

Diffusion of Ethane–Hydrogen Mixtures in LiLSX and CaA Zeolites Studied by Diffuse Reflectance IR Spectroscopy

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Abstract—The kinetics of the adsorption of ethane–hydrogen mixtures at low pressures (5–20 Torr) on the zeolites LiLSX and CaA are studied by diffuse reflectance IR spectroscopy. The adsorption of ethane mixed with hydrogen on the granulated zeolites is two orders of magnitude slower than the adsorption of pure ethane. Comparison of the adsorption kinetics of ethane–hydrogen mixtures on granulated samples and thin pellets shows that the transport of ethane into the microcrystals of the granular zeolites is retarded primarily by the counter-diffusion of ethane and hydrogen in the intercrystallite pores.

INTRODUCTION

Due to their unique molecular-sieve properties, zeolites are widely used in the adsorption separation and purification of gas and liquid mixtures and as catalysts in many chemical reactions. Most of the processes involving zeolites include the diffusion transport of reactants (or reactant mixtures) through micropores or secondary pores formed between microcrystals upon powder granulation. A detailed understanding of the complex diffusion behavior of reactants in the primary and secondary pores of zeolites is of crucial importance in the development and optimization of catalytic and adsorption processes.

Previously, we studied the diffusion of nitrogen–oxygen mixtures (O_2 –VSA process) in granulated zeolites by diffuse reflectance IR spectroscopy [1]. This method is based on the fact that symmetric molecules become IR-active upon adsorption and polarization with adsorption sites. The changes in the symmetry of molecules upon adsorption make it possible to observe vibrational absorption bands that are IR-inactive in the gas phase. Adsorption kinetics complicated by diffusion can be studied by monitoring the evolution of the intensities of these bands. It has been shown using this approach that the rate-determining step of the transport of nitrogen–oxygen mixtures in zeolites is diffusion in the intercrystallite space.

The latter work was continued by studying the diffusion of mixtures of other gases. Many reactions involving finely dispersed heterogeneous catalysts are accompanied by the transfer of reactants and reaction products in micropores and macropores. Most of these reactions are reactions of gaseous mixtures of hydrocarbons with hydrogen. For this reason, we applied the above method to the study of the simultaneous diffusion of ethane and hydrogen in zeolites with different micropore sizes. The zeolites LiLSX and CaA with effective window sizes of 7.4 and 5 Å, respectively,

were chosen for this study. The kinetic diameter of the ethane molecule is 3.8 Å (the critical diameter is 4.4 Å), and that of the hydrogen molecule is 2.9 Å. This allows both molecules to penetrate even into the narrowest pores of the zeolites. Since ethane is adsorbed on the zeolites more strongly than hydrogen (its heat of adsorption on CaA at room temperature is 7.5 kcal/mol [2], while the heat of adsorption of hydrogen does not exceed a few kcal/mol), we studied the kinetics of ethane adsorption complicated by diffusion because of the presence of hydrogen in the mixture. The evolution of the intensity of the absorption bands of adsorbed ethane, which are symmetry-forbidden in the gas phase, was measured by diffuse reflectance IR spectroscopy as in a previous study [1].

EXPERIMENTAL

The diffuse reflectance IR spectra of ethane adsorbed on the zeolites in the presence of gaseous ethane–hydrogen mixtures were recorded at room temperature according to a standard procedure [3] using a Nicolet Impact 410 FTIR spectrophotometer with a diffuse-reflectance attachment. The spectra obtained were converted to the Kubelka–Munk units using a standard program under the assumption that the reflectivity of the zeolites at 5000 cm^{-1} is 0.9. The background due to the zeolite was subtracted from the overall spectrum.

