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Effect of Decationation Procedure on the Textural Properties of High-Silica ZSM-5 Zeolite

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Abstract—The texture of the starting high-silica zeolite ZSM-5 and its decationated samples is studied by the low-temperature adsorption method. Mesopores with a diameter of 42 Å are found. Decationation of the zeolite is accompanied by an increase in the specific surface area and pore volume. It is suggested that the textural changes found are due to the removal of admixtures from some pores. A model for the formation of the secondary pore system is proposed. The secondary porosity is suggested to be due to the coordination of the zeolite crystals through the primary particles of aluminum hydroxide located on the surface of the zeolite crystals. The influence of the decationation conditions on the textural characteristics of ZSM-5 is shown.

INTRODUCTION

The activity and selectivity of zeolite-containing catalysts is mainly determined by the spectrum of zeolite acidity and the distribution of acid sites on its surface. This is due to the fact that some reactions (oligomerization and polymerization of olefins or dehydrocyclization of aliphatic hydrocarbons) occur in the interior of the zeolite grains, whereas other reactions (cracking or coke formation) occur on the outer surface [1–3]. Variations in the textural characteristics of the zeolite, including the size of the crystals, its inner and outer surface areas, significantly affect a catalytic process [4].

Earlier [5] we proposed a procedure for modifying a high-silica zeolite through its treatment in an electrolyzer compartment. We showed [6, 7] that the interaction of ions generated on the electrodes with the zeolite result in decationation up to the residual concentration of Na_2O < 0.1% and a change in the acid–base properties.

The aim of this work is to study the effect of electrochemical modification on the textural characteristics of a high-silica zeolite. The texture was investigated by adsorption methods [8, 9].

EXPERIMENTAL

A high-silica zeolite TsVM with the ZSM-5 structure (SiO_2/Al_2O_3 = 43; 4.15 wt % Na_2O) produced by Nizhegorodskie Sorbenty was studied. The zeolite was decationated either in a two-compartment bath electrolyzer or by known chemical methods. The performance attributes of the electrolyzer and the conditions of electrochemical decationation were described elsewhere [6]. Table 1 presents the regimes and conditions of the Na-TsVM modification. The textural characteristics were determined by the adsorption method in the Fenelonov’s Laboratory at the Institute of Catalysis, Siberian Division, Russian Academy of Sciences, on an ASAP-2400 Micromeritics setup. The adsorption isotherms were measured at 77 K, and the samples were degassed at 773 K to a residual pressure of 3×10^{-2} Torr. The specific surface area S_{sp} was determined by the BET method [8]. The S_{sp} values were calculated using the area of the nitrogen molecule of 16.2 Å^2. The density of liquid nitrogen was taken equal to 0.808 g/cm^3. The relative accuracy of S_{sp} measurements was 3%. The total pore volume and the pore size distribution were calculated from the desorption branch of the isotherm according to the standard Barrett–Joyner–Hailand procedure [8]. The statistical thickness of the adsorption film was calculated from the ratio $t = 3.54V_{ads}/V_m$ [9], and the monolayer capacity V_m was determined from the BET plots. The relative accuracy of the measurement of the pore volume and pore size distribution was 13%. The percentages of sodium and aluminum in the samples were estimated by flame photometry and complexometric analysis. The IR spectra in the region of the lattice vibrations were recorded on a Perkin Elmer 16 PC IR Fourier-transform spectrometer. The zeolite samples were pressed into pellets with KBr as a binding agent. The ^{27}Al MAS NMR spectra were recorded on a Varian Uniti-300 MAS instrument with a frequency of 78.18 MHz. All the NMR spectra were recorded for the samples hydrated at 295 K. A chemical shift is presented relative to $Al(H_2O)_6$. The degree of crystallinity was evaluated from the XRD data. The diffraction patterns were obtained on a DRON-2 instrument with FeK_α filtered monochromatic radiation according to a procedure described in [10]. The maximal degree of

Table 1. Decationation conditions and TsVM properties (SiO_2/Al_2O_3 = 43, 4.15 wt % Na_2O)

Sample no.	Method of decationation	Electrolyte	Concentration of electrolyte, mol/l	Conditions of modification				Degree of crystallinity, %
				pH	T, °C	I**, A	time, min	
1	Initial TsVM	–	–	–	–	–		81
2	Chemical	NH_4Cl	0.20	6.5	70	–	240	100
3	Chemical	HCl	7.00	–1.5*	90	–	240	90
4	Anodic compartment (diaphragm)	NH_4Cl	0.02	1.5	70	1.0–3.0	120	93
5	Anodic compartment (membrane)	NH_4Cl	0.02	2.5	70	1.0–3.0	120	88
6	Anodic compartment (diaphragm)	H_2O	–	3.3	50	0.1–0.5	240	91
7	Cathodic compartment (diaphragm)	NH_4Cl	0.02	10.0	70	1.0–3.0	120	84

* Measured by titrimetry.

