STATE OF Pt IN HIGH-SILICA ZEOLITES AND ITS CATALYTIC ACTIVITY IN ETHANE AROMATIZATION

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It has been established by means of XPS [1-3] that, as a result of interaction of highdispersity metal particles (Pt, Pd, Ru, Re) with electron-acceptor centers of γ -Al₂O₃ and Y zeolite, electron-deficient metal clusters are formed, manifesting high activity in a number of reactions. The state of the metal may be further changed as a result of exposure to the products and reactants of the catalytic reaction itself [4, 5]. Thus, in the course of aromatization of ethane and ethylene in the presence of a number of metal-zeolite catalysts, a "development" of the catalytic system M/H-TsVM* (M = Pt, Pd), accompanied by an increase in the yield of aromatic hydrocarbons [6], possibly due to changes in the valence state of the metal occur during the course of the reaction as a result of its interaction with the support and with the reaction products. In the present work we have used XPS to investigate the influence of pretreatment conditions (air, hydrogen, air-hydrogen) and the reaction medium on the electronic state of Pt in high-silica zeolites of the Pentasil type (H-TsVM) in the aromatization of ethane. In contrast to faujasites, in which the properties of Pt have been studied in detail [7, 8], practically no information is available on the valence state of Pt and its capability for migration in high-silica zeolites of the ZSM-5 type. In most studies [3, 5, 9-11], the catalyst structure has been investigated before performing the reaction (with some form of pretreatment) and after the reaction. More information can be obtained from data characterizing the catalyst in various stages of performing the reaction - data obtained by means of a procedure developed in [4] and improved in the present work.

DISCUSSION OF RESULTS

As catalysts for ethane aromatization we investigated samples of 0.5% Pt/H-TsVM (Ct-I) and 1.8% Pt/H-TsVM (Ct-II). The catalytic conversion of ethane in the presence of Ct-I was studied in the 300-600°C interval in a single-pass microreactor in the pulse mode (Fig. 1). Under these conditions, ethane undergoes mainly hydrogenolysis; it is converted to C_6-C_8 aromatic hydrocarbons and also to condensation products. Similar results on this catalyst have been obtained in the continuous-flow mode.

On the sample of Ct-II at 550°C (experiment series A), a catalyst development effect is observed, reaching a maximum activity in the region of 3-5 pulses (Fig. 2). It is significant that in the absence of metal (catalyst in the H form of the TsVM), no such development was observed in the case of ethylene, and its aromatization proceeded at a rather high level [6]. This means that the development effect is due to the presence of the metal in the catalyst composition and is apparently related to a change in the metal-support interaction during the course of the reaction. This sort of interaction has been observed when comparing the catalytic properties and photoelectron spectra of alumina-rhodium catalysts for ethylene cyclotrimerization [4]. In the course of that reaction, the activity of the catalyst and the electronic state of the Rh changed very substantially. On the Rh clusters in the Rh/ Al₂O₃·F catalyst, a new positive charge appeared (maximum shift $\Delta EbRh3d_{5/2} \sim 0.7$ eV).

In view of this situation, we performed another series of experiments B (see Fig. 2 and Table 1) in which, in parallel with the catalytic activity, we measured the electronic state of Pt in the course of aromatization of ethane on seven samples of Ct-II catalyst. As can

^{*}TsVM is the Russian designation for "zeolite, high modulus," i.e., zeolites with a high ratio of silica to alumina - Translator.

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Fig. 1



Fig. 1. Temperature dependence of ethane conversion product yield over 0.5% Pt/H-TsVM. a: 1) Yield of catalysate; 2) CH₄; 3) unreacted C_2H_6 ; 4) total C_6-C_8 aromatic hydrocarbons. b: 1) Benzene; 2) toluene; 3) xylenes.

Fig. 2. Yield of C_6 - C_8 aromatic hydrocarbons as a function of number of ethane pulses at 550°C over 1.8% Pt/H-TsVM that had been previously subjected to air-hydrogen treatment. Series A with 100 mg of catalyst, series B with 70 mg.

Fig. 3. XPS spectra of Pt4f + Al2p in 1.8% Pt/H-TsVM catalysts: a) original sample; b) 550°C in air; c) 550°C in air + 520°C in H₂; d) 550°C in air + 520°C in H₂ + 550°C in C₂H₆, 3 pulses. Dashed curves denote components obtained by computerized deconvolution; curves 1 and 2 and 1' and 2' are components of the spin doublet of Pt4f; curve 3 is the Al2p line.

be seen from these data (Fig. 2), in series b, as in series a, the maximum activity of the catalyst in ethane aromatization is reached during the course of 3-4 pulses.

