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Zinc-containing zeolite catalysts for ethane aromatization prepared by solid-state modification

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Solid-state modification was used to prepare zinc-containing zeolite catalysts based on pentasils with different framework SiO_2/Al_2O_3 ratios. The catalysts were studied by X-ray diffraction analysis and IR spectroscopy. The activity and selectivity of the Zn—pentasil systems prepared by the solid-state modification and impregnation methods were compared in the aromatization of ethane. The active and stable zeolite catalysts modified by transition metal ions can be obtained by the topochemical method.

Key words: Zn-containing catalysts, pentasils, solid-state modification, ethane aromatization, framework SiO_2/Al_2O_3 ratio.

Conversion of low-molecular paraffins, in particular, ethane, into aromatic C_6—C_{12} hydrocarbons is one of the promising routes of natural and oil gas processing. It has previously[1,2] been shown that highly siliceous zeolites of the pentasil family modified by transition metal ions are efficient catalysts of benzene formation from ethane in the reactions

$$3\,C_2H_6 \rightleftharpoons C_6H_6 + 6\,H_2$$

or

$$4\,C_2H_6 \rightleftharpoons C_6H_6 + 2\,CH_4 + 5\,H_2$$

These zeolites are bifunctional systems, whose activity is determined by the presence of both acid sites on the support and the centers containing metal ions.

Metal-containing zeolite catalysts of hydrocarbon conversion are usually prepared by the methods of ion exchange or impregnation of the zeolite support by solutions of compounds of the appropriate elements. However, a low ion-exchange capacity of the zeolites, in particular, pentasils, restricts the amount of metal cations introduced by ion exchange. On the other hand, impregnation does not ensure a uniform distribution of modifying ions in the bulk of the zeolite. In addition, solutions that need further utilization are used in both methods. Therefore, a search for new, more environmentally friendly methods for the preparation of active metal-containing zeolite-based catalytic systems seems urgent.

One of the promising methods for the preparation of such catalysts is the interaction of oxides or salts of transition elements with the zeolite matrix. This method is based on topochemical processes. The authors of several works[3—6] showed that metal ions can be introduced, in principle, into the zeolite structure by ion exchange in the solid state. It turned out that for some transition metals, which in aqueous solutions form large hydrated ions poorly penetrating into zeolite pores, topochemical reactions offer the way for ion-exchange sites to become easily accessible.

$$MO + 2\,H{—}O_{zeolite} \longrightarrow M(O_{zeolite})_2 + H_2O$$

M is metal

Thus, in some cases, isolated cations can be stabilized in zeolite channels and cavities to form metal-containing zeolite catalysts in one step without using solvents. The introduction of transition metal ions into the zeolite framework is accompanied by the neutralization of some protonic sites and the appearance of Lewis acid sites. This extends the range of surface groups capable of playing the role of active sites in aromatization. However, the role of Brönsted and Lewis sites in these catalysts in hydrocarbon transformations remains unclear. In particular, the first step of formation of aromatic structures from saturated C_2—C_5 hydrocarbons is assumed to be the dehydrogenation of paraffins involving strong Lewis acid sites containing ions of metal-modifiers.[2] The subsequent transformations of the olefins formed (oligomerization, ring closure) need protonic sites to occur.[7,8] Meanwhile, the concentration of Brönsted acid sites, which is low in highly siliceous zeolites, should decrease with the introduction of metal cations. In order to reveal the role of sites of different nature in the multistage aromatization of low-molecular paraffins, it is reasonable to use samples with different SiO_2/Al_2O_3 ratios as zeolite matrices.

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In this work, X-ray diffraction analysis and IR spectroscopy were used to study the formation of the Zn-containing zeolites of the pentasil family prepared by both the solid-state method and impregnation. Their activity and selectivity were compared in ethane aromatization.

Experimental

Hydrogen forms of pentasils ZSM-5 with different concentrations of aluminum in the framework (SiO_2/Al_2O_3 = 30, 56, 90, and 220) were used for the preparation of the catalysts. The zinc-containing systems were prepared by mechanically mixing ZnO powder with pentasils (ZnO+ZSM-5) or by the impregnation of the zeolites with an aqueous solution of zinc nitrate (ZnO/ZSM-5). The mechanical mixtures of zinc oxide and zeolite were stirred for 2 h until a homogeneous mixture was formed. Before catalytic experiments or physicochemical studies, the samples were treated in air, hydrogen, or consecutively in air and hydrogen (the flow rate of the gases was 3—3.5 L h^{-1}).