** Voltage is 75 V.

crystallinity of the zeolite in the series of samples was taken equal to 100%. The degree of crystallinity did not decrease upon decationation compared to the starting unmodified zeolite and even increased by ~19% (Table 1).

RESULTS AND DISCUSSION

The isotherms of nitrogen adsorption for all the samples belong to the I and IV mixed types according to the BDDT classification (Fig. 1). Hence, the zeolite contains mesopores, along with micropores determining the primary porosity. An H3–H4 hybrid hysteresis loop indicates the presence of slit pores open from all sides and formed by plane–parallel particles [8, 9]. The character of the t-curve and its deviation from a linear function at t = 3–5 Å (Fig. 2) provide further evidence for this fact.

The adsorption and desorption branches of the isotherm for the starting Na-TsVM (Fig. 1a) coincide at $P/P_0 \approx 0.05$. The hysteresis in the region of small pressures may be due to the hampered adsorption and desorption of the adsorbate molecules in zeolite micropores favored by compensatory sodium cations in zeolite channels. Decationation in acidic and close-to-neutral media disposes of these difficulties (Figs. 1b and 1c), and the desorption and adsorption branches of the isotherm coincide at P/P_0 = 0.4–0.5.

When modification is carried out in an alkaline medium (Fig. 1d), the hysteresis at small pressures is retained because of the partial removal of the compensatory cations upon such treatment.

It follows from pore distribution patterns of the samples (Fig. 3) that the secondary pore system of TsVM mainly comprises mesopores with a diameter of 42 Å. The texture observed cannot be formed by the direct coordination of primary zeolitic particles with each other or with additional non-zeolitic fragments on the surface of the zeolite crystals. In the first case, the sizes of secondary pores would be comparable with those of the zeolite crystals that are equal to 200–500 Å [11]. In the second case, the non-zeolitic compounds (e.g., both aluminate and silicate fragments) on the surface of the TsVM crystals would favor the formation of the developed mesopore system with pores of different shapes and sizes [12].

We assume that the TsVM texture is formed by the layer-by-layer coordination of the zeolite particles through the non-zeolitic fragments that are 42 Å in size, namely, through the primary particles (nuclei) [13] of the aluminum hydroxide phase, which can be formed under conditions of zeolite hydrothermal synthesis [14]. Several facts support this assumption. First, silicon and aluminum are distributed nonuniformly across the crystal layer [15], which is typical of high-module zeolites. According to [16], the aluminum concentration in the subsurface layers of the ZSM-5 crystals is considerably higher than that in the bulk. Second, the absorption band in the region of ν(OH) = 3670–3680 cm^{-1} is present in the IR spectra of the hydroxylated surface of the samples [17], which is due to the vibrations of OH groups bound to extraframework aluminum atoms [18]. This band is also typical of aluminum oxide [19]. Furthermore, the presence of mesopo-

