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Catalytic Aromatization of Light Alkanes

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Abstract—Experimental data on the application of pentasil-type zeolites in the aromatization of low-molecular-weight alkanes are surveyed. Examples of the transformation of ethane and propane into aromatics over pentasils containing Zn, Ga, or Ga–Pt are given. An important role of Pt in the formation of active and selective Ga–Pt catalysts for light alkane aromatization is shown.

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Aromatic hydrocarbons (ArH) are important starting materials in basic organic synthesis. They are used for manufacturing plastics, synthetic fibers, resins, various-purpose rubbers, dyes, surfactants, and and pharmaceutical and agricultural products. The most widely used are light arenes: benzene, toluene, and xylenes. In 2007 Russia planned to produce about 1250 thousand tons of benzene, 330 thousand tons of toluene, and 550 thousand tons of xylenes [1].

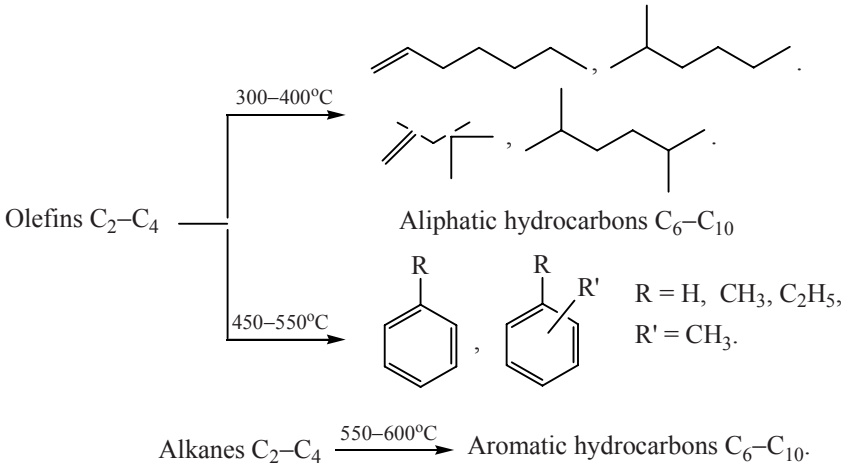
At present ArH are manufactured by catalytic reforming or pyrolysis of liquid oil hydrocarbons. Changes in the raw materials base of petrochemical complexes of Russia has resulted in a considerable deficiency of such hydrocarbons [2]. This makes quite urgent the problem of replacement of oil in the manufacture of arenes by alternative sources. The latter primarily include natural gas, and associated petroleum and refinery gases, that comprise C_2–C_5 paraffins and natural gas liquids (NGL) [3].

The development and setting in operation of new gas and gas condensate fields raise the problem of rational use of the low-molecular-weight paraffin fraction associated with methane. Taking into account the scale of natural gas production (more than 2.5 trillion m^3/year in the world; 500–550 billion m^3/year in Russia), light alkanes can undeniably be considered as an important potential source of raw materials for chemical industry [4]. However, the most part of hydrocarbon gases is still used as a technological or domestic fuel or flared on a large scale. Thus, according to estimates of a great number of Russian and foreign analysts [4, 5], in the beginning of XXI century, about 4% of produced natural gas is flared each year around the world (about 100 billion m^3). Along with that, much associated oil gas containing up to 40% of C_2–C_5 paraffins and olefin-containing refinery gases are lost. Probably, an optimal approach to these problems should involve complex processing all hydrocarbon components of natural and associated gases, as well as end gases of petrochemical enterprises by means of low-waste and ecologically friendly industrial technologies for manufacturing chemical products from light alkanes. Therewith, the key role should belong to catalytic processes.

Of particular interest is a one-stage catalytic synthesis of ArH from gaseous paraffins and olefins [6–9] (see Scheme 1). Its practical realization not only will create prerequisites for essential savings of constantly going-up oil and increased production of aromatic compounds, but also for effective use of fairly low-cost gaseous hydrocarbons as a raw material for valuable chemical substances.

