

REACTIONS OF ISOMERIZATION, HYDROGENATION AND DEHYDROGENATION OVER ZEOLITES CONTAINING NO TRANSITION METALS

By

KH. M. MINACHEV

Zelinsky Institute of Organic Chemistry, USSR Academy of Sciences, Moscow

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Hydrocarbon transformations such as isomerization, hydrogenation and dehydrogenation usually take place over the catalysts which include one of the VIII group metal. However, it was found recently that these reactions can be carried out over zeolites without transition elements. This paper describes new results of investigations of catalytic properties on various zeolites obtained in our laboratory. These include the reactions of saturated hydrocarbons, isomerization of unsaturated compounds, hydrogenation and dehydrogenation of cyclic hydrocarbons. The mechanisms of these reactions over zeolites without transition metals are discussed.

Introduction

Reactions of isomerization, hydrogenation and dehydrogenation of hydrocarbons play an important role in petroleum processing. As a rule, these reactions proceed over catalysts involving metals of group VIII on various supports, such as oxides, amorphous aluminosilicates and zeolites. It has been known for long that metals of group VIII can catalyze reactions of hydrogenation — dehydrogenation. The role of these metals in bifunctional catalysts for isomerization of saturated hydrocarbons is that of dehydrogenation of alkane to olefine which undergoes skeletal isomerization of the acidic centres of the catalyst followed by hydrogenation of the isomeric olefine into the corresponding isoparaffine.

Intensive studies of the catalytic properties of zeolites have demonstrated that most reactions effected earlier over catalysts involving metals of group VIII as an important component can proceed over zeolites without these metals. The studies by BENESI [1], VOORHIES [6, 7], KOUWENHOEVEN [8, 9] and in this laboratory [2—5] have demonstrated that *n*-pentane, cyclohexane, *n*-hexane isomerization proceeds at a high rate over the hydrogen form of mordenite. Introduction of palladium and platinum into this catalyst does not affect its activity in alkane isomerization. And this is an essential difference between H-mordenite, and bifunctional and metal-faujasite catalysts.

The catalytic activity of zeolites with no transition metals has been found by studying benzene [10] and ethylene [11] hydrogenation in our laboratory.

The catalytic studies with zeolites have developed intensively, and the catalytic properties of zeolites of type A, L, X, Y, erionite, mordenite, chabazite and omega

involving cations of group I, II, III in hydrogenation of aromatic hydrocarbons (benzene, toluene, xylois) [2, 4, 5, 12, 14], amylenes [12, 14—19], acetone [20, 21], aldehydes [22], alkylfurans [23], propylene [24—27], 1,2-epoxyhexane [28] have been extensively studied.

Other reactions accelerated by zeolites without transition metals are dehydrogenation of hydrocarbons [29—31], isopropyl alcohol into acetone [32], cumene into α -methylstyrene [33], hydrocarbon oxidation [34—37]. Recently we have demonstrated high activity and selectivity of Na-forms of various zeolites in hydrocarbon oxidative dehydrogenation [38, 39]. Thus, zeolites without metals of group VIII can catalyze both the reactions effected earlier over bifunctional catalysts (alkane isomerization) and those of a redox type (hydrogenation, oxidation, oxidative dehydrogenation). The redox properties of zeolite catalysts as well as their activity in acid-base reactions are of great importance and should be thoroughly studied.

The objective of this paper is to discuss the data obtained in the author's laboratory by studying the catalytic properties of various zeolites containing no transition metals in the reactions of saturated and unsaturated hydrocarbons and of a number of oxygen containing compounds. Special attention is given to the reactions of skeletal isomerization of saturated hydrocarbons, hydrogenation of aromatic, olefinic and dienic hydrocarbons, a carbonyl group of aldehyde and ketones, furane compounds, dehydrogenation of cyclane, cyclohexane and cyclohexene hydrocarbons.

Reactions of isomerization, hydrogenation and dehydrogenation over cationic forms of zeolites

1. *n*-Pentane and cyclohexane isomerization

Isomerization of saturated hydrocarbons over decationized and cationic forms of faujasites (X, Y) without metals proceeds at a much lower rate than that over bifunctional metal containing catalysts. The studies made by RABO, in this laboratory, and lately by many other workers have demonstrated that for example, with CaY a 15.5% yield of *isohexanes* is obtained at 420 °C, and with CaY involving 0.5% of Pt or Pd the yield of *isohexane* is nearly equilibrium (70—74%) at 360 °C [5, 40, 41].

Specific catalytic properties have been shown by decationized and cationic forms of synthetic mordenite [2—5]. It can be seen from Table I that the hydrogen form of mordenite is an active catalyst in isomerization of saturated hydrocarbons: at 280 °C

Table I

*The activity of mordenite catalysts in n-pentane
and cyclohexane isomerization*

$t = 280\text{ }^{\circ}\text{C}$; $P = 30\text{ atm}$; $P_{\text{H}_2}/P_{\text{CH}} = 3.2$; $V_{\text{CH}} = 1\text{ h}^{-1}$

Catalyst	Yield of isopentane, %	Yield of methylcyclo- pentane, %
HM	46.6	28.5
0.5% Pd/HM	45.4	44.3

and a pressure of 30 atm the yields of *isopentane* and *methylcyclopentane* amount to 46.6 and 28.5%, respectively.

An interesting specific feature of this zeolite is that in *n*-pentane isomerization, metal is not an important component of the catalyst as is the case for the bifunctional and metal — containing catalysts of the faujasite type [5, 40].

In *n*-pentane isomerization the activity of HM and Pd/HM is the same whereas in the case of cyclohexane Pd/HM is more active than H-mordenite. But the activity of H-mordenite is higher in isomerization of saturated hydrocarbons than that of the well-known bifunctional catalysts, including metal-zeolites.

The activity of mordenite depends on the degree of its decationization, and the extent of isomerization of cyclohexane, for example, is proportional to the degree of Na⁺ exchange for H⁺ (Fig. 1). This dependence shows uniformity of the active centres of the catalyst.

