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DRIFTS Study of Kinetics of Diffusion-Limited Adsorption of Ethane from Mixtures with Hydrogen by Cationic Forms of Zeolites*

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Abstract. The diffusion-limited adsorption of individual ethane or of ethane from mixtures with hydrogen by thin pellets of NaA, CaA and LiLSX zeolites or by thick layers of granulated zeolites was studied at room temperature. The rates of adsorption were monitored by development of the bands from the symmetry forbidden C—H stretching vibrations that were not observed for gaseous molecules. Diffusivity of individual ethane in the micropores of the thin NaA pellet obtained by this method is equal to $6 \cdot 10^{-16}$ m^2/s. This value agrees well with that one previously reported in literature. For adsorption of pure ethane in the larger primary micro pores of CaA or LiLSX only the lower limits of diffusivities were estimated. Diffusion-limited adsorption of ethane from mixtures with hydrogen by the thicker layers of granulated zeolites is much slower and is limited by counterdiffusion inside much larger channels between the zeolite granules. Estimation of diffusion coefficients of such counterdiffusion indicated that they are by two orders of magnitude lower than those for diffusion in gaseous mixtures of similar composition.

Keywords: DRIFTS, diffusion, ethane-hydrogen mixtures, zeolites

Introduction

Due to unique molecular-sieving properties, zeolites found a wide application for separation and purification of mixtures of gases or liquids by sorption and as catalysts of different chemical reactions. Most of such processes involve transport of reactants in micropores inside zeolite microcrystals or their aggregates. Therefore, detailed understanding of complex diffusion behavior of reactants inside micro- or secondary macropores of zeolites or other highly dispersed materials is of a decisive importance for development and optimization of catalytic and adsorption processes.

In our previous paper (Kazansky et al., 2004) we studied nitrogen diffusion in nitrogen-oxygen mixtures (O_2-VSA-process) in granulated zeolites by means of DRIFT spectroscopy. Advantages of DRIFTS in comparison with transmittance technique consist in ability to study diffusion process in thick zeolite layers and possibility of parallel volumetric measurements. This method is based on the property of symmetrical molecules to become IR-active due to polarization resulting from adsorption. Kinetics of the diffusion—limited adsorption of nitrogen was followed in this study by the time evolution of IR bands from the stretching $N = N$ vibrations. Using this approach, we concluded that the limiting step of nitrogen transport in the nitrogen-oxygen mixtures is connected with diffusion limitations inside macropores between the primary zeolite microparticles or in the channels between zeolite granules.

Many chemical reactions catalyzed by zeolites or by other highly dispersed heterogeneous catalysts also involve diffusion—limited transport of reactants or final products. Among them catalytic reactions of hydrocarbons are most interesting due to their practical importance and to the broad variety of different sizes of hydrocarbon molecules. Therefore, below we applied the similar approach to the study of diffusion-limited adsorption by cationic forms of zeolites of pure ethane and of ethane from mixtures with hydrogen. This choice

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*This paper is dedicated to the memory of Professor Wolfgang Schirmer.

was connected with numerous examples when catalytic transformations of hydrocarbons in mixtures with hydrogen, such as hydrocracking, hydroisomerization, hydrotreating etc., are of practical importance. As adsorbents we selected LiLSX, CaA and NaA zeolites with effective diameters of primary pores of 7.4, 5 or 4 Å, respectively. Kinetic diameter of ethane is equal to 3.8 Å, while that of hydrogen to 2.9 Å. This allowed penetration of both molecules inside even most narrow pores of NaA zeolite. Similar to the previous study (Kazansky et al., 2004), evolution of intensities of the symmetry-forbidden C—H stretching bands was monitored by DRIFTS measurements.

The zeolites under study were either pressed into thin semi-transparent pellets or were granulated into particles with dimensions of 0.5 ÷ 1 mm. In the first case the role of diffusion inside macropores between the primary zeolite microparticles was minimal, while diffusion in the channels between zeolite granules disappeared completely. In the second case adsorption by the granulated zeolites was carried out for the layers with the thickness of about two cm, while DRIFT spectra were measured at the bottom of the zeolite layers. Therefore, the diffusion-limited adsorption also involved the transport limitations inside macropores between the primary zeolite micro particles or in the gaseous phase in the channels between zeolite granules. Differences in adsorption rates by the thin pellets and by the very much thicker zeolite layers allowed discrimination between different steps of the diffusion—limited adsorption of pure ethane or of ethane adsorption from mixtures with hydrogen.

