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STUDIES OF PHYSICO-CHEMICAL PROPERTIES OF MIXED ADSORBENT IN THE ZEOLITE/SiO_2 SYSTEM

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The paper presents physico-chemical properties of mixed adsorbents in the clinoptylolite (mordenite)/SiO_2 system containing 30, 50, 80 mass% zeolite. Adsorption capacity towards polar (water, butanol) and non-polar (*n*-octane) substances as well as total surface heterogeneity (energetic and geometrical) were determined. Desorption energy distribution functions as well as fractal dimensions were also determined and compared with the low-temperature nitrogen adsorption data. Irregular shapes of the curves $q=f(E_d)$ as well as large values of volumetric fractal dimensions (D_f~2.6) revealed heterogeneous properties of the zeolite/SiO_2 system surfaces. Addition of zeolite increases total heterogeneity of the material.

Keywords: *energy distribution functions, fractal dimension, total heterogeneity, zeolite*

Introduction

Zeolites, aluminium oxides and silica gels are adsorbents widely applied in industry [1–4], environment protection [5–7], agriculture [8–10], medicine, optics, microelectronics and many other fields. Molecular sieve properties and high resistance to acid action are responsible for the fact that zeolites are used as catalysts. They find application in petrochemical industry in cracking [11], hydrocracking, isomerization and other processes. Zeolite catalysts are characterized by high activity, good selectivity, stability and capability of multiple regeneration. Zeolites are characterized by high ion exchange selectivity towards ^{137}Cs and ^{90}Sr as well as other radioactive elements [12–16, 23]. They are also used for purification of water and waste water containing heavy metal salts [5–7]. Ion exchange is the process most frequently applied for removal of these compounds on zeolites. In this process clinoptylolite, which, due to its properties, can be used not only for purification of waste water [17] but also for recovery of metals [18–22] found the widest applications. Owing to its large adsorption capacities towards vapours and gases it is used in environment protection to remove toxic gases, among others, SO_2, H_2S, NH_3, N_xO_y, Cl_2 and others from the atmosphere. To use them in practice, one must be familiar with physico-chemical properties of their surfaces. The properties of individual compounds are often examined. However, papers dealing with properties of mixed adsorbents are scarce in the literature. Porosity is one of the most important characteristics considered in determination of solid surface properties. Specific surface area, average pore radius and total pore volume have a significant effect on physico-chemical processes on the solid surface. Surface properties can be modified using high temperature or chemical modification. Thermal analysis is one of the methods used in determination of surface heterogeneity and adsorption properties. The paper presents determination of adsorption properties and functions of liquid desorption energy distribution mixed mesoporous adsorbent surfaces in the zeolite/SiO_2 system from the single curves of programmed thermodesorption under quasi-isothermal conditions Q-TG and Q-DTG [24–26].

Experimental

Materials

The following zeolites were used in these studies: mordenite (MN-369-2M), *trans*-carpation clinoptylolite and silica gel (Merck). The solvents of analytical purity, 1-butanol, *n*-octane (POCH Gliwice, Poland) and redistilled water were used.

Sample preparation

Ground zeolite (fraction >0.088 mm) was mixed with disintegrated silica in definite mass ratios; in which

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zeolite constituted 30, 50, 80% mixture. Then redistilled water was added and homogenized until a gel-like mass was obtained which was dehydrated and dried at 200°C for 2 h.

Measuring methods

Thermodesorption of polar (water, 1-butanol) and non-polar (*n*-octane) liquids from the synthesized material surfaces was made using a derivatograph of Q-1500D type (MOM, Hungary). The samples were dried at 200°C for 10 h to remove water. Then they were saturated with liquid vapours in a vacuum desiccator where $p/p_0=1$ for 30 h to establish liquid adsorption equilibrium.

Zeolite samples were moved into the measuring crucible placed in the derivatograph furnace and 3 measurements were made in the temperature range 20–250°C with the heating rate 6°C min^{-1}. The measurements closest to the average value were taken for calculations.

From the low-temperature nitrogen adsorption (sorptomat ASAP 2405 V1.01) specific surface areas and pore volume were determined and then fractal dimensions were calculated. Adsorption capacity and total surface heterogeneity of the studied samples were determined from the above mentioned experimental data.