Aromatization of C_2–C_4 Alkanes on Zeolites of Pentasil Family

Table 1 lists the thermodynamic characteristics of dehydrocyclooligomerization (aromatization) reactions of C_2–C_4 alkanes. The thermodynamic probability of aromatization of light alkanes is high at temperatures above 400°C for butanes, 500°C for propane, and 600°C for ethane.



Scheme 1. Scheme of transformations of C_2–C_4 olefins and alkanes on pentasils.

Catalytic transformations of light aliphatic hydrocarbons have long been studied in many research centers and abroad [11–17]. These studies have been much driven by the development of methods for synthesis of high-silica zeolites of pentasil family, such as ZSM-5 and ZSM-11, and their domestic analogs TsVK, TsVM, TsVN, etc. [6]. Pentasils have an unusual structure. Their frame consists of five-membered rings formed primarily by silicon–oxygen tetrahedra. The Si/Al ratio in pentasils varies from 15 to several hundreds [18]. The synthesis of pentasils is peculiar in that hydrothermal crystallization of aluminasilica gel is performed in the presence of various organic compounds (templates). During synthesis, as pentasil crystals grow, molecules of organic templates penetrate into the solid phase and ensure stabilization of the zeolite structure. The porous structure of ZSM-5 pentasil includes both straight (0.54×0.56 nm) and sinusoidal (0.51×0.55 nm) channels.

One of the most important features of the catalytic effect of pentasils is their ability to convert low-molecular-weight hydrocarbons into high-molecular-weight compounds. Scheme 1 shows what products can be obtained from gaseous hydrocarbons on pentasils. From C_2–C_4 olefins one can obtain, depending on reaction conditions, either a mixture of aliphatic hydrocarbons in the C_6–C_{10} gasoline fraction (primarily, isoparaffins) or ArH concentrate, mostly benzene, toluene, or xylenes. At temperatures above 500°C, gaseous paraffins undergo aromatization and cracking.

The peculiar feature of the catalytic properties of pentasils is that, being decationized, i.e. in the H-form, even with no additional promoters, they catalyze aromatization of light alkanes with a selectivity of up to 30%. The selectivity of aromatization [*S*(ArH)] can be much enhanced by means of chemical and thermal modification of pentasils. Chemical modification involves introduction of metal ions into the zeolite matrix (including isomorphous substitution of Al atoms in the frame), while thermal modification involves high-temperature treatment of decationized and metal-containing pentasils with air, hydrogen, or steam, thus controlling the relative fractions of protic and aprotic acid centers on the surface and selectivity of conversion over different routes [12, 16].

The depth and selectivity of light alkane conversions on modified pentasils depend on a number of

Table 1. Thermodynamic characteristics of aromatization of low-molecular alkanes [10]

Reaction	ΔH^0, kJ mol^{-1} at 800 K	ΔG^0, kJ mol^{-1} at 800 K	K_r^0		
			700 K	800 K	900 K
$3C_2H_6 \rightarrow C_6H_6 + 6H_2$	372.93	21.37	1.44×10^{-5}	4.02×10^{-2}	21.25
$2C_3H_8 \rightarrow C_6H_6 + 5H_2$	316.85	–33.72	0.185	1.59×10^{2}	3.23×10^{4}
$2C_4H_{10} \rightarrow C_6H_4(CH_3)_2 + 5H_2$	293.84	–54.93	7.326	3.86×10^{3}	5.39×10^{5}

Table 2. Aromatization of ethane on Zn-containing pentasils with varied (SiO_2/Al_2O_3) module; [Zn] = 5 wt %, T = 600°C, V = 450 h^{-1}