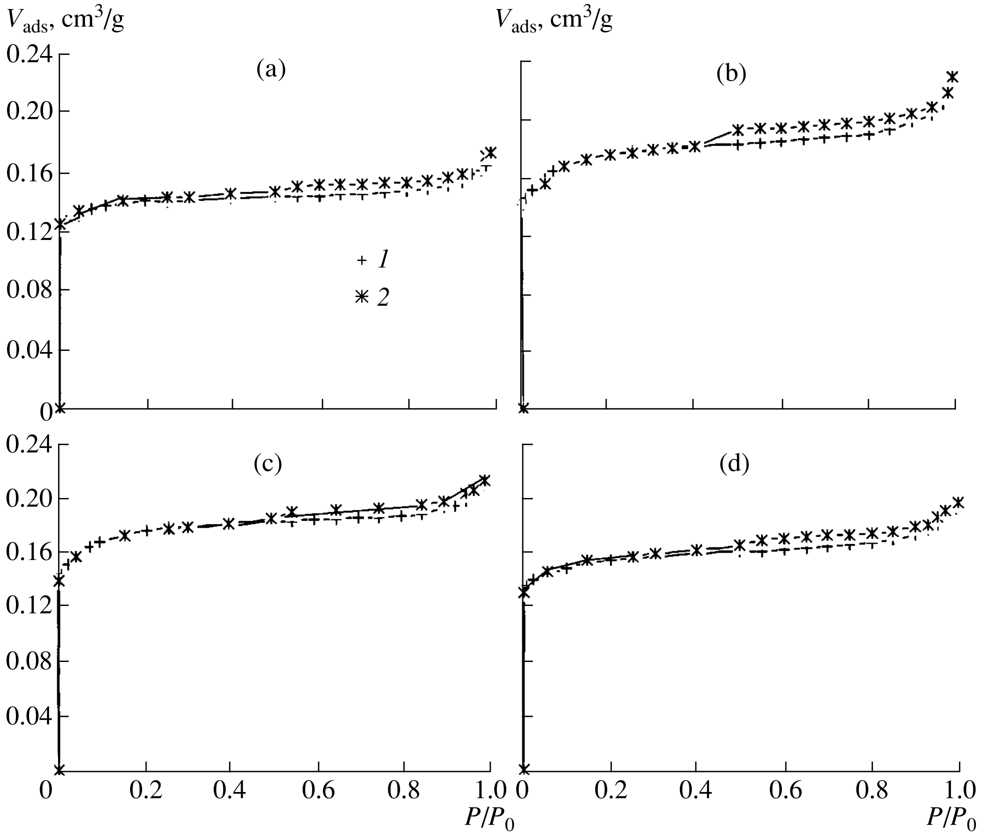

Fig. 1. (*1*) Adsorption and (*2*) desorption isotherms for $N_{2(liq)}$ at 77 K on samples (a) initial Na-TsVM and (b) H-TsVM prepared by chemical decationation in NH_4Cl solution in (c) the anode and (d) the cathode compartments of the electrolyzer in a NH_4Cl solution.

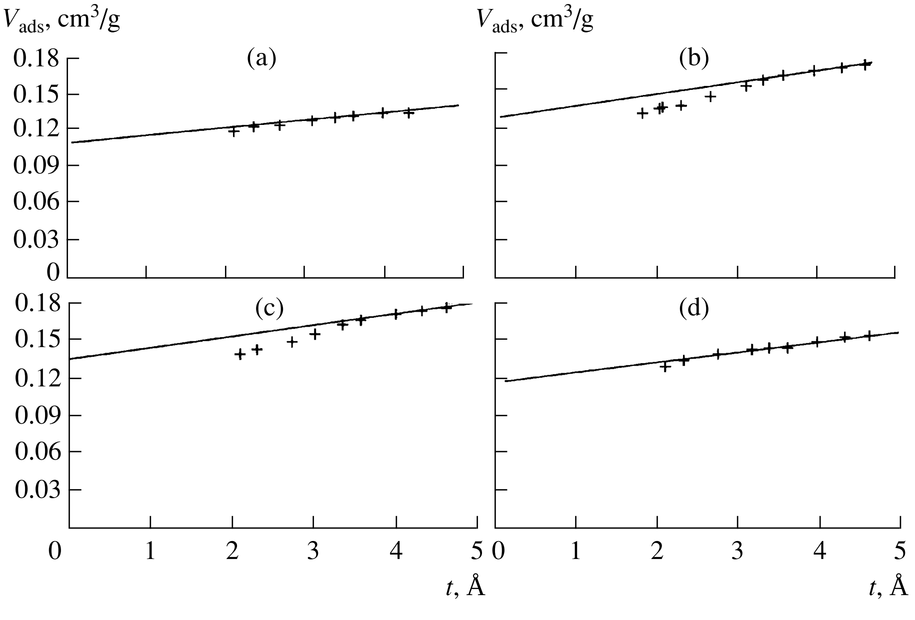

Fig. 2. The t-plot for nitrogen adsorption at 77 K on (a) starting Na-TsVM and (b) H-TsVM samples prepared by chemical decationation in a NH_4Cl solution in (c) the anode and (d) the cathode compartments of the electrolyzer in a NH_4Cl solution.

res with a diameter of 42 Å [13] formed by particles of similar size, which are probably the dimers of the hydroxide microcrystallites with sizes of 21–22 Å, is typical of aluminum hydroxides.

