Effect of Immobilized Carbon Nanoparticles on the Activity of Zeolites in the Oxidative Dehydrogenation of 4-Vinylcyclohexene and Ethylbenzene to Styrene

Kh. M. Alimardanov, A. A. Alieva, S. I. Abasov, M. F. Abbasov, and A. D. Kuliev

Mamedaliev Institute of Petrochemical Processes, National Academy of Sciences of Azerbaijan, Baku, 370025 Azerbaijan

e-mail: mayabdullayeva@rambler.ru; alreyhan@yahoo.com

Received May 16, 2011

Abstract—The results of studies on the oxidative dehydrogenation of 4-vinylcyclohexene to ethylbenzene and styrene and ethylbenzene to styrene on nanocomposite systems prepared by the immobilization of carbon nanoparticles on the H forms of zeolites and the modification of the resulting samples with platinum, gallium, and gadolinium are given. The activities of these catalysts are compared, and the synergism of the action of zeolite and carbon nanoparticles under the conditions of dehydrogenation is established. The immobilization of carbon nanoparticles into zeolite matrices contributes to an increase in their activity and stability and also to a decrease in the reaction temperature. The high yields of 4-vinylcyclohexene and ethylbenzene dehydrogenation products are reached at 425 and 470°C, respectively.

The target-oriented conversion of hydrocarbon raw materials into necessary products in the presence of nanocomposite systems, in particular, those prepared based on materials with zeolite or zeolite-like structures, is a priority trend in the development of present-day petroleum chemistry. It is well known that pentasils and mesoporous zeolite-like systems modified with Pt, Ga, and Gd exhibit high activity and selectivity in the aromatization, oligomerization, and alkylation of low-molecular-weight saturated and unsaturated hydrocarbons [1–6]; the conversion of methanol into aliphatic and aromatic hydrocarbons [7, 8]; the alkylation of benzene with propane [9] or isopropanol [10]; the dehydrodisproportionation [11] and dehydroalkylation of alkyl-substituted $C_7–C_8$ cyclohexanes with methanol [12, 13]; etc. However, there is almost no data on the use of these catalysts in the dehydrogenation reactions of hydrocarbons, in particular, ethylbenzene conversion into styrene, although other modified forms of different zeolite-containing catalysts are widely used in reactions for the production of styrene and its methyl derivatives by the dehydrogenation of ethylbenzene [14–16], the dehydration of methyl- and dimethylphenyl carbinols [17, 18], and the alkylation of alkenylbenzenes [19, 20] and toluene [21, 22] with methanol.

The butadiene method implemented with the participation of oxide and zeolite-containing catalysts [23–26] is currently considered an alternative method for expanding the range of raw materials for styrene production. This method is performed in the following two stages: the dimerization of butadiene to 4-vinylcyclohexene and the dehydrogenation of the latter to styrene. For the industrial implementation of this process, it is necessary to develop catalytic systems that are more efficient and provide high selectivity at either of the stages because of the presence of considerable 1,3-butadiene resources in the pyrolysis products of petroleum fractions.

The dehydrogenation of 4-vinylcyclohexene in the presence of well-known catalytic systems occurs with the predominant formation of ethylbenzene [25, 27] or a mixture of ethylbenzene and styrene with the predominance of the former [23, 24]. In this case, the ratio between the resulting reaction products—ethylbenzene and styrene—depends on the time of catalyst operation and changes significantly in the course of the process.

This work is the development of studies on the oxidative dehydrogenation of 4-vinylcyclohexene and ethylbenzene in the presence of zeolites TsVM modified with Pt and Ga. Here, we report the main experimental results of studying changes in the activity and selectivity of nanocomposite systems prepared based on these zeolites and carbon nanoparticles immobilized in them in the test reaction.

EXPERIMENTAL

The experiments were conducted on a laboratory setup at 0.1 MPa. A 3-g sample (fraction of 0.5–1 mm) of a catalyst, which was granulated without a binding agent, mixed with quartz grains in a ratio of 1 : 2 was loaded in a flow reactor and thermally treated at 500–550°C for 3–4 h in a flow of air. The hydrogen forms of HNa-mordenite (HNaM, $SiO_2/Al_2O_3 = x = 10$),
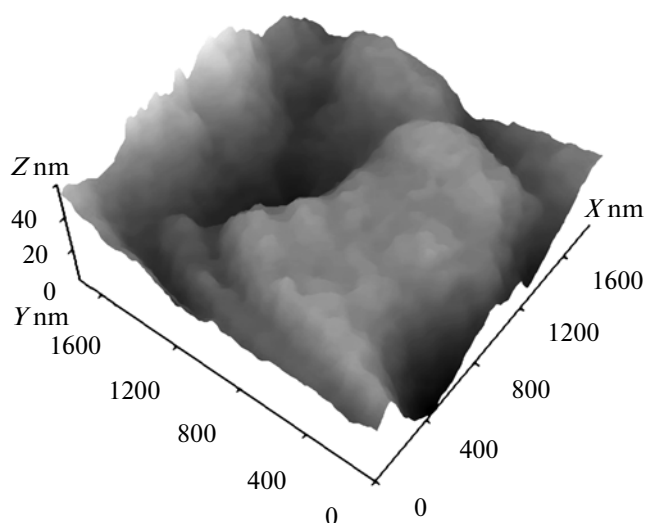
Fig. 1. AFM 3D image of the Pt, Ga, Gd/HNa-TsVM + 20% immobilized carbon nanoparticles.