Transformations of ethane were studied in a flow-type setup with a fixed bed of the catalyst (the volume of the sample loading was 1 cm^3) at an atmospheric pressure in the 475—650 °C temperature interval, while varying the ethane flow rate ($U_{C_2H_6}$) from 225 to 2800 h^{-1}. The catalytic activity was estimated using the conversion of the starting paraffin ($X_{C_2H_6}$) and the yield of aromatic hydrocarbons calculated per ethane passed (Y_{Ar}). The integral selectivities of formation of aromatic hydrocarbons (S_{Ar}), ethylene ($S_{C_2H_4}$), and methane (S_{CH_4}) were calculated as the ratio of the yield of the corresponding product to the ethane conversion.

The acidic properties of the catalysts were studied by IR spectroscopy using pyridine adsorption.[7]

X-ray powder diffraction analyses were carried out using a DRON-2 diffractometer (Cu-Kα radiation) with the 2 and 1 deg min^{-1} scanning rates in the intervals 2θ = 6—60 and 40—50°, respectively.

Results and Discussion

Aromatization of ethane on Zn-containing pentasils. The influence of the zinc concentration on the conversion of ethane, the yield of aromatic hydrocarbons, and the selectivity of formation of the reaction products was studied using the Zn—pentasil systems (SiO_2/Al_2O_3 = 30) prepared by impregnation and containing 0.75—7.50 wt.% zinc. The catalytic properties of the samples were compared at 600 °C and $U_{C_2H_6}$ = 450 h^{-1}. Under these conditions, the H-form of pentasil containing no metal manifested no substantial activity ($X_{C_2H_6}$ = 8.4%, Y_{Ar} = 2.3%).

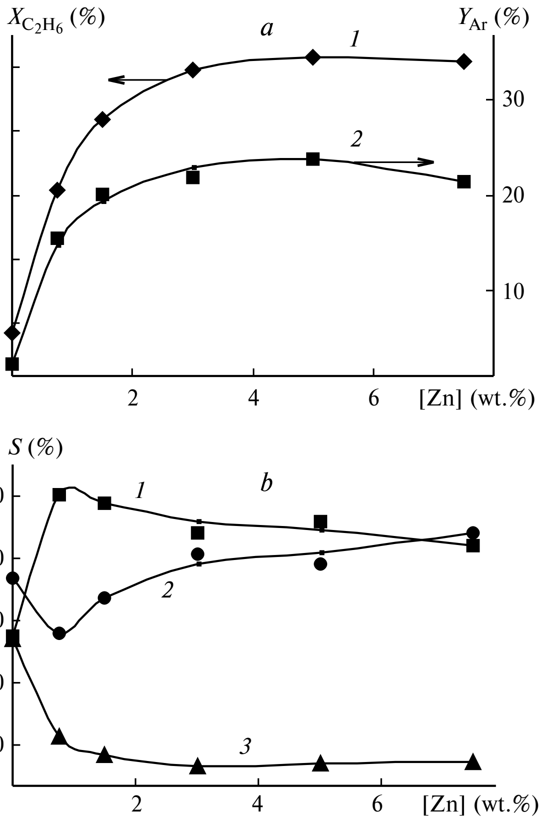

Fig. 1. Conversion of ethane ($X_{C_2H_6}$) (*1*), the yield of aromatic hydrocarbons calculated per passed ethane (Y_{Ar}) (*2*) (*a*), and the selectivities of formation of aromatic hydrocarbons (S_{Ar}) (*1*), methane (S_{CH_4}) (*2*), and ethylene ($S_{C_2H_4}$) (*3*) (*b*) as functions of the Zn concentration in the pentasil with SiO_2/Al_2O_3 = 30 (T = 600 °C, $U_{C_2H_6}$ = 450 h^{-1}).

