CONCLUSIONS

1. Heats of adsorption of O_2, N_2O, C_2H_4, and C_3H_6 by surface Mo^{4+}ions obtained by photoreduction of Mo^{6+}/SiO_2 by carbon monoxide have been determined for the first time.

2. It has been established that the heats of adsorption do not depend on the degree of coverage of the surface with adsorbed molecules, indicating a high degree of homogeneity of the Mo^{4+}ions obtained by photoreduction.

3. The calculated heat of adsorption of molecular oxygen in the form O^{2-} (653 kJ/mole) indicates high coordination unsaturation of the Mo^{4+} ions in the photoreduced specimens.

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EFFECT OF STEAMING ON COMPOSITION OF ACID CENTERS AND CATALYTIC PROPERTIES OF SUPERHIGH-SILICA ZEOLITES IN PSEUDOCUMENE ISOMERIZATION

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Superhigh-silica (SHS) zeolites of the Pentasil type have found extensive applications in recent years as acidic-type catalysts. The SHS zeolites have unique acid properties and pore structure, and are also good in terms of resistance to high temperatures and steaming. These catalysts are the most effective in reactions of liquid fuel synthesis from lower alcohols, the initial stages of which are accompanied by evolution of considerable quantities of water; they are also highly effective in the isomerization of alkylaromatic hydrocarbons (dimethylbenzenes and trimethylbenzenes). In the course of these reactions and in regenerations, SHS zeolites are repeatedly exposed to high temperatures and water vapor; therefore, it is logical to study the effect of preliminary steam treatment on the acidity of zeolite and on its catalytic properties as an aid in the development of optimum catalysts based on SHS zeolites.

In the work reported here, we applied spectroscopic methods in a study of the acid centers and state of aluminum in a TsVM [zeolite, high-modulus; i.e., a high-silica zeolite] after various thermal and steam treatments. These data are compared with the catalytic activity and selectivity of modified samples in the isomerization of pseudocumene.

EXPERIMENTAL

H-TsVM was synthesized without the use of any organic base, with subsequent decationization by treating with 0.5 N HCl down to $[Na_2O] < 0.05\%$. The TsVM had a structure character-

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TABLE 1. Influence of Conditions of Pretreating H-TsVM Zeolite on Distribution of Aluminum and Catalytic Properties in Isomerization of Pseudocumene

Sample	Pretreatment	Catalysate composition, %					Conversion, %	Selectivity with respect to isomerization products, %	Al/Si (surface)
		benzene + toluene	ΣO_2*	mesitylene	pseudocumene	hemimellitene			
(I)	Air, 820 K	7,8	20,8	16,9	47,5	6,9	52,5	45	0.047
(II)	Air, 1020 K	6,0	16,8	16,3	52,7	8,2	47,3	52	0,052
(III)	Steam, 820 K, 6 h	5,4	15,8	15.1	53,8	9,9	46.2	54	0.087
(IV)	6% steam/air mixture, 1020 K, 6 h	4.6	14,4	16,0	57,0	8,0	43,0	56	0,112
(V)	Sample (IV) treated with 0.5 N HCl	4,0	12,4	16,4	54.6	12,6	45.4	64	0,033

*As in Russian original — Translator.

istic for ZSM Pentasils, a 90% degree of crystallinity, and SiO_2/Al_2O_3 = 33. This zeolite was then subjected to thermal and steam treatments under conditions shown in Table 1. The sample that had been steamed at 1020 K in a 6% steam/air mixture was then treated with 0.5 N HCl to remove extralattice aluminum. Before performing the spectral measurements, the samples were conditioned at 820 K for 6 h and then at 1020 K for 2 h under vacuum. In this treatment, the temperature was raised at a rate of 5 K/min.

In studying the acid centers of the zeolite, we used IR spectroscopy in diffuse-scattered light. The spectra were measured in Perkin–Elmer 580B and Acta Beckman M-VII spectrophotometers, following procedures described in [1]. For identification of the Lewis acid centers, we used as a probe H_2 adsorbed at 77 K and a pressure to 50 mm Hg [2]. X-ray photoelectron spectra were obtained in an Escalab-5 instrument. In calculating the Al/Si ratios, the ionization section of the atoms was taken into account.

The catalytic activity of the samples in pseudocumene isomerization was measured in a flow-type laboratory unit with a fixed bed of catalyst at 77 K with a feedstock space velocity of 6.5 h^{-1}. The reaction products were analyzed by GLC.