HNa-TsVM ($x = 30$), and HNaY ($x = 4.8$) were used as parent zeolites. The degree of decationation was 75 wt %. The immobilization of carbon nanoparticles was performed by the in situ precipitation of them onto the zeolite. For obtaining the carbon nanoparticles, CCl$_4$ taken in an excess amount was stirred with aluminum metal chips in a glass reactor at 75–76°C. At the instant of carbon formation according to the equations

$$2Al + 3CCl_4 \rightarrow 2AlCl_3 + C_2Cl_6 + C$$

$$2Al + C_2Cl_6 \rightarrow 2AlCl_3 + 2C$$
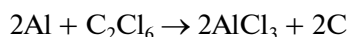
decationized zeolite was added to the mixture, and the stirring was continued until the complete consumption of aluminum for 2–8 h. The carbonized samples were separated from the mixture by filtration with the use of a Buchner funnel. Then, the precipitate was washed with CCl$_4$, dried at 80–120°C in a flow of nitrogen, and thermally treated at 200–250°C until the complete cessation of the release of HCl and the sublimation of AlCl$_3$. The specified degree of zeolite carbonization was reached by varying the amount of aluminum metal and the duration of stirring. Ga, Gd, and Pt were introduced into the composition of the H form of zeolites with immobilized carbon nanoparticles by impregnation with the aqueous solutions of Ga and Gd nitrates and ammonium hexachloroplatinate followed by heat treatment according to the known method [28]. Catalyst samples containing 3.0 wt % Ga$_2$O$_3$, 2.0 wt % Gd$_2$O$_3$, and 0.5 wt % Pt were used in the experiments. For the comparison of activities, Pt–Ga–Gd samples supported on immobilized carbon nanoparticles without a zeolite matrix and on zeolite that did not contain immobilized carbon nanoparticles were also prepared.

The X-ray diffraction patterns of the prepared catalysts were taken on a DRON-3M diffractometer using CuKα radiation with a Ni filter. The sizes of carbon nanoparticles in a zeolite matrix were determined on an NC-AFM scanning atomic force microscope.

The parent substances were 4-vinylcyclohexene, which was prepared in accordance with a well-known procedure [29], and chemically pure ethylbenzene. The physicochemical constants of these substances were consistent with reference data [30].

The reaction products were analyzed by GLC with a flame-ionization detector: a 6×2400 mm column packed with 10 wt % SE-30 on Chromosorb W ($T_{col} = 140$°C and $T_{inj} = 180$°C) and with 12 wt % bis(2-cyanoethyl) sulfide on the adsorbent Chromaton N AW-DMCS. Standard reference compounds were used for the identification of the products of catalysis.

RESULTS AND DISCUSSION

Previously, we found that the samples of HNa-TsVM modified with Pt, Ga, Gd, and potassium at 470–485°C exhibited high activity in the oxidative dehydrogenation of 4-vinylcyclohexene to ethylbenzene and styrene [31]. Further studies showed that the yield of dehydrogenation products on a freshly prepared sample initially increased in the course of the process and then somewhat decreased. The activity and stability of spent samples after their treatment in a flow of air at 450–500°C for 4 h were much higher than data obtained on the freshly prepared catalysts; this fact suggests the participation of specific reaction mixture components in the formation of the active centers of the catalyst. Analogous regularity was observed previously [1, 6] for the aromatization of C$_3$–C$_5$ paraffins on Ga and Pt, Ga pentasils. Dergachev et al. [1, 6] proposed the treatment of gallosilicates and galloaluminosilicates in a flow of hydrogen or water vapor in order to accelerate the stabilization of activity. On the other hand, such a change in the activity of oxide and zeolite catalysts in the oxidative dehydrogenation [32, 33] and alkylation [34] reactions of alkylaromatic hydrocarbons can be a consequence of the accumulated carbon deposits on their surface. To study the effect of carbon-containing deposits on the activity of zeolites in the oxidative dehydrogenation reaction of 4-vinylcyclohexene and ethylbenzene, we preliminarily investigated systems based on immobilized carbon nanoparticles containing modified forms of zeolites (HNaY, HNaM, and HNa-TsVM) with different concentrations of carbon nanoparticles in wide ranges of temperatures (320–525°C), hydrocarbon space velocities ($v = 0.5$–3 h^{-1}), and 4-vinylcyclohexene (ethylbenzene) : O$_2$ molar ratios (0.2–1.5). The relief of carbon nanoparticles in the prepared samples was studied on a scanning atomic force microscope (Figs. 1 and 2). Carbonization mainly occurs on the surface of a zeolite matrix. The sizes of the resulting carbon nanoparticles were as great as 30–67 nm. The atomic force

microscopic analysis of the samples revealed morphologically diverse surface structures. X-ray diffraction analysis demonstrated that the major portion of immobilized carbon nanoparticles was highly dispersed carbon-containing mass. As a rule, peaks due to carbon in the diffractograms merged into a wide halo with characteristic maximums at $d = 3.41–3.42$ Å.

