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Thermal Stability of Zeolites Y and ZSM-5 in Matrices of Various Compositions

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Abstract—Stability of the crystal structure of zeolites Y and ZSM-5 in the presence of the most frequently used matrix components was studied under conditions of thermal and hydrothermal treatments at high temperatures.

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Modern zeolite-containing catalysts are composite materials constituted by a matrix including a binder and a filler and an active component, zeolite. Zeolites of Y and ZSM-5 types are widely used as active components of catalysts in deep cracking of crude oil, hydrodeparaffinization, and hydrocracking. These processes occur at high temperatures and also in the presence of steam, as, e.g., in the case of catalyst regeneration in cracking processes. Therefore, development of thermally stable and highly active zeolite-containing catalysts requires an understanding of how the crystal structure of zeolites changes in severe thermal and hydrothermal conditions in the presence of matrices of various compositions.

The matrices used to prepare modern zeolite-containing catalysts are complex multicomponent systems capable to satisfy a number of requirements to catalysts in the course of their operation [1–4]. The behavior of catalysts is determined both by properties of separate constituents (zeolite and matrix components) and by their mutual influence. The presently used matrices are of multicomponent nature because separate components frequently fail to provide properties necessary for a catalyst.

One of ways to improve zeolite-containing systems consist in using montmorillonite as a matrix component. Montmorillonite has a high plasticity, which leads to a good moldability of its mixtures with other components of a catalyst. The high heat capacity of montmorillonite favors heat release from the zeolite component in the regeneration stage and thereby improves the thermal stability of the catalyst [4–6].

The number of studies concerned with zeolite-containing catalysts in matrices of various compositions is sufficiently large [7–11], whereas information about the effect of matrix components on the behavior of zeolites in severe temperature conditions of processes is comparatively scarce [12–14]. There have been reports about the role of the amorphous matrix in hydrothermal aging of cracking catalysts [10] and on the effect of Na-montmorillonite on the acidity and catalytic properties of zeolite-containing catalysts [11].

The aim of the present study was to determine how matrices of various compositions affect the thermal stability of zeolites Y and ZSM-5.

EXPERIMENTAL

As starting components for fabrication of model samples served zeolite Y in a mixed cation-decationized form, zeolites ZSM-5 with SiO_2/Al_2O_3 ratios in the lattice of 30 and 70, natural montmorillonite with SiO_2/Al_2O_3 ratios in the lattice of 30 and 70, natural montmorillonite in the calcium form, silicon dioxide sol, amorphous aluminosilicate, and reprecipitated aluminum hydroxide with a pseudoboehmite structure.

All the catalyst samples were prepared by mixing aqueous suspensions of components, with the subsequent filtration and molding of the mixture. The resulting catalyst has grains with a nearly spherical shape, 0.25–

0.15 mm in size. Further, the catalyst was dried at 100°C, calcined at 500–900°C, and hydrothermally treated in 100% steam in the temperature range 700–800°C.

Data on the phase composition of the samples and their degree of crystallinity were obtained using a DRON-3 diffractometer ($Cu_{K\alpha}$ monochromatized radiation). The relative crystallinity of zeolite Y in the samples was determined in accordance with ASTM.D 3906-03. It measuring the relative crystallinity of the zeolite in the samples subjected to thermal and hydrothermal treatments a sample calcined at $T = 500°C$ was used as reference. The degree of dealumination of zeolite was evaluated by the change in the lattice modulus M (SiO_2/Al_2O_3 ratio in the zeolite lattice) calculated from the results of an X-ray phase analysis

$$M = \{[1.6707/(a_0 - 24.19)] - 1\}2,$$

where a_0 is the zeolite lattice constant (Å) found in accordance with ASTM.D 3942-03.

The porous structure of the samples was studied by the method of low-temperature adsorption of nitrogen (Micromeritics ASAP-2020M instrument). The specific surface area S_{sp} was found by the BET technique, and values of the total adsorption pore volume V_{ads} were determined from the adsorption of nitrogen at $P/P_0 = 0.99$. The volume V_{micro} of micropores accessible to the adsorbate was found by the comparative method (t-method); the pore diameter D_{pore} was calculated by the formula $4V_{ads}/S_{sp}$.

The catalytic activity of the samples was found in accordance with the ASTM.D 3907-03 standard on a MAK-2M flow-through laboratory installation with a fixed catalyst bed at a temperature of 527°C and mass feed rate of the raw material of 24 h^{-1}. Hydropurified vacuum gas oil served as raw material. The catalyst charge was 5 g; amount of passed raw material, 1 g; and reaction duration, 30 s.