Experimental

The LiLSX zeolite sample under study was obtained from M. Bülow, BOC. It has a Si/Al ratio ~1.05, the extent of Na cation substitution by those of Li is close to 100%, and the average diameter of primary zeolite microparticles ~1÷ 3 μm. CaA zeolite also had the extent of sodium substitution by Ca close to 100%. The average diameter of the primary zeolite microparticles both for CaA and for the home-made NaA was equal to about ~3 μm. All samples were binder-free.

The zeolites were either granulated and crashed with selection of the granules with the size of 0.5÷1 mm or pressed into thin semi-transparent pellets with density of 25 ÷ 30 mg/cm^2. Then they were pre-evacuated at 673 K for 4 hours in the quartz part of the optical cell that was subsequently used for DRIFTS measurements.

DRIFT spectra of adsorbed ethane were recorded at room temperature by means of Nicolet “Impact 410” spectrophotometer equipped with a home-built diffuse-reflectance attachment. The measurements were carried out in the presence of ethane or ethane-hydrogen mixtures over the samples. All DRIFT spectra were transformed into Kubelka-Munk units by a standard program within an assumption that the reflective ability of the samples at 5000 cm^{-1} was equal to 0.9 units. After that the backgrounds created by the zeolites were subtracted.

For the spectral study of ethane adsorption the zeolite granules or pellets were transferred after cooling to the room temperature into the side finger of the optical cell equipped with CaF$_2$ window. The height of the layers of the zeolite granules was ca. 20 mm, while the DRIFT spectra were measured at the bottom part of the layers. Dimensions of the thin pellets fitted the size of the CaF$_2$ window. The first IR-spectra were recorded immediately after inlet of ethane or ethane-hydrogen mixtures into the pre-evacuated optical cell with the zeolites. The number of scans was equal to 16 with spectral resolution of 4 cm^{-1}. Subsequent DRIFTS measurements were carried out with the different time intervals depending on sorption rates.

Ethane was purified before spectral measurements by freezing at liquid nitrogen temperature with subsequent triple vacuum distillation at slowly increasing temperature. Hydrogen was purified from oxygen and other impurities by passing through the reduced chromium adsorbent at room temperature. Isotherms of ethane adsorption at room temperature were measured by volumetric method from the calibrated volume by means of the “Piezovac PV 20” pressure gauge.

Similar to the previous study (Kazansky et al., 2004) and to the generally accepted procedure (Kärger and Ruthven, 1992), the results on kinetics of diffusion—limited adsorption were presented in I/I_∞ versus square root of time (sqr(t)) plots, where I—are intensities of the adsorption-induced DRIFT bands at different time intervals after beginning of an experiment and I_∞—are intensities of these bands at the adsorption equilibrium. These data were then used for calculation of diffusivities both of the pure ethane and of ethane in mixtures with hydrogen. For this purpose we utilized the initial slopes of kinetic curves and Eq. (1) where A is the surface area of a single zeolite microparticle and V is its volume (Breck, 1976):

$$\gamma = \frac{I_t}{I_\infty} \approx \frac{2A}{V}\left(\frac{Dt}{\pi}\right)^{1/2} \qquad (1)$$

A similar approach was also used for estimation of coefficients of counterdiffusion in the thick layers of the zeolite granules with the only difference that in this case A was the cross section of the layer of zeolite granules, while *V* was the volume of the granules.

Experimental Results

DRIFT spectra of ethane adsorbed by LiLSX and CaA zeolites are shown in Fig. 1. Both of them contain four C—H stretching bands instead of only two ν_7 and ν_{10} bands for gaseous ethane (Herzberg, 1947). Appearance for adsorbed ethane of ν_1 band at 2860–2870 cm^{-1} from the fully symmetrical C—H stretching vibrations is most important. Below we used development of this band as a measure of adsorption rate.

To check the validity of our spectral approach we started with comparison of the isotherm of ethane adsorption by CaA obtained by the conventional volumetric measurements with that one reconstructed from intensities of ν_1 C—H stretching band at different pressures. The corresponding results are shown in Fig. 2. They indicate that both isotherms are very close to each other, while the slightly higher values of adsorption obtained from the spectral measurements are most likely connected with not completely exact choice of reflecting ability of CaA that was used for the Kubelka-Munk transformation. The linear parts of isotherms correspond to the pressures below 1.33 kPa. Since application of Eq. (1) requires the low surface coverages, the subsequent experiments on the study of kinetics of ethane diffusion—limited adsorption were carried out below this limit.