In the spectra of the original sample (Table 2 and Fig. 3) we observe only the $Pt4d_{5/2}$ line; the Pt4f doublet is completely masked by the Al2p line. The value of $E_bPt4f_{7/2}$, found as a result of deconvolution of these spectra, is close to that in the original complex. After calcining in air, along with this line we find in the spectrum a line with $E_bPtf_{7/2}$ = 72.2 eV, the position of which is close to that observed for the spectra of reduced samples. This line may pertain to high-dispersity particles of Pt(0) [3, 12]. Obviously, the decomposition of complex cations of Pt in air is accompanied by partial reduction of the Pt. The formation of Pt(0) has been observed in the oxidative treatment of $[Pt(NH_3)_4]^{2+} - NaY$ [7, 8].

Yield of Composition of catalysate, % catalysate, % Pulse No. on ethane Сн₊ C₂H C.H. benzene toluene passed through 0,4 1,0 1 35,6 27,076 1.6 6,5 8,7 $\frac{2}{3}$ 73 57,91,6 6.08056,6 3,29.0 2,3 2,2 2,2 2,0 $\frac{3}{4}$ 76 7,1 27,7 32,96.0 $\overline{70}$ 24,4 23,9 4,5 3,9 9,274 74 6 10.7 10.3 47,2 1,8 2,510 50.16.413.61,4

TABLE 1. Data on Conversion of Ethane on 1.8% Pt/H-TsVM at 550°C in Pulse Mode (series B)

TABLE 2.	Parameters	of	ХP	Spectra	of	1.8%	Pt/H-TsVM	Catalysts*
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Pretreatment Number of C_2H_6 pulses (550%)		Binding energy Pt Pt 4f _{7/2} , eV	TWHH Pt 4f _{7/2} , eV	E _b A1 2p, eV	<u>IPt 47</u> 1Al 2p	Pt Al	Si Al	
Original	_	73,4	2,1	74,8	0,9	0,027		
550℃ in air		73.6(55%); 72.2(45%)	2,4; 1,8	75,0	0,6	0,015	22	
520℃ in H ₂	-	72,0	2,4	75,0	3,2	0,1	28	
550°C in air + 520°C in H ₂	-	72,0	2,0	75,2	0,5	0,015	18	
-	1	72,2	2,1		0,5	0.015	20	
»	2	71,4(33%); 72,7(67%)	$egin{array}{c} 1,6 \\ 2,4 \end{array} 3,0 \dagger$	75,3	0.8	0.024	18	
»	3	71,7(33%); 72,7(67%)	$egin{array}{c} 1,6 \\ 2,4 \end{array} 2,9 \dagger$	75,3	0,7	0.021	20	
»	4	72,0	2,8	74.9	0,8	0.024	19	
»	5	72,2	2,4	75,2	0,6	0,018	18	
»	6	72,0	2,6	75,0	0,9	0,027	20	
» *	10	70,7(33%); 72,3(67%)	2,1; 1,8	74,9	0,8	0,024	25	

 E_b for $[Pt(NH_3)_4]Cl_2$ and Pt (metal) is 73.6 and 71.5 eV, respectively.

+TWHH upon deconvolution of one Pt4f spin-doublet.

Although the position of the principal Pt4f maxima for the two reduced samples are very close together, we find that when the sample has been reduced in H_2 without pretreatment in air, the Pt/Al ratio is considerably greater, by a factor of approximately 6. This is due to migration of Pt(0) to the outer surface of the zeolite [8, 12]. These results are consistent with data from electron microscope measurements, according to which the zeolite reduced in H_2 at 500°C contains, along with high-dispersity particles of Pt (<10 Å), large crystallites of metal with dimensions of 30-150 Å.

There are also differences in the catalytic activities of the three types of samples. The most active is the sample that had been calcined in air, giving a maximum yield of aromatic hydrocarbons amounting to 19.4%; the sample that had been reduced directly in H_2 is the least active (yield of aromatics 0.4%). Modification of the state of the Pt when exposed to the reaction medium was studied on the sample that had been reduced in H_2 after precalcination in air (maximum aromatics yield 11.3%), as this sample shows most clearly the stage of development of activity in the pulse reactor (see Fig. 2).