RESULTS AND DISCUSSION

In Fig. 1a we show IR spectra of the OH groups in samples of H-TsVM zeolite after various treatments. The absorption bands at 3740 and 3610 cm^{-1} pertain to the principal stretching vibrations of nonacidic silanol OH groups and acidic OH bridge groups, respectively. The broad line in the 3200-3300 cm^{-1} region pertains to bridge OH groups forming hydrogen bonds with neighboring oxygen atoms of the lattice. In the spectra of the steamed samples we find an additional band at 3680 cm^{-1}, which is usually ascribed to OH groups bonded to extralattice aluminum. From Fig. 1a it can be seen that whereas severe pretreating conditions (1020 K) have practically no effect on the state or concentration of the B-centers (spectrum 2), steaming gives a considerable reduction in the number of strong B-centers (spectra 3-5).

In Fig. 1b we show IR spectra of H_2 adsorbed at 77 K on samples of the zeolite that had been calcined under vacuum at 820 K (spectra 1-5) and 1020 K (6, 7). As was established previously [1, 2], the band at 4110 cm^{-1} pertains to complexes of H_2 molecules with bridge OH groups; the bands at 4000-4070 cm^{-1} correspond to H_2 molecules adsorbed on various types of L-centers. In particular, the bands at 4035 and 4060 cm^{-1} are ascribed to complexes of H_2 with tricoordinated lattice ions of silicon and extralattice centers of the type $^+[Al{=}O]$, bonded to aluminum that has left the skeleton. In the spectra of H_2 adsorbed on SHS zeolites, a third band had been observed previously, related to the presence of tricoordinated lattice atoms of aluminum; in the present study, however, we did not find any such band for these zeolites.

As can be seen from Fig. 1, steaming of the zeolite gives a considerable reduction of not only the number of strong B-centers, but also the total concentration of centers capable of adsorbing H_2. Moreover, in contrast to the thermally activated samples, in which the centers of H_2 adsorption are bridge OH groups (4110 cm^{-1}), we find that for the steamed zeolites, the probe molecules are adsorbed primarily on L-centers (4060, 4035 cm^{-1}). In other words, preliminary steaming facilitates the formation of L-centers in SHS zeolites, since thermal

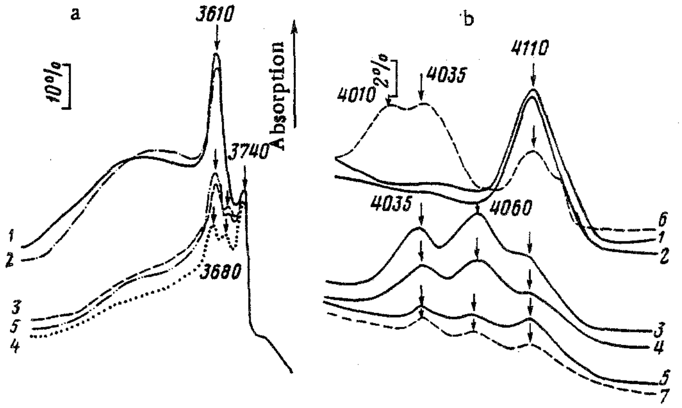

Fig. 1. IR spectra of OH groups (a) and H_2 (b) adsorbed at 77 K and 50 mm Hg on H-TsVM: 1, 6) (I), 2) (II), 3) (III), 4) (IV), 5, 7) (V). Treating temperature under vacuum 820 K (1-5) or 1020 K (6, 7).

activation requires temperatures of 870 K or higher for the appearance of these centers in any significant concentrations. It should also be noted that in the steamed samples that were almost completely dehydroxylated (Fig. 1b, spectrum 7), the total concentration of L-centers is considerably lower than in the thermally activated zeolites (spectrum 6).

A comparison of the spectra shows that steaming tends to remove a considerable quantity of aluminum from the lattice: In the IR spectra of adsorbed H_2, the most intense band is that at 4060 cm^{-1}, which had been previously assigned to complexes of H_2 with extralattice centers. This conclusion is consistent with data reported in [3] on the influence of steaming on the state of aluminum in zeolites, these data indicating that dealuminization of the lattice takes place in the course of such treatment.

Additional decationization of the steamed sample leads to an increase in intensity of the band at 3610 cm^{-1} and a simultaneous decrease in intensity of the band at 4060 cm^{-1}. This indicates that upon decationization, part of the extralattice aluminum is removed, and this makes it possible to form an additional quantity of acidic bridge OH groups.