Results and discussion

Catalytic and adsorption properties of materials depend on porosity and energetic heterogeneity of the surface. Composition change of one component results in the change of a number of active centres on the surface and affects the system geometry. The porosity parameters of the samples were determined from the nitrogen adsorption–desorption isotherms and are shown in Table 1.

Increase in the percentage content of zeolite in the sample mass results in decreasing specific surface area (S_{BET}) in the range 323–27.8 for for clinoptylolite and 323–27.6 $\text{m}^2\ \text{g}^{-1}$ for mordenite (Table 1). Increasing concentration of zeolite results in pore volume decrease in both cases (Fig. 1) and in insignificant changes of pore radius (Table 1). From the nitrogen adsorption–desorption isotherms fractal dimensions were calculated using the methods based on the theories by Frankel, Halsey and Hill as well as Kiselev from the following equations [27–30] and compared in Table 1:

$$D_{\text{f}}=2+\frac{\text{d}\left[\ln\int_{\text{a}}(-\ln x)\text{d}a\right]}{\text{d}[\ln(-\ln x)]} \tag{1}$$

$$D_{\text{f p}}=3-\text{d}[\ln a(x)]/\text{d}[\ln(\ln x)] \tag{2}$$

where a is the adsorption quantity, $x=p/p_0$.

The values of volumetric fractal dimension change in the range 2.5–2.7 and provide evidence for heterogeneous pore distribution. With increasing value of D_{f}, the relative contribution of the pores having the value close to the maximum increases and thus the sample heterogeneity increases.

The statistical number of liquid monolayers on the surface of the studied mixed adsorbents given in Table 2 was calculated from the Q-TG and Q-DTG curves in Fig. 2.

Figure 3 presents the curves of adsorption capacity as function of percentage content of zeolite in the sample. The curves $a=f$ (% of zeolite) are similar in both cases. Adsorption capacity decreases with the increasing concentration of zeolite due to the decrease in the adsorbent specific surface area; this is largest for water.

Figure 4 presents the dependence of statistical number of monolayers as a function of zeolite concentration. With increasing amount of zeolite in the sample there is observed a sudden increase of monolayer number for the water adsorption 6–44 for

Table 1 Adsorption and structural parameters of the mixed mesoporous adsorbent in the zeolite/SiO_2 system determined from the nitrogen adsorption isotherms

Zeolite/%	$S_{\text{BET}}/\text{m}^2\ \text{g}^{-1}$	$S_{\text{MIC}}/\text{m}^2\ \text{g}^{-1}$	$V_{\text{BJH ADS}}/\text{cm}^3\ \text{g}^{-1}$	$V_{\text{BJH DES}}/\text{cm}^3\ \text{g}^{-1}$	$V_{\text{MIC}}/\text{cm}^3\ \text{g}^{-1}$	D_{AV}/nm	D_{f}
			clinoptylolite				
100	27.8	3.7	0.11	0.11	0.0016	13.01	2.63
80	59.1	2.7	0.26	0.26	0.001	13.71	2.63
50	137.1	–	0.53	0.52	–	12.63	–
30	145.1	10.1	0.65	0.64	0.0037	12.92	2.61
			mordenite				
100	27.6	2.93	0.08	0.09	0.0012	10.97	2.67
80	91.2	–	0.19	0.23	–	8.57	2.64
30	116.9	2.57	0.56	0.54	–	14.98	2.62
SiO_2	323.1	0.39	0.94	0.84	–	9.23	2.51

S_{BET} – specific surface area, S_{MIC} – micropore area, V_{BJH} – pore volume, V_{MIC} – micropore volume, D_{AV} – average pore diameter, D_{f} – volumetric fractal dimension.

