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A Kinetic Model of the Dimerization of α-Methylstyrene in the Presence of High-Silica Zeolite Y

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Abstract—The kinetics of the dimerization of α-methylstyrene in the presence of high-silica zeolite HNaY has been studied, and a nine-stage scheme of the monomer conversion has been developed. Analysis of the kinetic models developed in the form of the Langmuir–Hinshelwood relationships and in terms of the mass action law has shown that the first model more adequately describes the experimental data. The numerical values of kinetic and adsorption parameters are represented.

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The development of effective methods for producing linear dimers of α-methylstyrene (4-methyl-2,4-diphenylpent-1- and -2-enes) has been given constant attention in the literature, because the application ranges of these compounds are very diverse: molecular weight regulators for polymers, solvents, components of synthetic lubricants, plasticizers of polymers and rubbers, and radiation-resistant heat-transfer agents [1–5].

The synthesis of dimers of α-methylstyrene (AMS) in the presence of different acid catalysts has been described in a large number of studies [6–14]. At the same time, a detailed kinetic study of the reaction is almost absent, except for [13], where the dimerization of AMS in the presence of cation-exchange resins has been studied in an environment of different solvents (cumene, anisole, phenol, substituted phenols), and [14] concerned with dimerization in an environment of ionic liquids. However, the analysis of the kinetics carried out in the mentioned studies is largely qualitative. There are no kinetic equations for the product formation rates; a mathematical processing of the experimental data has not been performed; therefore, it is impossible to quantitatively estimate the reaction rate.

We have previously developed [15] a kinetic model of the dimerization of AMS in the presence of a Y zeolite ($SiO_2/Al_2O_3 = 5.2$), which provides the synthesis of AMS linear dimers with a selectivity of 90–92% at a monomer conversion of 100%. At present, a method for producing a high-silica Y zeolite ($SiO_2/Al_2O_3 = 6.0$), which does not require a dealumination phase, has been assimilated in Salavatnefteorgsintez. This catalyst is much more resistant to high temperatures (up to 800°C) and is not destroyed at high degrees of decationation; therefore, it can be recommended for industrial implementation.

It is known that a necessary condition for calculating an industrial process is the knowledge of its kinetic model [16–17]. Therefore, the aim of the study was to analyze the kinetics of the dimerization of AMS in the presence of the Y zeolite ($SiO_2/Al_2O_3 = 6.0$) and to develop a kinetic model of the process.

EXPERIMENTAL

A NaY zeolite with a molar ratio of $SiO_2/Al_2O_3 = 6.0$ synthesized by the technique described in [18] was used. A HNaY zeolite with the degree of Na^+ H^+ ion exchange of 53 wt % ($0.53HNaY_{6.0}$) was prepared by decationation. The purity of the used AMS was 99.8%. To study the conversion of individual dimers, 4-methyl-2,4-diphenylpent-1-ene (**1**) with a base material concentration of 98.5% and 1,1,3-trimethyl-3-phenylindane (**2**) with a purity of 99.8% were isolated and used.

Kinetic experiments were performed in a batch thermostated reactor at atmospheric pressure. AMS was heated in the reactor to a desired temperature, and then the catalyst was charged. Samples for analysis were taken at regular intervals. The stirrer speed was 800–1200 rpm to provide the occurrence of the reaction in the kinetic region. During the experiments, the temperature was varied in a range of 60–100°C; the catalyst content, 2–20 wt %; and the experiment time, 1–6 h.

The quantitative composition of the reaction products was determined by GLC using a Carlo Erba HRGS 5300 Mega chromatograph with a FID and a 25-m glass capillary column and SE-30 as a phase. Conditions of analysis: a temperature program of 50 to 280°C at a rate of rise of 8°C/min; a detector temperature of 250°C; an evaporator temperature of 300°C; helium as a carrier gas, 30 mL/min. The products were

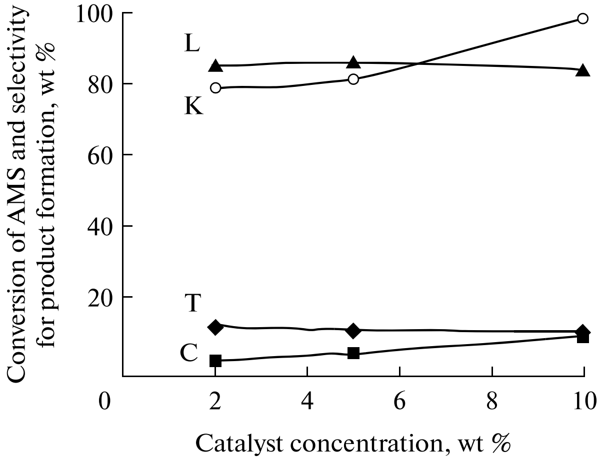


Fig. 1. Effect of catalyst concentration on the conversion (*K*) of AMS and the selectivity for the formation of linear (L) and cyclic dimers (C) and trimers (T). Reaction conditions: a temperature of 80°C, 2 h.