Before recording diffuse reflectance IR spectra, compacted powders of the zeolites with a granule size of 0.5–1.0 mm were aged *in vacuo* at 673 K for 4 h in quartz ampules having a side finger with a CaF_2 window. After aging, the zeolite granules were cooled to room temperature and placed into the side finger with the CaF_2 window to record IR spectra. The zeolite layer height in the side finger was ~20 mm, and IR spectra were recorded for the bottom part of the layer. The spectroscopic study of thin pellets compacted from LiLSX powder was also carried out in a quartz cell with

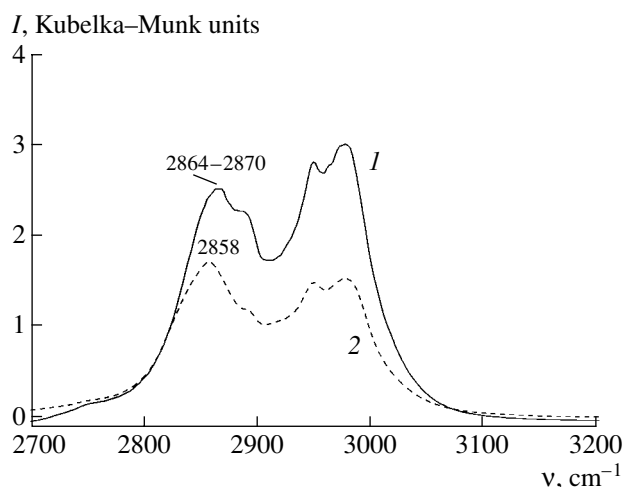


Fig. 1. IR spectra of ethane adsorbed at room temperature on (1) zeolite LiLSX at $P = 20$ Torr and (2) zeolite CaA at $P = 5$ Torr.

a CaF_2 window. The size of a thin pellet, whose density was 27 mg/cm^2 , was equal to the window size.

Ethane was frozen at the liquid-nitrogen temperature and then purified by triple vacuum distillation. Hydrogen was passed through a reduced chromium catalyst to remove oxygen and other impurities.

A mixture of gases was admitted into an IR cell (of volume 25 cm^3) from a 600-cm^3 glass flask directly in the spectrophotometer. The flask was connected with the IR cell through a flexible metallic bellow at whose ends were ground-glass joints. The first spectrum was recorded immediately after the gas mixture was admitted into the optical cell. Spectra were recorded with a scan number of 16 and a resolution of 4 cm^{-1} . Subsequent spectra were recorded at different time intervals, depending on the adsorption rate and the rate of the variation of band intensities.

The isotherms of ethane adsorption on the zeolites were measured volumetrically at room temperature using a calibrated volume and a Piezovac PV20 pressure gage. The adsorption kinetics of ethane–hydrogen mixtures were measured as the pressure drop over the sample in parallel with the spectroscopic measurements of the adsorption of pure ethane and ethane–hydrogen mixtures.

Zeolite LiLSX (BOC) had $\text{Si/Al} \geq 1.09$ and an average microcrystal size of $d = 1\text{--}3 \text{ }\mu\text{m}$; zeolite CaA was characterized by $\text{Si/Al} = 1$ and $d = 3 \text{ }\mu\text{m}$.

In the spectroscopic study of the kinetics of diffusion-controlled adsorption, we used the conventional method of plotting relative adsorption versus the square root of the time elapsed from the onset of adsorption. For a closed volume and low surface coverages, when the isotherm is described by the Henry law, the diffu-

sion-controlled adsorption rate is described by the following expression [4]:

$$Q_t/Q_\infty = 2A/V(1 + K)/K(Dt/\pi)^{1/2}, \quad (1)$$

where Q_t is the amount of gas adsorbed in time t , Q_∞ is the equilibrium adsorption, A is the external surface area of the particles (cm^2/g), V is the crystal volume (cm^3/g), D is the diffusion coefficient (cm^2/s), and K is the ratio of the amount of adsorbate in the gas phase to the amount of adsorbate in the crystallites at equilibrium.

When plotting the adsorption kinetics for pure ethane and ethane mixed with hydrogen, relative adsorption was expressed in terms of the ratio I/I_{max} , where I and I_{max} are the intensities of the absorption bands due to adsorbed ethane at the time point t and at equilibrium, respectively.