Gaseous cracking products (C_1–C_5) were analyzed with a Kristall 5000.1 chromatograph. A quantitative analysis of liquid products was made with a Shimadzu GC-2010 chromatograph in accordance with ASTM.D 2887 standard.

All the catalysts prepared contained 25 wt % zeolite Y and 75 wt % matrix. The chemical composition of the components used is presented in Table 1.

The variation of the relative crystallinity of the zeolite in various matrices depending on the steam treatment temperature is shown in Fig. 1.

Table 1. Chemical composition of the catalysts

Component	Content, wt %			
	Na_2O	Al_2O_3	SiO_2	$(REE)_2O_3$*
Zeolite Y	1.77	21.49	62.91	13.83
Montmorillonite	0.21	23.59	60.43	–
Silicon dioxide	–	–	100.00	–
Aluminosilicate	0.20	12.50	87.30	–
Aluminum oxide	0.10	99.90	–	–

* $(REE)_2O_3$ is a mixture of oxides of rare-earth elements (Ln + Ce + Pr > 95%).

The highest thermal stability is observed for the zeolite in an amorphous aluminosilicate matrix. The aluminum oxide matrix fails to preserve the high crystallinity of the zeolite in the temperature range 550–775°C under study. The silicon dioxide matrix leads to a decrease in the zeolite crystallinity at 550–650°C. However, the crystallinity of the zeolite remains at higher temperatures (750–775°C) in the presence of silicon dioxide. Montmorillonite exerts the weakest influence on the manner in which the crystallinity of the zeolite changes in calcination.

The change in the zeolite crystallinity in hydrothermal treatments can be attributed to redistribution of sodium cations among the zeolite and the matrix. As shown in [3, 15], sodium cations tend to be evenly distributed among

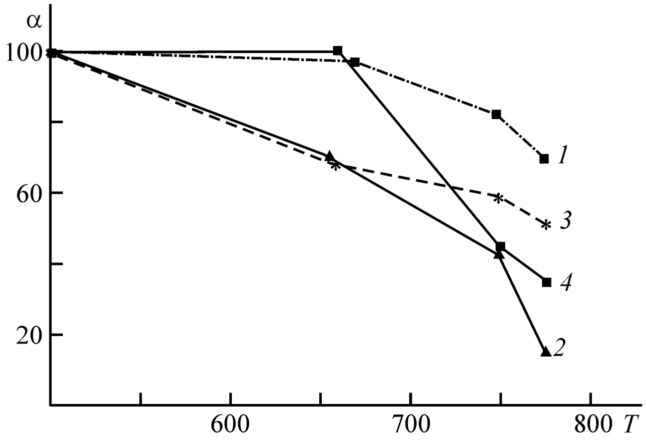

Fig. 1. Relative crystallinity α of zeolite Y in various matrices vs. the temperature T of hydrothermal treatment. Matrix: (1) aluminosilicate, (2) aluminum oxide, (3) silicon dioxide, and (4) montmorillonite.

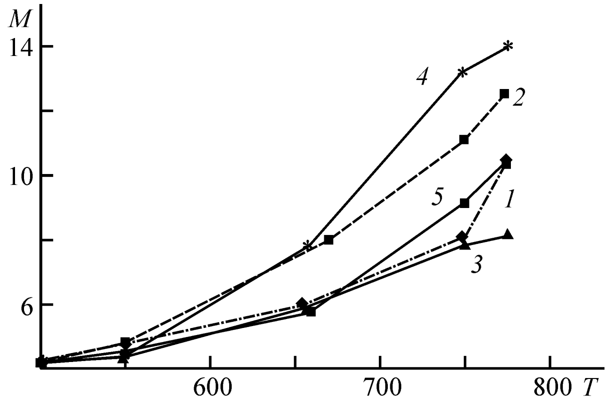

Fig. 2. Lattice modulus of zeolite Y vs. the treatment temperature *T*. Matrix: (*1*) absent, (*2*) aluminosilicate, (*3*) aluminum oxide, (*4*) silicon dioxide, and (*5*) montmorillonite; the same for Fig. 3.

the zeolite and the matrix in a high-temperature treatment. Commonly, the zeolite component of a catalyst contains a greater amount of sodium cations than the matrix (Table 1) because of the localization of these cations in difficultly accessible places of the zeolite. In the course of a high-temperature treatment, sodium cations migrate from the zeolite component into the matrix, and the decrease in the content of sodium cations leads to an increase in the structural stability of the zeolite. The amorphous aluminosilicate matrix has a higher cation capacity, and the redistribution of the cations leads to a lower content of sodium in the zeolite and, consequently, to a higher thermal stability of the zeolite. The cation capacity of the calcium form of montmorillonite, aluminum oxide, and silicon dioxide is lower than that of the amorphous aluminosilicate and, therefore, the thermal stability is substantially poorer in matrices of this kind.