The corresponding results on comparison of ethane adsorption by the thin pellet and the thick layer of NaA grains are shown in Fig. 3. In both cases the rates of adsorption are very close to each other. They indicate a similar origin of transport limitations. In other words, for NaA the transport limitations are connected with diffusion inside micro pores. Therefore, using the slope of the plot in Fig. 3 and Eq. (1) we calculated diffusivity of pure ethane inside micropores of NaA primary particles with dimensions of 3 mμ as equal to D $\approx 6 \cdot 10^{-16}$ m^2/s. This value well agrees with that one ($4.6 \cdot 10^{-16}$ m^2/s) measured by gravimetric uptake method, previously reported in Kondis, and Dranoff (1971). In addition, the results of Fig. 4 indicate that the rates of the diffusion—limited adsorption of pure ethane and of ethane from the mixtures with hydrogen of different compositions by the thin NaA pellet are also very close to each other. Thus, the presence in the C_2H_6—H_2 mixtures of hydrogen does not create any additional limitations for diffusion inside micro pores of the primary NaA microparticles.

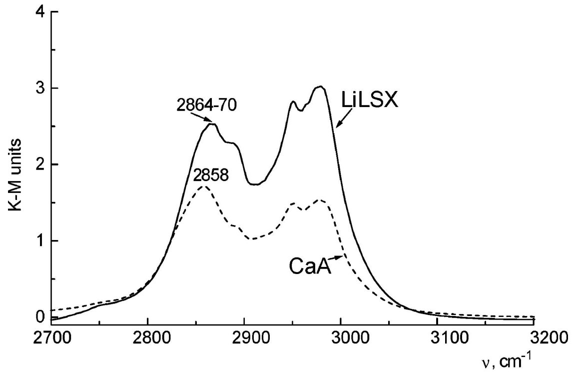

Figure 1. DRIFT spectra of ethane adsorbed by LiLSX or CaA zeolites at room temperature.

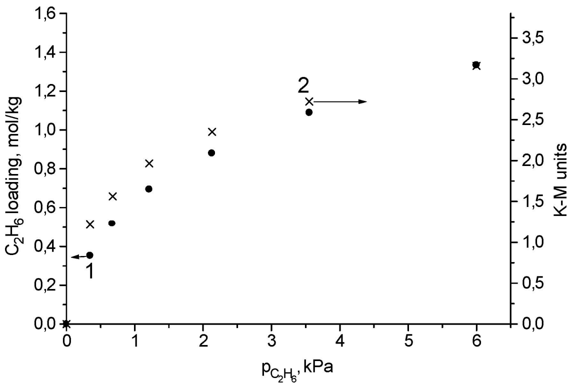

Figure 2. Comparison of isotherms of ethane adsorption on CaA zeolite at room temperature obtained by volumetric (1) and by DRIFT (2) methods.

As follows from Fig. 5, this situation is different for ethane adsorption by the much thicker layer of NaA granules from the very strongly enriched in hydrogen mixture. The much slower adsorption rate obviously indicates existence of some additional transport limitations created by the presence of hydrogen inside the channels between NaA granules.

Results on diffusion—limited adsorption of ethane by CaA are shown in Figs. 6–8. Comparison of kinetic curves (a) and (b) in the first of these figures indicates that the rate of diffusion—limited adsorption of pure ethane by the thin pellet of the former zeolite is much higher than in the latter. This is certainly connected with the larger micropore size in CaA of 5 Å in comparison with only 4 Å for NaA. For CaA adsorption was

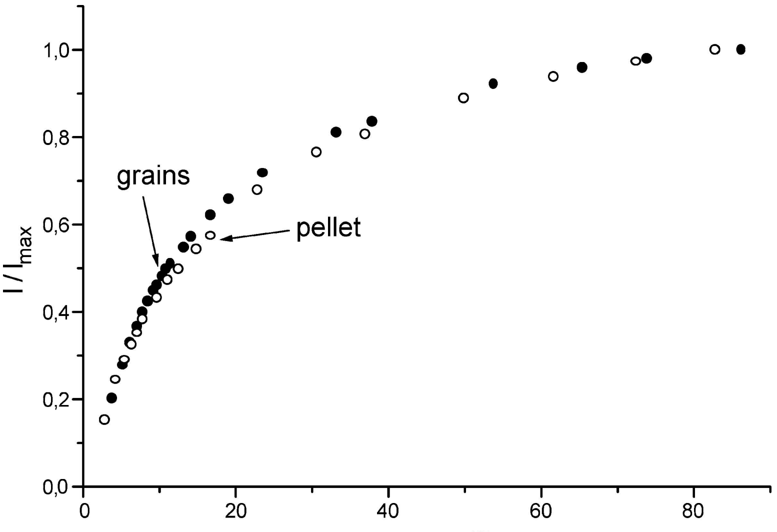

Figure 3. Kinetics of diffusion—limited adsorption of pure ethane by the thin NaA pellet (open circles) or by the thick layer of the granulated zeolite (black circles).