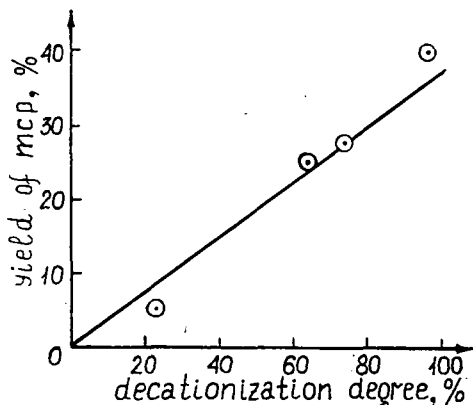


Figure 1. Isomerization rate of cyclohexane vs. mordenite decationization degree at $t=300^{\circ}\text{C}$, $P=30\text{ atm}$, $V=1\text{ h}^{-1}$

The catalytic properties of H-mordenite are greatly different from those of its cationic forms. Table II shows that the activity of di- and tri-valent mordenite cationic forms is inferior to that of H-mordenite. For instance, over Al-mordenite at 300 °C the yield of methylcyclopentane is twice as small as that over H-mordenite. The activity of Cd- and Zn-zeolites is higher than that of Mg- and Ca-modifications

Table II

Cyclohexane isomerization on the cationic forms of mordenite

$P = 30\text{ atm}$; $P_{\text{H}_2}/P_{\text{C}_6\text{H}_{12}} = 3.2$; $V_{\text{C}_6\text{H}_{12}} = 1\text{ h}^{-1}$

Catalyst	HM	LiM NaM KM	MgM	CaM	ZnM	CdM	AlM	Pd/CaM	
$t^{\circ}\text{C}$	300	300—450	360	420	374	374	300	300	350
Yield of Mcp*	39.2	no reaction	9.9	6.2	27.1	34.6	18.7	0.0	28.0

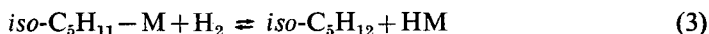
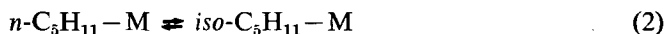
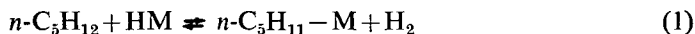
* Mcp — methylcyclopentane.

of mordenite, whereas over Li-, Na- and K-forms the reactions does not take place at all. The fact that univalent cationic forms of mordenite as well as faujasite do not show any activity can be accounted for by the absence of proton acidity in zeolites. On the other hand, the activities of decationized and cationic forms of mordenite are different, whereas for zeolites of type Y this is not the case.

Absence of catalytic activity in polyvalent cationic forms of mordenite in the reaction of isomerization may be explained by very low acidity of the samples. Therefore introduction of Pd, for example, into Ca-mordenite does not produce active isomerization catalysts. At 300 °C they are not active, and at 350 °C the yield of methylcyclopentane is 28%, *i. e.* much lower than that of Pd/CaY (60%), for example.

The ability of H-mordenite to effect isomerization of saturated hydrocarbons in the absence of metals may indicate to a specific mechanism of the reactions with this catalyst. The kinetic studies of *n*-pentane isomerization over H-mordenite provide evidence to support this supposition [3, 5]. It has been found that for the reaction to proceed, the presence of hydrogen is necessary, and an increase in the partial H₂ pressure decreases the rate of isomerization as is the case with bifunctional catalysts. Since H-mordenite is not a bifunctional catalyst (it does not contain metals of group VIII) the isomerization mechanism involving the stage of saturated hydrocarbon dehydrogenation into olefine (cycloolefine) should be excluded.

To account for the kinetic regularities observed it may be assumed that isomerization over this catalyst would proceed according to the following scheme:



where HM is H-form of mordenite; $n\text{-C}_5\text{H}_{11} - \text{M}$, $\textit{iso}\text{-C}_5\text{H}_{11} - \text{M}$ are carbonium ions bound to the active centres of the catalyst.

Assuming that carbonium ion isomerization is slow (stage 2) whereas the other intermediate stages are fast and in equilibrium one can obtain the following kinetic equation:

$$r = \frac{K_2 a_1 \frac{P_{n\text{-C}_5}}{P_{\text{H}_2}} - K_{-2} \frac{P_{\textit{iso}\text{-C}_5}}{P_{\text{H}_2}}}{1 + a_1 \frac{P_{n\text{-C}_5}}{P_{\text{H}_2}} + \frac{1}{a_3} \frac{P_{\textit{iso}\text{-C}_5}}{P_{\text{H}_2}}}$$

where r is the reaction rate, K is the rate constant of the corresponding step, a is the equilibrium constant of the corresponding step; P is the partial pressure of the reagents.

According to this equation the rate of the direct reaction at a constant temperature depends on the ratios of *n*-pentane and hydrogen partial pressures only ($P_{n\text{-C}_5}/P_{\text{H}_2}$). At low $P_{n\text{-C}_5}/P_{\text{H}_2}$, with $a_1 P_{n\text{-C}_5}/P_{\text{H}_2} \ll 1$, $r = K_2 a_1 \frac{P_{n\text{-C}_5}}{P_{\text{H}_2}}$, whereas at high $P_{n\text{-C}_5}/P_{\text{H}_2}$, with $a_1 P_{n\text{-C}_5}/P_{\text{H}_2} \gg 1$, $r = K$.

Fig. 2 presents the experimental data in terms of $r \sim \frac{P_{n\text{-C}_5}}{P_{\text{H}_2}}$ which shows that they are in agreement with the kinetic equation for the direct reaction. It should be noted that at low partial hydrogen pressure the operation of the catalyst is unstable and therefore the experimental dots on the right-hand branch of the curves in Fig. 2 have been obtained taking into account the degree of catalyst poisoning [42]. From the temperature dependence of the equilibrium constant of the first stage of the pro-

cess the thermal effect and entropy of *n*-alkyl cation formation on the catalyst surface was calculated, which were found to be equal to 11 kcal/mol and 20 cal/mol. degr., respectively. Independent approximate estimation of these values from the energies of bond cleavage and reagent entropies gives 16 kcal/mol and $12 \frac{\text{cal}}{\text{mol. degr.}}$ [42]. The agreement may be considered satisfactory, with insufficiently high accuracy of the experiment and approximate calculations. Thus, according to the mechanism suggested hydrocarbon isomerization proceeds via a carbonium ion resulting from splitting off a hydride-ion from a molecule of the initial hydrocarbon rather than by addition a proton of the catalyst to the intermediate olefine.

The ability of H-mordenite to split off a hydride ion is likely to be due to the presence of strong acidic centres [43], whereas the low activity of di-valent forms may be due to the absence of the Brönsted acidity (according to the i. r.-spectroscopic studies of the adsorbed pyridine [44]). The same conclusion can be made from the results of studying the hydrogen content in mordenites by isotopic exchange with deuterium performed in this laboratory. For example, the protium concentration in 0.8 CaNa-mordenite was found to be an order lower than that in H-mordenite [45]. As to a relatively high isomerization activity of Zn- and Cd-forms of mordenite it should be taken into consideration that

these cations can be reduced to metals with simultaneous formation of H-form.