The results of processing the adsorption isotherms are presented in Table 2. The total specific surface areas were estimated by the BET method (S_{BET}), and the total pore volumes (V_t) were found from the adsorption when the pore system was completely filled. Decationation is accompanied by an increase in the specific surface area and pore volume: S_{BET} increases by 11.0–28.5% and V_t increases by 14.1–41.1%.

The micropore volumes (V_{micro}) were calculated by two methods: from the intercept on the *y* axis of the *t*-plot and by the Dubinin–Radushkevich method [20]. Figure 4 shows the isotherms in the Dubinin–Radushkevich coordinates. The values of V_{micro} were 0.11–0.12 cm^3/g for the first case and 0.13–0.16 cm^3/g for the second case. The values found in the literature [4] for zeolite ZSM-5 range from 0.13 to 0.15 cm^3/g. Therefore, the most reliable values determined by the Dubinin–Radushkevich method were used in further calculations.

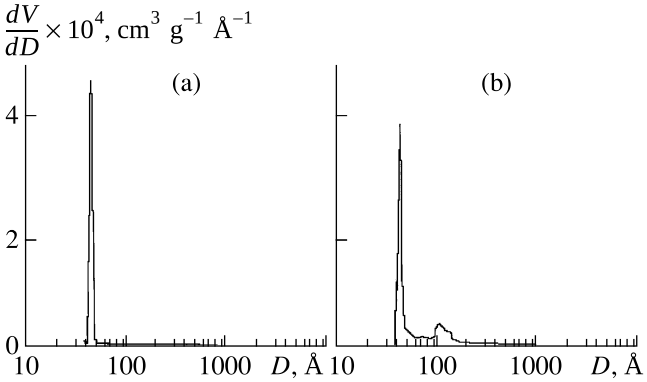

Fig. 3. Pore size distributions for (a) Na-TsVM and (b) H-TsVM prepared in the anode compartment (pH 3.3).

The mesopore volumes (V_{meso}) were calculated by subtracting V_{micro} from the total pore volume, and the mesopore surface was estimated by the equation $S = 4V/D$ [9], assuming mesoporosity to be uniform with $D = 42$ Å. The results of calculations listed in Table 2 show that the specific surface area and pore volume in the zeolite are largely determined by micropores, whose fraction is 89–82% in S_{BET} (similarly to [21]) and 68–79% in V_t. Decationation is accompanied by a change in the volume and surface of micropores, which increase 1.1–1.2 times. However, the inner crystalline structure of the zeolite remains almost unchanged as follows from the IR-spectroscopic study of the samples in the region of the zeolite lattice vibrations (400–1300 cm^{-1}) (Fig. 5). Modification does not cause significant changes in the regions of the IR spectra at ν = 1224, 1094, 794, and 554 cm^{-1}, which are typical [22, 23] of high-module zeolites (Fig. 5).

The parameters of mesopores increase more significantly (by 2.1 times) than those of micropores. The V_{meso} and S_{meso} values increase simultaneously and in nearly the same manner. This indicates that decationation does not change the pore system. One can suggest that a fraction of the pores in the zeolite is freed from

Table 2. Textural characteristics of TsVM as a function of the conditions of modification

No. of sample	Sample* (pH of treatment)	S_{BET}, m^2/g	V_t, cm^3/g	*t*-method		Dubinin–Radushkevich method			S_{micro}, m^2/g
				V_{micro}, cm^3/g	V_{meso}, cm^3/g	V_{micro}, cm^3/g	V_{meso}, cm^3/g	S_{meso}, m^2/g	
1	Na-TsVM	313	0.169	0.113	0.056	0.133	0.036	34	279
2	CD (6.5)	402	0.227	0.124	0.103	0.167	0.060	57	345
3	CD (–1.5)	396	0.211	0.116	0.095	0.163	0.048	46	350
4	EA (1.5)	394	0.209	0.129	0.080	0.166	0.043	41	353
5	EA (2.5)	364	0.212	0.119	0.094	0.153	0.059	56	308
6	EA (3.3)	392	0.238	0.115	0.124	0.161	0.077	73	319
7	EC (10.0)	348	0.193	0.119	0.075	0.150	0.040	45	309

* CD is chemical decationation, EA is electrochemical anode treatment, and EC is electrochemical cathode treatment.

