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The Oxidative Dehydrogenation of 4-Vinylcyclohexene in the Presence of Modified Ga, Pt-Pentasils

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Abstract—The oxidative dehydrogenation reaction of 4-vinylcyclohexene (4-VCH) in the presence of a pentasil zeolite (TsVM) modified by platinum, gallium, gadolinium, and potassium was investigated. The influence of the nature of the modifiers on the progression of the reaction and the yields of the desired product, ethylbenzene and styrene, was established. It was found that the conversion of 4-VCH into ethylbenzene and styrene proceeds along two parallel routes, the oxidative dehydroisomerization and dehydrogenation of the reactant hydrocarbon. Conditions for the maximal yield of styrene on potassium hydroxide–promoted Pt,Ga,Gd/HNa–TsVM were determined.

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The dehydrogenation of hydrocarbons in the presence of various hydrogen acceptors has been extensively developed in recent years [1–3]. Research in this area has focused on the problem of the preparation of C_4 and C_5 unsaturated aliphatic hydrocarbons and alkenylarenes (styrene and its methyl derivatives). Among the traditional methods used for the dehydrogenation of benzene and its derivatives, alkenylated aromatic compounds are prepared in some cases via the reaction of ethylbenzene hydroperoxide with propylene followed by the dehydration of the resulting methyl phenyl carbinol [4, 5] or via the alkylation of toluene and other alkyl- and alkenylbenzenes with C_1–C_3 monohydric alcohols in the presence of various zeolite catalysts [6–9]. A commercially more available and less expensive feedstock is used in the latter case as compared to the conventional styrene manufacture process according to the scheme: toluene $\longrightarrow$ benzene $\longrightarrow$ ethylbenzene $\longrightarrow$ styrene.

As shown by published data, the styrene synthesis according to the scheme butadiene-1,3 $\longrightarrow$ 4-vinylcyclohexene $\longrightarrow$ styrene is of great practical importance as well. Its value is due to both the presence of a considerable source of butadiene-1,3 available with the C_4 pyrolysis fraction [10, 11] and the ease of its conversion into 4-vinylcyclohexene (4-VCH) [12, 13].

In a number of studies devoted to the dehydrogenation of 4-VCH, high yields of ethylbenzene and only traces of styrene have been obtained [14, 15]. At the same time, some processes for the oxidative dehydrogenation of 4-VCH into styrene have been patented [16, 17].

However, the nonsystematic and controversial character of the investigations in this area does not make it possible to reveal the general trends and mechanism of the reaction; to consider the influence of various parameters and individual components formed in the reaction on the selective conversion of 4-VCH; and, hence, to find the optimal conditions for the synthesis of the desired product.

Earlier, we have shown [18] the feasibility of the simultaneous preparation of ethylbenzene and styrene by the oxidative dehydrogenation of 4-VCH in the presence of some rare-earth elements and alkali metals (potassium) of iron oxide–modified natural clinoptilolite or synthetic mordenite.

This work was devoted to the investigation of the catalytic transformation of 4-VCH in the presence of pentasil zeolite modified with platinum metal, gallium, and gadolinium oxides; the influence of admixed byproducts of the reaction on the selectivity of the process was also studied.

EXPERIMENTAL

The reactant hydrocarbon 4-vinylcyclohexene was prepared by the dimerization of butadiene-1,3 and the sharp rectification of the dimer fraction. The following hydrocarbons were also used in the work: ethylbenzene, styrene, ethylcyclohexane, vinylcyclohexane, and ethylcyclohexene isomers whose purity was determined by GLC. The physicochemical characteristics of the aforementioned hydrocarbons were in good agreement with the published data [19].

The metal-containing pentasil samples were prepared from the HNa-TsVM zeolite (manufactured by VNIINP) having the ZSM-5 structure (SiO_2/Al_2O_3 = 30) according to the following procedures:

(1) joint impregnation of the zeolite matrix with an aqueous solution of a mixture of gallium nitrate, gad-

olinium nitrate, and ammonium hexachloroplatinate followed by their thermal decomposition at 450–500°C;

(2) successive impregnation of HNa-TsVM in individual solutions of the relevant salts followed by their thermal treatment at 500–550°C after impregnation with each individual solution [20];

(3) cation exchange of Na^+ ions for Me^{n+} ions at pH 5–6.5 according to the procedure [21]; or

(4) mechanical mixing of gallium oxide, gadolinium oxide, and ammonium hexachloroplatinate with HNa-TsVM.