The acidic properties of Al-mordenite have not been studied yet. One may suggest, however, that it is a cation-decationated form of zeolite since in the process of ion-exchange together with substitution of Al^{3+} for Na^+ the exchange of Na^+ for H^+ is also possible (pH of the solution is 2.6). Besides, Al^{3+} cations are capable of decomposing water molecules to generate protons to a greater extent than divalent metal cations. Therefore the activity of AlM catalyst is only twice as low as that of H-mordenite.

To conclude, the chemical composition and structure of mordenite seem to be responsible for unusually high activity of its H-form in hydrocarbon isomerization. The acidity of this catalyst appears to be so high that metals of group VIII are not necessary in alkane isomerization, which distinguishes mordenite from other zeolites.

2. Hydrogenation of unsaturated compounds

High catalytic activity of zeolites in hydrogenation of various unsaturated compounds is illustrated in Table III. These data show that synthetic zeolites containing no ions or atoms of transition elements are active in hydrogenation of various unsaturated compounds [10, 12, 14]. It should be noted that hydrogenation of aroma-

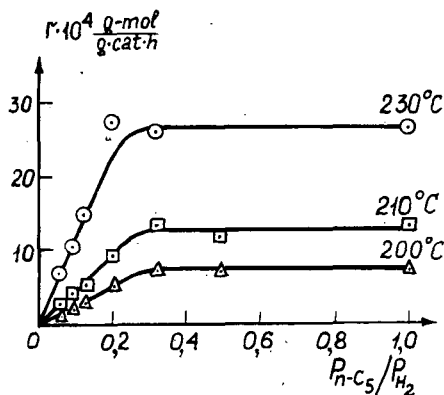


Figure 2. Reaction rate vs. ratio of *n*-pentane and hydrogen partial pressure (P_{n-C_5}/P_{H_2}) plots for *n*-pentane isomerization over HM



Table III
Hydrogenation reactions over zeolites without transition metals

Unsaturated compound (A)	Catalyst	Reaction conditions				Conversion, %
		<i>t</i> , °C	<i>P</i> , atm	<i>V_A</i> , h ⁻¹	H ₂ :A	
C ₅ H ₁₀	NaY	300	30	1.0	3	96.5
CH ₃ —CO—CH ₃	NaM	300	30	1.0	3	51.5
CH ₃ —CHO	Na, K—Ch	300	30	1.0	3	40.0
silvane	NaA	300	60	0.5	4	44.0
toluene	NaΩ	270	30	1.0	5	95.5

tic hydrocarbons and olefines proceeds selectively without formation of side products but in the case of acetone, aldehydes and silvan one can observe secondary reactions, dehydration of *isopropyl* alcohol and tetrahydrosilvan, and also hydrogenolysis of the latter. Selectivity of primary hydrogenation product formation varies from 20 to 100% with the catalyst and condition of the process.

In hydrocarbon hydrogenation zeolite catalysts are more active than sulphide and oxide catalysts (WS₂, MoS₂, MoO₃, NiS and their combinations on supports). For instance, benzene hydrogenation over zeolites proceeds at 200—250 °C and a pressure of 30 atm whereas with the former at 300—450 °C and 50—250 atm [46]. Metals of group VIII (Pt, Pd, Ni) on Al₂O₃, Al₂O₃·SiO₂ and other supports, *i. e.* the most active hydrogenation catalysts are superior to cationic forms of zeolites in their activity since the latter do not effect hydrogenation of aromatic hydrocarbons at atmospheric pressure. In spite of zeolite catalysts being of lower activity than metal containing catalysts it should be stressed, however, that practically important processes of hydrogenation, that of benzene, for example, are carried out at elevated hydrogen pressure even over metal containing catalysts to attain a high degree of transformation [47, 48]. Therefore, zeolites without transition metals may be promising in hydrogenation of unsaturated compounds under hydrogen pressure. The comparison of the zeolites studied and other hydrogenation catalysts containing metals of group VIII, such as chromium, zinc, metal oxides [49, 50] shows that they are comparable in conversion and selectivity of oxygen containing compounds although over metal containing contacts reactions proceed at lower temperatures.

The catalytic activity of zeolites without transition metals in hydrogenation of aromatic hydrocarbons, olefines, and oxygen containing compounds depends on their structure and composition [12, 14]. The concentration of cations in zeolites of various structure contributes most significantly to their hydrogenating activity. For instance, the rate of 2-methylbutene-2, benzene and acetone hydrogenation decreases with zeolite decationization and increases with introduction of sodium ions, exchange into their ammonium form (Fig. 3).

However, there are differences due to the structure of mordenite and faujasite (Y). Linear dependence is characteristic of Na-mordenite whereas for zeolite NaY one can observe hysteresis of the hydrogenating activity upon decationation-recationation (Fig. 3). This indicates that upon decationation-recationation Na⁺ cations are first to be removed from the accessible places (occupy the accessible places) in the zeolite lattice, for example, in large cavities.

The hydrogenating activity of zeolites depends not only on the cation concentration but also on their nature. Consideration should be given to the dependence of zeolite activity on the value of the electrostatic potential of a cation e/r^2 . The validity of this dependence can be supported by the data obtained from the studies of cations in zeolites by X-ray photoelectron spectroscopy [51]. They indicate to a predominant

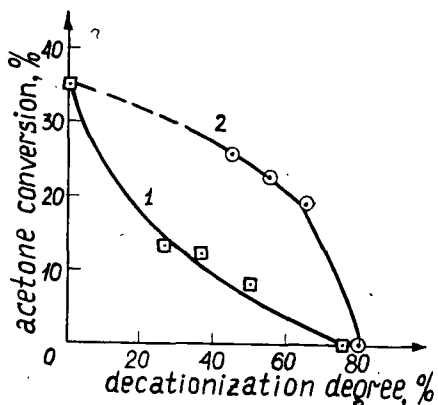


Figure 3. Activity of zeolite NaY vs. Na⁺ concentration plots for acetone hydrogenation. 1 — decationization NaY 2 — decationization NH₄Y

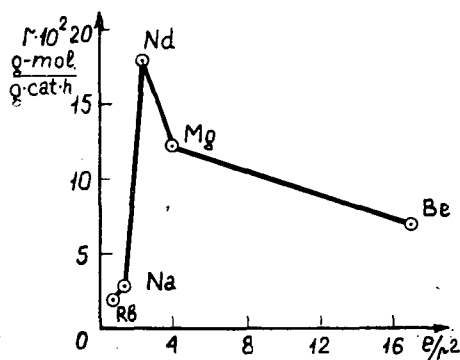


Figure 4. Activity of cationic forms of zeolite Y vs. value of cation electrostatic potential (e/r^2) plots for 2-methylbutene-2 hydrogenation

ionic character of the cation bond with the lattice of zeolites. It has been shown that in hydrogenation of 2-methylbutene-2 and acetone the dependence of the activity on the e/r^2 value passes through a maximum indicating optimal energy of the reagent molecular bonds with the active centres of the catalyst (Fig. 4).