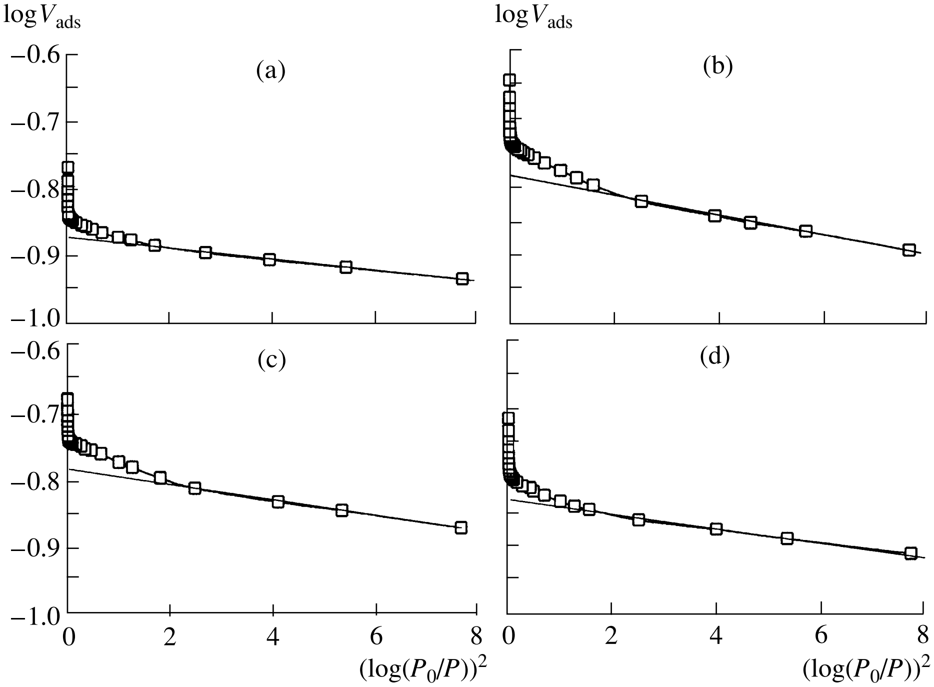

Fig. 4. Adsorption and desorption isotherms for $N_{2(liq)}$ at 77 K on samples (a) starting Na-TsVM and (b) H-TsVM prepared by chemical decationation in a NH_4Cl solution in (c) the anode and (d) the cathode compartments of the electrolyzer in a NH_4Cl solution in the coordinates of the Dubinin–Radushkevich equation.

admixtures upon treatment (Fig. 6). These admixtures may be residual compounds of hydrothermal synthesis (alkali and sodium polyaluminate [13]) and sodium polysilicates formed during the synthesis along with the zeolite [21, 24]. According to data from chemical analysis (Table 3), ~43% of the sodium ions in Na-TsVM are not compensatory. This fact was also noted in [25].

Table 3. The influence of the decationation method on the chemical composition of TsVM samples

No. of sample	Sample* (pH of medium)	Na_2O, wt %	Al_2O_3, μmol/g
1	Na-TsVM	4.15	983
2	CD (6.5)	0.03	934
3	CD (–1.5)	0.02	718
4	EA (1.5)	0.07	907
5	EA (2.5)	0.02	917
6	EA (3.3)	0.06	921
7	EC (10.0)	0.86	909

* For abbreviations, see Table 2.

The presence of $NaAlO_2$ in TsVM is confirmed by the findings of the IR-spectroscopic study (Fig. 5). The absorption band at 876 cm^{-1}, which is not typical of zeolites with the ZSM-5 structure, is present in the spectrum of the starting Na-TsVM (sample no. 1). This band disappears in the spectra of decationated samples. The absorption in the 870–700 cm^{-1} range is usually attributed to the Al–O vibrations in aluminum–oxygen compounds formed by polymerized AlO_4 tetrahedrons, including aluminate compounds of alkali and alkaline earth metals [26].