The thermal stability of the zeolite can be affected not only by the migration of sodium cations, but also by that of silicon from the matrix into the zeolite structure. It was demonstrated in [10] by a number of methods (STEM, 29Si MAS-NMR) that, under the severe conditions of hydrothermal treatment of zeolite Y, the crystal structure of the zeolite in the amorphous aluminosilicate matrix is “restored” via migration of silicon from the matrix into the zeolite.

The lattice modulus of the zeolite (SiO_2/Al_2O_3) can serve, together with the degree of crystallinity, for analysis of changes in the crystal structure of the zeolite. A change in the modulus is a measure of the amount of aluminum removed from the zeolite skeleton in the course of hydrothermal treatment. Figure 2 shows how the lattice modulus of the zeolite depends on the temperature of treatment with steam.

The degree of dealumination of the zeolite is determined by the content of aluminum in the matrix used (Table 1). Accordingly, the smallest zeolite dealumination is observed for the aluminum oxide matrix, and a high degree of dealumination, for the silicon dioxide matrix. The content of aluminum in montmorillonite (23.6 wt % in terms of Al_2O_3) is close to its content in the given zeolite Y (21.5 wt % Al_2O_3), which means that the presence of montmorillonite has nearly no effect on the variation of the modulus of the zeolite with increasing temperature. The observed pattern can be attributed to enhancement or weakening of aluminum migration induced by the difference in its concentration between the zeolite and matrix phases.

The change in the crystal structure of the zeolite in the course of hydrothermal treatments can also be attributed to a change in the volume of micropores in the samples, calculated from data obtained in analysis of nitrogen adsorption isotherms. Because the matrix components have no micropores (montmorillonite contains an insignificant amount of micropores), the observed changes in this parameter of the samples can be attributed to disintegration of the crystal lattice of the zeolite [16].

Figure 3 shows data on a decrease in the micropore volume in relation to the hydrothermal treatment temperature. The change in the volume of micropores for the zeolite without matrix is recalculated with account of the fact that the content of the zeolite in samples with various matrices is 25%, i.e., the volume of micropores for a zeolite without matrix is multiplied by 0.25.

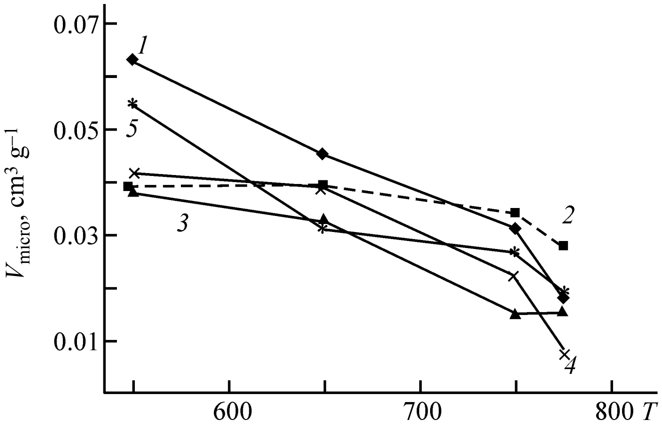

Fig. 3. Micropore volume $V_{micropore}$ of the composites vs. the treatment temperature *T*.

Table 2. Catalytic properties of zeolite-containing catalysts in relation to the matrix nature

Property	Matrix			
	amorphous aluminosilicate	silicon dioxide	aluminum oxide	montmorillonite
Conversion, %	80.9	46.0	75.8	69.3
Yield, wt %				
Gases	26.4	11.6	21.6	18.6
Gasoline	46.3	31.3	45.9	45.6
light gas oil	13.5	18.9	18.3	17.1
heavy gas oil	5.6	35.1	5.9	13.6
Coke	8.2	3.1	8.3	5.1

The highest thermal stability is observed for the zeolite in the amorphous aluminosilicate matrix, as also in the case of estimation by the relative crystallinity of the zeolite. As the treatment temperature increases, these two parameters change for the given sample to about the same extent. In the presence of other matrices, the manners in which the volume of micropores and the relative crystallinity vary may be strongly different. This may be due to blocking of entrances into the zeolite channels by matrix fragments. As additional evidence in favor of this version serves the fact that, at comparatively low temperatures, when there are no changes in the crystallinity of the zeolite, the volumes of micropores in the samples are already substantially smaller than those expected from calculations from the zeolite content. As the composite treatment temperature is raised, pores of the matrix become coarser, which probably leads to a better accessibility of the micropores of the zeolite.