Thus, the data on the dependence of the catalytic activity of zeolites in hydrogenation reactions on the concentration and nature of the exchange cations allow a conclusion that either zeolite cations themselves are the active centres of the catalysts or are involved with them.

In the studies of the activity of zeolite Y, with various degrees of decationization, in hydrogenation of 2-methylbutene-2 an attempt has been made to estimate the number of the Na⁺ cations involved in the active centre of the zeolite [52]. A formula was derived to calculate the probable distribution of cations as a singlet or doublet *etc.* in zeolite large cavities. This formula is

$$P_k = \frac{m!}{m^k(m-K)!} \cdot \frac{v^k}{K!} \cdot e^{-v}$$

where P_k is the probability of multiplet formation of K -order, m is the number of localizing cation sites in zeolite large cavities, K is the multiplet order: v is the average number of cations in the large cavity of a zeolite sample (measured from the number of Na⁺ cations going into solution upon treatment of the zeolite sample with an excess amount of NH₄Cl solution).

The formula allowed calculation of the number of large cavities containing a certain amount of Na^+ cations in zeolite Y samples with various degrees of decationization, that is, the number of cationic multiplets of different order is calculated followed by estimation of the specific activity of the multiplets. The results of these calculations are presented in Table IV.

Table IV
Specific activity of different multiplets (molecules/active site·sec· 10^2) in 2-methylbutene-2 hydrogenation over NaY with various decationization degrees at 200 °C, $P = 30$ atm, $\text{H}_2 : \text{C}_5\text{H}_{10} = 3$

Multiplet order K	Decationization degree, %				Standard deviation of multiplet specific activity, %
	0	38	55	75	
1	0.71	0.93	0.68	0.47	23.8
2	1.88	2.51	1.89	1.53	18.0
3	3.95	6.67	5.43	6.67	39.4
4	3.95	28.90	26.30	50.00	59.8
5	3.95	328.0	342.0	1000.0	86.5
hydrogenation rate $\text{g}\cdot\text{mol}/\text{g}\cdot\text{cat}\cdot\text{h}\cdot 10^2$	9.0	5.9	4.1	1.8	

As seen from the table it is only in the case of the multiplets of the first and second order that the specific activity remains constant within the experimental error. Hence, the active center involves one or two- Na^+ cations.

A considerable contribution into the activity of hydrogenation zeolite catalysts is made by crystalline aluminosilicate lattice which is responsible for the concentration, distribution and accessibility of the cations for the reacting molecules.

Fig. 5 shows that the rate of 2-methylbutene-2 hydrogenation passes through a maximum with an increase of silica and alumina ratio in Na-zeolites. The studies of 2-methylbutene-2 molecule thermodesorption from various zeolites have demonstrated that a similar dependence is observed also for The coefficient of the initial hydrocarbon diffusion in the intracrystalline pores of zeolites [53]. The catalyst efficiency factor proved to be close to a unity in the case of zeolite Y only. In narrow porous zeolites of type A, chabazite, erionite, mordenite the efficiency factor is much lower than a unity, which indicates to inner diffusion area of the reaction and thereby the dependence of the hydrogenation rate on the zeolite composition becomes understandable.

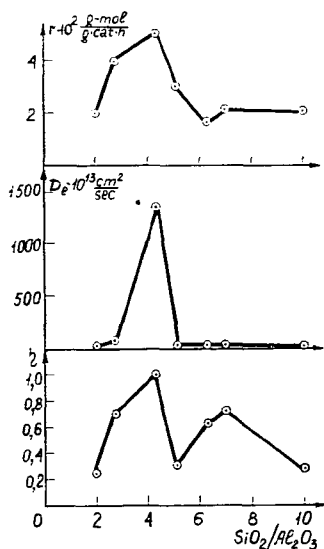


Figure 5. Activity, diffusion coefficient and effectiveness factor vs. zeolite composition plots for 2-methylbutene-2 hydrogenation

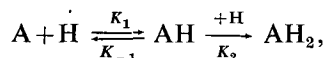
A different picture is observed in the case of acetone and toluene hydrogenation [12, 14]. During hydrogenation of these compounds the reaction rate first decreases when going from zeolite A to faujasites, and then it increases, mordenite showing the highest activity. To explain the differences of these dependences and those observed in hydrogenation of 2-methylbutene-2 it can be assumed that in this case we have inner kinetic region of the reaction over all the catalysts. The reason for it is a considerably lower activity of zeolites in acetone and toluene hydrogenation as compared with that of 2-methylbutene-2.

To elucidate the mechanism of the reaction kinetic studies were made of 2-methylbutene-2, acetone and toluene hydrogenation. The results obtained [13, 14, 18] are presented in Table V. To account for the kinetics observed it may be assumed

Table V
Kinetics of unsaturated compounds hydrogenation over zeolites

Catalyst	Unsaturated compound (A)	Reaction order		E _{app} kcal/mol	Kinetic equation
		H ₂	A		
RbY	2-methylbutene-2	1	1	15.0	$r = k \cdot P_A \cdot P_{H_2}$
NaM	acetone	1	0	10.0	$r = \frac{k \cdot P_A \cdot P_{H_2}}{(1 + a_A \cdot P_{H_2})^2}$
NaM	toluene	0.5	0	22.4	$r = \frac{k \cdot P_A \cdot P_{H_2}^{1/2}}{(1 + a_A \cdot P_A)^2}$

that a successive addition of hydrogen atoms takes place on the catalyst surface to the unsaturated bonds of the hydrogenated compound according to the scheme:



where A is the hydrogenated compound. Assuming the Langmuir character of the adsorption of the initial compounds one may obtain the following kinetic equation:

$$r = \frac{K_2 a_A a_{H_2} P_A P_{H_2}}{\left(1 + \frac{K_2}{K_1} a_{H_2}^{1/2} P_{H_2}^{1/2}\right) (1 + a_A P_A + a_{H_2}^{1/2} P_{H_2}^{1/2})^2} \quad (1)$$