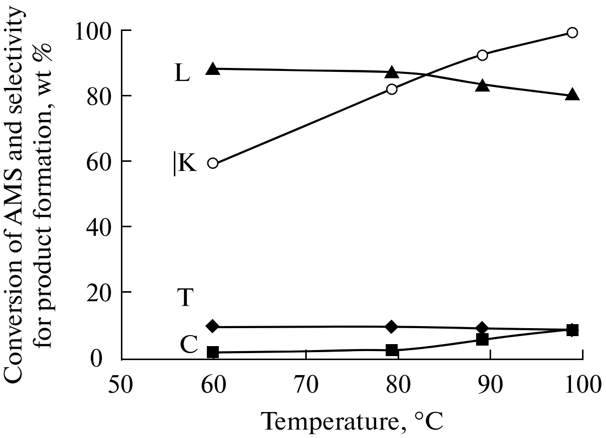
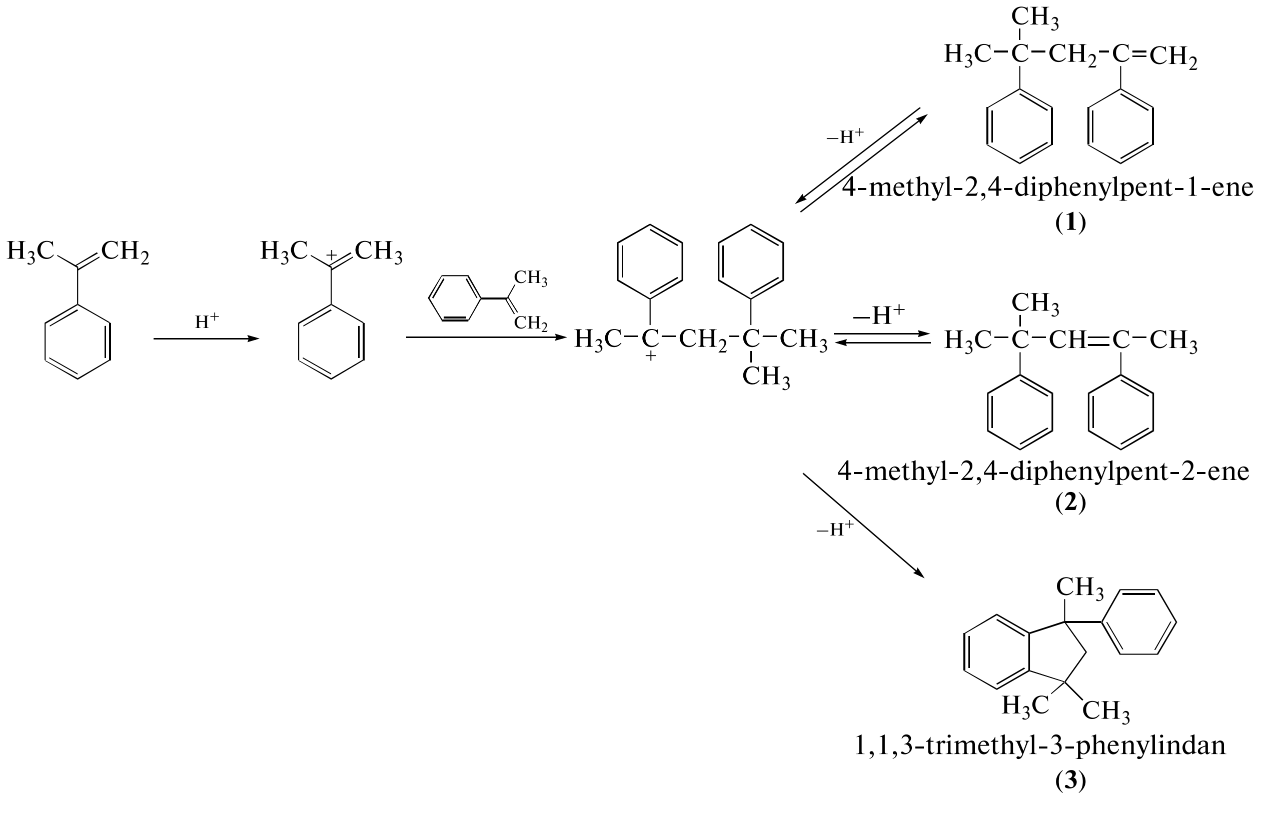


Fig. 2. Effect of temperature on the conversion (K) of AMS and the selectivity for the formation of linear (L) and cyclic dimers (C) and trimers (T). Reaction conditions: 10 wt % catalyst, 1 h.

identified according to known retention times. The *cis*-4-methyl-2,4-diphenylpent-2-ene, 1,1,3-trimethyl-3-phenylindanem, and *trans*-4-methyl-2,4-diphenylpent-2-ene dimers and trimers (seven peaks) were determined according to the time of yield.