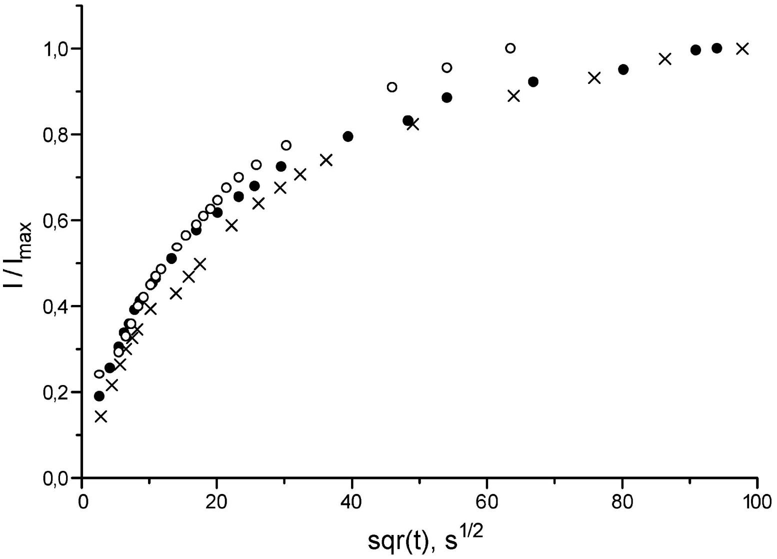

Figure 4. Kinetics of diffusion–limited adsorption of ethane by the thin NaA pellet: the open circles—adsorption of pure ethane; crosses—adsorption of ethane from the 95% C_2H_6 + 5% H_2 mixture; black circles adsorption from the 50% C_2H_6 + 50% H_2 mixture. Partial pressure of ethane was equal to 0.67 kPa.

probably even too fast for proper DRIFTS measurements. Indeed, the I/I_∞ value of the first point in Fig. 6 (a) is already as high as 0.8. In addition, recording of the first DRIFT spectrum required 16 scans. Therefore, this point corresponds to some average value within 10 first seconds after beginning of the experiment, while the diffusivity of pure ethane in CaA $D \sim 10^{-14}$ m^2/s estimated from this point corresponds only to the lowest limit of the real value. Anyway, in accordance with the larger micropore size, diffusivity of pure ethane in CaA is more than by one order of magnitude higher than in NaA.

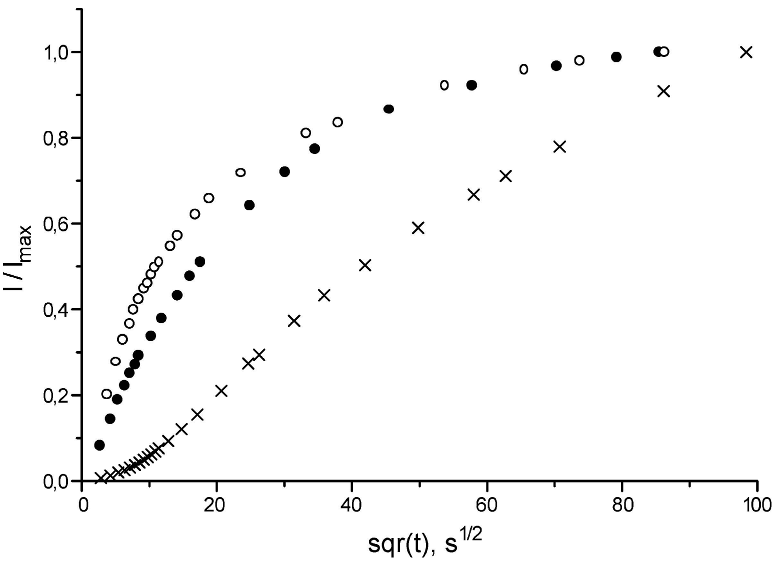

Figure 5. Kinetics of diffusion—limited adsorption of ethane at room temperature by the thick layer of NaA grains: open circles—adsorption of pure ethane; black circles—adsorption of ethane from the 50% C_2H_6 + 50% H_2 mixture; crosses—adsorption of ethane from the 2% C_2H_6 + 98% H_2 mixture. Partial pressure of ethane was equal to 0.67 kPa.