The plots of $X_{C_2H_6}$, Y_{Ar}, and the selectivity of formation of gaseous and liquid products *vs*. Zn concentration in the zeolite are presented in Fig. 1, *a*, *b*. The promotion effect of zinc appears even when 0.75 wt.% metal are introduced into the pentasil: at $X_{C_2H_6}$ = 30% Y_{Ar} ≈ 16%, S_{Ar} ≈ 50%. The conversion of ethane and Y_{Ar} are much higher on the catalysts containing 3.0 wt.% zinc. The highest yield of the aromatization products (~24%) was achieved for the ZnO/ZSM-5 sample containing 5.0 wt.% metal. A further increase in the zinc concentration to 7.5 wt.% did not increase Y_{Ar} and resulted in a slight decrease in S_{Ar} along with some increase in S_{CH_4}. The qualitative composition of the products of ethane aromatization is virtually independent of the zinc content in the catalysts (Table 1), and only the ratios of concentrations

Table 1. Transformations of ethane into aromatic hydrocarbons on the ZnO/ZSM-5 catalysts (T = 600 °C, $U_{C_2H_6}$ = 450 h^{-1})

[Zn] (wt.%)	$X_{C_2H_6}$	Y_{Ar}	Composition of products (wt.%)				
	(%)		C_6	C_7	C_8	C_9	C_{10}—C_{12}
0	8.4	2.3	37.2	39.0	11.5	1.4	10.9
0.75	30.7	15.5	33.2	27.0	6.0	1.9	31.9
1.5	41.9	20.1	29.4	27.0	6.4	1.1	41.8
3.0	49.5	21.9	25.3	25.2	6.6	1.1	41.8
5.0	51.5	23.7	26.7	24.2	6.0	1.3	41.8
7.5	50.9	21.4	25.6	25.0	5.9	0.8	42.7

Note. Here and in Table 2 $U_{C_2H_6}$ is the volume hourly space velocity of ethane, $X_{C_2H_6}$ is the conversion of ethane, and Y_{Ar} is the yield of aromatic hydrocarbons calculated per passed ethane.

Table 2. Aromatization of ethane on Zn-containing pentasils with different framework compositions ([Zn] = 5 wt.%, T = 600 °C, $U_{C_2H_6}$ = 450 h^{-1})

Method of preparation	SiO_2/Al_2O_3 [a]	$X_{C_2H_6}$	Y_{Ar}	S_{Ar} [b]	S_{CH_4} [b]	$S_{C_2H_4}$ [b]	Composition of products (wt.%)				
		%					C_6	C_7	C_8	C_9	C_{10}—C_{12}
Impregnation	30	51.5	23.7	46.0	39.2	7.0	26.7	24.2	6.0	1.3	41.8
	56	51.3	24.0	46.8	37.8	9.4	25.3	27.1	9.0	3.5	35.1
	90	57.2	26.1	45.6	40.4	6.1	22.1	24.1	6.9	1.8	45.0
	220	38.1	17.7	46.5	33.9	12.1	28.9	29.1	8.1	3.3	30.6
Mechanical mixing	30	58.2	24.2	41.6	45.7	6.5	23.6	23.1	5.8	1.1	46.4
	56	46.5	22.9	49.2	33.5	9.5	27.8	29.3	8.9	3.2	30.8
	90	55.0	25.1	45.6	40.0	6.4	23.8	25.9	7.5	1.7	41.1
	220	44.7	20.7	46.3	36.2	11.2	27.7	29.6	8.0	2.9	31.8

[a] Molar ratio.

[b] S_{Ar}, S_{CH_4}, and $S_{C_2H_4}$ are the selectivities of formation of aromatic hydrocarbons, methane, and ethylene, respectively.

of particular hydrocarbons change insignificantly: an increase in the metal concentration decreases the content of benzene and alkylbenzenes C_7—C_8 and increases the content of aromatic C_{10}—C_{12} hydrocarbons.

The catalysts containing 5.0 wt.% zinc were chosen to compare the catalytic properties of the Zn—pentasil systems with different compositions of the framework prepared using impregnation and solid-state modification. As follows from the data presented in Table 2, the catalysts for ethane aromatization prepared by the introduction of zinc into the pentasils using the solid-state reaction are not inferior in terms of activity and selectivity to the samples prepared by the impregnation of the zeolites with a solution of zinc nitrate and containing the same metal content. A decrease in the aluminum concentration in the pentasil framework down to ~0.9 Al atoms in the unit cell (SiO_2/Al_2O_3 = 220) has almost no effect on the selectivity of formation of aromatic hydrocarbons. This concerns the catalysts prepared using both solid-state modification and impregnation.