Before use, the catalysts granulated by alumina hydrogel taken in the amount of 30 wt % (particle size, 0.5–1.5 mm) were activated during 2–3 h at 500°C in an air flow. The experiments were carried out in a fused-silica flow reactor with a fixed catalyst bed in the temperature range from 250 to 520°C at a pressure of 0.1 MPa. The products were analyzed by GLC on a 2.4 m × 6-mm column packed with 10 wt % SE-30 silicone elastomer–coated Chromosorb W (T_{col} = 140°C, T_{vap} = 180°C) or 5 wt % bis-(2-cyanoethyl)sulfide-coated Chromaton N-AW-HNDS (T_{col} = 80°C, T_{vap} = 170°C) using nitrogen as the carrier gas.

RESULTS AND DISCUSSION

The Na-TsVM zeolite at 300–500°C displays almost no activity in the dehydrogenation of 4-VCH. The partial substitution of Na^+ cations for NH_4^+ and the subsequent high-temperature treatment of the resulting samples at 500–550°C lead to the formation of active centers responsible for the isomerization of the initial hydrocarbon. The isomerization of 4-VCH in the presence of HNa-TsVM in the temperature range of 250–350°C results in the migration of the multiple bond from the vinyl group to the cyclohexene moiety in order to form a conjugated diene system. The products of 4-VCH disproportionation and dehydrogenation on this catalyst are detected only at higher temperatures (400–450°C). Although the yield of the products is insignificant, the maximal amount of aromatic hydrocarbons (15.7% of ethylcyclohexene) is contained in the products of the reaction run at 450°C over the HNa-TsVM with a degree of Na^+ exchange of 75 wt %. The use of oxygen as an oxidant (4-VCH : O_2 = 1 : 0.2) has almost no effect on the isomerization and dehydrogenation activity of HNa-TsVM.

The introduction of platinum and the Ga and Gd cations into HNa-TsVM leads to a dramatic increase in the catalyst activity towards dehydrogenation. It is known that Ga- and PtGa-pentasils exhibit high activity in the dehydrogenation and aromatization of C_2–C_4 saturated hydrocarbons [22–26] and in the dehydroalkylation of naphthenes [27]. The results of our investigations have shown that the ternary system Pt,Ga,Gd/HNa-TsVM with various contents of the active components display a particularly high activity in the oxidation mode. They are characterized by the most optimal combination of oxidation–reduction and acid–base properties.

The highest activity in the dehydrogenation of 4-VCH is displayed by the Pt,Ga,Gd/HNa-TsVM and Ga,Gd/HNa-TsVM samples prepared according to procedures 1 and 2, which are characterized by a higher dispersion of the modifying additives and a higher stability.

Both the level and selectivity of the 4-VCH conversion depend largely on their preparation procedure, the ratio between the concentrations of the modifiers, and the reaction temperature (Tables 1, 2). As can be seen from Table 1, quite high yields of ethylbenzene and styrene are reached in the presence of the sample containing 3.0 wt % Ga_2O_3, 2.0 wt % Gd_2O_3, and 0.5 wt % Pt. The products obtained in this sample contain, along with ethylbenzene and styrene, some amount of the 4-VCH isomerization and disproportionation products whose yield decreases with increasing the temperature (Table 2). These data suggest that the catalyst surface is modified by the formed compounds and condensation products.

It is known that the formation of coke deposits during the catalytic conversion of hydrocarbons over modified forms of TsVM is mediated mainly by their strong acid sites responsible for the hydrogen-atom redistribution and arene dealkylation reactions [21]. Therefore, the blocking of these sites by condensation products leads to a decrease in the yield of benzene and toluene, however, the yield of ethylbenzene and styrene remains almost at the previous level.