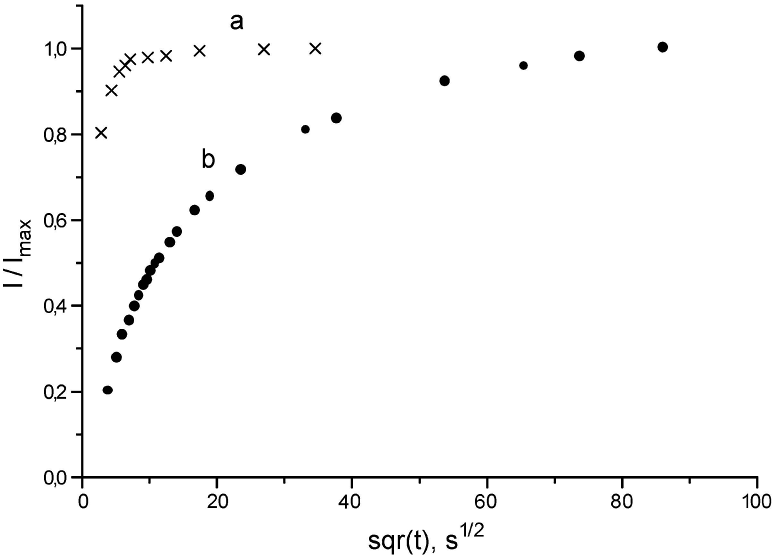

Figure 6. Kinetics of diffusion—limited adsorption of pure ethane by the thin CaA pellet (a) and by the NaA pellet (b). Partial pressure of ethane was equal to 0.67 kPa.

Results on diffusion—limited adsorption of ethane from mixtures with hydrogen by the thin pellet of CaA are shown in Fig. 7. Similar to adsorption of pure ethane, the rate of ethane adsorption by CaA in the presence of hydrogen is also faster than by NaA. However, for CaA it decreased in the hydrogen-rich mixtures much stronger. This indicates the stronger hindering influence of hydrogen inside the broader micropores of CaA.

As follows from Fig. 8, diffusion-limited adsorption of ethane from ethane—hydrogen mixtures by the thicker layer of the CaA granules was also considerably slower than by the thin pellet. Similar to the granulated NaA, this also indicates additional transport limitations

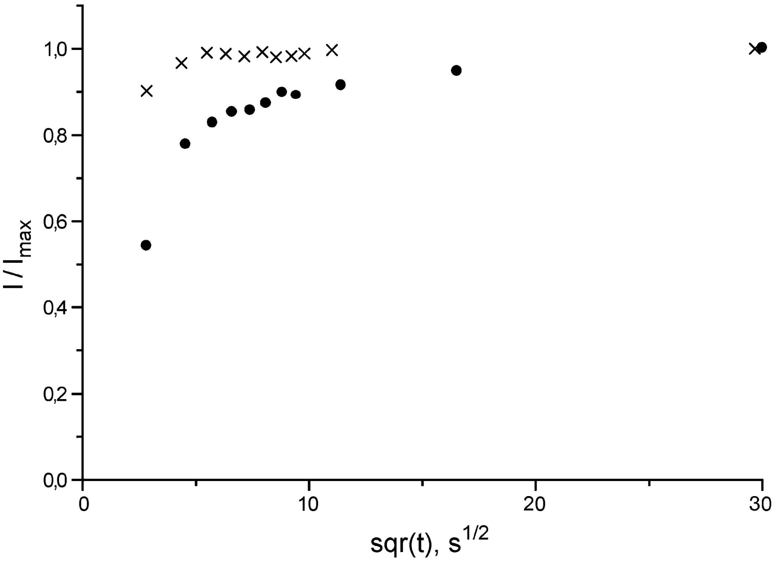

Figure 7. Kinetics of diffusion—limited adsorption by the thin pellet of CaA of ethane from the mixtures of the following compositions: 80% C_2H_6 + 20% H_2 (crosses) or 20% C_2H_6 + 80% H_2 (black circles). Partial pressures of ethane were equal to 0.67 or 0.17 kPa respectively.