According to X-ray diffraction data, the structure of zeolites remained almost unchanged upon carbonization and impregnation with corresponding salt solutions. Only a decrease in crystallinity was observed in HNaY samples. Tables 1 and 2 compare results concerning catalyst activity. As can be seen in Table 1, the introduction of immobilized carbon nanoparticles into the composition of zeolites had almost no effect on the qualitative composition of the liquid products of catalysis. The ratios between and the yields of the dehydrogenation products of 4-vinylcyclohexene (ethylbenzene and styrene) depend on structure and the degree of carbonization of zeolites. Of zeolite catalysts, the greatest amounts of ethylbenzene and styrene in a non-steady state at 470°C were obtained on Pt, Ga, Gd/HNaY (51.9%) and Pt, Ga, Gd/HNaM (20.4%), respectively. The presence of immobilized carbon nanoparticles (INCs) in the composition of zeolite catalysts contributes to an increase in their dehydrogenating activity. However, from data in Table 1, it follows that the yields of ethylbenzene and styrene upon the oxidative dehydrogenation of 4-vinylcyclohexene on Pt, Ga, Gd/INC were lower than those on the zeolite catalysts containing no immobilized carbon nanoparticles by a factor of almost 1.5. It is also of interest that the activity of Pt, Ga, Gd/INC was twice as high as the activity of the Pt, Ga, Gd/AG-3 sample prepared based on AG-3 carbon.

A somewhat different behavior was observed in the oxidative dehydrogenation of ethylbenzene on these samples. An increase in the amount of immobilized carbon nanoparticles to 5 wt % (Table 2) had almost no effect on the activity of the catalysts, although it facilitated an increase in selectivity for styrene from 82.0 to 88.0%. A further increase in the amount of immobilized carbon nanoparticles in the composition of a catalyst led to a decrease in its activity, whereas the selectivity remained almost unchanged.

It is likely that the chemical modification of zeolites with nanosized carbon particles leads to their accumulation in the channels of the structure and, thus, in the blocking of the accessibility of active centers to a reactant with these particles. Furthermore, this nanocomposite system can facilitate a redistribution of metal cations into surface sites accessible to hydrocarbons upon the modification of this system with Ga, Gd, and Pt compounds. As a result, ionic-type side reactions (isomerization and disproportionation) are inhibited and selectivity for radical–ion reactions, including the oxidative dehydrogenation of
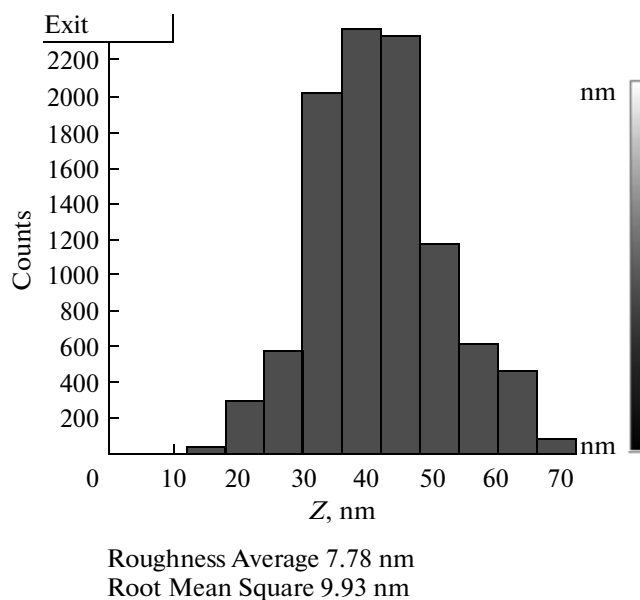

Fig. 2. Bar diagram of the distribution of carbon nanoparticles on the surface of a zeolite matrix.

hydrocarbons, increases. It is likely that this is responsible for the observed high selectivity of the process for the target products.

Our studies performed using zeolite samples modified with Pt, Ga, and Gd with different degrees of dealumination of mordenite ($Al_2O_3/SiO_2 = x = 10–17$; TsVM, $x = 33–50$) showed that the dealumination of zeolites in the specified range had almost no effect on the activity of the used catalysts.

We chose Pt, Ga, Gd/HNaTsVM samples containing 5 and 20 wt % immobilized carbon particles for the subsequent studies of catalytic properties.

The ratios between and the yields of the oxidative dehydrogenation products of 4-vinylcyclohexene and ethylbenzene with the participation of this sample depend on both the conditions of catalysis (Tables 3, 4) and the hydrocarbon : oxygen molar ratio (Figs. 3a, 3b). For the comparison of results, Tables 3 and 4 also summarize data obtained on noncarbonized TsVM and immobilized carbon nanoparticles containing corresponding amounts of Pt, Ga, and Gd. It is well known that, on the decationized forms of zeolites like mordenite and pentasil modified with the oxides of polyvalent metals in the range of 250–340°C, the sequential displacement of multiple bonds mainly occurs in the ring and from the side vinyl group toward the ring until their conjugation occurs according to the following scheme: 4-vinylcyclohexene → 3-vinylcyclohexene → 3-ethylidenecyclohexene → ethyl-1,2-cyclohexadiene isomers [23]. The isomerization of 4-vinylcyclohexene in the presence of the above catalysts precedes the dehydrogenation reaction; this is likely due to its lower activation energy. In this case, the dehydrogenation of the above