X-ray diffraction analysis. The crystalline phases of zinc oxide and zeolites of the ZSM-5 type exhibit distinct X-ray diffraction patterns. Therefore, the specific features of formation of the catalysts active in the aromatization of low-molecular paraffins can be revealed by comparing the diffraction patterns of individual components of the catalysts prepared by the solid-state method with those of mixed catalytic systems.

The diffraction pattern of the starting pentasil with SiO_2/Al_2O_3 = 30 in the region of 2θ = 6—60° exhibits several diffraction maxima, the most intense of which are the doublet at 7.94—8.84°, the triplet at 23.12, 23.90, and 24.40°, the maxima at 29.26 and 29.86°, and the doublet at 44.95—45.40°. The positions of these maxima, their indices, and relative intensities are presented in Table 3.

The X-ray diffraction pattern of crystalline ZnO contains three reflections at 2θ = 31.9, 34.6, and 36.4°, and the latter is most strong. The pure ZSM-5 zeolite exhibits no diffraction peaks in this region. At the same time, as shown by analysis of the X-ray diffraction patterns of the samples prepared by mechanical mixing and containing 0.5—20.0% ZnO, the plot of the intensity of the maximum at 36.4° *vs.* the concentration of the crystalline phase of zinc oxide (ZnO_{cryst}) is linear. Therefore, the intensity of the reflection at 36.4° (I) can be used for the estimation of the ZnO_{cryst} concentration in the samples of the zinc-containing zeolite catalysts subjected to different treatments. The results of the corresponding calculations are presented in Table 4.

Table 3. Positions, indices, and relative intensities of diffraction maxima of the zeolite ZSM-5 with SiO_2/Al_2O_3 = 30

2θ/deg	[hkl]			I/I_{max} (%)
	h	k	l	
7.94	1	0	1	30
8.84	0	2	0	28
23.12	5	0	1	100
23.90	3	0	3	50
24.40	1	3	3	30
29.26	3	5	2	10
29.86	5	0	3	15
44.95	0	10	0	10
45.40	10	0	0	10

According to the data in Table 4, all samples under study contain the individual phase of zinc oxide. However, its concentration can substantially decrease due to different conditions of treatment. The treatment of the freshly prepared mechanical mixture of zeolite and zinc oxide by hydrogen causes more than twofold reduction in [ZnO_{cryst}], and after the "reaction—regeneration" cycle this concentration decreases more than tenfold. This indicates the strong interaction of the zeolite with zinc oxide resulting in a substantial change in the state of zinc in

Table 4. Content of the crystalline phase of ZnO ([ZnO_{cryst}]) in the catalysts prepared by the introduction of 5 wt.% Zn into the zeolite matrix (X-ray diffraction estimate)

Catalyst[a]	Conditions of preparation and treatment[c]	$I^b \cdot 10^{-3}$ /pulse	[ZnO_{cryst}] (%)
ZnO/ZSM-5 (30)	*A*	2.1	0.30
ZnO+ZSM-5 (30)	*B*	9.9	5.20
ZnO+ZSM-5 (30)	*C*	10.0	5.30
ZnO+ZSM-5 (30)	*D*	4.9	2.10
ZnO+ZSM-5 (30)	*E*	2.3	0.50
ZnO+ZSM-5 (56)	*E*	2.1	0.30
ZnO+ZSM-5 (90)	*E*	2.1	0.30
ZnO+ZSM-5 (220)	*E*	2.0	0.28

[a] The SiO_2/Al_2O_3 molar ratio in the zeolite in given in parentheses.

[b] Intensity of the reflection at 36.4°.

[c] *A* stands for impregnation with a solution of $Zn(NO_3)_2$; *B*, mechanical mixing; *C*, mechanical mixing, air; *D*, mechanical mixing, H_2; *E*, mechanical mixing, after the "reaction—regeneration" cycle.

the catalysts prepared by mechanical mixing. Probably, the treatment with hydrogen favors the decomposition of ZnO_{cryst} followed by the migration of some Zn atoms deep inside the zeolite channels. The amount of the Zn ions, which changed the state after contact with H_2, corresponds to the concentration of the ion-exchange sites in the pentasil with $SiO_2/Al_2O_3 = 30$ (0.28 mg-equiv. g^{-1}).