The change in activity was accompanied by definite changes in the Pt4f parameters (see Table 2). Thus, after the second pulse of C_2H_6 the Pt4f lines are broadened from 2 to about 3 eV and remain at this level after pulses 3 and 4. They subsequently become slightly narrower, but their TWHH is still greater than for the original sample. The increase in TWHH may be due to the appearance of several nonequivalent states of the Pt. And, indeed, an analysis of the Pt4f + Al2p spectra after pulses 2 and 3 shows that they are better approximated by the Al2p singlet and two Pt4f spin-doublets with respective $Pt4f_{7/2}$ binding energies of 71.3-71.7 and 72.7 eV. After 10 pulses, the C_2H_6 spectrum is also broadened and split into two doublets; in this case, however, the high-energy doublet has parameters close to

those of the original spectrum (see Table 2). The spectra of the samples after 4-6 pulses are approximated quite well by one Pt4f spin-doublet and the Al2p line.

Thus, it is evident that the state of the Pt changes during the course of development of the catalyst. According to the XPS data, two types of Pt centers can be distinguished, differing in their spectral characteristics: particles of Pt for which the spectra are shifted significantly (+1.3 eV) relative to the spectrum of the metal, and Pt particles with spectra in which there is no positive shift whatever, or a small negative shift (for example, after 10 pulses of C_2H_6). Positive shifts in the spectra of high-dispersity metals are explained by a number of factors [1, 3, 12]: by a decrease in the energy of hyperatomic relaxation, by metal-support interaction, and by the inherent electronic structure of small particles. According to approximate estimates in [13], the relaxation shift for Pt particles with dimensions of 10-15 Å is no greater than 0.5 eV. This means that the observed shifts are at least partly due to transfer of electron density from the Pt to acceptor sections of the support. In the course of development of activity, the positive charge on the Pt increases; then, after passing through the maximum in activity, the charge drops off slightly, even though some of the Pt centers in the original sample and also in deactivated samples apparently carry a positive charge.

The second type of center, constituting some 30% of the total number of centers after pulses 2 and 3, is characterized by either an absence of charge or a slight negative charge, according to the XPS data. We can class as such centers the large crystallites of Pt which, according to the data of electron microscopy, are present on the outer surface of the zeolite. For particles of such a size, relaxation effects are insignificant, and the parameters of their spectra should not differ from those of the bulk metal. With such an assignment, the clearer manifestation of centers of the second type after the first pulses of ethane must mean that the occurrence of the reaction is accompanied by additional sintering of the Pt. Even though the increase in the Pt/Al ratio that is observed during the course of the reaction could be attributed to additional migration of Pt(0) to the outer surface, this increase is quite small, and it changes very little during the course of the reaction. Further evidence against this hypothesis is the fact that catalysts containing greater amounts of crystallites on the outer surface are less active. Another factor responsible for the appearance of Pt centers of the second type may be the so-called strong metal-support interaction (SMSI) [14], leading to suppression of the adsorption capability of the metals with respect to H_2 and a decrease in their activity in reactions of hydrogenolysis and hydrogenation of hydrocarbons [15]. Although the SMSI effect is most characteristic for metals supported on readily reduced oxides (TiO₂, Nb₂O₅, V₂O₅, ZrO₂), such data have also appeared recently for Pt/Al₂O₃ [16]. We can assume that under severe conditions of the reaction (550°C; hydrocarbons, H_2), oxygen vacancies are formed in the zeolite lattice, and Al³⁺ ions located close to the Pt are reduced. Interaction of Pt with such electron-donor centers will lead to the appearance of excess electron density on the Pt, which is actually observed according to the XPS data.

Thus, the same as in the case of faujasites, the reduction of Pt in high-silica zeolites leads to localization of atoms or clusters of Pt in the zeolite structure and partial migration to the outer surface. In view of geometric limitations in the structure of ZSM-5, it is impossible to localize large clusters, the formation of which in large void spaces of Y zeolite was postulated in [6]. In the case of Pt/H-TsVM zeolite, we also observed a more substantial migration of Pt atoms to the outer surface in the course of H₂ treatment. Along with this, preliminary dehydration (treatment with air) of the zeolite makes it possible to retain a considerable part of the Pt within the structure. As a result of interaction with acceptor sections of the zeolite skeleton (possibly with Brønsted centers), a positive charge appears on part of the Pt atoms. As in the case of Rh/Al_2O_3 [4], the charge increases with increasing degree of ethane or ethylene conversion to aromatic hydrocarbons. Along with this, part of the Pt centers are in the zero-valent state or are negatively charged, possibly because of strong interaction with reduced Al ions. These Pt centers may be responsible for the change in selectivity of the reaction, in particular the suppression of hydrogenolysis of the original ethane.