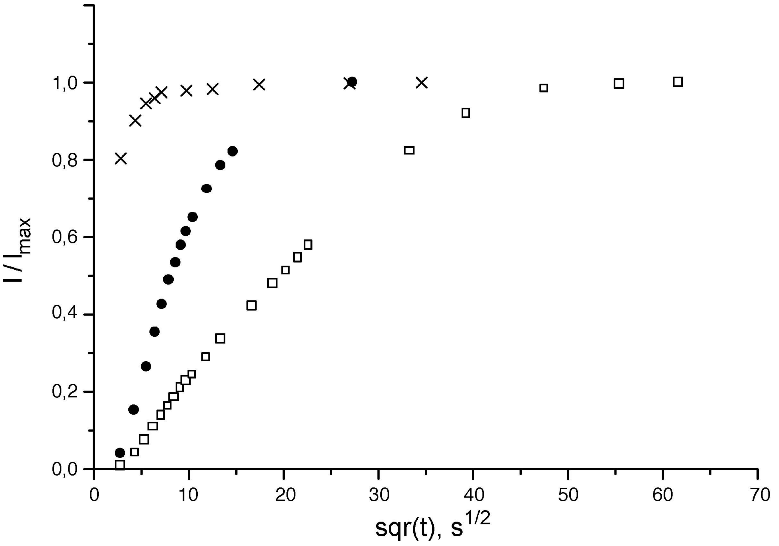

Figure 8. Kinetics of diffusion—limited adsorption of pure ethane by the thick layer of CaA grains (crosses) or of ethane from ethane-hydrogen mixtures of the following compositions: black circles—the 95% C_2H_6 + 5% H_2 mixture; open squares—50% C_2H_6 + 50% H_2 mixture. Partial pressures of ethane were equal to 0.67 kPa.

created by the presence of hydrogen in the channels between the zeolite granules.

Results on ethane adsorption by LiLSX zeolite are essentially similar to those for CaA. In accordance with even larger micropore diameter of 7.5 Å, the rate of the diffusion—limited adsorption of pure ethane was also too fast for the proper DRIFTS measurements. On the other hand, similar to CaA, ethane adsorption from ethane–hydrogen mixtures both by the thin LiLSX pellet and by the much thicker layer of zeolite granules were much slower than for the pure ethane. (Compare in this connection Figs. 9 and 10). Therefore, for LiLSX the rates of the diffusion limited adsorption of ethane from the mixtures with hydrogen were also measured quite properly.

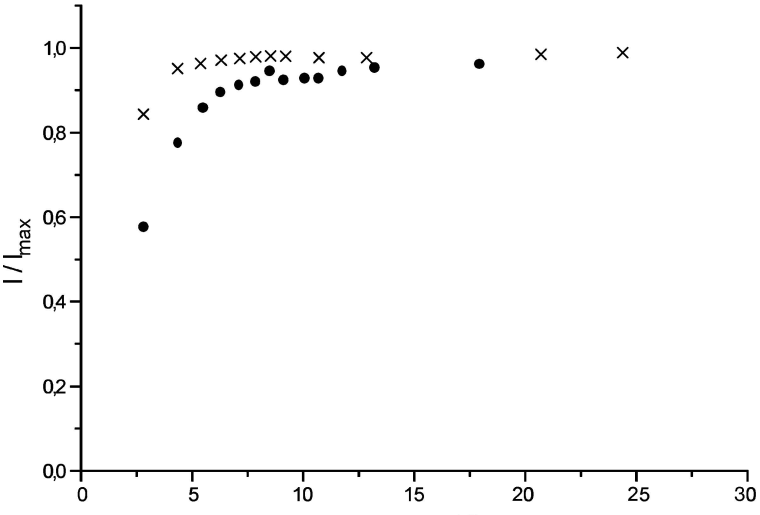

Figure 9. Kinetics of diffusion—limited adsorption of ethane by the thin pellet of LiLSX zeolite from ethane-hydrogen mixtures of different compositions: crosses the 80% C_2H_6 + 20% H_2 mixture; black circles—the 20% C_2H_6 + 80% H_2 mixture. Partial pressures of ethane were equal to 2.1 and 0.53 kPa respectively.

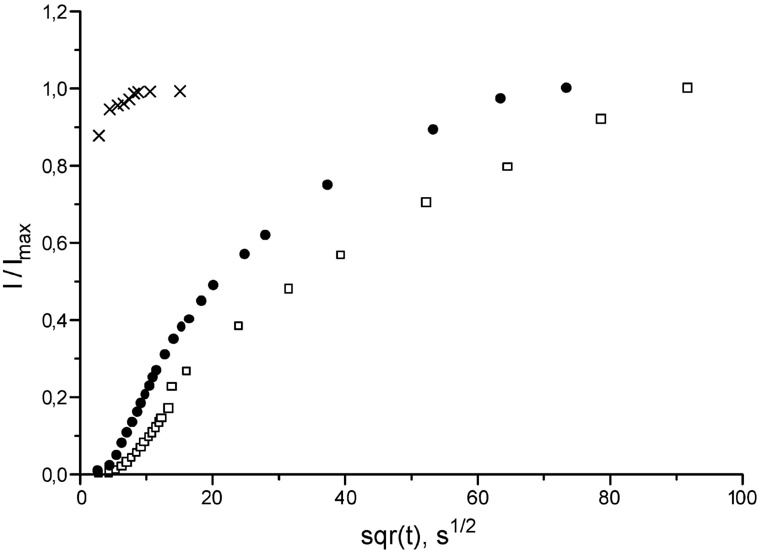

Figure 10. Kinetics of diffusion—limited adsorption by thick layer of LiLSX grains of pure ethane (crosses) or of ethane from ethane-hydrogen mixtures of different compositions: black circles—the 50% C_2H_6 + 50% H_2 mixture; open squares 25% C_2H_6 + 75% H_2 mixture. Partial pressures of ethane were equal to 2.66 kPa.