SiO_2/Al_2O_3, mol	$K(C_2H_6)$, %	B(ArH), %	S(ArH), %	$B(CH_4)$, %	$S(CH_4)$, %	$B(C_2H_4)$, %	$S(C_2H_4)$, %
Impregnation							
30	51.5	23.7	46.0	17.5	39.2	4.2	7.0
56	51.3	24.0	46.8	19.4	37.8	4.8	9.4
90	57.2	26.1	45.6	23.1	40.4	3.5	6.1
220	38.1	17.7	46.5	12.9	33.9	4.6	12.1
230	32.8	16.8	51.2	7.6	23.2	6.0	18.3
Solid-phase modification							
30	58.2	24.2	41.6	26.6	45.7	3.8	6.5
56	46.5	22.9	48.9	15.6	33.5	5.6	9.5
90	51.5	24.6	47.8	19.8	38.4	3.5	6.8
220	44.7	20.7	46.3	16.2	36.2	5.0	11.2
230	38.7	18.4	47.5	11.8	30.5	5.6	14.5

factors. Apart from the zeolite frame and reaction conditions, important factors are the nature of the modifier element and its concentration, as well as conditions of catalyst pretreatment [19]. Modified pentasils are most commonly prepared by ion exchange, impregnation with corresponding salt solutions, and isomorphous substitution of lattice aluminum atoms to obtain ferrosilicates, borosilicates, gallosilicates, and galloalumosilicates with the pentasil structure [20].

Testing various metals as aromatization promoters (Cu, Zn, Cd, rare-earth metals, Al, Ga, In, Sn, V, Cr, Mo, Co, Ni, Fe, and Pt) showed that the most effective modifiers for pentasil catalysts are zinc, gallium, and platinum [12, 16, 20].

Varying reaction conditions (temperature, contact time, and partial pressures of reagents) allowed optimal parameters of aromatization in the presence of these catalytic systems to be determined: Ethane and propane are best aromatized at higher temperatures (≥500°C) than butane (350–450°C). In what follows we give examples illustrative of the influence of the above factors on the catalytic activity of modified pentasils.

Zinc Pentasils

It was found that the optimal concentrations of the promoter in aromatization of light alkanes on Zn-modified pentasils are 5.0 wt % for ethane [21] and 1.5–2.0 wt % for propane and butane [12, 20]. A promising procedure for preparing metal-containing zeolite catalysts is solid-phase reaction of transition metal oxides or salts under various conditions. Therewith, topochemical processes occur [21–24]. This procedure allows stabilization of isolated cations in zeolite channels and cavities and preparation of metal-containing zeolite catalysts in one stage in the absence of solvents.

Table 2 presents the results of aromatization of ethane on Zn-modified pentasils with varied modulus (SiO_2/Al_2O_3 molar ratio). As seen, in principal parameters, such as ethane conversion (K), yield of aromatic hydrocarbons (B), and selectivity (S), the catalysts prepared by impregnation and solid-phase modification are quite close to each other. This finding means that both methods form in the zeolite structure the same number of active centers of similar nature, which activate ethane molecules and their further conversion into aromatic hydrocarbons.

When assessing the selectivity of ethane aromatization on zinc-containing samples with various modules one should bear in mind that comparisons were performed at different ethane conversions. Figure 1 shows the dependence of the yield of aromatics on the conversion of ethane. As seen from the figure, the yield of aromatic hydrocarbons is linearly related to the conversion of ethane; therewith, all points for catalysts of various compositions fall on a straight line starting from the origin. This finding means that, within experimental error, the selectivity in aromatic hydrocarbons is independent on the zeolite module as

the SiO_2/Al_2O_3 ratio is varied from 30 to 230. The same conclusion follows from the results for aromatization of propane on Zn pentasils with various frame structure, reported in [25]. From the slopes of the $B(ArH) = f(K)$ straight lines, mean selectivities of formation of ArH and gaseous reaction products were estimated (Table 3). Note first of all that the S(ArH) for ethane (47.0%) and propane (44.2%) differ only slightly.

By contrast, the difference in the selectivities of formation of gaseous products is much greater [cf. $S(CH_4)$ 19.5 and 34.0 % for propane and ethane, respectively]. With C_2 hydrocarbons, the situation is reverse.