The topochemical interaction of zinc oxide with the pentasil framework occurs much more strongly during ethane aromatization in the reaction medium containing evolved hydrogen. Under these conditions, the phase of crystalline ZnO almost completely disappears. The number of the Zn atoms in the decomposed crystalline phase is approximately twice as much as the ion-exchange capacity of the pentasil with $SiO_2/Al_2O_3 = 30$, whereas this excess is greater for the samples with a lower content of aluminum in the framework. Perhaps, after the reaction followed by the regeneration of the catalysts, the Zn atoms, which migrated inside the zeolite, are localized near the ion-exchange sites. The state of zinc after the interaction of the catalyst with the reaction medium remains unclear. The reduction of the Zn cations to the metal is improbable, because the diffraction pattern contains no reflections indicating a particular phase or large clusters of metallic zinc. According to the recently published results of the quantum-chemical density functional calculations[9] of the structure and reactivity of clusters of the Zn ions in the framework of the ZSM-5 zeolite, the stabilization of the isolated Zn ion in the five-membered ring is energetically unfavorable in the zeolites with the low aluminum content, and zinc exists in these zeolites, most likely, as dimeric ZnZnO clusters. In addition, the presence of the zinc clusters results in strong distortions of the Al—O and Si—O bond lengths compared to the lengths of the same bonds in zeolites containing no zinc. The introduction of zinc shortens the Al—O bond lengths by 0.08 Å, whereas the Si—O bonds are elongated by 0.15 Å.

The strong interaction between the elements of the pentasil structure and zinc oxide is confirmed by analysis of the state of the framework of the zeolites with different SiO_2/Al_2O_3 ratios. As follows from the data presented in Table 4, ZnO_{cryst} almost completely disintegrates by the reaction medium, and the content of the remained ZnO_{cryst} is almost independent of the aluminum concentration in the framework. This indicates the important role of inner pores in the interaction of ZnO with the pentasils. The diffraction patterns of the catalysts obtained by the solid-state method contain no reflections related to the products of ZnO conversion. However, the known X-ray diffraction criteria of the state of the framework of high-silica zeolites make it possible to elucidate the influence of the presence of zinc in the intracrystalline space of the zeolite on the framework volume.

It has previously[10] been shown that the diffraction patterns of the ZSM-5 zeolites in the region of $2\theta = 40—45°$ contain a doublet, with the distance between the components being sensitive to the change in the framework composition. It is established, in particular, that the distance between two peaks (Δ) at $2\theta \approx 45.0$ and 45.5° increases with a decrease in the aluminum content in the unit cell. Since the Si—O bond length is shorter than the Al—O bond length, the increase in the distance between two reflections indicates the reduction of the unit cell parameters and contraction of the lattice. This procedure is conventionally used for the simplified estimation of the aluminum content in the framework from the X-ray diffraction data.[11] It was applied to reveal the influence of the presence of zinc in the catalysts after the "reaction—regeneration" cycle on the volume of the pentasil framework. With this purpose, we constructed the plot, which reflects the dependence of Δ on the number of Al atoms in the framework (Fig. 2). As follows from the data in Fig. 2, this plot is well approximated by the linear equation

$$[Al] = 17.3 - 33.3\Delta.$$

A decrease in the aluminum content in the unit cell from 6.0 to 0.9 atoms, *i.e.*, an increase in the SiO_2/Al_2O_3 ratio from 30 to 220, is accompanied by an increase in Δ from 0.34 to 0.50° (see Fig. 2). The data for the ZnO+ZSM-5 samples subjected to regeneration with air after aromatization are also presented in Fig. 2 (see line *2*). The obtained results indicate a considerable change in the state of the framework after the decomposition of ZnO_{cryst} during the interaction of the catalyst with the reaction medium. For example, for the sample with $SiO_2/Al_2O_3 = 30$, the Δ value increases from 0.34 to 0.43, indicating the considerable contraction of the unit cell