Summarizing the data on the state of Pt in Pt/H-TsVM and also considering the change in catalytic activity, we can assume that a form of Pt exists ($Pt^{\delta+}$ with a shift of approximately 1.3 eV), this form apparently determining the aromatizing activity of Ct-II in conversions of ethane. As the pore size in zeolites of the ZSM type is 5.5-6 Å [17], the most probable site of occurrence of the reaction is apparently the mouths of the pores in the zeolite catalyst. It appears that the catalysis is accomplished on that part of the Pt which, in the dispersed state (crystallite dimension about 10 Å), is located at the mouths of these pores. Apparently, the partial dehydrogenation of ethane to ethylene takes place on exactly these same sites; the ethylene, penetrating into the zeolite pores, undergoes further conversions to aliphatic oligomers and aromatic hydrocarbons, the formation of which proceeds with the participation of acidic bridge OH groups of the zeolite, which have been identified by diffuse reflectance IR spectroscopy.

EXPERIMENTAL

<u>Catalysts</u>. We used two samples of Pt catalysts prepared from NH₄-TsVM: 0.48% Pt-H-TsVM (Ct-I) and 1.78% Pt/H-TsVM (Ct-II). These were originally prepared from the Na form of the TSVM, obtained by crystallization of alumina-silica gels under hydrothermal conditions without the use of any organic cation [19]; the mole ratio $SiO_2/Al_2O_3 = 35$; the content of Na₂O = 3%, Fe₂O₃ = 0.12%; phase purity about 100%. The Pt-containing zeolites were prepared by treating NH₄=TsVM (after decationization, residual content Na₂O < 0.1%) with the calculated quantity of aqueous Pt(NH₃)₄Cl₂ aqueous solution under conditions of ion exchange; the degree of exchange was monitored according to the residual content of Pt in the mother solution. By this procedure, samples Ct-I and Ct-II were obtained. The powdered preparations were dried and pressed without binder. The 0.5-1 mm fraction was used in the experiments.

For the spectral studies, samples of the catalyst (Ct-II) were subjected to different pretreatments: a) calcination in a flow of air for 5 h at 550°C; b) in a flow of air for 5 h at 550°C and then in a flow of H_2 for 3 h at 520°C. After each such treatment, the catalysts were cooled to about 20°C in a medium of dry Ar and transferred to the spectrometer (see below).

<u>Catalytic experiments</u> with ethane were performed in a pulse microcatalytic unit [20]. The U-shaped reactor was charged with a sample of Ct-II, which was then calcined at 550° C, first for 5 h in a flow of air and then 3 h in a flow of H₂, after which the H₂ was replaced by He (20 ml/min); then, after about 20 min, ethane was fed in (0.082 ml). At the end of the reaction (about 30 min), the catalyst was cooled in a flow of He and then analyzed. The XP spectrum of the first sample was taken after one pulse of ethane, the second sample after two pulses, etc. (see Table 2). A fresh portion of Ct-II was used for each sample.

<u>Spectrometric Studies</u>. Samples from the catalytic reactor were transferred to the spectrometer in an inert atmosphere. This was done by placing the reactor in a box filled with purified Ar; the sample was pressed onto a Pb substrate and mounted on a holder. Then the box was connected to the sample introduction section of the spectrometer, and the sample holder was transferred, in a counterflow of Ar, to the vacuum section of the spectrometer.

The XP spectra were recorded in an FS-200V spectrometer, following procedures given in [12]. For all of the measurements of spectra, the vacuum was almost $5 \cdot 10^{-8}$ torr. As standards we used the lines 1s ($E_b = 285.0 \text{ eV}$) and Si2p ($E_b = 103.8 \text{ eV}$). No significant distortion in the form of the C1s line was observed after catalysis. The Pt/Al and Si/Al atomic ratios were estimated on the basis of the corresponding integral intensities, with a correction for the photoionization cross section [12]. Since the Pt4f spin-doublet and the Al2p line overlap partially, in determining the parameters of the spectra we analyzed these lines by a program for deconvolution of unresolved Gaussian lines in a PDP 11/03 L computer. The accuracy in determining E_b was 0.2 eV, in determining the atomic ratios 20-30%.

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CONCLUSIONS

1. In an investigation of the catalytic properties and photoelectron spectra of Pt-containing high-silica zeolites of the Pentasil type (Pt/H-TsVM) in the aromatization of ethane, it has been established that the catalyst activity and the electronic state of the Pt depend considerably on the conditions of pretreatment and will change under the influence of the reaction medium.

2. In the course of ethane aromatization in the pulse mode, development of activity is observed in the Pt/H-TsVM catalyst, accompanied by an increase in the positive charge on the high-dispersity platinum particles, the presence of which apparently determines the aromatizing activity of Pt/H-TsVM in ethane conversions.

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