Table 2 lists the catalytic parameters of catalysts based on zeolite Y in the presence of various matrices after a hydrothermal treatment (775°C, 100% steam).

It can be seen from the presented data that the activity of the catalysts in various reactions characteristic of the cracking process strongly depend on the type of the matrix used. The intrinsic activity of the zeolite can be judged from its operation in the presence of an inert matrix, silicon dioxide. The high activity of the sample with the aluminosilicate matrix is due to the contribution of the matrix activity and to the enhanced thermal stability of the zeolite.

A comparison of the results obtained in studies of the thermal stability of zeolites Y in various matrices demonstrated that the behavior of zeolites under the conditions of severe hydrothermal treatments is largely determined by the type of the matrix used.

The aluminosilicate matrix provides a higher activity, better crystallinity of the zeolite, and preservation of the micropore volume of the zeolite. If the thermal stability of the zeolite in the presence of the aluminosilicate is due to redistribution of not only sodium, but also silicon, then this should be accompanied by a change in the acidity of the zeolite component and, consequently, should affect the intrinsic activity of the zeolite. In this case, an acceptable thermal stability of the zeolite can be obtained, with a high activity of the catalyst as a whole, by varying the chemical and phase composition of the catalyst.

The composition of the matrix is determined not only by the conditions, but also by the goal of the process. When, for example, zeolite ZSM-5 is used as the active component of the hydrodeparaffinization catalyst, presence of the aluminosilicate in the matrix is undesirable because of its high cracking activity, and, therefore, aluminum oxide matrices are used more frequently [17]. Montmorillonite and aluminum hydroxide are frequently used as matrices for various zeolite-containing catalysts. Specific features of formation of the porous structure of a system constituted by montmorillonite and aluminum oxide, taken in various ratios, were described in detail in [6, 18].

The variation of the porous structure of zeolite ZSM-5 having a lattice modulus of 30 with thermal treatment

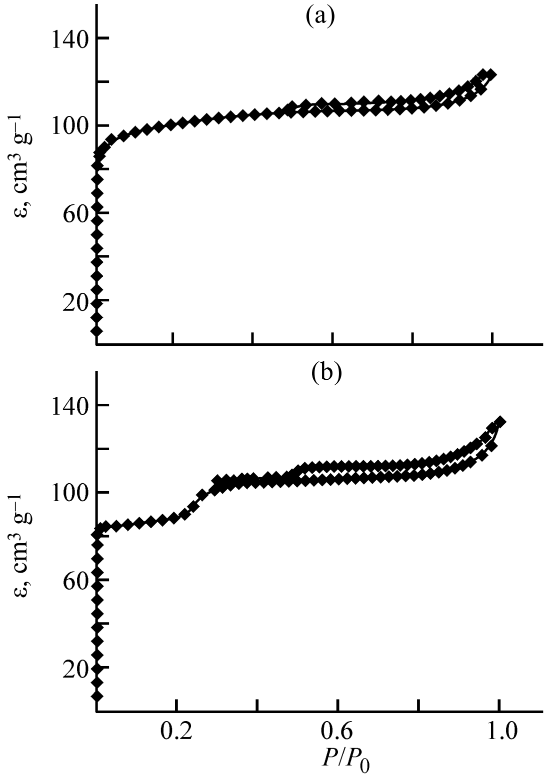

Fig. 4. Isotherms of nitrogen adsorption on zeolite ZSM-5 (a) calcined at $T = 700°C$ and (b) hydrothermally treated (100% steam) at $T = 800°C$. (ε) Amount of the adsorbate and (P/P_0) relative pressure; the same for Fig. 5.

conditions is shown in Figs. 4a, 4b. In the case of thermal treatment of the zeolite in the temperature range 500–700°C, no significant changes occur in the zeolite structure, and the type of the nitrogen adsorption isotherm corresponds to that shown in Fig. 4a.

Upon treatment of the zeolite at a higher temperature in the presence of steam, the adsorption isotherm (Fig. 4b) acquires an additional step at relative pressures of 0.2–0.3. This step is due to the appearance of an additional volume of narrow (20–40 Å) mesopores [19, 20].

In the case of a hydrothermal treatment of a zeolite ZSM-5 with a large lattice modulus (70), an additional volume of mesopores also appears. For the zeolite with a modulus of 70, the fraction of the adsorbate related to the region in which a step appears in the adsorption isotherm is somewhat larger (20%) than that for the zeolite with a modulus of 30 (10–14%).