In the Henry region, I/I_{max} is proportional to the square root of the time elapsed from the process onset. The slope of the initial, linear portion of the adsorption curve on the $I/I_{\text{max}} - \sqrt{t}$ coordinates enables one to calculate the diffusion coefficient D .

RESULTS AND DISCUSSION

The diffuse reflectance IR spectra of ethane adsorbed on zeolites LiLSX and CaA at room temperature are presented in Fig. 1.

The ethane bands peaking at 2864 cm^{-1} for LiLSX and at 2858 cm^{-1} for CaA are due to the symmetrical C–H stretching vibrations and appear only in the IR spectrum of adsorbed ethane. On the assumption that the intensities of these bands are proportional to the amount of ethane adsorbed at the given time point, they can be used for plotting the kinetics of diffusion-controlled adsorption. To validate this approach, we compared the adsorption isotherms of ethane on CaA measured volumetrically at room temperature with the isotherm derived from the intensities of the 2858 cm^{-1} band (Fig. 2).

It is clear from Fig. 2 that the curves are similar; therefore, it is possible to use the intensity of the 2858 cm^{-1} band as a measure of ethane adsorption on CaA zeolite. The slight discrepancy between the isotherms at low pressures is most likely to be due to the insufficiently precise parametrization of the program that converts the reflectance spectra to the Kubelka–Munk units.

The ethane adsorption isotherms measured volumetrically at room temperatures for LiLSX and CaA are presented in Fig. 3. The linear portion of the isotherm (Henry's region) is limited by equilibrium pressures of 20 and 5 Torr for LiLSX and CaA, respectively. For this reason, we set the upper limit of ethane pressure at 20 Torr for LiLSX and at 5 Torr for CaA in the measurement of the adsorption kinetics of pure ethane and ethane mixed with hydrogen.

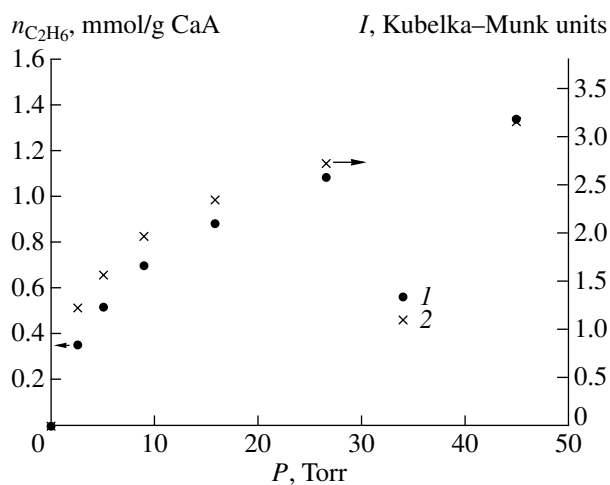


Fig. 2. Isotherms of ethane adsorption on zeolite CaA at room temperature from (1) volumetric and (2) diffuse reflectance IR spectroscopy data.

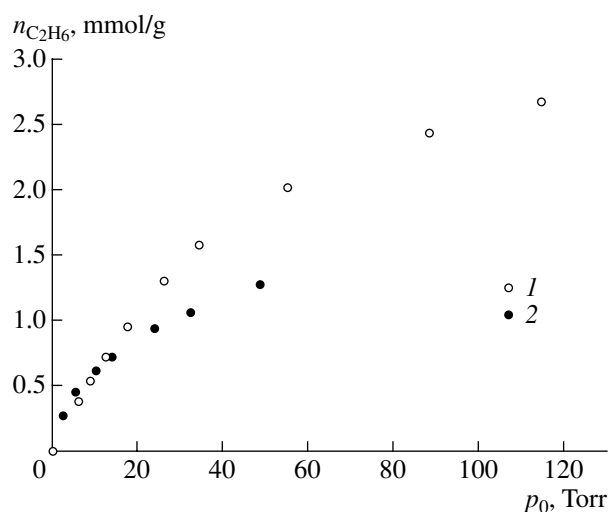


Fig. 3. Isotherms of ethane adsorption on zeolites (1) LiLSX and (2) CaA at room temperature from volumetric data.