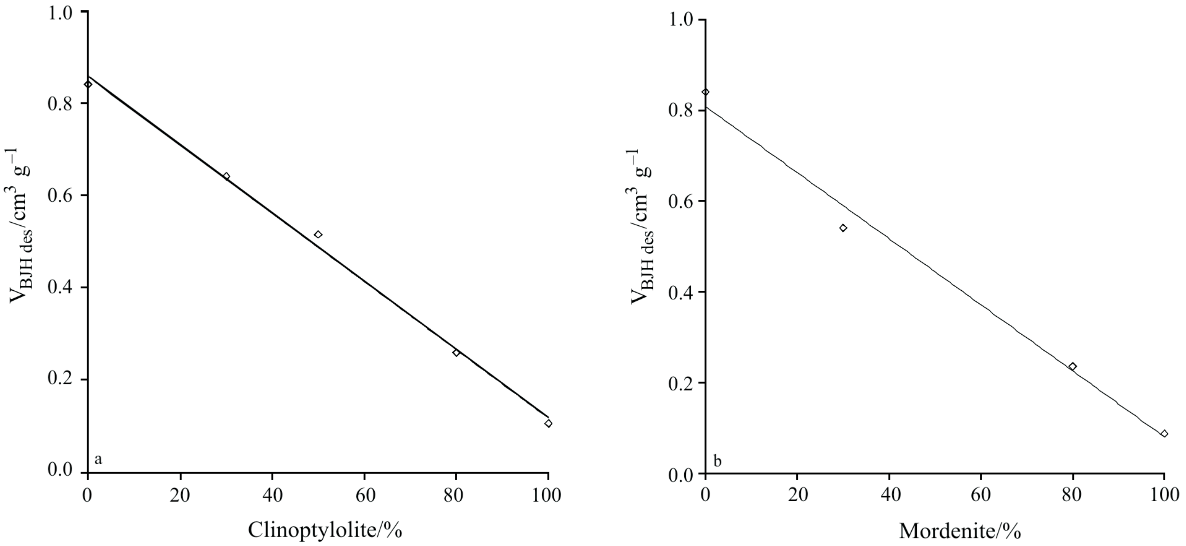

Fig. 1 The dependency of pore volume on the percentage content of a – clynoptylolite and b – mordenite in the samples

