CHANGES IN PHYSICO-CHEMICAL AND CATALYTIC PROPERTIES OF SYNTHETIC ERIONITE AFTER VARIOUS TREATMENT*

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Influence of decationization by ammonium ions and dealumination by HCl as well as calcination under self-steaming conditions at 1 053 K with following treatment by ammonium ions or by HCl solution on the extent of alkali metals extraction was studied together with surface, sorption, acidic and catalytic properties of synthetic erionite. Samples were also characterized by X-ray diffraction spectra and IR skeletal vibration spectra. Results showed increasing catalytic activity and acidity after thermal treatment, followed by ion exchange with HCl or ammonium ions, which can be connected with deeper substitution of potassium cations of erionite. At the same time by the treatment under self-steaming conditions, as a result of framework dealumination, the zeolite obtained a secondary pore system, which resulted in increasing sorption capacity for aromatics, suppression of coking during *o*-xylene conversion and also increased diffusion of Hammet indicators into the zeolite.

Erionite belongs to the group of narrow-pores zeolites, having both synthetic and natural forms (ref.[1]). Generally, the composition of an elementary cell is $(K, Na)_9 . [(AlO_2)_9(SiO_2)_{27}] . 27\,H_2O$. The content of potassium is obviously about three times higher than that of sodium.

Three types of structural units are present in erionite: *1*) hexagonal prismas, *2*) cancrinite cells and *3*) erionite cavities. While erionite cavities are quite large (0·63 × 1·3 nm), windows to the cavities are very small – 0·36 × 0·52 nm (ref.[2]), allowing the entrance only to the smallest molecules.

To the main catalytic applications of erionite belongs the selective catalytic cracking of n-alkanes in a mixture with isoalkanes and other bigger molecules[3–5], where the shape-selective properties of the narrow diameter of windows are employed. This effect is mainly applied to increase the octane number of reformate in selectoforming, or in the deparaffination of higher naphtha fractions[6–9].

For using erionite in acid and bifunctional catalysis, one has to convert it from the original, inactive Na, K-form into active acid H-form. Sodium can be exchanged

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relatively easily but about 15% of potassium remains in erionite even after the repeated ion exchange accompanied by calcination at 770 K (ref.[10]). In this work we studied the influence of various methods of H-erionite preparation on extraction of potassium and sodium from erionite, and consequently the changes in acidity, surface and sorption properties and in catalytic activity.

EXPERIMENTAL

Synthetic erionite was prepared in Research Institute for Petroleum and Hydrocarbon Gases in Bratislava, Si/Al ratio was 3·16 (sample NaKE).

Decationisation of parent zeolite was carried out by repeated treatment with 2M NH_4NO_3 solution (sample HE).

Dealumination was carried out by repeated treatment with 1M HCl (sample DE). Both decationisation and dealumination were described in detail in our previous work[11].

Self-steaming treatment of decationised samples was carried out at 1 053 K for 3 h (sample SE). After this thermal treatment, sample SE was exchanged either with 2M NH_4NO_3 solution (sample SE-H) or with 0·1M HCl (sample SE-D).

Surface characteristics were measured by physical adsorption of nitrogen at 77 K, and treated by BET isotherm and *t*-plot method[12]. *Adsorption capacity* for n-hexane and benzene was determined by the static method at 298 K. *X-ray diffraction spectra* were taken by CuK_α with Ni-filter. *Infrared spectra* were measured by KBr-technique.

Acidity of samples prepared was determined by two methods: 1. Titration by 1-buthylamine in benzene with the use of Hammet indicators (time for reaching the equilibrium was kept to 48 h). 2. TPD of ammonia; after calcination of samples in the flow of argon at 773 K for 3 h and cooling to 453 K, ammonia was sorbed on the samples during 30 min; after 2 h of purging with argon, the temperature was increased to 823 K (20 K/min), the quantity of ammonia released was determined.

Catalytic activity was tested by two methods: 1. Conversion of *o*-xylene in pulse microreactor (0·2 ccm of catalyst, nitrogen flow, 60 ml/min, 693 K, pulse 2 μl). 2. Conversion of n-heptane in flow microreactor at 723 K, on line connected with gas chromatograph (0·2 cm^3 of catalyst, hydrogen flow 60 ml/min, partial pressure of n-heptane 4·71 kPa).

RESULTS AND DISCUSSION

The chemical composition of erionite samples, prepared by various methods, is given in Table I. It can be seen that the potassium content cannot be significantly decreased to a smaller value even after severe treatment with hydrochloric acid (sample DE). As it has been shown in our previous work[11], the content of potassium did not decrease even after multiple treatment. This fact is probably connected with the strong bonding of potassium ions in cancrinite cages. Sodium is released from the structure almost completely even after two steps of decationization.