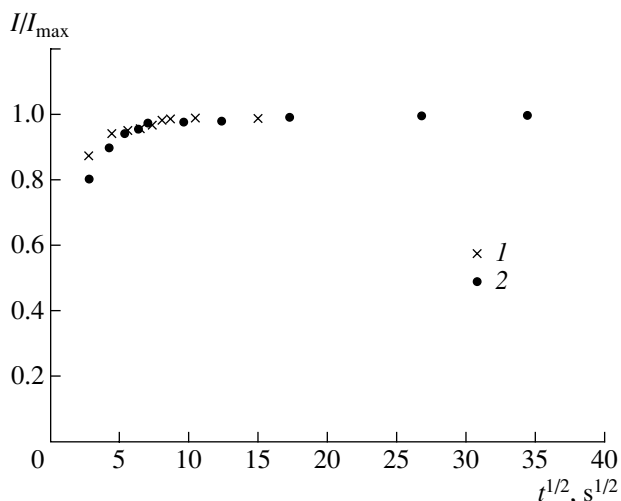


Fig. 4. Kinetics of the adsorption of pure ethane on granular zeolites (1) LiLSX and (2) CaA at room temperature.

The kinetics of the adsorption of pure ethane on the granular zeolites LiLSX and CaA at room temperature are illustrated in Fig. 4. Pure ethane is adsorbed rapidly on both zeolites, and the process is almost complete within 1 min. Since recording one diffuse reflectance spectrum takes ~8 s, the adsorption curve of pure ethane begins at a relative adsorption of 0.8 for CaA and ~0.9 for LiLSX. Therefore, it is difficult to quantitatively determine the initial amounts of pure ethane adsorbed at room temperature. At the same time, the results presented in Fig. 5 show that the rate of the diffusion-controlled adsorption of ethane from ethane-hydrogen mixtures on LiLSX zeolite is at least two

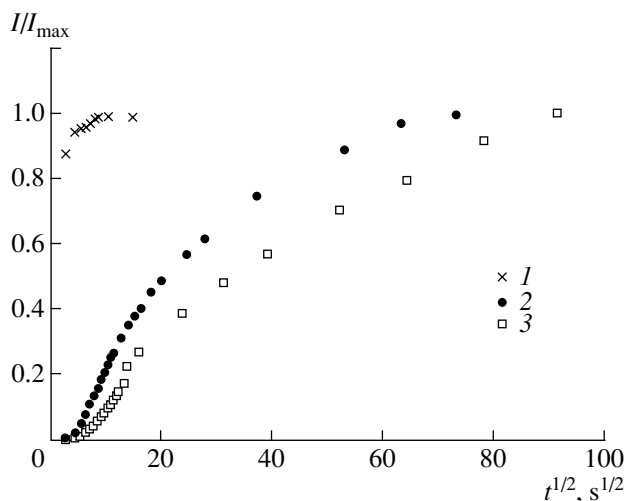


Fig. 5. Kinetics of ethane adsorption on granular zeolite LiLSX at room temperature for (1) pure ethane, (2) 50% C₂H₆ + 50% H₂, and (3) 25% C₂H₆ + 75% H₂.

orders of magnitude lower and depends on the hydrogen content of the mixture.

Unlike the adsorption of pure ethane, which is complete in less than 1 min (curve 1), ethane adsorption from ethane-hydrogen mixtures lasts for more than 1 h. The adsorption equilibration time lengthens with increasing hydrogen content of the mixture (curves 2, 3). The initial portions of the kinetic curves indicate that no absorption due to adsorbed ethane is observed at the initial time point, which is ~30 s after the beginning of the experiment. This is most likely to be due to the fact that the diffusion rate of dihydrogen in zeolite micropores is much higher than that of ethane.