The process of formation of new mesopores in the zeolite may be due to its dealumination and may occur by the mechanism suggested in [4], via redistribution of tetrahedral groups of aluminum and silicon in the crystal structure of the zeolite. However, the observed changes cannot by fully attributed to the dealumination process, because the content of aluminum in zeolites ZSM-5 is 3.3 wt % (at a modulus of 30) and 1.4 wt % (at a modulus of 70). Therefore, if the additional volume of mesopores appeared only via dealumination of the zeolite, the process would be more pronounced for a zeolite with a higher content of aluminum in the lattice and, on the whole, the additional volume of mesopores would constitute a smaller fraction of the total pore volume of the zeolite.

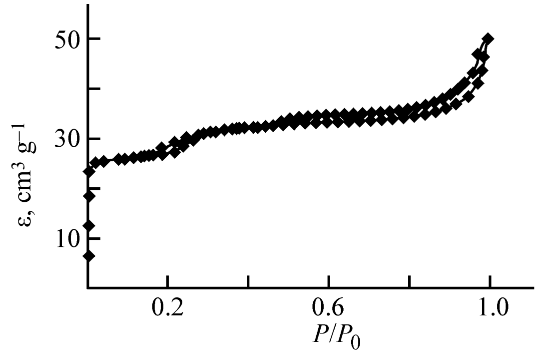

Fig. 5. Isotherm of nitrogen adsorption on a sample composed of 60% ZSM-5 and 40% montmorillonite, after its treatment at 800°C in 100% steam.

In a hydrothermal treatment of the zeolite in the presence of a matrix or its separate components, the appearance of a “secondary” mesoporosity is determined by the amount of the zeolite introduced. The type of the adsorption isotherm is determined by the matrix composition. As an example, Fig. 5 shows the nitrogen adsorption isotherm for a sample with 40% montmorillonite and 60% ZSM-5, subjected to a hydrothermal treatment at $T = 800°C$. The appearance of a hysteresis loop at $0.15 < P/P_0 < 0.30$ confirms that capillary condensation occurs in this region, which can serve as evidence in favor of formation of secondary mesopores.

The change upon various treatments in the volume of micropores of composites formed by the zeolite with a matrix and its components was used to evaluate the extent to which the crystal structure of ZSM-5 changed. Table 3 lists the volumes of micropores in the composites and in a pure zeolite treated under similar conditions. The calculated volumes of micropores in the composites are given on the basis of the percentage content of the zeolite.

The data in Table 3 demonstrate that the smallest difference between the calculated and experimental values

Table 3. Micropore volume of the composites

Composition of the composites, wt %	V_{micro}, cm^3 g^{-1}			
	700°C		800°C, 100% H_2O	
	found	cacld.	found	cacld.
ZSM-5 – 30	0.13	–	0.12	–
MM – 20, Al_2O_3 – 20, ZSM-5 – 60	0.080	0.078	0.070	0.072
MM – 0, Al_2O_3 – 40, ZSM-5 – 60	0.068	0.078	0.050	0.072
MM – 40, Al_2O_3 – 0,ZSM-5 – 60	0.046	0.078	0.036	0.072

is observed for the matrix constituted by montmorillonite and aluminum oxide. Consequently, the matrix of this composition preserves the crystal lattice of the zeolite to the greatest extent. It should be noted that separately taken matrix components cannot improve the thermal stability of zeolite ZSM-5 in a hydrothermal treatment.

CONCLUSIONS

(1) It was demonstrated that characteristics of zeolites Y and ZSM-5 studied are strongly changed under the severe conditions of hydrothermal treatments. The extent of these changes is determined by the composition of the matrix components.

(2) Zeolite Y shows the best thermal stability in the presence of an aluminosilicate. This composition is also characterized by the highest activity in cracking.

(3) The changes in zeolite ZSM-5 upon treatment under hydrothermal conditions consist in that a considerable amount of micropores in the zeolite are disintegrated and an additional amount of narrow mesopores is formed. For the zeolite with a larger modulus, this effect is more pronounced, although this zeolite is less subject to dealumination. The zeolite structure remains the most stable in the presence of a matrix composed of montmorillonite and aluminum oxide.

(4) With account of the specific features of the influence exerted by different matrix components on such zeolite parameters as the degree of crystallinity, lattice modulus, and volume of micropores, both the catalytic and physical parameters of catalysts based on zeolites Y and ZSM-5 can be optimized in relation to their purpose and working conditions.

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