If we are to assume small values of the adsorption coefficients of the initial components in 2-methylbutene-2 hydrogenation, then equation (1) is reduced to the dependence observed experimentally (Table V). In the case of acetone a zero order against the hydrogenated substance indicates more or less strong adsorption of this component, and, hence, equation (1) may give the kinetic equation observed (Table V) which describes well the experimental data (Fig. 6). To bring the above scheme of the reac-

tion in the case of toluene hydrogenation into agreement with the experimental data it is necessary to assume that the slow step is addition of the first hydrogen atom to the benzene ring. The resulting kinetic equation (Table V) is in good agreement with the experimental data (Fig. 7).

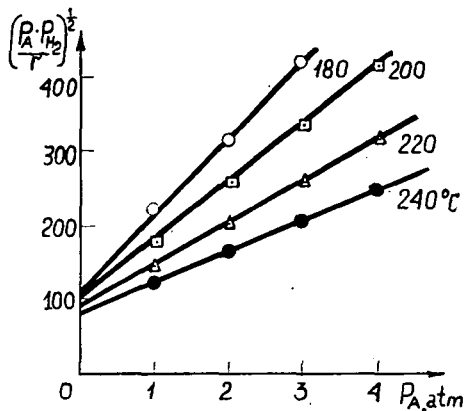


Figure 6. $\left(\frac{P_A P_{H_2}}{r}\right)^{1/2}$ vs. P_A plots for acetone hydrogenation over NaM.

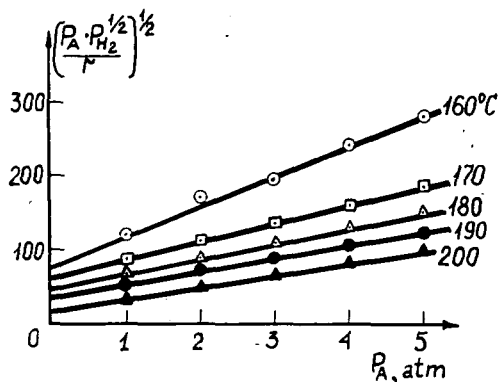
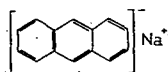


Figure 7. $\left(\frac{P_A P_{H_2}^{1/2}}{r}\right)^{1/2}$ vs. P_A plots for toluene hydrogenation over NaM.

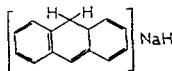
The nature of the activity of the new hydrogenation catalysts should be somehow dependent on activation of hydrogen and the unsaturated compound. The assumption about dissociative adsorption of hydrogen on zeolites without transition metals is in agreement with the kinetics of toluene, acetone and 2-methylbutene-2 hydrogenation. Moreover, hydrogen dissociative adsorption and successive addition of hydrogen atoms to the unsaturated bonds of the hydrogenated compound are indicated also by the results obtained from the reaction of piperylene hydrogenation over Na-forms of zeolites A, Y, chabasite, erionite and mordenite. It is possible to demonstrate that the ratio pentene-1: pentene-2 in the reaction products should be 0.5, with successive presence of hydrogen atoms, and 1.0 if molecular hydrogen is added to piperylene. The experimental value obtained is 0.5 which is indicative of dissociative adsorption. As to the ratio of *cis*-pentene-2: *trans*-pentene-2, it is not characteristic of the reaction mechanisms involved and is dependent on the ratio of syn/anti configurations of piperylene isomers under the reaction conditions.

The mechanism of the reaction involving hydrogen dissociative adsorption and successive addition of hydrogen atoms to unsaturated bonds of the hydrogenated compounds explains satisfactorily the experimental data obtained. Since zeolite cations are responsible for the reaction hydrogen adsorption with dissociation on atoms may proceed, for example, on the dipole formed by a cation and oxygen of zeolite lattice.

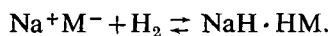
This mechanism is also supported by high catalytic activity of a dative complex of the type



found by TAMARU [54] in the reactions of unsaturated hydrocarbon hydrogenation. These reaction can be catalysed by such complexes in a temperature range of 50—120 °C. Molecular hydrogen is supposed to undergo chemisorption on the complex to give



involving sodium hydride and monohydroanthracene, which is a hydrogen donor in hydrogenation of unsaturated compounds. With these ideas extended to the cationic forms of zeolites considered as dative complexes of the atoms of alkaline and alkaline-earth compounds with aluminosilicate zeolite framework, hydrogen chemisorption can be presented as follows (*e. g.* mordenite):

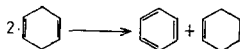


Upon heterolytic cleavage of the H—H bond the hydride-ion passes to the metal cation and the proton forms a hydroxyl group with the oxygen of the lattice. One may suggest also that the H—H bond would not break completely, and the extent of the cleavage would depend on the nature of the metal cation, which would affect the catalyst activity.

3. Cyclic hydrocarbon transformations on zeolites

High catalytic activity of various cationic forms of zeolites in hydrogenation of unsaturated hydrocarbons allowed us to suggest that these catalysts would be active also in the reactions of dehydrogenation. To verify this assumption we have studied transformation of cyclohexane, cyclohexene and cyclohexadiene-1,4 in an impulse microreactor over various cationic forms of zeolites.

Over Na-zeolites cyclohexane did not undergo any transformation up to 500 °C. In the case of cyclohexene the reaction products were methylcyclopentane and cyclohexane (Table VI). As seen from the table the most active catalyst is Na-mordenite. It is well-known that cyclohexene transformation into methylcyclopentane and cyclohexane proceeds over acidic catalysts [55]. In the case of Na-forms of zeolites the acidic centres may be due to deficient Na⁺ cations in the zeolite structure. Cyclohexadiene-1,4 is converted over Na-zeolites into benzene, cyclohexene and cyclohexadiene-1,3 (Table VII). The most active catalyst in benzene formation is NaY. Small amounts of cyclohexene in the reaction products indicate that benzene is formed not only as a result of direct dehydrogenation of cyclohexadiene-1,4 but also from disproportionation reaction



Calculations show that 85—90% of benzene is formed by direct dehydrogenation.