The mean selectivity of ethylene formation from ethane is no higher than 12.5%; at the same time, among the reaction products of propane fairly much C_2 hydrocarbons are formed $\{S(\sum C_2) = 30.9\%$ at $[C_2H_6]/[C_2H_4] > 10–15\}$. Apparently, under milder conditions, the ethane that forms fails to react and is accumulated. Essentially, ethane and propane are aromatized in high yield on high-module Zn pentasils.

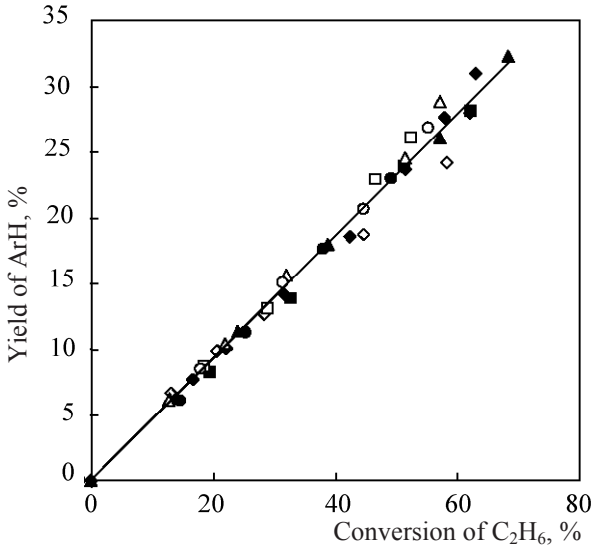


Fig. 1. Dependence on the yield of aromatic hydrocarbons on the conversion of ethane on Zn pentasils with varied module, prepared by (light symbols) solid-phase modification and (dark symbols) impregnation. Catalyst: (◊) Zn + NTsVM (30); (□) Zn + HZSM-5 (56); (Δ) Zn + HZSM-5 (90); and (○) Zn + HZSM-5 (220).

Gallium Pentasils

The catalytic properties of pentasils with varied content of gallium in aromatization of $C_2–C_4$ hydrocarbons have been studied in detail in [11, 12, 14, 16, 20, 26]. Introduction of even 0.5% of gallium appreciably accelerate ethane and propane aromatization and increases the yield of aromatic hydrocarbons 1.3–1.5-fold compared with H zeolite [12, 14]. The activity of Ga-modified pentasils depends considerable on the frame of the starting zeolite [8, 14, 20]. Active and selective catalysts were only obtained with a low-module Ga pentasil (SiO_2/Al_2O_3 = 40): S(ArH) for isobutane and propane are 60 and 50%, respectively. With the carrier with a low aluminum content (SiO_2/Al_2O_3 = 280), the S(ArH) value was lower 1.5 times [19, 20]. This trend is only characteristic of Ga pentasils. As mentioned above, ethane and propane aromatized with close selectivities on various-composition Zn pentasils [21, 25]. Probably, to form highly active aromatizing centers in Ga pentasils, a combination of a great number of strongly acidic centers and gallium atoms is required.

Evidence for this conclusion comes from the results of aromatization of ethane on Ga and Ga–Pt pentasils [27–30]. To find out how the activity of pentasils depends on the concentration of gallium, we performed aromatization of ethane in the presence of H-ZSM-5 (module 30) modified with 0.1–5.0% Ga (Fig. 2a) and Ga–Pt pentasils (Fig. 2b). The highest yield of aromatics (16.7%) was obtained on 2.0% Ga/H-ZSM-5 and the highest selectivity [S(ArH) ~62%] on catalysts containing 0.5 and 1.0% Ga.

Comparison of the activities of catalysts with varied Ga/Pt ratio showed that introduction of even 0.1% of gallium into a Pt-containing pentasil appreciably increased the yield of aromatics (Fig. 2b). Therewith, the conversion of ethane increased ~1.5 times, and the selectivity did not change. With samples containing 0.5–2.0% Ga, the yield of aromatic hydrocarbons was ~30% (selectivity 62–64%).