To determine the influence of the individual components of the reaction mixture on the catalyst activity and selectivity for styrene, the transformation of binary mixtures of 4-VCH with some hydrocarbons which are contained in the liquid reaction products has been studied (Figs. 1a–1d). It has been found that the introduction of an additional amount of styrene into the reaction zone increases the amount of ethylbenzene in the products. It is likely that the dehydrogenation of 4-VCH over the given temperature range is accompanied by the coupled hydrogenation process, and ethylbenzene in all of the experiments is formed with higher yields as compared to styrene. The presence of some amount of ethyl- and vinylcyclohexane in the products of the conversion of 4-VCH per se in the temperature range of 350–400°C (Table 2) provides indirect evidence for this assumption. Therefore, 4-VCH adsorbed on the surface can partially act as a hydrogen acceptor (along with the nucleophilic oxygen of the catalyst surface) in the dehydrogenation process. The addition of ethyl- and vinylcyclohexane into the starting 4-VCH at 485°C contributes mainly to an increase in the yield of the dehydrodealkylation products—benzene and toluene; however, the yield of ethylbenzene and styrene on a converted 4-VCH basis remains almost unchanged.

Table 1. Influence of the mass ratio of modifiers supported on 0.75 HNa-TsVM on the yield of 4-VCH oxidative dehydrogenation products ($T = 470°C$, $V_{4\text{-VCH}} = 1\ h^{-1}$, 4-VCH : O_2 molar ratio = 1 : 0.3)

Me^{n+}, wt %			Yield, %			Yield of ethylbenzene, %	Yield of styrene, %
Ga^{3+}	Gd^{3+}	Pt	of liquid products	of gas	of coke		
1.0	0.5	–	92.3	5.6	2.1	10.8	2.5
1.0	0.5	0.3	93.0	5.0	2.0	26.4	4.2
2.0	0.5	0.3	90.5	7.0	2.5	31.8	12.4
2.0	0.5	0.5	90.4	7.5	2.1	35.2	15.1
3.0	0.5	0.5	91.1	7.1	1.8	37.9	17.5
3.0	1.0	0.5	91.6	6.2	2.2	38.6	17.8
3.0	2.0	0.5	93.8	4.7	1.5	40.2	19.6
3.0	2.0	–	92.4	5.8	1.8	32.5	14.0

Table 2. Influence of the temperature and space velocity on the composition and yield of 4-VCH oxidative dehydrogenation products (catalyst 3% Ga_2O_3, 2% Gd_2O_3, 0.5% Pt/0.75 HNa-TsVM)

T, °C	$V_{4\text{-VCH}}$, h^{-1}	Liquid products, wt %							Yield of ethylbenzene, %	Yield of styrene, %
		C_6–C_8 cycloalkanes	ethylcyclohexene*	ethylidenecyclohexene**	4-VCH	benzene, toluene, xylenes =	ethylbenzene	styrene		
370	1.0	3.6	4.2	14.5	49.5	3.0	20.0	5.2	18.0	4.6
400	1.0	2.1	3.8	15.6	40.1	6.1	23.3	9.0	20.8	8.0
450	1.0	1.0	5.1	16.1	21.8	5.7	37.3	13.0	32.5	11.3
470	1.0	0.8	5.4	13.4	10.9	5.8	42.8	20.9	40.2	19.6
485	1.0	–	2.1	7.2	9.2	5.0	52.1	24.4	44.8	21.0
500	1.0	–	1.0	4.4	6.3	3.9	54.8	29.6	45.7	24.7
520	1.0	–	2.1	4.8	10.3	7.7	48.9	26.2	40.2	27.4
485	0.5	–	2.5	2.9	7.5	6.4	52.8	27.9	45.0	23.8
485	2.0	–	2.0	13.6	35.8	3.8	31.1	13.7	27.4	12.1
485	3.0	–	1.6	16.1	44.7	3.9	23.0	10.7	20.6	9.3

Notes: * Together with vinylcyclohexane.
** Together with ethylcyclohexadiene isomers.

It is known that the hydrogenation of hydrocarbons in the presence of solid catalysts involves nucleophilic surface oxygen (base sites), whereas the isomerization (or disproportionation) occurs on Lewis and Broensted acid sites [28]. The isomerization of 4-VCH in the presence of the acid sites of Pt,Ga,Gd/HNa-TsVM, as in the case of the unmodified HNa-zeolite catalyst, proceeds only as the double bond migration and leads to ethylcyclohexadiene or ethylidenecyclohexene isomers, which are readily dehydrogenated into ethylbenzene.