Table 1. Oxidative dehydrogenation of 4-vinylcyclohexene on zeolites with different concentrations of immobilized carbon nanoparticles ($T = 470°C$; $v_{\text{4-vinylcyclohexene}}$, 1 h^{-1}; molar ratio 4-vinylcyclohexene : O_2 = 1 : 0.3)

Amount of immobilized carbon nanoparticles, wt %	Composition of liquid products of catalysis, wt %							Yield, %	
	C_6–C_8 cyclanes and cyclenes	C_8H_{12} dienes *	4-Vinylcyclohexene	Benzene, toluene	Xylene isomers	Ethylbenzene	Styrene	Ethylbenzene	Styrene
Pt, Ga, Gd/HNaY									
–	1.2	10.6	12.2	5.5	1.7	53.6	15.2	51.9	15.0
2	2.0	11.6	9.4	4.4	1.6	53.5	17.5	51.8	17.3
5	2.4	9.0	9.4	5.0	1.0	55.0	18.2	53.2	18.0
20	1.8	7.5	9.9	4.5	0.4	60.6	15.3	58.7	15.1
Pt, Ga, Gd/HNaM									
–	3.7	12.0	9.4	3.0	1.0	50.2	20.7	48.5	20.4
2	2.8	12.3	10.4	3.6	0.8	51.0	19.1	49.4	18.8
5	2.1	10.0	11.2	3.0	0.9	51.7	21.1	50.0	20.8
20	2.5	9.1	12.4	3.4	0.6	55.4	16.6	55.6	16.4
Pt, Ga, Gd/HNaTsVM									
–	2,5	14.8	13.2	4.1	1.7	42.8	20.9	40.2	19.6
2	1,8	12.0	10.9	4.7	1.8	44.1	24.7	42.7	24.4
5	1,7	10.5	13.2	2.2	1.5	46.3	24.6	44.8	24.3
20	3,2	7.0	11.5	2.9	1.0	49.4	25.0	47.8	24.7
Pt, Ga, Gd/ICN									
–	0.6	5.3	35.6	2.5	0.5	38.6	16.9	37.4	16.7
Pt, Ga, Gd/AG									
–	0.9	4.0	62.9	1.0	–	24.3	6.9	24.0	7.0

* Ethylidene and ethylcyclohexadiene isomers.

Table 2. Oxidative dehydrogenation of ethylbenzene on zeolites with different concentrations of immobilized carbon nanoparticles ($T = 470°C$; $v_{\text{ethylbenzene}}$, 1 h^{-1}; molar ratio ethylbenzene : O_2 = 1 : 0.5)

Zeolite	Amount of immobilized carbon nanoparticles, wt %	Composition of liquid products of catalysis, wt %					Ethylbenzene conversion, %	Selectivity for styrene, %
		Light hydrocarbons	Benzene, toluene	Xylene	Ethylbenzene	Styrene		
Pt,Ga,Gd/HNaY	–	1.0	7.8	4.2	30.4	56.6	70.5	79.4
	2	0.9	5.6	4.7	33.5	55.3	67.5	81.0
	5	0.5	6.2	3.4	32.5	57.4	68.5	82.9
	20	0.2	3.6	3.0	41.3	51.9	59.9	85.6
Pt,Ga,Gd/HNaM	–	0.6	6.7	3.2	35.1	54.4	66.7	81.5
	2	0.4	5.8	4.0	34.0	55.8	67.0	82.3
	5	0.5	6.3	3.2	36.2	53.8	64.9	82.0
	20	0.4	2.4	2.2	43.8	51.2	58.4	84.9
Pt,Ga,Gd/HNaTsVM	–	0.4	5.2	2.6	41.4	50.0	59.8	82.0
	2	0.4	2.8	2.3	40.0	54.5	61.2	88.0
	5	0.3	2.3	2.2	42.3	52.9	59.0	88.7
	20	0.3	2.5	2.0	47.4	47.8	55.0	84.3
–	Pt,Ga,Gd/ICN	0.3	1.5	1.2	57.6	39.4	44.1	88.3
	Pt,Ga,Gd/AG-3	–	0.9	0.8	81.4	16.9	22.7	78.6

Table 3. Effect of temperature on the yield of products in the oxidative dehydrogenation of 4-vinylcyclohexene in the presence of Pt, Ga, Gd/HNaTsVM with immobilized carbon nanoparticles ($v_{\text{4-vinylcyclohexene}}$, 1 h^{-1}; molar ratio 4-vinylcyclohexene : O$_2$ = 1 : 0.3)