The effect of the module of pentasils on ethane aromatization was studied using bimetallic catalysts (Table 4). The resulting data showed that the activity and selectivity of Ga–Pt systems markedly decreased with increasing SiO_2/Al_2O_3 ratio. Thus, the yield of

Table 3. Selectivity of transformations of ethane and propane on Zn-containing pentasils

Starting hydrocarbon	S(ArH), %	$S(CH_4)$, %	$S(\Sigma C_2)$, %	S(ArH)/S (CH_4)	S(ArH)/ $S(\Sigma C_2)$
Ethane	47.9	37.1	12.5[a]	1.27	3.76
Propane	44.2	19.5	30.9	2.27	1.43

[a] Selectivity of C_2H_4 formation.

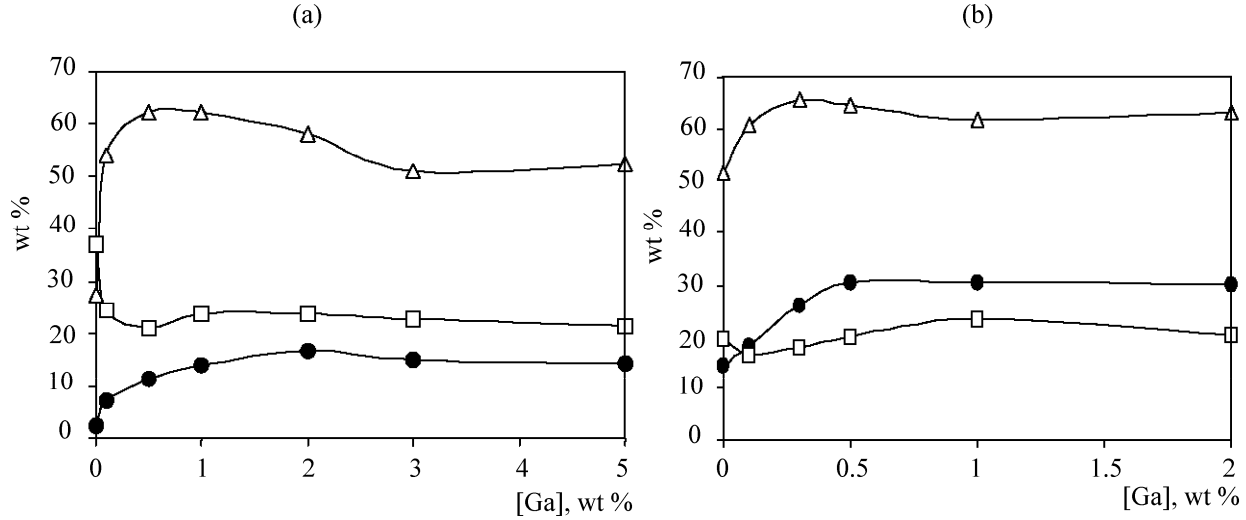


Fig. 2. Dependence of parameters of ethane aromatization on the concentration of gallium in the catalysts (a) Ga/H-ZSM-5 and (b) Ga-0.3%Pt/H-ZSM-5. $SiO_2/Al_2O_3 = 30$; $T = 600°C$; $V = 450\ h^{-1}$.

aromatics on (0.5%Ga–0.3%Pt)/H-ZSM-5 samples decreased two times: from 30.3% ($SiO_2/Al_2O_3 = 30$) to ~15% ($SiO_2/Al_2O_3 = 90$). The strongest changes were observed with (2.0%Ga–0.3%Pt)/pentasil samples: On the catalyst with the SiO_2/Al_2O_3 ratio of 56, as little as 12.7% of ethane converted into products with a 51.4% selectivity. Therewith, the conversion of ethane decreased two times. On (2.0%Ga–0.3%Pt)/H-ZSM-5 (module 90) the major conversion pathway of ethane in chosen conditions was dehydrogenation with S_{C2H4} 53.9%. The calculated overall conversion rate constants (k) and initial rates of accumulation of aromatic hydrocarbons [W(ArH)], presented in Table 5, reveal mutual effect of Ga and Pt on the catalytic properties of zeolite systems. When both Ga and Pt are present together, synergistic effect in their catalytic action takes place, evidenced by strongly increased yields of aromatic hydrocarbons and enhanced selectivity of their formation.