The comparison of the data of Table 2 shows that one of the main factors affecting the yield of ethylbenzene and styrene, along with the acid–base and oxida-

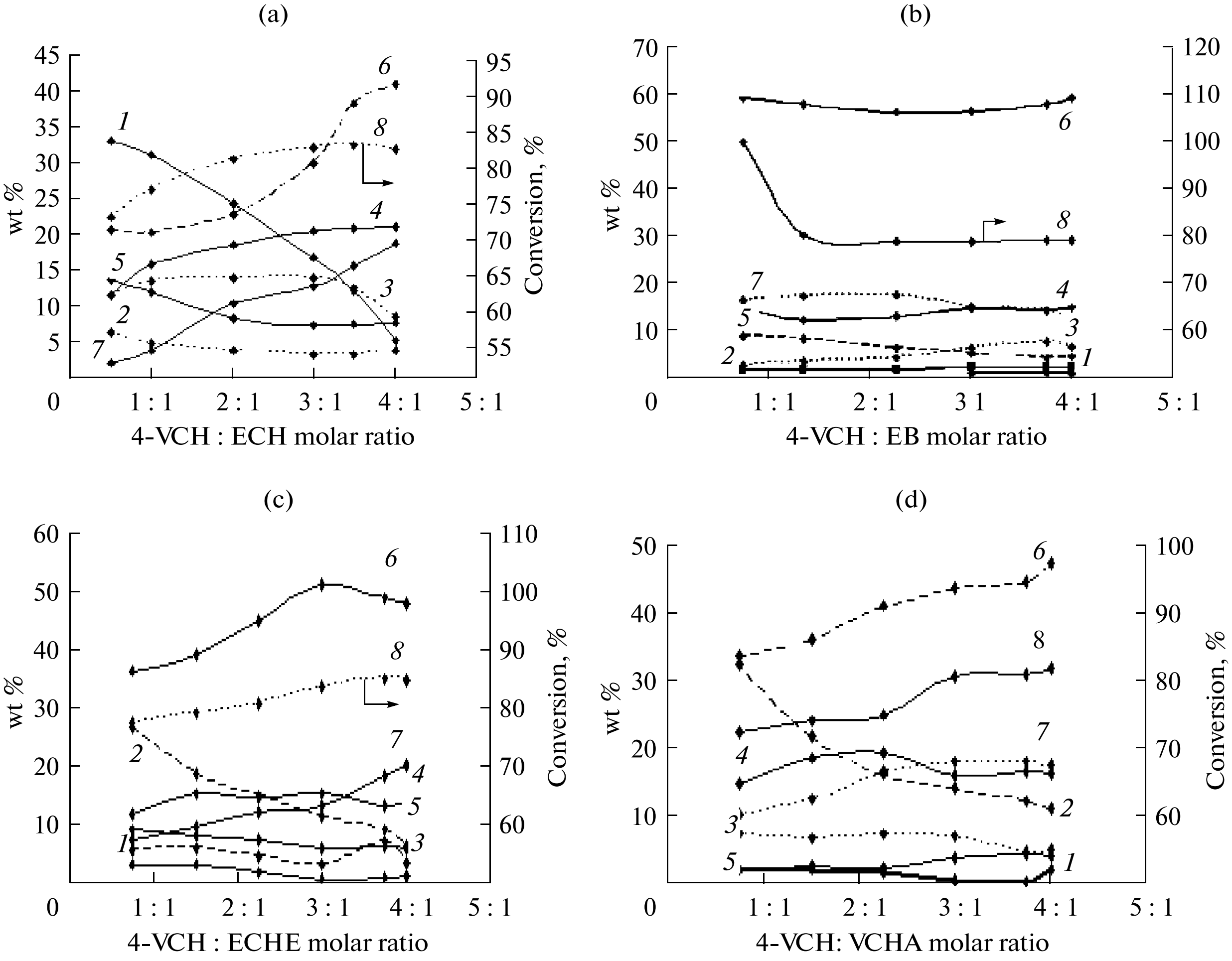

Fig. 1. Catalytic transformation of a binary mixture of 4-vinylcyclohexene (4-VCH) with (a) ethylcyclohexane (ECH), (b) ethylbenzene (EB), (c) ethylcyclohexene (ECHE), and (d) vinylcyclohexane (VCHA) in the presence of Pt,Ga,Gd/HNa–TsVM: (*1*) C_6–C_8 cycloalkanes; (*2*) vinylcyclohexane and ethylcyclohexene isomers; (*3*) ethylidenecyclohexene and ethylcyclohexadiene isomers; (*4*) 4-VCH; (*5*) benzene, toluene, and xylene isomers; (*6*) ethylbenzene; (*7*) styrene; and (*8*) the conversion of 4-VCH.

tion–reduction properties of the catalyst, is the reaction temperature. The highest yields of these hydrocarbons are reached at 470–485°C. It should be pointed out that the yields of ethylbenzene and styrene at 500°C are 45.7 and 24.7%, respectively; however, the reaction selectivity is considerably less as compared to the data obtained at 470–485°C.

The predominance of ethylbenzene in the catalysis product indicates that the reaction proceeds via the following consecutive steps:

4-VCH ⟶ ethylidenecyclohexene + isomers of ethylcyclohexadiene ⟶ ethylbenzene ⟶ styrene.