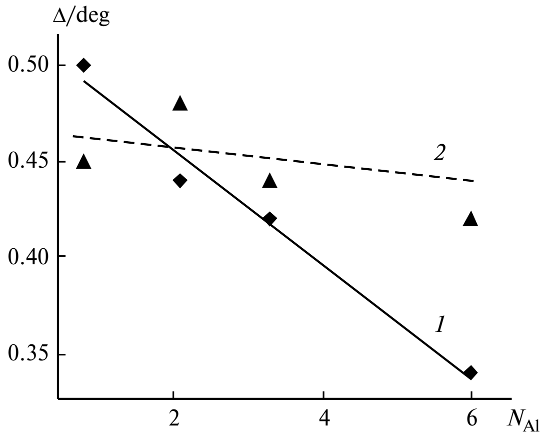

Fig. 2. Distance between the diffraction maxima (Δ) at about 45 and 45.5° as a function of the number of Al atoms (N_{Al}) in the unit cell of the pentasils: *1*, initial samples and *2*, the same samples after the "reaction—regeneration" cycle.

parameters due to framework compression. However, with an increase in the SiO_2/Al_2O_3 ratio in the framework, Δ increases less remarkably, while for the sample with $SiO_2/Al_2O_3 = 220$ this value even decreases compared to that of the nonmodified zeolite. Since an increase in the SiO_2/Al_2O_3 ratio decreases the fraction of ion-exchange sites, we can assume that their number gradually decreases to such an extent that the interaction with the Zn ions does not result in the contraction of the framework. Perhaps, in the sample containing only 0.9 Al atoms per unit cell, finely dispersed zinc-oxide clusters are formed inside the pentasil channels accompanied by some expansion of the framework instead of compression.

IR spectroscopic data. The IR spectroscopic study of the adsorption and thermal desorption of pyridine showed that the adsorption of this base on the ZnO/ZSM-5 catalyst ($SiO_2/Al_2O_3 = 30$) prepared by impregnation and containing 5.0 wt.% zinc resulted in the appearance of an absorption band (AB) at 1456 cm^{-1} corresponding to coordinatively bound pyridine. This band corresponds to the formation of new aprotonic acid sites containing zinc cations.[7] The identical AB was detected in the spectrum of pyridine adsorbed on the ZnO+ZSM-5 sample ($SiO_2/Al_2O_3 = 30$) after ethane aromatization followed by the treatment of the catalyst with air at 550 °C (Fig. 3, spectra *1* and *2*). The detailed study of the adsorption and thermal desorption of pyridine on the Zn-containing pentasil with $SiO_2/Al_2O_3 = 30$ prepared by the solid-state method gave the following results. The spectrum of pyridine adsorbed on the freshly prepared ZnO+ZSM-5 sample at the desorption temperature $T_{des} = 215$ °C contains an AB at 1453 cm^{-1} (see Fig. 3, spectrum *4*). When this mixture of powders after heating in the air flow was treated with hydrogen at 550 °C, an intense AB appeared in the spectrum at 1456 cm^{-1} (see Fig. 3, spectra *5* and *6*). This implies that new Lewis (L) sites are formed under these conditions, *i.e.*, the solid-state interaction of the zeolite with ZnO occurs. The intensity of the AB at 1549 cm^{-1}, which is attributed to pyridine adsorption on the Brönsted (B) acid sites, substantially decreases simultaneously with the appearance of the AB at 1456 cm^{-1}. Note that the AB at 1456 cm^{-1} does not disappear even after heating of the reduced samples in oxygen with further pyridine adsorption (see Fig. 3, spectra *7* and *8*), indicating that the solid-state interaction is irreversible and the formed L sites are stable toward oxidants.

The comparison of the IR spectra of the samples prepared by mechanical mixing of ZnO with SiO_2 or with amorphous aluminosilicate showed that the necessary condition for the formation of aprotonic zinc-containing sites is the involvement of the zeolite with the pentasil struc-

