

Investigation of the surface properties of ZSM zeolite decationized in the electrolyzer chamber by physical and chemical methods

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1. Introduction

The effectiveness of zeolite catalytic systems in acid-base reactions is due to the presence of active acid sites on their surface. Hence, the problem of determining the nature of Lewis acid sites is of practical interest.

2. Experimental

The H-forms of the high-silica zeolites ZSM were obtained by treating aqueous Na-zeolite suspensions in the anode or cathode chambers of a diaphragm electrolyzer with or without an electrolyte (H₂O).

The treatment conditions used in the diaphragm electrolyzer: the anode — a ruthenium–titanium oxide plate; the cathode — a steel plate, $T = 343$ K, $\tau = 120$ min; the hydro-module in chambers (zeolite mass/solution volume) $G = 5.7$ g/l, $\Delta U = 75$ V.

The decationation of the Na-ZSM samples was carried out by treating in 25% HCl solution for 240 min and in 0.8% NH₄Cl solution for 120 min.

IR spectra of the H-ZSM samples were measured on a UR-20 spectrometer before and after carbon monoxide adsorption [1].

²⁷Al NMR spectra were measured on a VARIAN UNITI-30 MAS spectrometer at the frequency of 78.157 MHz with sample rotation at “magic” angle. The rotation rate was 2.5 kHz. Chemical shifts were measured with respect to Al(H₂O)₆³⁺ used as an external standard.

Aluminum concentration of the initial Na-ZSM and the decationized samples were determined by titrimetric method. The sodium concentrations in the initial Na-ZSM and the decationized samples were determined by flame photometry method.

3. Results and discussion

Previously, we have shown the possibility of the zeolite decationation in the anode or cathode chamber of a double-chamber electrolyzer. The treatment of zeolite in the anode chamber causes its decationation to the Na₂O concentration below 0.1 wt.% [2].

The present paper shows the results of investigating the effect of this treatment on the acid-base properties of zeolites and the state of alu-

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Table 1

Treatment conditions and acid properties of zeolite samples

(1) Treatment in the anode chamber — 0.2% NH_4Cl solution. (2) Treatment in the anode chamber — H_2O . (3) Treatment in the anode chamber — 0.1% NH_4Cl solution. (4) Decationation in 25% HCl solution. (5) Decationation in NH_4Cl solution and treatment in the anode chamber (0.2 % NH_4Cl solution). (6) Decationation in NH_4Cl solution and treatment in the cathode chamber (0.2% NH_4Cl solution). (7) Treatment in the anode and cathode chambers (0.2% NH_4Cl solution).

Sample	Crystallization degree (%)	Na_2O (%)	Experimental data							Calculated data				
			Lewis acid sites ($\mu\text{mol/g}$)				Breasted acid sites ($\mu\text{mol/g}$)			$\Sigma L_i + B_i$	L_3 ($\mu\text{mol/g}$)	L_1 ($\mu\text{mol/g}$)	B_1 ($\mu\text{mol/g}$)	L (%)
			L_1	L_2	L_3	ΣL_i	B_1	B_2	ΣB_i					
1	104	0.07	121	40	14	175	235	64	299	474	14.1	112.8	239	37
2	112	0.06	100	33	18	151	220	34	254	405	13.2	105.6	185	37
3	102	0.05	132	32	–	164	165	41	206	370	9.9	78.7	205	44
4	98	0.03	67	31	9	107	150	20	170	277	9.0	72	127	39
5	103	0.02	91	46	12	149	175	90	265	414	10.5	84	239	36
6	101	0.03	220	46	11	277	175	55	230	507	10.5	84	–	55
7	104	0.02	240	32	–	272	155	75	230	502	9.3	74.4	–	54

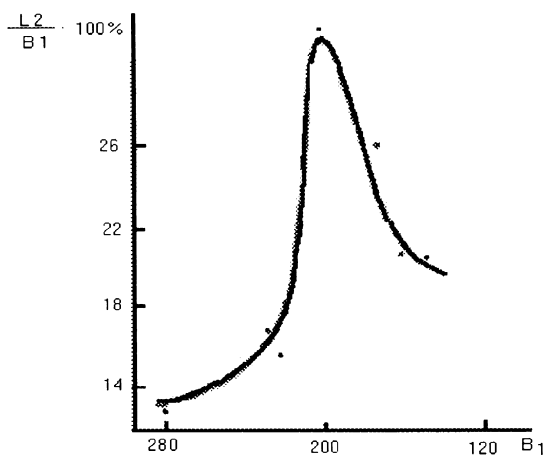


Fig. 1. Relation between the concentrations of L_2 and B_1 sites.

minum atoms in their framework. The acid-base properties were estimated by the analysis of the IR spectra of evacuated samples recorded before and after the carbon monoxide adsorption. Table 1 shows some data obtained.

The degree of zeolite crystallization often increases after electrochemical treatment. This is caused by the recrystallization of the layer of siliceous fragments on their surface.