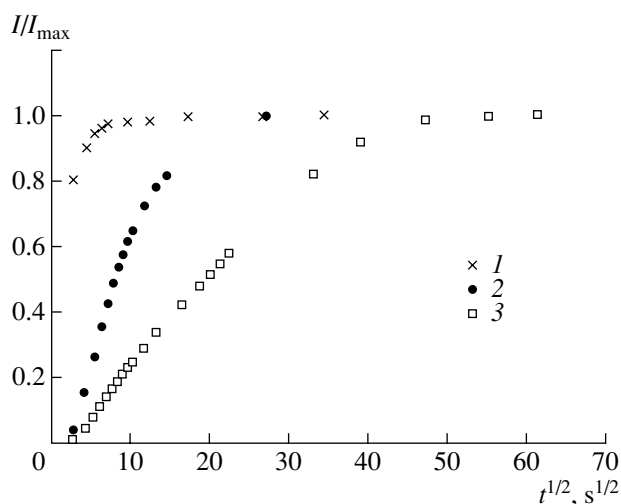


Fig. 6. Kinetics of ethane adsorption on granular zeolite CaA at room temperature for (1) pure ethane, (2) 95% C₂H₆ + 5% H₂, and (3) 50% C₂H₆ + 50% H₂.

The diffusion coefficient of hydrogen at room temperature is 3×10^{-8} m²/s [5] for zeolite NaA, which has a smaller pore diameter (4 Å) than zeolite LiLSX (7.4 Å). This value is one order of magnitude larger than the diffusion coefficient of ethane in zeolite NaX with a window diameter of 7.4 Å (5×10^{-9} m²/s) [6]. Hydrogen is known to be virtually unadsorbable at room temperature. Therefore, the several-seconds delay in the appearance of the absorption bands of adsorbed ethane early in the run is most likely to be a consequence of the fact that hydrogen rapidly fills the internal zeolite pores. Ethane is adsorbed later, displacing hydrogen from the zeolite micropores. Ethane and hydrogen interdiffuse in opposite directions, strongly retarding ethane adsorption.

The retardation of the diffusion of ethane mixed with hydrogen is also observed for granular zeolite CaA (Fig. 6). Even a small amount of hydrogen (5%) noticeably decreases the rate of ethane adsorption. As a consequence, unlike pure ethane (Fig. 6, curve 1), ethane–hydrogen mixtures allow the spectroscopic observation of the early stages of adsorption (Fig. 6, curve 2).

The retardation of ethane diffusion by hydrogen can take place both in primary (intracrystallite) and secondary (intercrystallite) zeolite pores. To distinguish between these effects, we compared the kinetics of the adsorption of ethane from a hydrogen-rich mixture (25% C₂H₆ + 75% H₂) on zeolite LiLSX as granules and a thin pellet (Fig. 7).

Ethane adsorption from this mixture on the thin pellet is rapid and is complete as soon as 2.5 min after the beginning of the run (Fig. 7, curve 1). This process takes more than 2 h (Fig. 7, curve 2) for the granular sample with a granule size of 0.5–1 mm and a layer height of about 20 mm. Since the sizes of microcrystals

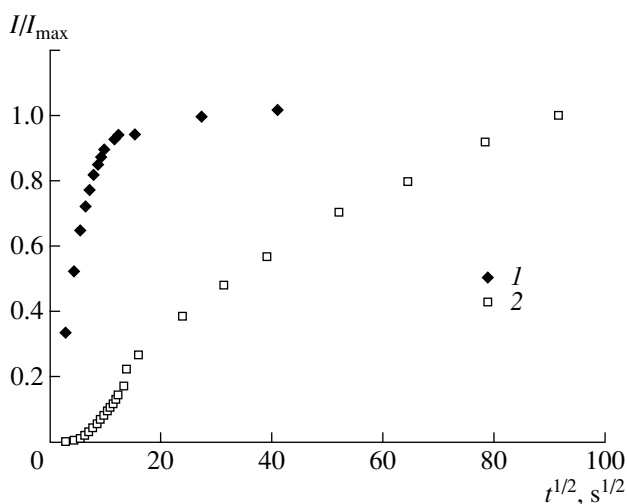


Fig. 7. Kinetics of the adsorption of the mixture 25% C₂H₆ + 75% H₂ on (1) pellets and (2) granules of zeolite LiLSX at room temperature.