The IR spectroscopic data that we have obtained are consistent with the results obtained on these samples by means of XPES. In Table 1 we have entered data illustrating the influence of zeolite pretreating conditions on the Si/Al ratio on the surface of the microcrystallites. These data indicate that thermal treatment of the zeolite under severe conditions (1020 K) has practically no effect on the content of aluminum in the lattice, whereas steaming tends to enrich the surface layer of the crystallites with aluminum, apparently because of dealuminization of the volume and migration of extralattice aluminum to the surface of the microcrystallites.

The data obtained by physicochemical methods explain the difference in activity and selectivity of steamed and thermally activated zeolites in pseudocumene isomerization. Results are presented in Table 1 from a study of the catalytic properties of the modified TsVM samples. Steaming leads to a certain decrease in pseudocumene conversion, probably related to the decrease in total concentration of acid centers that was observed in the spectra. At the same time, however, there is an increase in the selectivity with respect to isomerization products. The maximum selectivity is observed for the steamed sample that had then been subjected to additional decationization; this sample also gave a higher conversion. Apparently this is related to an increase in the concentration of B-centers (see Fig. 1a), these centers usually being regarded as the active centers in the isomerization of alkylaromatic hydrocarbons. The main side reaction in pseudocumene isomerization is dealkylation to form benzene, toluene, xylene isomers, and gas consisting primarily of C_1-C_3 light paraffins and H_2 (2-3% of feed). It should be noted that there was practically no disproportionation of trimethylbenzenes, and the quantity of coke formed in the first 30 min of the reaction was $\leq$0.6%.

The data obtained in the isomerization experiments indicate that for all of the catalyst samples, the composition of the trimethylbenzene mixture is close to equilibrium under these particular process conditions: mesitylene/pseudocumene/hemimellitene = 22.5/62.3/15.2. Even at low pseudocumene conversions, the ratio of mesitylene and hemimellitene yields remains practically constant, equal to the corresponding ratio for the equilibrium mixture. In contrast, in isomerization of xylenes on zeolites of the ZSM type, as was shown in [4], considerable deviations are usually found from the equilibrium composition of the xylene mixture; in particular, the reaction is more highly selective with respect to the para isomer, the molecules of which are the smallest. This fact is explained by the occurrence of a reaction of dimethylbenzene isomerization in the zeolite pores and by steric hindrance imposed by the dimensions of the passages on the structure of the product that is formed. In the isomerization of trimethylbenzenes on these same zeolites, we did not find any significant deviations of the isomer mixture composition from the equilibrium composition, even though the molecules of mesitylene and hemimellitene do differ in size; therefore, we can conclude that the reaction of pseudocumene conversion does not take place in the pores of the zeolite, but rather at the mouths of the pores or on the outer surface, where there is no steric limitation.

This hypothesis is also consistent with the data obtained in physicochemical studies of these zeolites by means of IR and XPES spectroscopies. For example, when the change is made from sample (I) to sample (II) (Table 1), the latter sample having been activated at a higher temperature, we do not observe any differences in the IR spectra of the OH groups or adsorbed H_2, thus indicating the absence of any change in the acid centers located within the zeolite structure. At the same time, according to the XPES data, in the near-surface layer under these conditions, the process of dealuminization has already begun, probably in connection with the low thermal stability of aluminum ions located close to or on the outer surface of the microcrystals. Simultaneous with the start of changes in the chemical composition of the outer surface, we observe a decrease in conversion of pseudocumene and an increase in selectivity.

Steaming, which is far more severe, affects the volume of the microcrystallites; the dealuminization process proceeds to a greater degree, and it leads to further migration of aluminum to the outer surface. In turn, this results in a lower conversion of pseudocumene, since the extralattice aluminum ions block an ever-increasing part of the active centers located on the outer surface. Subseqeunt treatment of the zeolite with HCl tends to wash out the extralattice aluminum mainly from the outer surface, and this is accompanied by liberation of surface centers that are active in the isomerization of pseudocumene. Moreover, such treatment may result in widening of the pore mouths, and this will also lend to an increase in the number of active centers.

CONCLUSIONS

1. By means of diffuse scattering IR spectroscopy and x-ray photoelectron spectroscopy, it has been shown that thermal treatment leads to dealuminization of the lattice of TsVM zeolite and to a substantial decrease in the total number of acid centers with an increase in the relative number of Lewis acid centers, related in particular to extralattice aluminum.

2. The decrease in the total number of acid centers results in a decrease in pseudocumene conversion, but an increase in selectivity of isomerization. It is concluded that the reaction takes place in the mouths of the pores or on the outer surface of the zeolite.

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