There are three types of Lewis acid sites on the surface of electrochemically decationized zeolites: weak — L_1 ($Q_{co} = 34\text{--}40$ kJ/mol), medium strength — L_2 ($Q_{co} = 41\text{--}48$ kJ/mol), and strong — L_3 ($Q_{co} = 49\text{--}51$ kJ/mol). Also, there are two types of Brönsted sites (B_1 and B_2 , respectively) inside the zeolite crystals and on their surface ($\nu_{OH} = 3610$ cm^{-1} and $\nu_{OH} = 3720$ cm^{-1}) [1].

The zeolite treatment in the anode chamber ($\text{pH} < 7$) leads to the decrease of the concentration of the strongest Lewis sites L_3 . The treatment in the cathode chamber ($\text{pH} > 7$) leads to a significant increase of the number of the weakest sites.

We have found empirical relationships between the concentrations of Lewis sites and Brönsted sites in the zeolite channels B_1 :

$$L_1 = 0.48 B_1,$$

$$L_3 = 0.06 B_1.$$

There is a maximum of the dependence of the concentration of L_2 on that of B_1 (Fig. 1). There is no relation between B_1 and B_2 concentrations, probably, due to the influence of the crystallite size on B_1 concentration.

The total concentration of acid sites on the zeolite surface (all types of Lewis sites and surface Brönsted sites) is proportional to the concentration of Brönsted ones in the zeolite channels $\sum L_{1-3} + B_2 \approx B_1$.

The zeolite is subjected to dealumination during its treatment in the electrolyzer chamber. Table 2 shows the experimental data on the dealumination of zeolites. The initial zeolite form ZSM has 8% of free aluminum ions that can be substituted with sodium ions. These aluminum ions occupy the cation positions in $\text{Al}(\text{OH})_{3-n}^{(3-n)+}$ forms in the zeolite. Consequently, the concentration of the framework aluminum is somewhat lower than the total aluminum concentration. The decationation with HCl leads to deep dealumination (25%) of the framework and is accompanied by removal of all free aluminum atoms. A complex zeolite treatment (decationation + electrochemical) has an analogous effect. A direct electrochemical treatment of sodium zeolite forms in the anode and cathode electrolyzer chambers leads either to the dealumination with aluminum removal from the zeolite or to the formation of “compensation” aluminum. This effect depends on

Table 2
The effect of treatment on dealumination of Na-ZSM

Samples	pH	Aluminum concentration (mol/g)	
		I ^a	II
0 ^b	–	401	378
1	1.5	373	336
2	2.2	357	352
4	–1.5	293	292
5	1.5	304	296
6	10.5	379	357
7	10.0	358	352

^aI — before the substitution of sodium for aluminum; II — after the substitution of sodium for aluminum.

^b0 — initial Na-ZSM ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 43$).

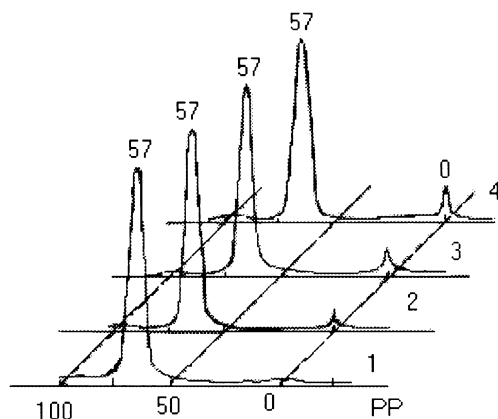


Fig. 2. ^{27}Al NMR spectra of zeolite samples: (1) initial Na-ZSM; (2) treatment in the anode chamber (H_2O); (3) treatment in the anode chamber (NH_4Cl solution); and (4) treatment in the anode and cathode chambers (NH_4Cl solution).

the electrolysis regime. For the samples treated, a decrease of the total concentration of acid sites may be observed alongside the dealumination. The degrees of zeolite decationation and dealumination during the treatment in the anode chamber are regulated by the electrolysis regime.

A proton is transferred from an aluminum atom to an extra-lattice position, and the Al_2O_3 phase is formed on the crystallite surface. In high resolution ^{27}Al NMR spectra besides the signal with a chemical shift of $\delta = 57$ ppm referred to the tetrahedral framework aluminum,

an intensive signal appears at $\delta = 0$ ppm (Fig. 2). It corresponds to six-coordinated extra-lattice aluminum atoms. Probably, the Al_2O_3 phase is responsible for the formation of weak L_1 sites. Its morphology is determined by pH of the zeolite suspension. Treatment in the electrolyzer anode chamber ($\text{pH} = 1.2\text{--}1.5$) is useful for forming X-ray amorphous Al_2O_3 with low concentration of L_1 sites. Subsequent treatment in the cathode chamber ($\text{pH} = 10.0\text{--}11.0$) is accompanied by a phase transformation producing $\eta\text{-Al}_2\text{O}_3$ with a higher concentration of L_1 sites.

4. Conclusions

The data obtained show that the decationation of high-silica zeolites in the electrolyzer chamber changes their acid-base properties. This can be used for producing active and steadily operating catalysts.

References

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- [2] A.A. Lamberov, A.G. Liakumovich, I.V. Kalinina, in: Int. Conf. "Zeolite Catalysis and Industrial Progress". September