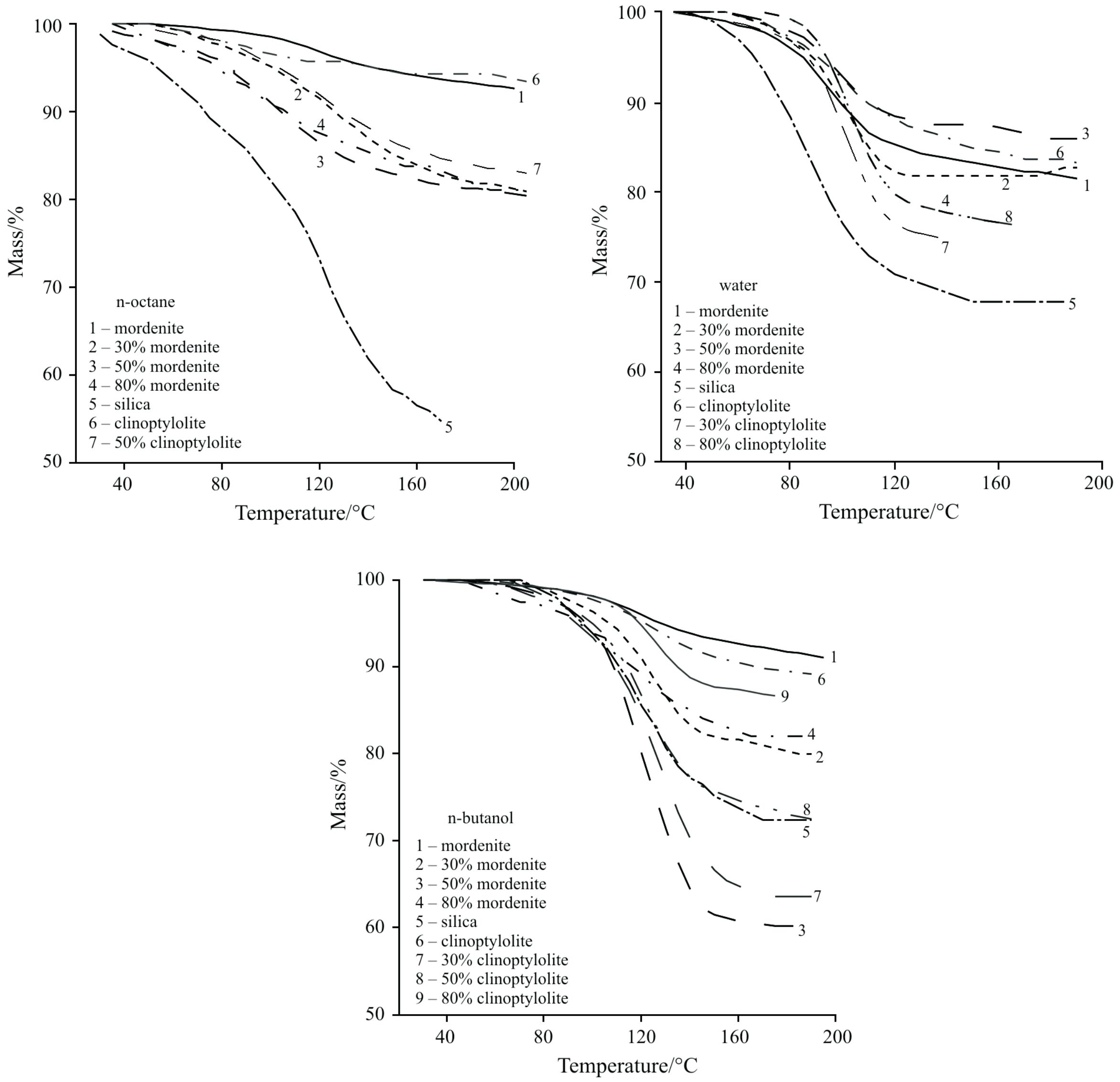

Fig. 2 The mass loss curves Q-TG of liquids thermodesorption from the mixed adsorbents

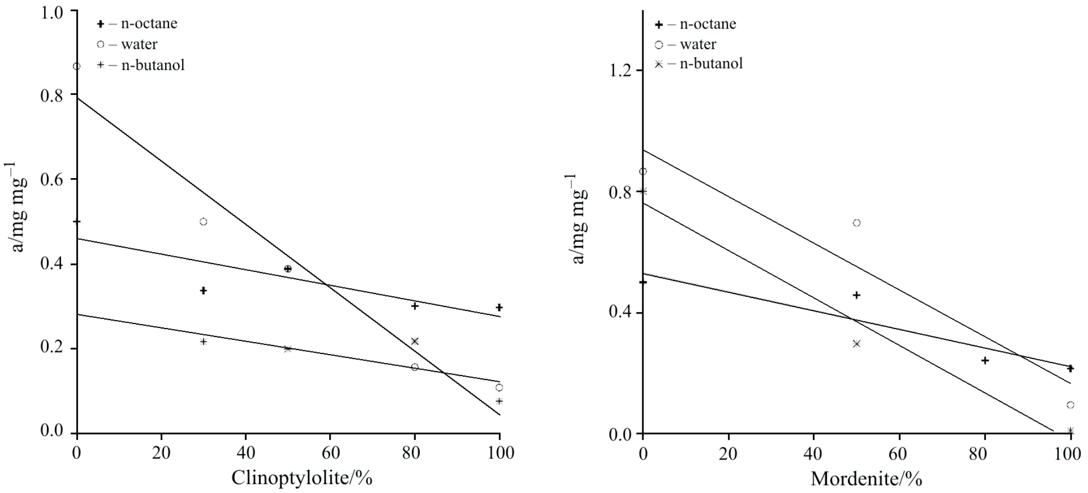

Fig. 3 The dependency of adsorption capacity on the percentage content of the zeolite in the sample

clinoptylolite and 5–34 for mordenite due to the increase in active centres of hydrophilic character on the material surface and in the interactive adsorbent–adsorbate forces. In the case of butanol or octane an insignificant increase of the value *n* in both cases is observed.