Analysis of the starting and decationated TsVM samples for the aluminum (see Table 3) showed that the samples undergo dealumination during decationation. The degree of dealumination is determined by the treatment conditions and increases with increasing acidity of the medium [17]. As follows from the constancy of the position of the absorption band at 1094 cm^{-1} (Fig. 5), the zeolite framework is not dealuminated. Therefore, we conclude that the samples are dealuminated by the removal of the extraframework aluminum compounds from zeolite pores.

An increase in the mesopore parameters in H-TsVM is determined by the treatment conditions. The most pronounced increase in V_{meso} (by 67–114%) was found for TsVM modified in an almost neutral or weak acidic media (sample nos. 2 and 6, respectively). Treatment in an acidic medium (pH 1.5–2.5) changed the V_{meso} value by 19–63%. The least pronounced increase (by 11%) was found for the sample decationated in an alkaline medium (sample no. 7). These facts suggest that changes in the TsVM texture are also due to the transformations of admixtures.

The most pronounced increase in the parameters of mesopores in the H-TsVM samples prepared by chemical decationation in a medium close to neutral or by anode treatment at pH 3.3 (sample no. 6) is probably due to the formation of the aluminum hydroxide phase with intrinsic secondary pores of ~100 Å in diameter (Fig. 3b). According to chemical analysis, these samples are the least dealuminated because, during the hydrolysis of $NaAlO_2$ in an aqueous medium at a pH value close to neutral, fragments of the aluminum hydroxide phase are probably formed and remain in the zeolite. The results of the IR study confirm this suggestion (Fig. 4, sample nos. 2 and 5). The absorption band at 876 cm^{-1} disappears and simultaneously a broad band appears in the 750–600 cm^{-1} range. According to [26], the absorption in this spectral region is due to the Al–O vibrations in the polymeric aluminum–oxygen compounds formed by the AlO_4 tetrahedrons (ν = 700 cm^{-1}) and AlO_6 octahedrons (ν = 650–600 cm^{-1}). The appearance of the broad bands in the regions 900–700 and 650–500 cm^{-1} in the IR spectra of silica gel with deposited aluminum oxide was also reported in [27].

An increase in V_{meso} and S_{meso} of TsVM treated in an acidic medium (samples nos. 3–5) is likely due only to the removal of admixtures. Up to 27% aluminum is removed. Only fragments of the aluminum hydroxide phase are formed in small amounts. The weak absorption band in the range 650–600 cm^{-1} appears in the IR spectra of these samples (Fig. 4, samples nos. 3 and 4). Small amounts of hydroxide are due to the fact that the conversion of sodium aluminate at low pH is accompanied by the formation of acid or base aluminum salts, which are then partially removed from the zeolite. The high-resolution ^{27}Al NMR spectroscopy data support these assumptions (Fig. 7). The signals with the chemical shift δ = 0 ppm typical of six-coordinated aluminum cations [28] appear in the spectra of the samples.

The least changes in the texture of TsVM are seen upon modification in the cathode compartment of the electrolyzer probably because of the partial removal of admixtures from the zeolite pores at high pH values up to pH 10. Weak absorption in the range ν = 750–600 cm^{-1} of the IR spectrum (Fig. 5, sample no. 6) may indicate that the aluminum–oxygen compounds are not formed, and the data of ^{27}Al NMR confirm this suggestion. One signal with the chemical shift δ = 57 ppm typical of the framework aluminum atoms tetrahedrally coordinated to oxygen is seen in the ^{27}Al NMR spectrum of the sample that is decationated in the cathode compartment.