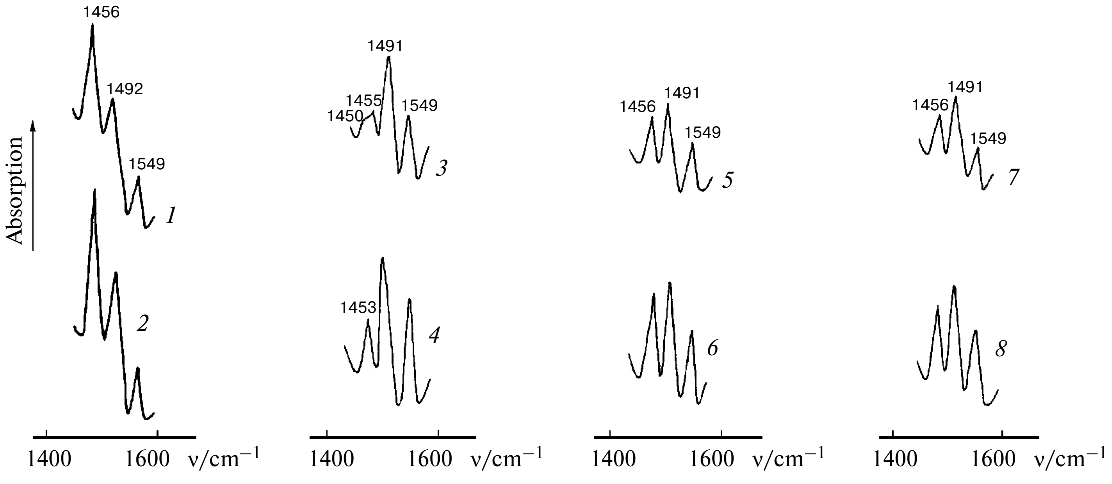

Fig. 3. IR spectra of pyridine adsorbed on the ZnO+ZSM-5 catalyst ($SiO_2/Al_2O_3 = 30$) containing 5.0 wt.% Zn: after the "reaction—regeneration" cycle (*1*, *2*), on the starting sample (*3*, *4*), after treatment with H_2 (*5*, *6*), and after treatment with H_2 and O_2 (*7*, *8*). Temperature of desorption: 480 (*1*), 218 (*2*), 565 (*3*), 215 (*4*, *6*), 550 (*5*), 575 (*7*), and 223 °C (*8*).

ture in the solid-state reaction, because the band at 1456 cm^{-1} is observed only in this case. The amount of the formed L sites depends on the aluminum content in the pentasil framework: for the sample with $SiO_2/Al_2O_3 = 30$ the intensity of this AB and, correspondingly, the fraction of the Zn-containing aprotonic sites are much higher than those for the catalyst with $SiO_2/Al_2O_3 = 220$.

Thus, the catalytic systems with high activity and selectivity in ethane aromatization can be prepared by the solid-state interaction of zinc oxide with zeolites of the pentasil family. The effect of hydrogen and the reaction medium on the catalyst changes the state of zinc, which is expressed, first of all, as the decomposition of the crystalline phase of bulk ZnO and the formation of L sites containing Zn atoms in the zeolite channels. Taking into account that the treatment of bulk zinc oxide with hydrogen can result in the formation of semihydride forms of the $[Zn—H]^+$ type,[12] we can assume that similar intermediates appear at the first step of the solid-state reaction. The interaction of these forms with the B sites of the pentasil results, most likely, in the formation of zinc-containing L sites. The semihydride forms migrate to the bridging hydroxyls of the zeolite, most likely, in the course of the topochemical process rather than through the gas phase. The formation of the ZnZnO clusters or $[ZnO_2]^{2-}$ ions dispersed in the pentasil channels cannot be excluded. A decrease in the aluminum content in the framework substantially changes the character of interaction of the Zn atoms with the ion-exchange sites of the pentasils during solid-phase modification. The contraction of the lattice, which is manifested in the samples containing from 6 to 2 Al atoms in the unit cell, is followed by a small expansion of the pentasil framework in the sample containing 0.9 Al atoms. The changes in the framework volume indicate the strong interaction of the Zn ions with the atoms of the silica-alumina framework. The high catalytic activity of the samples with the low aluminum content ($SiO_2/Al_2O_3 > 50$) indicates that the role of the protonic sites in the Zn-containing pentasils in the aromatization of low-molecular hydrocarbons is relatively not important and all reactions leading to the formation of aromatic hydrocarbons (oligomerization, cyclization, and others) can occur on the L sites formed upon the interaction of zinc with the zeolite.[13]

The results obtained imply the following conclusions. First, the method of solid-state interaction of ZnO with the ZSM-5 zeolite provides active and selective catalysts for ethane aromatization in one step. Second, the catalytic systems containing 3—5 wt.% Zn demonstrate the highest activity and selectivity in aromatization. Third, the ZSM-5 zeolites with the SiO_2/Al_2O_3 ratio from 30 to 100 are the optimal zeolite matrices for the preparation of such catalysts. Fourth, the active sites of the Zn—pentasil systems obtained by the solid-state reaction are finely dispersed zinc-containing clusters localized in the zeolite channels and possessing the pronounced electron-acceptor properties.

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