From the Q-TG and Q-DTG data the statistical number of liquid monolayers, n_{aver}, were determined as well as the functions of desorption energy distribution from the dependences [24]:

$$-\frac{1}{1-\theta_i}\frac{\mathrm{d}\theta_i}{\mathrm{d}T}=\frac{\nu_i}{\beta}\exp\left(-\frac{E_i}{RT}\right) \qquad (3)$$

$$\varphi_n(E)=-\frac{\mathrm{d}\theta}{\mathrm{d}T}\frac{1}{T} \qquad (4)$$

Table 2 Properties of liquid adsorption layers of the surface mixed mesoporous adsorbent in the zeolite/SiO_2 system

Zeolite/%	liquid	Δm/mg	a/mg mg^{-1}	k/mmol g^{-1}	n
			clinoptylolite		
100	*n*-octane	5	0.0769	0.00067	6
	water	11	0.2972	0.0018	45
	n-butanol	12	0.1090	0.0014	11
80	*n*-octane	48	0.2181	0.0019	8
	water	63	0.3014	0.0167	21
	n-butanol	30	0.1570	0.0021	8
50	*n*-octane	8	0.2000	0.00175	3
	water	21	0.3888	0.21604	12
	n-butanol	21	0.3888	0.00525	8
30	*n*-octane	38	0.2171	0.0019	3
	water	29	0.03372	0.0187	9
	n-butanol	11	0.5000	0.00675	10
			mordenite		
100	*n*-octane	17	0.00982	0.00086	8
	water	14	0.21538	0.0119	33
	n-butanol	13	0.09489	0.00128	10
80	*n*-octane	10	0.38461	0.00336	9
	water	7	0.2414	0.0134	11
	n-butanol	6	0.1818	0.00245	6
50	*n*-octane	22	0.2973	0.0026	4
	water	16	0.4571	0.02539	13
	n-butanol	32	0.6956	0.0094	14
30	*n*-octane	14	0.2800	0.0024	6
	water	6	0.1578	0.0087	6
	n-butanol	15	0.3333	0.0045	7
SiO_2	*n*-octane	25	0.8064	0.00705	6
	water	9	0.5000	0.0278	6
	n-butanol	13	0.8666	0.0177	8

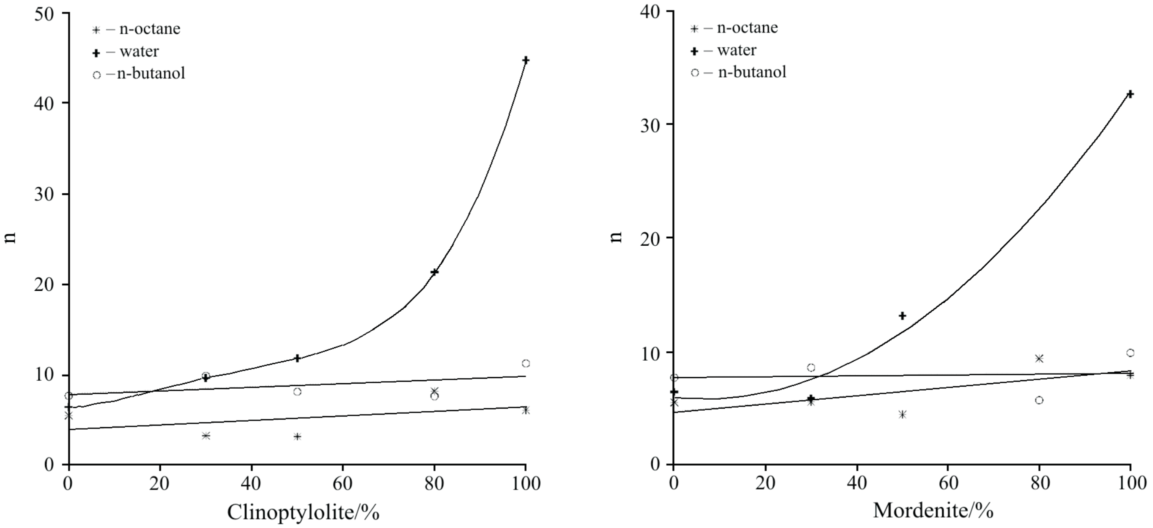

Fig. 4 The dependency of number monolayer of liquids on the percentage content of the zeolite in the sample