T, °C	Composition of liquid products of catalysis, wt %							4-Vinylcyclohexene conversion**, %	Yield of oxidative dehydrogenation products, %	Ethylbenzene : styrene molar ratio
	C_6–C_8 cyclanes and cyclenes	C_8H_{12}*-dienes	4-vinylcyclohexene	Benzene, toluene	Xylene isomers	Ethylbenzene	Styrene			
Pt, Ga, Gd/HNaTsVM + 5% immobilized carbon nanoparticles										
320	0.7	13.2	73.7	1.0	—	11.4	—	14.8	11.3	—
345	0.7	14.0	65.0	1.0	—	18.3	1.0	23.4	19.1	18 : 1
370	1.2	10.2	58.2	1.5	1.0	24.2	3.7	35.0	27.1	6.3 : 1
400	2.0	10.0	35.0	2.5	1.5	34.8	14.2	57.7	47.7	2.4 : 1
425	2.0	13.1	19.0	3.0	1.5	41.1	20.7	70.1	60.2	1.9 : 1
470	1.7	10.5	13.2	2.2	1.5	46.3	24.6	78.0	69.1	1.85 : 1
500	2.2	7.7	10.7	4.0	1.6	50.8	23.0	83.2	70.3	2.2 : 1
Pt, Ga, Gd/HNaTsVM + 20% immobilized carbon nanoparticles										
320	0.5	11.7	77.8	—	—	10.0	—	12.3	9.9	—
345	0.6	12.0	70.5	0.5	—	15.8	0.6	20.0	16.2	—
370	1.1	10.5	58.4	0.8	—	26.3	2.9	34.5	28.9	9 : 1
400	2.4	9.2	34.4	1.6	1.0	38.6	12.8	59.0	50.0	3 : 1
425	2.4	9.6	27.2	2.4	1.1	40.0	17.3	65.7	55.8	2.3 : 1
470	3.2	7.0	11.5	2.9	1.0	49.4	25.0	82.8	72.5	1.9 : 1
500	2.0	8.1	14.9	3.5	1.4	49.2	20.9	79.9	66.8	2.3 : 1
Pt, Ga, Gd/HNaTsVM										
320	2.0	17.5	79.3	—	—	1.2	—	5.1	1.2	—
345	3.6	17.2	71.4	—	—	7.8	—	14.1	7.7	—
370	7.8	14.5	49.6	2.5	0.5	20.0	5.2	39.2	22.6	3.9 : 1
400	5.9	15.6	40.1	4.8	1.3	23.3	9.0	48.1	28.8	2.6 : 1
425	6.1	16.1	21.8	4.8	0.9	37.3	13.0	64.7	43.8	2.9 : 1
470	6.2	13.4	10.9	4.5	1.3	42.8	20.9	77.2	59.8	2.05 : 1
500	1.0	4.4	6.3	3.0	0.9	54.8	29.6	90.2	70.4	1.85 : 1
Pt, Ga, Gd/ICN										
320	—	3.4	90.2	—	—	6.4	—	8.3	6.3	—
345	—	3.5	87.3	—	—	9.2	—	11.9	9.1	—
370	0.5	6.4	73.1	1.1	—	16.4	2.5	24.5	18.7	6.5 : 1
400	2.8	7.3	56.6	1.4	0.6	23.0	8.3	39.9	30.5	2.7 : 1
425	3.0	7.1	40.8	2.0	0.6	33.1	13.4	54.3	46.2	2.4 : 1
470	4.2	6.0	31.3	2.5	0.5	38.6	16.9	65.3	54.1	2.2 : 1
500	2.2	4.8	32.2	2.7	1.0	41.0	16.1	66.1	54.3	2.5 : 1

* Ethylidene and ethylcyclohexadiene isomers. ** In the calculation of conversion, the migration of double bonds in the 4-vinylcyclohexene molecule was ignored.

Table 4. Temperature effect on the conversion of ethylbenzene and the yield of styrene in the oxidative dehydrogenation of ethylbenzene on Pt, Ga, Gd/HNaTsVM with immobilized carbon nanoparticles ($v_{ethylbenzene}$, 1 h^{-1}; molar ratio ethylbenzene : O_2 = 1 : 0.5)

| T, °C	Composition of liquid products of catalysis, wt %					Ethylbenzene conversion, %	Selectivity for styrene, %
	Light hydrocarbons	benzene, toluene	xylenes	ethylbenzene	styrene		
Pt,Ga,Gd/HNaTsVM + 5% immobilized carbon nanoparticles							
370	–	1.0	1.0	91.6	6.4	11.1	56.7
400	–	1.0	1.0	85.3	12.7	19.0	64.9
430	0.2	1.2	1.2	75.9	21.5	27.9	74.6
470	0.3	2.3	2.2	42.3	52.9	59.0	88.7
500	0.5	3.0	2.7	40.1	53.7	61.9	89.1
525	1.8	4.6	2.8	38.7	52.1	64.0	81.8
Pt,Ga,Gd/HNaTsVM + 20% immobilized carbon nanoparticles							
370	–	1.0	1.0	93.8	4.2	7.1	59.6
400	–	1.2	1.0	88.1	9.7	14.5	65.9
430	0.3	0.8	1.1	77.6	20.2	24.7	80.8
470	0.3	2.5	2.0	47.4	47.8	55.0	84.3
500	0.7	3.4	2.0	46.8	47.1	55.5	82.1
525	1.6	5.2	2.4	46.5	44.3	56.8	74.0
Pt,Ga,Gd/ICN							
350	0.1	–	–	97.4	2.5	3.5	72.9
370	0.2	–	–	94.7	5.1	7.2	71.6
430	0.4	1.0	0.8	74.8	23.0	27.4	82.9
470	0.3	1.5	1.2	57.6	39.4	44.1	88.3
500	0.7	2.1	0.9	56.6	39.7	46.8	81.3
530	0.9	5.0	1.6	56.3	36.2	47.6	72.5

intermediates also leads to the formation of a mixture of ethylbenzene and styrene. Therefore, we did not take into account the migration of double bonds in the calculation of the conversion of 4-vinylcyclohexene.