Over H-forms of zeolites the major product of cyclohexane transformation is coke, cracking products, methylcyclopentane, and at a high degree of decationization benzene and toluene are also formed. The most active in this process is zeolite HY,

Table VI

Cyclohexene conversion in pulse reactor over Na-forms of zeolites* at $V_{He} = 20 \text{ cm}^3/\text{min}$, $t = 450^\circ\text{C}$, catalyst weight 40 mg

Zeolite ($\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$)	Yield of reaction products**, %	
	Methylcyclopentane	Cyclohexane
A (2.0)	2.9	7.8
Y (4.3)	1.3	1.7
erionite (6.2)	1.7	4.4
mordenite (10.0)	11.6	32.6

* Zeolite types X, L and chabazite were inactive at these conditions.

** Conversion of the hydrocarbons to coke was not observed in the range of chromatographic method sensitivity.

Table VII

Cyclohexadiene conversion in pulse reactor over Na-zeolites at $t = 400^\circ\text{C}$, $V_{He} = 20 \text{ cm}^3/\text{min}$, catalyst weight 40 mg

Zeolite ($\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$)	Yield of reaction products*, %		
	Cyclohexene	Cyclohexadiene-1,3	Benzene
A (2.0)	1.0	20.6	11.7
X (2.9)	0.7	8.8	<1.0
Y (4.3)	4.7	14.9	31.6
chabazite (5.1)	0	4.5	7.8
erionite (6.2)	2.2	14.3	5.6
L (7.1)	1.6	20.9	18.2
mordenite (10.0)	1.2	16.8	<1.0

* Conversion of the hydrocarbons to coke was not observed in the range of chromatographic method sensitivity.

Table VIII

Cyclohexane conversion over HY (98%) at $t=500^\circ\text{C}$,
 $V_{\text{He}}=20\text{ cm}^3/\text{min}$, catalyst weight 0.2 g

Slug number	Hydrocarbons quantity converted to the coke, %	The composition of gaseous products, %			
		C ₁ -C ₃	Cyclohexane	Benzene	Toluene
1	62	100.0	—	—	—
2	56	84.0	2.5	4.5	9.0
3	53	75.9	4.1	5.8	14.2
4	50	82.3	2.7	7.6	7.4

Table IX

Cyclohexane conversion over HY (98%) at $t=500^\circ\text{C}$,
 $V_{\text{He}}=20\text{ cm}^3/\text{min}$, catalyst weight 0.2 g

Slug number	Hydrocarbons quantity converted to coke, %	The composition of gaseous products, %		
		C ₁ -C ₃	Benzene	Toluene
1	71	76.0	10.1	13.9
2	66	59.0	17.8	23.2
3	60	57.9	14.9	25.2
4	56	55.9	17.4	26.7
5	58	58.9	16.0	25.1

with decationation equal to 98% (Table VIII). As seen from the table, cyclohexane is first converted into coke and cracking products followed by formation of benzene and toluene the latter resulting from benzene alkylation by the cracking products. Over H-zeolites cyclohexane gives benzene and toluene in addition to the cracking products. With an increased decationization of zeolite Y its activity in this process increases. Table IX presents the data obtained from the studies of cyclohexane transformations over zeolite HY (98%). Over this catalyst the initial cyclohexane is fully converted into coke, cracking products benzene and toluene. Over H-zeolites cyclohexadiene is converted into coke, methylcyclopentane, cyclohexane, cyclohexene, cyclohexadiene-1,3 and benzene the activity of the zeolite increasing with decationation (Fig. 8). This figure shows that benzene is the major product of cyclohexadiene-1,4 transformations over decationated zeolites.

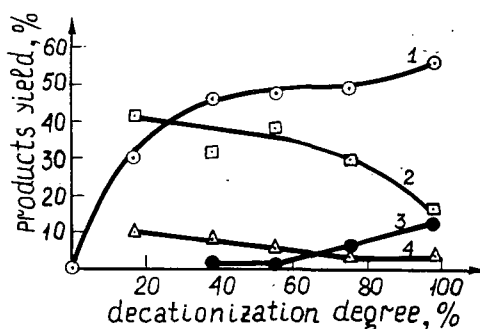


Figure 8. Yield of reaction products vs. decationization degree plots for cyclohexadiene-1,4 conversion over zeolite NaY. 1 — benzene, 2 — coke, 3 — cyclohexane, 4 — cyclohexene

Over Mg- and Nd-forms of zeolite Y cyclohexane undergoes cracking and isomerization into methylcyclopentane only. In the case of cyclohexene the products obtained over multivalent forms of zeolite Y are not only those of cracking, isomerization and disproportionation but also benzene and toluene (Table X). Thus, the

Table X
Cyclohexene conversion* over cationic forms of zeolite Y at $t = 500^\circ\text{C}$,
 $V_{\text{He}} = 20 \text{ cm}^3/\text{min}$, catalyst weight 0.2 g

Zeolite	Hydrocarbons quantity converted to coke, %	The composition of the gaseous products, %					
		C ₁ -C ₃	Methylcyclopentane	Cyclohexane	Cyclohexene	Benzene	Toluene
BeY**	65	45.9	49.9	4.2	—	—	—
MgY	58	55.3	30.0	1.7	—	3.0	10.0
NdY	67	73.6	11.8	—	—	3.7	10.9

*. The data of the first slug.

** Some amount of benzene and toluene in reaction products on BeY was observed in the second and third slugs.

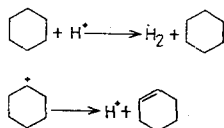
composition of the products of cyclohexene transformation over H- and multivalent forms of zeolite Y is about the same, which indicates to their similar activity in this process. Cyclohexadiene-1,4 over multivalent forms of zeolite Y gives the same products as those of cyclohexene, but in this case benzene is formed with higher selectivity (Table XI).