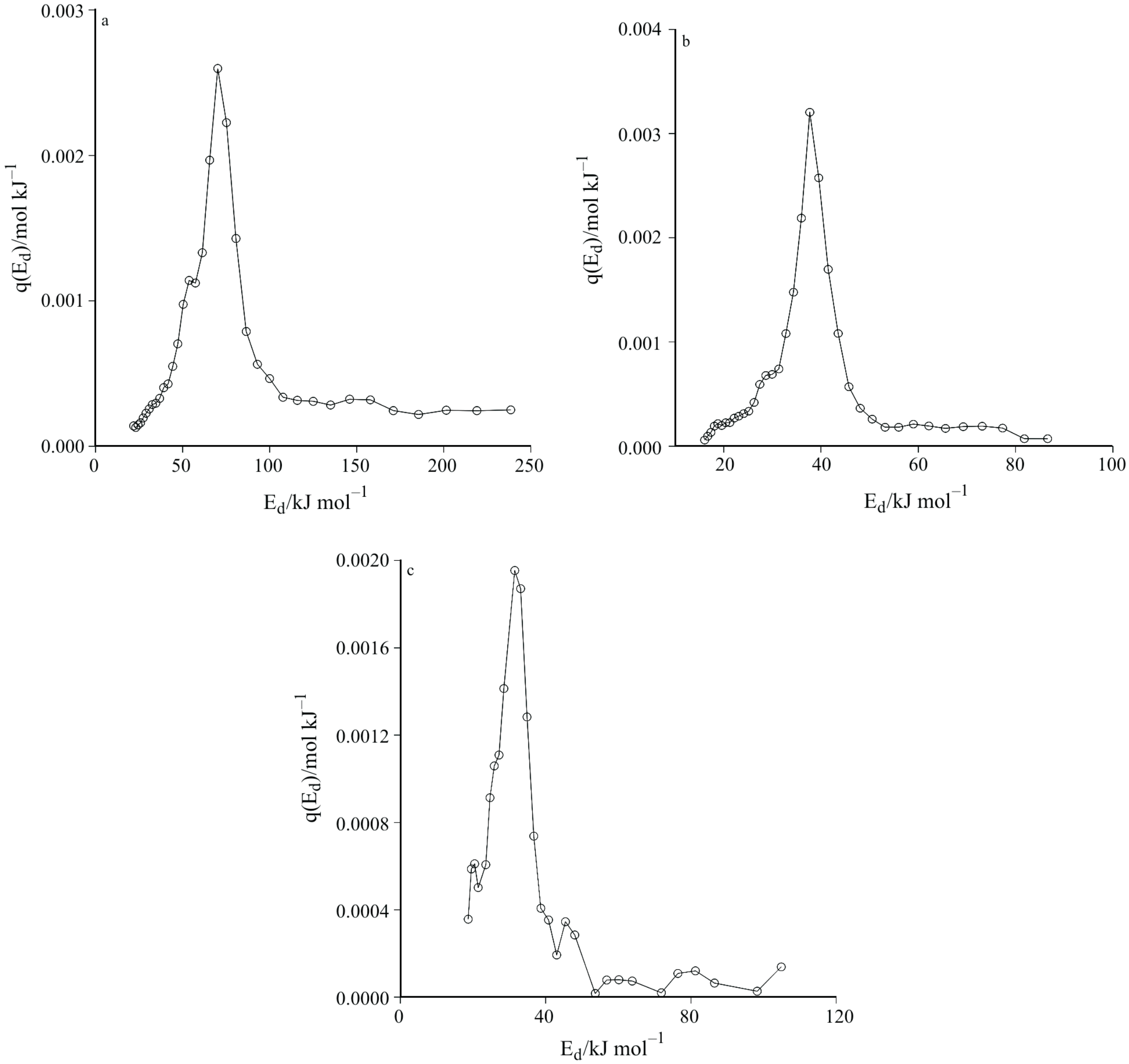

Fig. 5 Energy distribution function of water desorption from: a – mordenite, b – clinoptylolite, c – silica surface