Active Centers of Modified Pentasils

Obviously, the catalytic properties of modified pentasils are directly related to their acid properties. First of all this relates to the strength and stability of acid centers and, what is especially important, to localization of acid centers in the zeolite structure and their possible evolution under the action of the reaction medium and under thermal treatment [6].

The relative fractions of the Brönsted (B) and Lewis (L) acid centers depends on the structure of zeolites, composition of their frame, thermal stability of the hydroxyl shell, and chemical nature of modifiers [20].

IR spectral monitoring of the adsorption of various probe molecules revealed specific features of acid properties of pentasils and gave insight into the distribution of acid centers over the structure. Our

Table 4. Aromatization of ethane on Pt–Ga pentasils with varied SiO_2/Al_2O_3 ratio; $T = 600°C$, $V = 450\ h^{-1}$

SiO_2/Al_2O_3, mole	[M], wt %		$K(C_2H_6)$, %	B(ArH), %	S(ArH), %	$S(CH_4)$, %	$S(C_2H_4)$, %	$S(C_3–C_4)$, %
	Ga	Pt						
30	0.5	0.3	47.1	30.3	64.3	19.5	7.0	–
56	0.5	0.3	39.9	24.0	60.2	23.3	6.5	–
90	0.5	0.3	27.2	14.8	54.5	11.1	19.5	4.1
30	2.0	0.3	47.6	30.1	63.2	20.1	7.8	–
56	2.0	0.3	24.7	12.7	51.4	7.7	21.5	8.9
90	2.0	0.3	17.0	4.2	24.8	3.5	53.9	7.6

spectral studies on zeolites [20, 31–35] showed that modification of pentasils with nickel, cobalt, zinc, or gallium forms new aprotic acid centers that adsorb pyridine much stronger that Lewis centers (Al^{3+}) of the parent zeolite. The strength of these centers depends on the nature of the modifying cation and their stability is determined by the ability of the cation to change its charge under the action of reductive medium. If the cation is readily susceptible to reduction (for example, Ni^{2+}), after treatment with hydrogen the cationic center disappears. In the case of difficultly reducible cations (Zn^{2+}) such treatment produces no changes in the spectra and, probably, has no effect on the structure and concentration of Lewis centers. Moreover, in certain cases hydrogen treatment is necessary for forming strong aprotic acid centers. This relates to catalysts prepared by mixing the zeolite matrix with ZnO [21, 24] or Ga_2O_3 [36], as well as to gallosilicates and galloalumosilicates with the pentasil structure [11, 20].

Stages of formation of Lewis centers in Ga pentasils were studied by IR spectroscopy in combination with X-ray photoelectron spectroscopy, ESR, and NMR [11, 12, 20, 24, 34, 35].

Aprotic gallium-containing centers include out-of-frame Ga atoms, and, therewith, the mechanism of their formation depends on the methods of synthesis and modification of catalysts. When catalysts are prepared by impregnation of the zeolite matrix with a $Ga(NO_3)_3$ solution, most gallium does not enter into channels but localize on the outer surface of zeolite crystals. Obviously, this is associated with a larger radius of the salvation shell of Ga^{3+} cations and

Table 5. Calculated k and W(ArH) for gallium- and platinum-modified H-ZSM pentasils with the module 30; T = 600°C

Catalyst	$k\times10^2$, s^{-1}	W(ArH)$\times10^4$, mol s^{-1} g^{-1}
2%Ga/H–ZSM	6.0	1.5
0.3%Pt/H–ZSM	6.0	1.3
2%Ga-0.3%Pt/H–ZSM	13.4	4.4

electrostatic hindrances arising from the compensation of isolated negative charges of the lattice with polyvalent cations. Treatment of such catalysts in a reductive medium results in that a part of gallium migrates from the outer surface inward crystals [11, 34, 35].