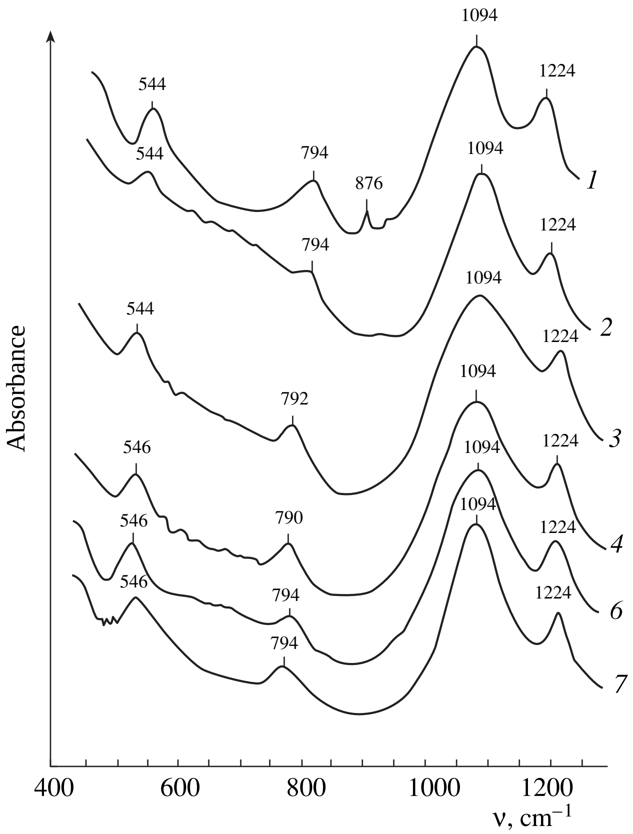

Fig. 5. IR spectra of framework vibrations for TsVM samples modified under different conditions.

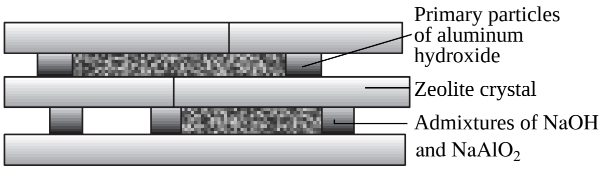

Fig. 6. Model of TsVM secondary pore structure.

To summarize, we conclude that the decationation of the zeolite TsVM in the electrolyzer compartment does not alter the zeolite structure. An increase in the specific surface area and pore volume upon modification is due to the removal of admixtures from some fraction of the zeolite pores.

TsVM mesopores are probably formed by the mutual coordination of the zeolite crystals through the mediation of the primary particles of the aluminum hydroxide phase, 42 Å in diameter.

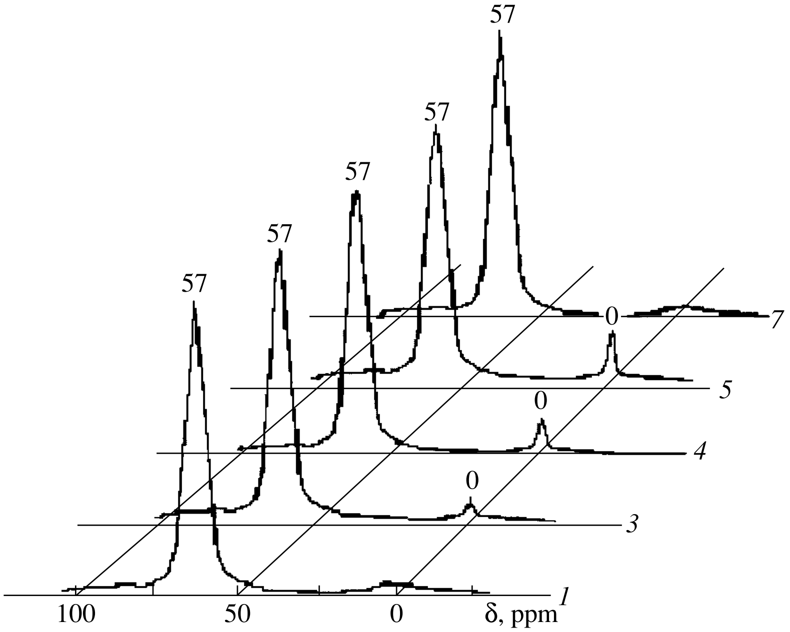

Fig. 7. The ^{27}Al NMR spectra for (*1*) initial Na-TsVM and (*3*) H-TsVM samples prepared by chemical decationation in a HCl solution in (*4*) the anode compartment in a NH_4Cl solution; (*5*) the anode and cathode compartments in a NH_4Cl solution; (*7*) the cathode compartment in a NH_4Cl solution (numbers of curves correspond to those of samples in Tables).

Modification in weak-acidic or neutral media is accompanied by the most pronounced increase in S_{meso} and V_{meso} due to the formation of an additional phase of aluminum hydroxide with its own mesopore system.

Acidic decationation favors the removal of the extraframework aluminum compounds. The degree of decationation is proportional to the acidity of a medium. The aluminum hydroxide phase is formed in small amounts.

Partial removal of admixtures occurs during alkaline modification, and, as a result, the changes in the parameters of mesopores are minimal.

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