Table XI
Cyclohexadiene-1,4 conversion over cationic forms of zeolite Y
at $t = 200^\circ\text{C}$, $V_{\text{He}} = 20 \text{ cm}^3/\text{min}$, catalyst weight 10 mg

Zeolite	Hydrocarbons quantity converted to coke, %	The composition of the gaseous products, %				
		Methylcyclopentane	Cyclohexane	Cyclohexene	1,4-cyclohexadiene	Benzene
BeY	50	2.2	6.9	6.3	3.1	81.5
MgY	75	5.9	13.2	6.5	—	74.5
NdY	30	8.8	14.2	5.5	—	71.6

The results obtained allow certain conclusions to be made about hydrocarbon dehydrogenation over zeolites. First, the ease of benzene formation increases in the series: cyclohexane < cyclohexene < cyclohexadiene. Second, the activity of zeolites in dehydrogenation increases when going on from Na- to H- or multivalent forms. For instance, over zeolite HY, with a degree of decationation equal to 98%, even cyclohexane is partially converted into benzene, whereas with decationization of 75% and lower the reaction products indicate to the reactions of cracking and isomeriza-

tion only. It seems likely that in the reaction conditions studied the active centres of cyclic hydrocarbon dehydrogenation can be not only metal cations but also the Brönsted acidic centers, and the reaction may be presented as follows:



Conclusion

As is shown in this paper zeolites containing neither atoms nor ions of transition metals can be active and selective in isomerization of saturated hydrocarbons and hydrogenation of various unsaturated compounds. As to dehydrogenation of the cyclic hydrocarbons studied over Na-forms of various zeolites it is cyclohexadiene-1,4 only which can be converted into benzene to some extent. In the case of cyclohexene, cyclohexane and methylcyclopentane are formed, and cyclohexane, taken as an initial reactant, does not undergo any transformations over Na-zeolites. Introduction of multivalent cations into NaY zeolite or its decationization results in an increase of its dehydrogenating activity in cyclohexadiene transformation. It should be noted that over multivalent and decationated forms of zeolites cyclohexene is also partially converted into benzene, and over highly decationated zeolite Y even cyclohexane is partially dehydrogenated to benzene, although the principal direction is cracking. From the data obtained by studying transformations of cyclic hydrocarbons over various zeolites we may conclude that although the catalysts studied show some dehydrogenating activity it is much lower than that which could be expected on the basis of the catalytic activity in hydrogenation. What is responsible for it remains to be clarified.

As to hydrogenation over zeolites containing no transition elements we can conclude from the dependence of catalytic activity on zeolite composition, nature and concentration of cations that ion-exchange cations are involved into the active centre, with the number of sodium cations in the active centre of zeolite Y not exceeding two as in hydrogenation of 2-methylbutene-2. The mechanistic studies of hydrogenation reactions have shown that the problem of hydrogen activation over cationic forms of zeolites is of great importance. It seems likely that hydrogen molecule dissociation into atoms takes place on the active centers of catalysts. This assumption is in agreement with the kinetics of hydrogenation reactions, isomerization of the double bond upon hydrogenation of 2-methylbutene-2 over NaY and the ratio of pentene-1: pentene-2 in the reaction products of piperylene hydrogenation.

As is mentioned above there are many examples at present which illustrate that zeolites without transition elements show high activity in the reactions which were effected earlier over catalysts involving transition metals or their oxides as an indispensable component. This property of zeolites which is of great scientific and practical importance should be thoroughly studied.

References

- [1] *Benesi, H. A.*: J. Catal., **8**, 368 (1967).
- [2] *Minachev, Kh. M., V. I. Garanin, V. V. Kharlamov, T. A. Isakova, E. E. Senderov*: Izv. Akad. Nauk SSSR, Ser. Khim., **1969**, 1737.
- [3] *Minachev, Kh. M., V. I. Garanin, V. V. Kharlamov*: Izv. Akad. Nauk SSSR, Ser. Khim., **1970**, 835.
- [4] *Minachev, Kh. M., V. I. Garanin, T. A. Isakova, V. V. Kharlamov, V. I. Bogomolov*: Adv. Chem. Ser., No. 102, 441 (1971).
- [5] *Minachev, Kh. M., V. I. Garanin, V. V. Kharlamov, T. A. Isakova*: Kin. i Kat., **13**, 1101 (1972).
- [6] *Voorhies, A., P. A. Bryant*: AIChE Journal, **14**, 852 (1968).
- [7] *Beecher, R., A. Voorhies*: Ind. Eng. Chem., Proc. Res. Development, **8**, 366 (1969).
- [8] *Kouwenhoeven, H. W., W. C. van Zyll Langhout*: Chem. Eng. Progr., **67**, No. 4, 65 (1971).
- [9] *Kouwenhoeven, H. W.*: Adv. Chem. Ser., No. 121, 529 (1973).
- [10] *Minachev, Kh. M., V. I. Garanin, T. A. Isakova, V. V. Kharlamov*: Izv. Akad. Nauk SSSR, Ser. Khim., **1969**, 481.
- [11] *Minachev, Kh. M., O. K. Shchukina, M. A. Markov, R. V. Dmitriev*: Neftekhimiya, **8**, 37 (1968).
- [12] *Minachev, Kh. M., V. I. Garanin, V. V. Kharlamov*: III Sovietsko-Yaponsky seminar po katalizu, Preprinty dokladov, pr. No. 19, Alma-Ata, 1975.
- [13] *Minachev, Kh. M., V. V. Kharlamov, V. I. Garanin, T. A. Isakova*: Izv. Akad. Nauk SSSR, Ser. Khim., **1976**, 294.
- [14] *Minachev, Kh. M., V. V. Kharlamov, V. I. Garanin, T. A. Isakova, D. B. Tagiev, M. A. Kapustin*: I-Vsesoyuznaya Konferentsiya „Primenenie zeolitov v Katalize“, Novosibirsk, 1976, Sb, mater., p. 25.
- [15] *Kharlamov, V. V., V. I. Garanin, D. B. Tagiev, Kh. M. Minachev*: Vsesoyuznaya Konferentsiya po mekhanizmu geteroe nno-kataliticheskikh reaktsy, preprint No. 41, Moskva, 1974.
- [16] *Kharlamov, V. V., V. I. Garanin, D. B. Tagiev, Kh. M. Minachev, A. A. Goryachev*: Izv. Akad. Nauk SSSR, Ser. Khim., **1975**, 673.
- [17] *Kharlamov, V. V., V. I. Garanin, D. B. Tagiev, Kh. M. Minachev, A. A. Goryachev*: Izv. Akad. Nauk SSSR, Ser. Khim., **1975**, 845.
- [18] *Kharlamov, V. V., V. I. Garanin, D. B. Tagiev, Kh. M. Minachev*: Izv. Akad. Nauk SSSR, Ser. Khim., **1975**, 2406.
- [19] *Minachev, Kh. M., V. V. Kharlamov, V. I. Garanin, D. B. Tagiev*: Izv. Akad. Nauk SSSR, Ser. Khim., **1975**, 2410.
- [20] *Minachev, Kh. M., V. I. Garanin, V. V. Kharlamov, M. A. Kapustin*: Izv. Akad. Nauk SSSR, Ser. Khim., **1974**, 1554.
- [21] *Minachev, Kh. M., V. I. Garanin, V. V. Kharlamov, M. A. Kapustin*: Izv. Akad. Nauk SSSR, Ser., Khim., **1975**, 2673.
- [22] *Minachev, Kh. M., V. I. Garanin, V. V. Kharlamov, M. A. Kapustin*: Izv. Akad. Nauk SSSR, Ser. Khim., **1978**, No. 7.
- [23] *Karakhanov, R. A., V. I. Garanin, V. V. Kharlamov, M. A. Kapustin, B. B. Blinov, Kh. M. Minachev*: Izv. Akad. Nauk SSSR, Ser. Khim., **1975**, 445.
- [24] *Topchieva, K. V., O. L. Shakhnovskaya, E. N. Rosolovskaya, S. P. Zhdanov, N. N. Samulevich*: Kinet, Catal., **13**, 1453 (1972).
- [25] *Topchieva, K. V., S. P. Zhdanov, E. N. Rosolovskaya, O. L. Shakhnovskaya, N. N. Samulevich*: Zh. Fizich. Khim., **48**, 2461 (1974).
- [26] *Topchieva, K. V., E. N. Rosolovskaya, O. A. Shakhnovskaya*: Sb. „Sovremennyye problemy fizicheskoi khimii“, **8**, M., Izd. MGU, 1975, p. 199.
- [27] *Topchieva, K. V., O. L. Shakhnovskaya, E. N. Rosolovskaya*: Kin. i Kat., **10**, 1381 (1969).
- [28] *Chernishikova, F. A., D. V. Mushenko, L. A. Blandina*: Neftekhimiya, **14**, 188 (1974).
- [29] *Galich, P. N., I. T. Golubchenko, A. A. Gutirya*: Sb. „Sintetycheske zeolity“, Izd. AN SSSR, M., 1962, p. 260.
- [30] *Galich, P. N., A. A. Gutirya, V. S. Gutirya, I. E. Neimark*: Dokl. Akad. Nauk SSSR, **144**, 147 (1962).
- [31] *Galich, P. N., V. S. Gutirya, I. E. Neimark*: Sb. „Neftekhimiya“, Naukova Dumka, Kiev, 1964, p. 13.
- [32] *Yashima, T., H. Suzuki, N. Nara*: J. Catal., **33**, 486 (1974).
- [33] *Richardson, J. T.*: J. Catal., **9**, 182 (1967).