and micropores are the same in these LiLSX samples, it is evident that the diffusion resistance inside the zeolite microcrystals is the same for the granules and the pellet. For the transport of a mixture, the difference is that the number of micropores in the granular sample is much larger than that in the pellet. Furthermore, in the pellet, ethane is transferred into micropores simultaneously from two sides. Therefore, in the granular sample, the substance is transferred to the lower zeolite layers through secondary pores, whose number depends on the height of the zeolite layer. Thus, the lower rate of ethane adsorption on the granular samples observed for the ethane–hydrogen mixtures is mainly due to the counterdiffusion of ethane and hydrogen, which occurs in the secondary pores of the zeolite granules or between the granules.

The kinetics of ethane adsorption on granular CaA samples from the (50% C₂H₆ + 50% H₂) mixture are presented in Fig. 8. These curves were derived from the variation of the intensity of the 2858 cm⁻¹ band (curve 1) and from the pressure drop over the sample (volumetric data) (curve 2). The curves almost coincide. The slight discrepancy between the initial portions of the curves can be explained as follows. Since one IR spectrum is recorded for ~8 s and band intensity in the initial regions of the curves increases very rapidly, the band intensities measured early in the run correspond to some adsorption values averaged over the measurement period rather than to current adsorption values. This decreases the accuracy of the adsorption data measured early in the run. The accuracy of these measurements increases with decreasing adsorption rate. Thus, the satisfactory agreement between the spectroscopic and volumetric kinetic data for gas mixtures whose components differ markedly in terms of adsorption strengths suggests that the adsorption kinetics of such mixtures

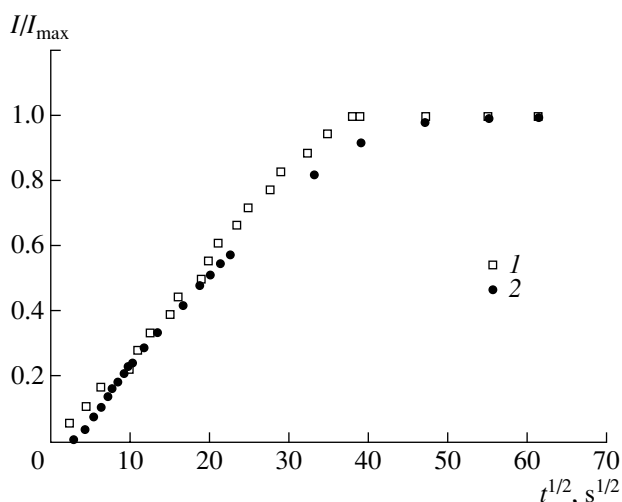


Fig. 8. Kinetics of the adsorption of the mixture 50% C_2H_6 + 50% H_2 on granulated zeolite CaA at room temperature from (1) pressure drop and (2) diffuse reflectance IR spectroscopic data.

can be measured with a sufficient accuracy by the volumetric method as well.

CONCLUSIONS

In this work, we have demonstrated the successful application of a new approach to the study of the diffusion-controlled kinetics of the adsorption of gas mixtures on microporous materials. The evolution of absorption bands absent from the IR spectrum of gas-

eous molecules makes it possible to measure the kinetics of ethane adsorption from ethane–hydrogen mixtures with different compositions. The rate of ethane sorption from ethane–hydrogen mixtures on granular zeolites LiLSX and CaA is almost 100 times lower than the adsorption rate of pure ethane and decreases with increasing hydrogen content of the gas mixture.

Comparison of equilibration rate data for the adsorption of a hydrogen-rich mixture on a granulated sample and a thin pellet of LiLSX has demonstrated that the main contribution to the retardation of ethane adsorption on the granulated sample is from the counterdiffusion of ethane and hydrogen in the secondary zeolite pores. It has been demonstrated using the adsorption of the 50% C_2H_6 + 50% H_2 mixture on zeolite CaA as an example that the kinetics of the adsorption of gases with very different adsorption properties from their mixtures can be studied by the volumetric method.

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