After the thermal treatment with following extraction by ammonium ions (Se-H) or diluted hydrochloric acid (SE-D), the content of potassium significantly decreased. At the same time, the Si/Al ratio of the sample SE-D slightly increased. The highest Si/Al ratio was obtained after dealumination with 1M HCl (DE). But it is necessary to say that all the Si/Al ratios are calculated for the bulk of zeolite, in the case of SE, Se-H and SE-D samples the Si/Al ratios of the lattice could be larger.

X-Ray diffraction spectra confirmed a good degree of crystallinity of all samples with the exception of strongly dealuminated sample DE (Fig. 1). The presence of an amorphous phase is also indicated by a slight increase of background at 2θ

TABLE I

Chemical composition of original (NaKE) and modified samples of erionite

Sample	Composition, wt. %					Si/Al mol/mol
	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	
NaKE	67·24	18·02	3·65	10·27	0·63	3·16
HE	77·35	19·70	0·09	2·42	0·53	3·30
DE	90·28	7·15	0·05	2·17	0·36	10·70
SE-H	78·37	20·64	0·10	0·51	0·30	3·22
SE-D	84·40	15·33	0·07	0·48	0·40	4·61

TABLE II

X-ray characteristics of samples NaKE and SE

hkl	Sample NaKE		Sample SE	
	d, Å	*I*	*d*, Å	*I*
100	11·51	100	11·04	100
002	7·55	10	7·49	8
110	6·63	57	6·41	66
102	6·30	5	6·23	7
200	5·75	7	5·58	10
210	4·340	50	4·225	18
212	3·756	70	3·696	27
104	3·582	32	3·565	22
213	3·304	18	3·234	13
204	3·159	23	3·117	13
214	2·849	73	2·806	30
402	2·677	14	2·634	8

angle 20 – 25°. Besides this, in the case of samples SE, Se-H and SE-D there is observed a small shift of diffraction lines to greater values of 2θ angle (lower d-values). In Table II diffraction data of main lines are compared of parent erionite (NaKE) and thermally treated sample (SE). It is assumed that this shift is caused by the unit cell-parameter decreases a consequence of framework dealumination during thermal treatment.

IR spectra of the lattice vibrations are shown in Fig. 2. Bands of framework vibration of parent erionite (NaKE) are in good agreement with published values[13]. The spectrum of decationizated sample (HE) is practically the same, the band at 1 400 cm^{-1} is connected with the ammonium ions in the zeolite (IR spectra of this sample, as well as of the sample SE-H were taken with uncalcined materials).

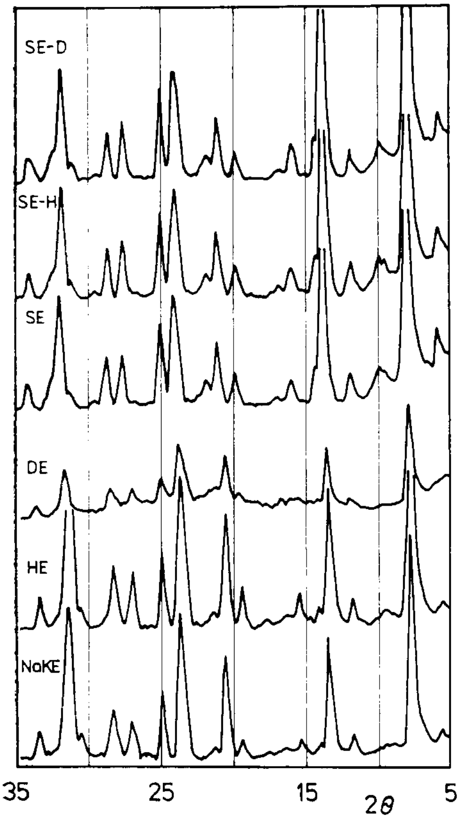

FIG. 1
X-Ray diffraction spectra of erionite samples

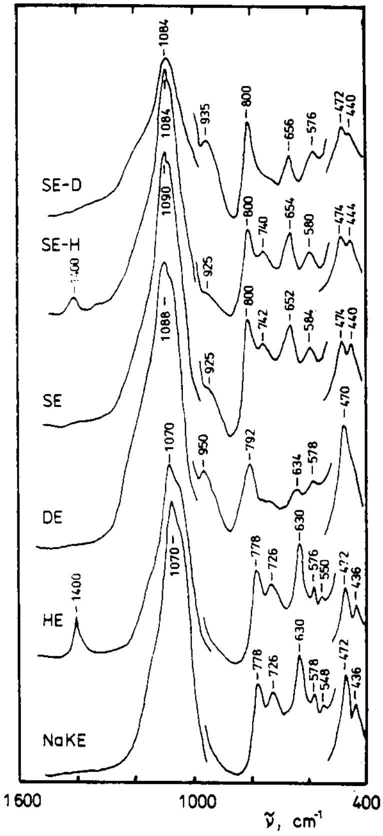

FIG. 2
IR spectra of skeletal vibration

In the samples SE, SE-H and SE-D, all vibration bands are shifted to higher wavenumbers which could be ascribed to the Si/Al ratio increase. This assumption is in agreement with the X-ray diffraction results.