As can be seen in Table 3, unlike noncarbonized Pt, Ga, Gd/HNaTsVM, the oxidative dehydrogenation of 4-vinylcyclohexene on the carbonized samples begins at a lower temperature (320–340°C). In this case, the main product of 4-vinylcyclohexene dehydrogenation is ethylbenzene. Styrene is formed starting from 370°C, and its buildup is intensified at 400–425°C. The maximum yields of ethylbenzene and styrene (39.8–44.8 and 20.4–22.3%, respectively) are reached on the nanocomposite Pt, Ga, Gd/HNaTsVM system containing 5 wt % immobilized carbon nanoparticles at 425–470°C. On this system, the oxidative dehydrogenation of ethylbenzene begins at a temperature of 370°C and the highest yield of styrene (52.5–55.2%) with 88.7–89.1% selectivity is reached at 470–500°C (Table 4). Note that the dehydrogenation of ethylbenzene on the zeolite-containing Pt, Ga, Gd/ICN sample, as in the case of 4-vinylcyclohexene, begins at a lower temperature (320–350°C); however, the activity

of this system is low and the maximum yield of styrene does not exceed 39.0% (at 470°C).

According to the results given in Tables 1–4, it is possible to conclude that the immobilization of carbon nanoparticles on the zeolite HNa-TsVM matrix leads to the synergism of their action. This is likely due to their mutual influence on the distribution of metal cations in the process of modification.
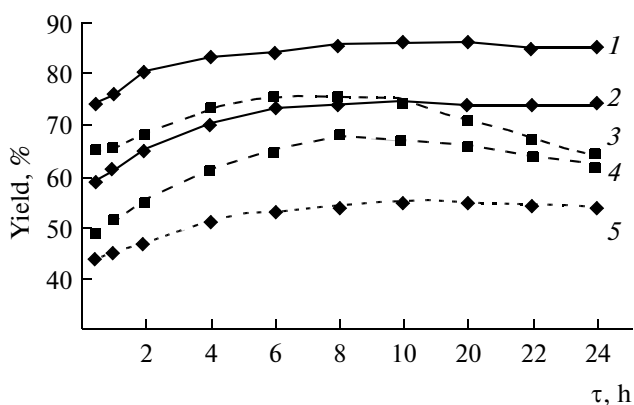
The dehydrogenation of 4-vinylcyclohexene on noncarbonized samples is accompanied by the isomerization and disproportionation of the initial substances and dehydrogenation products in significant amounts. The isomerization of 4-vinylcyclohexene occurs by the migration of multiple bonds in the molecule without changes in the structure of the initial hydrocarbon and leads to the formation of a mixture of 3-ethylidene-1-cyclohexene and ethyl-1,3-cyclohexadienes. These latter are easily dehydrogenated to ethylbenzene and styrene. The disproportionation of the dehydrogenation products occurs more intensely as the temperature is increased from 470 to 525°C and leads to the accumulation of an amount of benzene and toluene in the products of catalysis. As the amount of immobilized carbon nanoparticles in the composi-
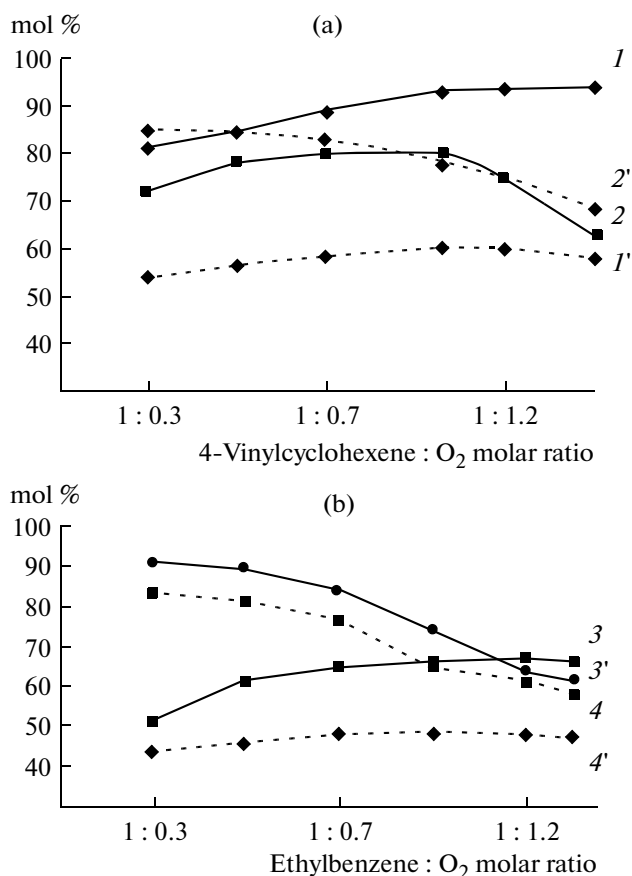
Fig. 3. Dependence of the conversion of (a) 4-vinylcyclo-hexene (at 425°C) and (b) ethylbenzene (at 470°C) and selectivity for dehydrogenation products on the hydrocar-bon : oxygen : (1−4) Pt, Ga, Gd/(HNaTsVM + 5% immo-bilized carbon nanoparticles) or ((1'−4') Pt, Ga, Gd/ICN catalyst molar ratios: (1, 1') 4-vinylcyclohexene conver-sion, (2, 2') selectivity for ethylbenzene + styrene, (3, 3') ethylbenzene conversion, and (4, 4') selectivity for styrene.