Despite large difference in the micropore sizes, the close rates of ethane adsorption from the 50% C_2H_6 + 50% H_2 mixtures by the thick layers of NaA, CaA or LiLSX grains in Figs. 5, 8 and 10 are quite remarkable. This definitely indicates existence for all of these zeolites of similar transport limitations connected with ethane diffusion in the ethane—hydrogen gaseous mixtures inside broader channels between the zeolite granules.

Discussion

The granulated zeolites under the study contain two different kinds of particles:

(i) The small primary microparticles with dimensions of ca. 3 mμ for NaA and CaA or about 1÷3 μm for LiLSX.

(ii) The much bigger granules with dimensions of 0.5 ÷ 1 mm pressed from the zeolite powder. Therefore, the porous structure of the granulated zeolites is the following:

(i) Inside primary microparticles they contain narrow windows with molecular sieving properties with diameters of 4 Å, 5 Å or 7.5 Å for NaA, CaA or LiLSX respectively.

(ii) Diameters of macropores between the primary zeolite microparticles are much larger. They are comparable with those of the microparticles i.e. are equal to several μm.

(iii) The very much larger channels between the zeolite granules also have dimensions comparable with those of the granules, i.e. of about 0.5 ÷ 1 mm.

In accordance with such porous structure, ethane diffusion in the granulated zeolites should be described by three different diffusion coefficients that correspond to the different pore sizes and different mechanisms of diffusion. Diffusivity of pure ethane in the narrow micropores with dimensions of $4 \cdot 10^{-8}$ cm of NaA was experimentally detected as equal to $6 \cdot 10^{-16}$ m^2/s. For CaA or LiLSX, the micropore sizes are larger. Therefore only the lowest limits of diffusivity were estimated. The corresponding Figures are collected in Table 1.

At pressures below ~1.33 kPa ethane transport in the larger macropores between primary zeolite microparticles with diameter of ~10^{-4} cm most likely corresponds to the Knudsen diffusion with D ~ $3 \cdot 10^{-4}$ m^2/s that was estimated from the following well-known expression (Kärger and Ruthven, 1992):

$$D = 9700\, r\, (T/M)^{0.5} \quad (2)$$

Herein, r is the pore radius and M the molecular weight of ethane. The coefficient of molecular diffusion about 10^{-5} m^2/s at higher pressures should be similar to that one for the gaseous molecules. The diffusivities of ethane and hydrogen inside the channels between much larger zeolite granules should be also similar to those in the gas phase.

Using these diffusion coefficients, and Eq. (3) for the Random-walk model of diffusion

$$\tau \sim x^2/D \quad (3)$$

(where τ—is the time required for the diffusion–limited adsorption by the micro or macroparticles; x—are dimensions of the particles or the length of channels between the granules if diffusion takes place in the gas inside the channels; D—is the diffusion coefficient), we estimated the following characteristic times for different rate—limiting steps of diffusion-limited adsorption by the thick layers of granulated zeolites.

For the Knudsen or molecular diffusion-limited adsorption by the aggregates of primary microparticles with dimensions of ~1 mm this time is equal to $\tau \approx 10^{-2}$ s. The characteristic time of molecular

Table 1. Diffusivities of pure ethane and of ethane in ethane—hydrogen mixtures of different compositions in the thin pellets of different zeolites.

The zeolite	Diameter of windows (Å)	Compositions of gaseous mixtures	D (m^2/s)	The times of diffusion-limited adsorption by the zeolite pellets
NaA	4	C_2H_6	$6 \cdot 10^{-16}$	10^2 s
		95% C_2H_6 + 5% H_2	$6 \cdot 10^{-16}$	
		50% C_2H_6 + 50% H_2	$6 \cdot 10^{-16}$	
CaA	5	C_2H_6	$\geq 10^{-14}$	≤ 10 s
		80% C_2H_6 + 20% H_2	$2 \cdot 10^{-14}$	
		20% C_2H_6 + 80% H_2	$0.6 \cdot 10^{-14}$	
LiLSX	7.4	C_2H_6	$\geq 10^{-14}$	≤ 10 s
		80% C_2H_6 + 20% H_2	$0.8 \cdot 10^{-14}$	
		20% C_2H_6 + 80% H_2	$0.3 \cdot 10^{-14}$	

diffusion of ethane in the gas phase between the zeolite granules of $\tau \sim 40$ s in the layer with the thickness of 2 cm is very much longer. Hence, diffusion limitations never arise in the macropores between primary zeolite microparticles. Instead they may be connected either with diffusion limitations inside micropores or in the gas phase in the channels between the zeolite granules.