The main changes in IR spectra were observed for dealuminated sample DE, where the bands at 436, 545 – 730 cm^{-1}, which could be attributed to the presence of double-six-rings, almost disappeared as a consequence of partial loss of crystallinity. On the other hand, the band at 950 cm^{-1} increased (this band was observed also in sample SE-D, and partially in samples SE and SE-H).

Adsorption isotherms of nitrogen for samples NaKE, HE and DE in Fig. 3*a* show identical adsorption and desorption parts without a hysthereis loop for all these samples.

Sample SE, as well as Se-H and SE-D showed very narrow hystheresis loops, connected with the creation of a secondary pore structure as the consequence of lattice dealumination by the thermal treatment. The example of adsorption hystheresis for sample SE is given in Fig. 3*b*.

The changes in the surface and sorption properties of modified samples of erionite are summarized in Table III. The increase of specific surface area BET by 170 m^2/g in the decationized erionite HE in comparison with parent erionite NaKE is caused by the cation-exchange from the cavities (increased volume of micropores). Severe dealumination (DE) resulted in a decrease of specific surface area as well as specific volume of micropores by 30% (in comparison with HE), which shows a considerable loss of crystallinity.

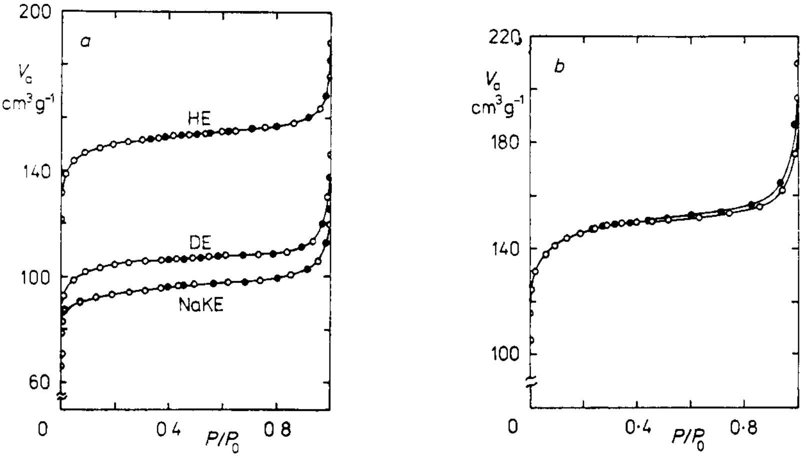

FIG. 3

Adsorption-desorption isotherms of samples NaKE, HE, DE (*a*) and SE-D (*b*): ○ adsorption, ● desorption

It is assumed that by the thermal treatment, the potassium cations diffuse from the cancrinite cages into great erionite cages, where they can be easily extracted by ammonium ions or hydrochloric acid. At the same time, during the thermal treatment under self-steaming conditions, the partial hydrolysis of structural aluminium can proceed. This phenomena can be connected with the production of extra-lattice aluminum species in micropore volume and with the creation of secondary pore structure. Both above-mentioned processes have to result in a micropore volume decrease, as it can be seen from the values for sample SE in Table III. By the following treatment with ammonium ions (SE-H) or with dilute hydrochloric acid (SE-D), the micropore volumes increased.

The changes in the pore system of modified erionite samples are also characterized by sorption capacity values in Table III. The sorption capacity of n-hexane after decationisation increased by 50%, but those of benzene and *o*-xylene are almost the same as for parent erionite. The sorption capacity of benzene increased twice after severe dealumination (DE) or after thermal treatment (SE), and almost three times after extraction with HCl (SE-D). High values of sorption capacities of *o*-xylene were obtained only for the samples DE and SE-D. The increase of sorption capacities for benzene and *o*-xylene is connected with the pore openings increasing after the thermal treatment (SE, SE-H and SE-D). The high values of sorption capacities of benzene and o-xylene in the sample DE could be attributed also to the amorphous phase.