Fig. 4. Effect of catalyst operation time on catalyst activity in the oxidative dehydrogenation of 4-vinylcyclohexene (at 425°C; 4-vinylcyclohexene : O_2 = 1 : 0.5). Catalysts: (1) Pt, Ga, Gd/HNaTsVM + 5% immobilized carbon nanoparticles; (2) Pt, Ga, Gd/HNaTsVM + 20%; (3) Pt, Ga, Gd/HNaY + 5% immobilized carbon nanoparticles; (4) Pt, Ga, Gd/HNaTsVM; and (5) Pt, Ga, Gd/ICN.

tion of a catalyst is increased, the benzene and toluene content of the liquid reaction products decreases. As noted above, this is likely due to the fact that, upon the immobilization of carbon on the surface of a zeolite matrix, its localization preferably occurs at strong acid sites, which are responsible for the occurrence of ion-type reactions, in particular, the disproportionation of the alkyl derivatives of benzene [35].

The yield of products of the oxidative dehydroge-nation of 4-vinylcyclohexene and ethylbenzene on Pt, Ga, Gd/HNaTsVM + 5% immobilized carbon nano-particles initially increased with the hydrocarbon : oxygen molar ratio (Figs. 3a, 3b) to reach maximum values at 1 : 0.9−1.1 or 1 : 0.5 for 4-vinylcyclohexene or ethylbenzene, respectively, but then decreased. This was due to the fact that the products of the deep and partial oxidation of hydrocarbons increased with the concentration of oxygen in the initial mixture; this more intensely manifested itself in the case of 4-vinyl-

cyclohexene. Note that the same regularity was also observed on Pt, Ga, Gd/ICN.

The yield of the dehydrogenation products of 4-vinylcyclohexene and ethylbenzene substantially depends on the operation time of the above catalysts (Figs. 4, 5). As a rule, in all of the zeolite catalysts modified with immobilized carbon nanoparticles, an increase in the yield of the main products (ethylben-zene and styrene) was observed upon the oxidative dehydrogenation of 4-vinylcyclohexene for 4–6 h (Fig. 4). Pt, Ga, Gd/HNa-TsVM and Pt, Ga, Gd/ICN exhibited the same properties. In all cases, an increase in the yield of target products during the indicated period occurred due to an increase in the reaction selectivity (from 74.3 to 93%) with a simulta-neous decrease in the conversion of 4-vinylcyclohex-ene and in the yields of by-products—disproportion-ation (benzene and toluene) and deep oxidation (CO_2) products. After reaching a maximum, the yield of dehydrogenation products remained almost unchanged for ~20 h. The exception is provided by the Pt, Ga, Gd/HNaY + 5% immobilized carbon nano-particles and Pt, Ga, Gd/HNaTsVM samples, whose activity gradually decreased. According to atomic force microscopic data, the structure of immobilized carbon nanoparticles and the sizes of the carbon nano-particles underwent considerable changes upon the operation of the carbonized forms of zeolites for 10 h.

The sizes of the carbon nanoparticles reached 80–90 nm. In this case, the structure of HNaTsVM remained almost unchanged (according to X-ray dif-fraction data). A decrease in the crystal structure was observed in the carbonized Pt, Ga, Gd/HNaY sample.

Approximately the same behavior was observed in the oxidative dehydrogenation of ethylbenzene (Fig. 5); however, in this case, unlike 4-vinylcyclohex-
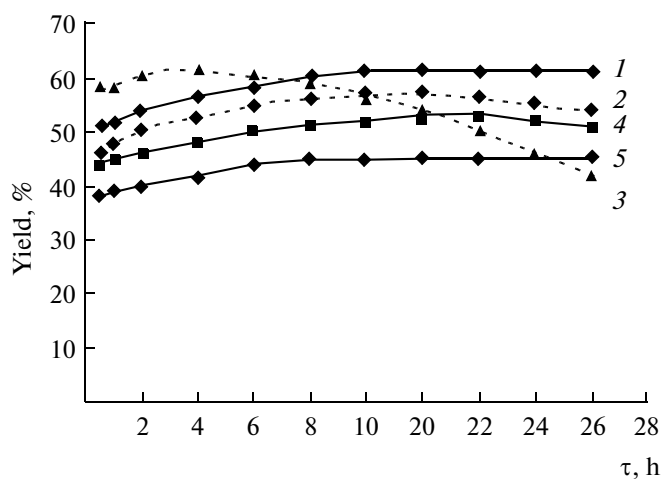
Fig. 5. Effect of the catalyst on-stream time on catalyst activity in the oxidative dehydrogenation of ethylbenzene (at 470°C; ethylbenzene : $O_2 = 1 : 0.5$).

ene, the catalyst activity slowly increased for 10—15 h, and then it was stabilized. It is likely that the catalytic properties of these systems changed in the course of the process due to the additional modification of their surface by coke deposits, whose composition was differed from the composition of immobilized carbon nanoparticles. The greatest coke deposition was observed in the oxidative dehydrogenation of 4-vinyl-cyclohexene.