- [34] *Agudo, A. L., F. S. Bedkok, F. S. Stoun*: „Trudy IV Mezhdunarodnogo kongressa po Katalizu”, Moskva, 1968, „Nauka”, 1970. 2, p. 169.
- [35] *Roginskiy, S. Z., O. V. Altshuler, O. M. Vinogradova, V. A. Seleznev, I. L. Tsitovskaya*: Dokl. Akad. Nauk SSSR, **196**, No. 4, 872 (1971).
- [36] *Tsitovskaya, I. L., O. V. Altshuler, O. V. Krilov*: Dokl. Akad. Nauk SSSR, **212**, 1400 (1973).
- [37] *Altshuler, O. V., I. L. Tsitovskaya*: Izv. Akad. Nauk SSSR, Ser. Khim., **1974**, 825.
- [38] *Minachev, Kh. M., D. B. Tagiev, V. V. Kharlamov*: Izv. Akad. Nauk SSSR, Ser. Khim., **1977**, 1931.
- [39] *Minachev, Kh. M., D. B. Tagiev, Z. G. Zulfugarov, V. V. Kharlamov*; Kin. i Kat., **18**, 1368 (1977).
- [40] *Pickert, P. E., J. A. Rabo, E. Dempsey, V. Schomaher*: Proc. of the 3rd Internat. Congress on Catalysis, Amsterdam, 1964; **1**, 714 (1965).
- [41] *Minachev, Kh. M., V. I. Garanin, Ya. I. Isakov*: Usp. Khim., **35**, 2151 (1966).
- [42] *Kharlamov, V. V., V. I. Garanin, Kh. M. Minachev*: Izv. Akad. Nauk SSSR, Ser. Khim., **1973**, 1006.
- [43] *Minachev, Kh. M., R. V. Dmitriev, Ya. I. Isakov, O. D. Bronnikov*: Kin. i Kat., **12**, 712 (1971).
- [44] *Zefrancois, M., G. Malbois*: J. Catal., **20**, 350 (1971).
- [45] *Minachev, Kh. M., R. V. Dmitriev, O. D. Bronnikov, V. I. Garanin, T. A. Isakova*: Izv. Akad. Nauk SSSR, Ser. Khim., **1976**, 2426.
- [46] *Kalechiz, I. V.*: „Khimiya gidrogenizatsionnykh protsessov v pererabotke topliv”, M., 1973, p. 96.
- [47] *Minachev, Kh. M., Ya. I. Isakov*: „Metallsoderzhashchie zeolity v Katalize”, Nauka, M., 1976, p. 58.
- [48] *Minachev, Kh. M., Ya. I. Isakov*: Catalytic properties of Metall-containing Zeolites, in ACS monograph 171, *J. A. Rabo*: „Zeolite Chemistry and Catalysis”.
- [49] *Dolgov, B. N.*: „Kataliz v organicheskoi khimii”, L., 1959.
- [50] *Belskiy, I. F., V. M. Shostakovskiy*: „Kataliz v khimii furana”, Nauka, M., 1972.
- [51] *Minachev, Kh. M., G. V. Antoshin, E. S. Shpiro*: Sb. „Problemy Kinetiki i Kataliza”, M., Nauka, 1975, p. 189.
- [52] *Kharlamov, V. V., Kh. M. Minachev*: Izv. Akad. Nauk SSSR, Ser. Khim., **1977**, 280.
- [53] *Minachev, Kh. M., V. V. Kharlamov, V. I. Garanin, D. B. Tagiev*: Izv. Akad. Nauk SSSR, Ser. Khim., **1976**, 1700.
- [54] *Tamaru, K.*: Catalysis Rev., **4**, 161 (1970).
- [55] *Kubasov, A. A., A. N. Ratov, K. V. Topchieva, L. V. Vishnevskaya*: Vestn. Mosk. Univ., Ser. Khim., **1970**, 406.