The catalytic activity of modified erionite samples for *o*-xylene conversion in pulse reactor is connected with the changes in pore structure. While the conversion of *o*-xylene for the decationized sample HE sharply decreased with the number of impulses because of coking, in the case of dealuminated and partially destroyed sample DE the activity remained stable (Fig. 4). Similar comparison could be made

TABLE III
Surface and adsorption properties of modified erionites

Sample	S_{BET} m^2/g	S_{mezo} m^2/g	V_{micro} cm^3/g	Sorption capacity, wt. % n-hexane	benzene	*o*-xylene
NaKE	292	27	0·133	10·3	5·6	2·4
HE	466	28	0·219	15·0	6·2	2·4
DE	324	22	0·152	13·6	12·4	7·0
SE	439	41	0·159	15·1	13·1	2·9
SE-H	443	59	0·199	17·2	14·6	3·7
SE-D	419	75	0·177	17·2	16·3	6·0

for the samples SE-H and SE-D but even at higher conversion degree. This fact can be explained by the presence of the secondary pore structure, which allows the entering of aromatics molecules inside and outside of zeolite pores.

In the case of n-heptane conversion in flow reactor, the situation is different (Table IV). Molecules of n-alkane can enter the pores of erionite without any problem, thus the efficiency of the acid centers inside the cavities for n-alkanes is high. The highest activity of samples SE-H and SE-D could be ascribed to higher degree of potassium extraction (in comparison with the HE sample).

The acidity determination by two different methods supports the assumption of pore structure changes and alkali metals extraction in the prepared samples. The values of acidity, determined by Hammet's indicators, are very small because of the

TABLE IV

Acidity and catalytic activity of modified erionite samples (catalytic activity by conversion of n-heptane at 723 K in flow atmospheric reactor)

Sample	Acidity, mmol g^{-1}		Conversion of n-heptane wt. %
	by Hammet's indicator	by TPD of ammonia	
HE	0·10	2·67	10·0
DE	0·35	1·23	2·3
SE	0·10	1·44	2·5
SE-H	0·15	2·04	30·8
SE-D	0·60	1·72	17·0

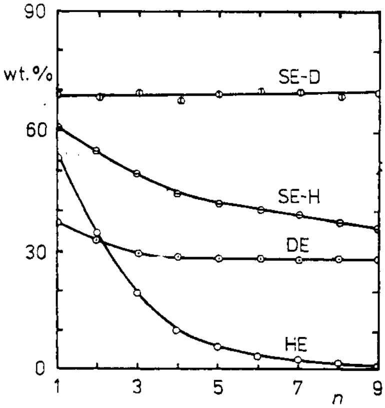

FIG. 4

Changes of catalytic activity in pulse reactor for *o*-xylene conversion (%) with the number of pulses (*n*) small pore openings for indicators (the greatest values were obtained for samples, treated with hydrochloric acid). The total acidity, determined by the TPD of ammonia, showed the highest value for the sample SE-H, which were deeply decationized as the HE sample, but less dealuminated than the SE-D sample.

CONCLUSION

The experimental results showed that the remained potassium cations, which were strongly bonded in the erionite structure even after repeated ion exchange, could be released by the action of the thermal treatment of ammonium form of erionite under self-steaming conditions with following treatment by ammonium ions or diluted hydrochloric acid.

After such treatment, the total acidity and catalytic activity increased, but at the same time, the zeolite obtained a secondary pore system, connected with the increase of adsorption capacity as well as catalytic conversion activity for aromatic hydrocarbons.

REFERENCES

1. Breck D. W. in: *Zeolitic Molecular Sieves*, pp. 28, 71, 85, 252. Wiley, New York 1974.
2. Kawahara A., Curien H.: Bull. Soc. Fr. Mineral. Crystallogr. *92*, 250 (1969).
3. Barrer R. M., Galabova I.: Adv. Chem. Ser. *121*, 356 (1973).
4. Chen Y. Y., Garwood W. E.: J. Catal. *53*, 284 (1978).
5. Robson H. E., Hammer G. P., Arey W. F.: Adv. Chem. Ser. *102*, 417 (1971).
6. Roselius R. R., Edeleanu, A. G. (Chevron Res. Comp.): U.S. 4,036 735 (1977).
7. Maziuk J. (Mobil Oil Corp.): U.S. 4,010 093 (1977).
8. Becker K. (VEB Leuna Werke): Ger. (GDR) 149 941 (1980).
9. Shell Francaise: Fr. 2,260 381 (1974).
10. Kogelbauer A., Lercher J. A., Steinberg K. H., Roessner F., Soelner A., Dmitriev V.: Zeolites *9*, 224 (1989).
11. Hudec P., Novanský J., Phuong N. T.: Ropa Uhlie *28*, 215 (1986).
12. Hudec P., Novanský J., Šilhár S., Trung T. N., Zubek M., Maďar J.: Ads. Sci. Technol. *3*, 159 (1986).
13. Occelli M. L., Ritz G. P., Iyer P. S., Walker R. D., Gerstein B. C.: Zeolites *9*, 104 (1989).

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