Thus, the modification of pentasil zeolites with immobilized carbon nanoparticles leads to an increase in their activity and selectivity in radical—ion reactions, in particular, the oxidative dehydrogenation of 4-vinylcyclohexene and ethylbenzene. The introduction of immobilized carbon nanoparticles facilitates the blocking of strong acid sites in the catalysts, the highly dispersed redistribution of metal cations, and an increase in the stability of the catalyst.

REFERENCES

1. Kh. M. Minachev and A. A. Dergachev, Izv. Akad. Nauk SSSR, Ser. Khim., No. 6, 1018 (1993).

2. D. Seddon, Catal. Today, No. 6, 351 (1998).

3. V. R. Choudhary, P. Devadas, S. Banerjee, and A. K. Kinage, Microporous Mezoporous Mater. **47**, 253 (2001).

4. V. R. Choudhary, S. Banerjee, and P. Devadas, J. Catal. **205**, 398 (2002).

5. R. V. Dmitriev, D. P. Shevchenko, E. S. Shpiro, et al., Stud. Surf. Sci. Catal. **69**, 381 (1991).

6. A. L. Lapidus, A. A. Dergachev, V. A. Kostina, and A. A. Silakova, Pet Chem. **48**, 83 (2008).

7. D. Freeman, R. P. K. Wells, and G. J. Hutschings, J. Catal. **205**, 358 (2002).

8. O. A. Sinitsyna, V. N. Chumakova, and I. F. Moskovskaya, Neftekhimiya **27**, 194 (1987).

9. C. Bigey and B. -L. Su, J. Mol. Catal. A **209**, 179 (2004).

10. S. Gnanapragasam, V. Krishnasamy, and V. Mohan, Indian J. Chem., Sect. A: Inorg., Bioinorg., Phys., Theor. Anal. Chem. **40**, 947 (2001).

11. Kh. M. Alimardanov, S. I. Abasov, A. F. Abdullaev, et al., Pet. Chem. **41**, 431 (2001).

12. Kh. M. Alimardanov, L. A. Tairova, and S. I. Abasov, Pet. Chem. **43**, 403 (2003).

13. Kh. M. Alimardanov, F. M. Velieva, L. A. Dadasheva, and M. I. Rustamov, Pet. Chem. **46**, 353 (2006).

14. N. S. Nesterenko, O. A. Ponomerova, V. V. Yuschenko, et al., Appl. Catal. A: Gen/ **254**, 261 (2003).

15. She-Tin Wong, Hong-Ping Lin, and Chung-Yuan Mou, Appl. Catal. A: Gen. **198**, 103 (2000).

16. Y. Qiao, C. Miao, Y. Yue, et al., Micropor. Mezopor. Mater. **119**, 150 (2009).

17. I. G. Shmelev, A. A. Lamberov, and R. G. Romanova, in *Modern Problems of Theoretical and Experimental Chemistry* (2001) [in Russian], p. 69.

18. E. M. Mamedov, M. A. Gagarin, and Kh. E. Kharlampidi, Zh. Prikl. Khim. **75**, 599 (2002).

19. O. A. Ponomareva, I. F. Moskovskaya, and B. V. Romanovskii, Pet. Chem. **41**, 257 (2001).

20. O. A. Ponomareva, I. F. Moskovskaya, and B. V. Romanovskii, Pet. Chem. **39**, 83 (1999).

21. Yu. I. Sidorenko, P. N. Galich, V. S. Gutyrya, et al., Dokl. Akad. Nauk SSSR **173**, 132 (1967).

22. K. I. Patrilyak, Yu. I. Sidorenko, and V. A. Bortyshevskii, *Alkylation on Zeolites* (Naukova Dumka, Kiev, 1991) [in Russian].

23. Kh. M. Alimardanov and A. F. Abdullaev, Neftekhimiya **35**, 526 (1995).

24. Y. S. Choi, Y.-K. Park, J.-S. Chang, et al., Catal. Lett. **69**, 93 (2000).

25. J.-S. Chang, S.-E. Park, Q. Gao, et al., Chem. Commun., 859 (2001).

26. R. Neumann and I. Dror, Appl. Catal. **172**, 67 (1998).

27. G. G. Garifzyanov, I. Kh. Bikbulatov, and R. B. Valitov, Neftekhimiya **10**, 28 (1970).

28. Kh. M. Minachev and Ya. I. Isakov, *Preparation, Activation, and Regeneration of Zeolite Catalysts* (TsNIITENeftekhimii, Moscow, 1971) [in Russian].

29. I. E. Maxwell, R. S. Downing, and S. A. J. van Langen, J. Catal. **61**, 485 (1980).

30. R. C. Weast and M. J. Astle, *Handbook of Data on Organic Compounds* (CRC, Boca Raton, 1985), Vol. 1.

31. Kh. M. Alimardanov, A. A. Alieva, and S. I. Abasov, Pet. Chem. **50**, 124 (2010).

32. T. G. Alkhazov and A. E. Lisovskii, *Oxidative Dehydrogenation of Hydrocarbons* (Khimiya, Moscow, 1980) [in Russian].

33. O. V. Krylov, *Heterogeneous Catalysis* (Akademkniga, Moscow, 2004) [in Russian].

34. S. J. Kulkarni, H. Hattori, and K. Tanabe, Appl. Catal. **49**, 27 (1989).

35. P. A. Jacobs, *Carboniogenic Activity of Zeolites* (Elsevier, Amsterdam, 1977; Khimiya, Moscow, 1983).