This conclusion is well consistent with the experimentally detected characteristic time of $\tau \sim 50$ s for the diffusion-limited adsorption of pure ethane by primary microparticles in the thin NaA pellet. For this zeolite the rates of adsorption by the thick layer of granules and by the thin pellet are practically equal to each other (Fig. 3). This indicates the absence of additional diffusion limitations inside the channels between the granules with the only exception of the very strongly enriched in hydrogen mixture.

Diffusion inside larger primary micropores of CaA or LiLSX is qicker. Therefore, for these zeolites the rate-limiting step is different. Instead of ethane diffusion in the primary micropores it corresponds to the transport limitations in the gas mixture in the channels between the zeolite granules. This conclusion is supported by close adsorption rates of ethane for all three granulated zeolites from mixtures of similar composition. (Compare in this connection kinetics of ethane adsorption from the 50% H_2 + 50% C_2H_6 mixture by the granulated NaA, CaA and LiLSX zeolites in Fig. 5, 8 and 10). The similar conclusion also follows from the close values of diffusivities for the granulated zeolites with the thickness of the layers of 2 cm in Table 2. The corresponding diffusion coefficients differ only within one order of magnitude. It is also quite remarkable that the diffusivities in the channels of granulated zeolites are by 2–3 orders of magnitude lower than those in ethane-hydrogen gaseous mixtures (10^{-6}–10^{-7} m^2/s instead of $\sim 10^{-4}$–10^{-5} m^2 /s). Such difference is connected with different mechanisms of diffusion-limited mixing of ethane with hydrogen in the gas phase and of the counterdiffusion in the similar mixtures inside the cannels between the zeolite granules.

Table 2. Coefficients of counterdiffusion in ethane—hydrogen mixtures of different compositions in the channels between granules of the thick layers of different zeolites.

The zeolite	Diameter of windows (Å)	Compositions of gaseous mixtures	D (m^2/s)
NaA	4	50% C_2H_6 + 50% H_2	$4 \cdot 10^{-7}$
		2% C_2H_6 + 98% H_2	$0.7 \cdot 10^{-7}$
CaA	5	95% C_2H_6 + 5% H_2	$2 \cdot 10^{-6}$
		50% C_2H_6 + 50% H_2	$3 \cdot 10^{-7}$
LiLSX	7.4	50% C_2H_6 + 50% H_2	$4 \cdot 10^{-7}$
		25% C_2H_6 + 75% H_2	$1.5 \cdot 10^{-7}$

Indeed, due to the higher diffusivity of hydrogen, ethane adsorption by the granulated zeolites from H_2 + C_2H_6 mixtures with hydrogen starts with fast filling of internal micro and macro pores with hydrogen. The rate of subsequent adsorption is limited by replacement of hydrogen by ethane via counterdiffusion. The latter is much slower than the diffusion-limited ethane-hydrogen mixing in the gas phase. Another difference with the gaseous mixtures is the slower counterdiffusion at higher hydrogen contents, while due to higher diffusivity of hydrogen, the rate of ethane-hydrogen mixing in the gas phase is increasing. Counterdiffusion also results in appearance of induction periods for ethane adsorption that are connected with initial strong enriched of internal zeolite micropores with hydrogen (Figs. 5, 8 and 10).

Conclusion

DRIFT spectroscopy that has been earlier applied to the study of the diffusion—limited adsorption by zeolites of nitrogen was successively used for the similar study of adsorption of ethane as a simplest hydrocarbon. It was concluded that the rate of adsorption of pure ethane by NaA is limited by the transport phenomena inside the narrow internal micropores of this zeolite. The obtained value of diffusivity of $6 \cdot 10^{-16}$ m^2/s well agrees with that one previously reported in literature. For diffusivity of pure ethane in the larger primary micropores of CaA and LiLSX zeolites only the lowest limits of diffusivities were estimated.

It was also concluded that the rate of ethane adsorption from mixtures with hydrogen by the much thicker layers of granulated zeolites is controlled by the counterdiffusion in ethane-hydrogen gaseous mixtures that fill the channels between the zeolite granules. The corresponding diffusivities are by 3–4 orders of magnitude lower than for diffusion in ethane-hydrogen gaseous mixtures of similar composition. In addition, unlike gaseous mixtures, the coefficients of ethane counterdiffusion decreased at higher hydrogen contents. Counterdiffusion also results in appearance of induction periods for ethane adsorption.

Acknowledgments

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