Table 3 Changes of desorption energy of the liquids from the tested samples

Zeolite/%	*n*-octane			water			*n*-butanol		
	dE_d	$E_{d,max}$	q_{max}	dE_d	$E_{d,max}$	q_{max}	dE_d	$E_{d,max}$	q_{max}
clinoptylolite	18–40	16	$1.6\cdot10^{-3}$	13–60	40	$4.2\cdot10^{-4}$	12–40	27	$5.5\cdot10^{-4}$
80	10–55	35	$7.1\cdot10^{-3}$	17–80	49	$7.4\cdot10^{-3}$	10–80	44	$6.4\cdot10^{-3}$
50	12–60	30	$4.5\cdot10^{-4}$	20–60	39	$3.1\cdot10^{-4}$	11–60	27	$5.5\cdot10^{-4}$
30	12–85	43	$8.0\cdot10^{-4}$	20–60	35	$6.4\cdot10^{-3}$	18–80	54	$7.6\cdot10^{-4}$
mordenite	15–60	30	$1.1\cdot10^{-4}$	15–45	30	$2.5\cdot10^{-3}$	17–35	19	$3.0\cdot10^{-4}$
80	10–35	25	$2.3\cdot10^{-4}$	16–45	31	$2.8\cdot10^{-4}$	15–90	65	$1.1\cdot10^{-3}$
50	12–55	28	$6.4\cdot10^{-4}$	18–60	30	$1.3\cdot10^{-3}$	30–90	54	$8.2\cdot10^{-3}$
30	18–50	22	$4.9\cdot10^{-4}$	16–63	46	$7.7\cdot10^{-4}$	14–83	48	$7.7\cdot10^{-4}$
SiO_2	25–68	43	$2.5\cdot10^{-3}$	12–53	32	$1.9\cdot10^{-4}$	18–30	21	$1.7\cdot10^{-3}$

where $T=T_0+\beta t$, θ the degree of surface coverage, ν the entropy factor, E_i the desorption energy calculated for each temperature, T_0 and T the initial and given temperatures of desorption, respectively, β the heating rate of the sample, t the time and R the universal gas constant. Table 3 presents the comparison of value E_d change ranges for individual systems and Fig. 4 presents energy distribution function of water desorption from pure: a) mordenite, b) clinoptylolite, c) silica surface.

The functions of material energy distribution on the basis of clinoptylolite and mordenite presented in Fig. 5 differ in desorption energy values and shape of curve which indicates a complex mechanism of desorption and influence of zeolite concentration on this process. Higher distribution function values correspond to a larger number of active centres of a given energy on the surface. The increase in $E_{d,max}$ value indicates also the increase in the adsorbate–adsorbent interaction force (Table 3).

Conclusions

The paper presents the description of physico-chemical and adsorption properties of mixed adsorbents in the zeolite/SiO_2 system with different contents of clinoptylolite and mordenite. The research showed that desorption of the studied liquids proceeds in a discontinuous way as shown by the inflections of the Q-TG curves which are due to the energy difference of the adsorbate–adsorbent interactions, nature of active centre and solid surface porosity. The Q-TG and Q-DTG curves were used for calculation of the number of monolayers and of the desorption energy distribution. Adsorption capacity dependences on zeolite concentration in the sample showed a decrease in the adsorbed liquid amount compared with pure silica gel with simultaneous increase of a monolayer number which were the same in both cases. Zeolite content increase affects adsorption–structural properties of the obtained materials. Studies of low-temperature nitrogen adsorption showed a decrease in the specific surface area (S_{BET}) and the total pore volume with increasing zeolite fraction concentration compared with silica gel. Addition of zeolite results in the increase of complete heterogeneity of the material. In order to characterize the complete heterogeneity of the material, function of pore volume distribution in relation to the radius, fractal dimensions and of desorption energy distribution were calculated. Irregular shapes of the curves $q=f(E_d)$ and large values of volumetric fractal dimensions (D_f~2.6) confirmed heterogeneous properties of the zeolite SiO_2 system surface. As far as surface is concerned the programmed thermo-desorption method under quasi-isothermal conditions combined with the sorptomatic method proved to be very useful in studies of mixed systems.

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