations to the total intensity of the adsorbate spectrum.

Our experimental results on the integral molar absorption coefficients of C−H bands, which indicate a weaker polarization of ethane by Mg^{2+} than by Ca^{2+} cations, are in agreement with the adsorption isotherms presented in Figure 2. However, these findings are not obvious; because of the larger charge-to-ionic radius ratio of Mg^{2+} in comparison with Ca^{2+}, one could expect a stronger polarization of ethane by Mg^{2+} than by Ca^{2+} cations. A possible explanation of this discrepancy could be the much smaller ionic radius of Mg^{2+} in comparison with Ca^{2+} (0.72 Å vs 1.00 Å in 6-fold coordination).[23] Therefore, the Mg^{2+} ions could be more strongly shielded than Ca^{2+} ions by the surrounding oxygen atoms of the zeolite framework, resulting in a decreased polarizing ability. Indeed, quantum-chemical modeling of alkane adsorption on cation-exchanged Y zeolites shows that shielding prevents significant "nondirected" electrostatic interaction with Mg^{2+} cations, whereas this type of contribution to the overall interaction is substantial in CaY.[24] Ethane adsorption energies were calculated to be similar for MgY and CaY (around 45 kJ/mol), whereas the interaction of a hydrocarbon with free Mg^{2+} ions was found to be stronger than with free Ca^{2+} ions. Thus, our experimental results reflect the shielding postulated by the quantum-chemical calculations. It seems that the shielding leads to a weaker interaction of ethane with Mg^{2+} than with Ca^{2+} ions, as indicated by the adsorption isotherms and the absorption coefficients. However, the positions of the low-frequency bands at 2848 cm^{-1} for CaY and 2813 cm^{-1} for MgY suggest a stronger interaction on MgY and do not fit the trend predicted by the quantum-chemical modeling. Thus, the integral molar absorption coefficients of IR C−H bands are a better indicator of the polarizing ability of cations than the low-frequency shifts and better reflect the trend in polarizing power of cations in zeolites.

The obtained results are in good agreement with our previous investigations of the adsorption of ethane on zeolites by DRIFTS.[5,7] It had been demonstrated that the adsorption of light alkanes by various cationic forms of various zeolites results in a variation of the distribution of the relative intensities of the absorption bands, which strongly depends both on the nature of the cations and on the zeolite framework. It was also shown that the most strongly perturbed and polarized vibrations are the initially fully symmetric C−H stretching vibrations, which are directly connected with the chemical activation of adsorbed molecules. These results allowed us to suggest the utilization of the intensities of vibrational IR bands as a new spectral criterion of activation of adsorbed molecules in heterogeneous acid and acid−base catalysis.

Indeed, intensities of IR bands are directly connected to the change of the dipole moments of chemical bonds resulting from their vibration; that is, they reflect the polarization of chemical bonds resulting from their stretching upon excitation. Therefore, the polarizing power of cations in zeolites is expressed not only in the low-frequency shifts and increasing relative intensities of the most strongly red-shifted IR band of the initially fully symmetric C−H stretching vibrations of adsorbed alkanes as shown earlier[7] but also in the changing and increasing integral molar absorption coefficients.

Conclusions

The polarizing power of cations in zeolites is reflected not only by the low-frequency shifts of the IR bands of adsorbed molecules, but also by the absolute and relative intensities of the most strongly red-shifted bands.

The perturbation of adsorbed alkane species by bivalent cations results in a strongly increasing spectral contribution of low-frequency C−H stretching bands, which arise from the initially (i.e., before adsorption) optically inactive fully symmetric C−H stretching vibrations.

The integral molar absorption coefficient of all IR C−H stretching bands of ethane adsorbed by sodium cations in Y zeolite is smaller than that for the free ethane molecule. In contrast, for adsorption by bivalent alkaline earth cations the integral molar absorption coefficients of the C−H stretching bands are higher than for the free molecule.

The integral molar absorption coefficients of C−H bands indicate a weaker adsorption and polarization of ethane by Mg^{2+}

in Y zeolite than by Ca^{2+} cations. This behavior can be explained by the much smaller ionic radius of Mg^{2+} in comparison with Ca^{2+}. Therefore, the former ion is more strongly shielded by the surrounding oxygen atoms of the zeolite framework, resulting in a reduced polarizing ability. The polarizing power of cations in zeolite Y increases thus in the following sequence: $Na^+ < Mg^{2+} < Ca^{2+}$.

The intensities of C−H stretching vibrations are sensitive to the chemical activation arising from the polarization of the adsorbed molecules by the active site. Therefore, in addition to the low-frequency shifts generally used to assess the influence of the surface on the reactant, absorption coefficients may also be used as a criterion of perturbation of light alkanes upon their interaction with adsorption sites.

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