To lower the isomerizing activity of Pt,Ga,Gd/HNa-TsVM, a certain amount (0.3–2.0 wt %) of potassium hydroxide was additionally introduced into the catalyst (Fig. 2). As seen from the figure, in the presence of potassium hydroxide–promoted catalysts, the ethylbenzene : styrene ratio is changed in favor of the latter; i.e., the selectivity for styrene increases. At the same time, the conversion of 4-VCH on the catalyst samples promoted with 0.3–1.0 wt % KOH remains almost at the previous level. Therefore, these samples catalyze, along with the above transformation, the direct dehydrogenation of 4-VCH into styrene, omitting the steps of double bond migration from the vinyl group to the six-membered ring. However, with an increase in the amount of KOH from 1.0 to 2.0 wt %, the conversion of 4-VCH decreases.

Thus, the transformation of 4-VCH over the above heterogeneous catalysts proceeds via two parallel routes. In the presence of Pt,Ga,Gd/HNa-TsVM, the oxidative dehydroisomerization of 4-VCH into ethylbenzene and styrene prevails with the former product prevailing (molar ratio 2–2.5 : 1), and the sample promoted with potassium hydroxide mainly catalyzes the dehydrogenation of 4-VCH to form equal amounts of ethylbenzene and styrene (molar ratio 1–1.2 : 1).

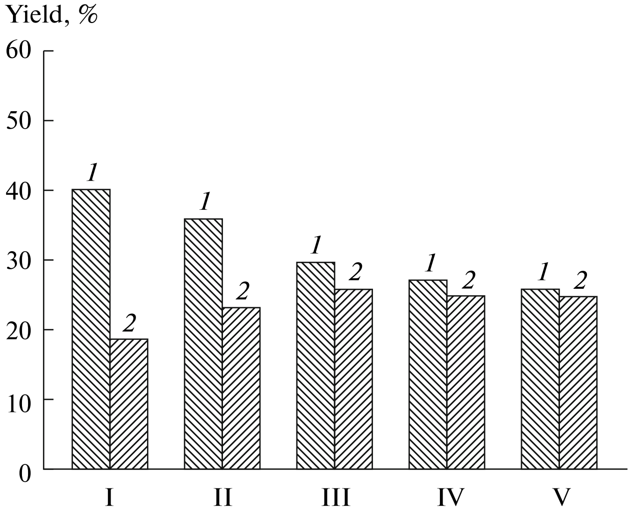

Fig. 2. Dehydrogenation of 4-VCH over Pt,Ga,Gd/HNa-TsVM ($T = 481°C$, 4-VCH : O_2 molar ratio = 1 : 0.3) (I) unpromoted and promoted with (II) 0.3 KOH, (III) 0.75, (IV) 1.5, and (V) 2 wt % potassium hydroxide: (*1*) ethylbenzene and (*2*) styrene.

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