X-ray phase analysis in combination with quantum-chemical calculations gave a new insight into the formation of active centers of Ga and Ga–Pt pentasils [27, 28, 30]. It was shown that on reduction of zeolites at temperatures above 500ºC the crystal phase of gallium oxide disappears almost completely. Under these conditions gallium more actively passes into the finely dispersed state, and in pentasils containing both gallium and platinum we observed formation of particles with a higher Ga/Pt ratio.

A fragment of the pentasil frame was modeled by a cluster containing a six-membered ring of four Si and two Al atoms, placed in a direct zeolite channel. The resulting cluster with the stoichiometry $Al_2Si_4O_6H_{12}$ is shown in Fig. 3a. A Ga_2Pt_4 particle was chosen as compensating the lattice frame charge. This particle was placed in the center of the ring so that Ga atoms resided in cationic sites. An optimized structure of the

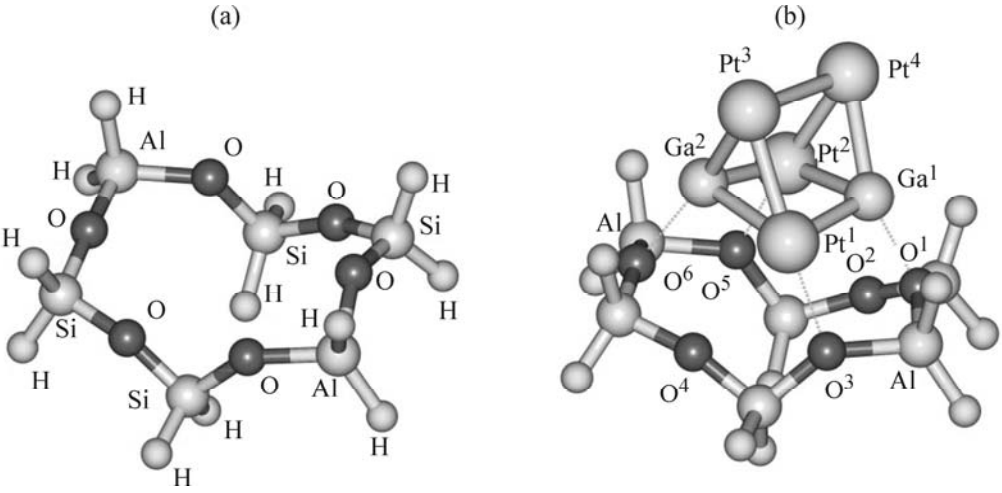


Fig. 3. Clusters modeling (a) fragment of the zeolite H-ZSM-5 frame and (b) active center of the Ga-Pt/H-ZSM-5 catalyst.

$Ga_2Pt_4Al_2Si_4O_6H_{12}$ cluster modeling the active center in the Ga–Pt/H-ZSM-5 catalyst is shown in Fig. 3b.

Quantum-chemical calculations gave grounds to suggest that introduction of platinum into Ga pentasils forms bimetallic particles like intermetallids. Apparently, gallium ions reside in cation-exchange sites and favor stabilization of such particles inside the zeolite frame and formation of active centers for dehydration of alkanes, specifically ethane. Introduction of platinum into Ga pentasils accelerates the stage of ethane dehydrogenation compared with what is observed with catalysts modified with gallium only and also facilities hydrogen and ethylene desorption [36].

CONCLUSIONS

The presented data provide evidence showing that metal-containing pentasils are highly active in the aromatization of lower alkanes. Based on these results we can suggest that the mechanisms of the catalytic action of modified pentasils obtained by different methods have much in common. The catalysts all contain strong aprotic acid centers that favor faster dehydrogenation of saturated molecules, which is the key stage of alkane aromatization. At the same time, each of the catalysts have characteristic features associated, first of all, with the localization of active centers in the pentasil structure and their acidity, as well as the electronic structure of modifiers. Furthermore, of importance is also the ratio between aprotic and protic acid centers, which depends on the composition of the frame and out-of-frame environment. The results of spectral studies of the physicochemical properties of modified pentasils are presented in more detail by V.B. Kazanskii and coworkers [37–40].

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