RESULTS AND DISCUSSION

The dimerization of AMS in the presence of the Y zeolite occurs via the carbenium ion mechanism characteristic of the oligomerization of olefins [20], the main chemical reactions of which are shown in the scheme.



Scheme of the dimerization of AMS.

Table 1. Conversions of linear dimer (**1**) in the presence of the $0.53HNaY_{6.0}$ zeolite

No.	Catalyst amount	T, °C	Time, h	Composition, wt %		
				dimer (**1**)	dimer (**2**)	dimer (**3**)
Initial	–	–	–	98.6	1.4	–
1	5	80	1	97.6	2.3	0.1
			3	91.8	8.0	0.2
2	10	60	1	98.5	1.4	0.1
			3	93.4	6.3	0.3
3	10	80	1	95.1	3.4	1.5
			3	86.2	10.1	3.7
4	10	100	1	92.9	5.2	1.9
			3	82.6	12.9	4.5
5	20	80	1	85.6	10.9	3.9
			3	63.9	27.0	9.1

The resulting dimeric carbocation is stabilized owing to proton abstraction. Deprotonation can occur both to form olefin (linear dimers **1** and **2**) and by intramolecular alkylation with the respective loss of a proton by the resulting phenylindan (**3**).

Results of kinetic experiments on studying the effect of temperature, the content (concentration) of the $0.53HNaY_{6.0}$ catalyst, and experiment time on the conversion of AMS and the yield of dimerization products are shown in Figs. 1–3. It should be noted that, under the studied conditions, the main reaction products are linear dimers (**1**, **2**). It is evident from the figures, the conversion of AMS increases with an increase in the catalyst content, temperature, and reaction time: an increase in the catalyst concentration up to 10 wt % and in temperature up to 80–90°C leads to almost 100% conversion of AMS. At the same time, selectivity for linear dimers decreases from 90–92% to 84–88%, and the selectivity for the formation of a cyclic dimer increases.

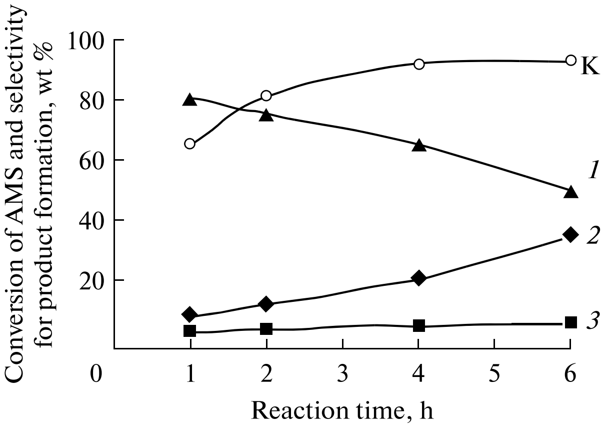


Fig. 3. Change in conversion (K) and selectivity for the formation of AMS dimers in time: (*1*) dimer (**1**); (*2*) dimer (**2**); and (*3*) dimer (**3**). Reaction conditions: 5.0 wt % catalyst, 80°C.

As the temperature increases to 100°C, the cyclodimerization reaction is accelerated and the cyclic dimer content increases by 2–3 times (Fig. 2). At temperatures above 140°C, the nearly single reaction product is dimer (**3**).

The composition of dimers varies with time (Fig. 3). At the beginning of the reaction, dimer (**1**) is dominant; then the selectivity for its formation decreases with a simultaneous increase in the selectivity for the formation of isomer (**2**). The selectivity for the formation of cyclic dimer (**3**) gradually increases.

To better understand the reaction mechanism, we studied the conversion of individual compounds: linear (**1**) and cyclic dimer (**3**) at 60–100ºC in the presence of 5–20% of the catalyst (Table 1). It is shown that dimer (**1**) isomerizes to dimer (**2**) and is converted to dimer (**3**) owing to the intramolecular alkylation reaction. These reactions are accelerated with increasing temperature and, to a lesser extent, with increasing catalyst concentration. Conversion of cyclic dimer (**3**) on the zeolite does not occur; this confirms the irreversibility of the conversion of linear dimers to a cyclic dimer.

Therefore, the formation of dimers (**1–3**) on zeolites, as on other acid catalysts, is a series–parallel process. A feature of a zeolite catalyst is that linear dimers are mostly formed inside the cavities with the participation of structural OH groups, while a cyclic dimer and trimers are formed on the surface acid sites (acid AlOH and SiOH groups) [19].

It was suggested in [7, 13] that 4-methyl-2,4-diphenylpent-1-ene (**1**) is first kinetically formed, then it isomerizes to dimer (**2**); after that, both linear isomers can be converted to cyclic dimer (**3**). In our

Table 2. Numerical values of kinetic parameters of the oligomerization of AMS in the presence of the HNaY catalyst for rate equations in the form of the L–H relations

Constant no.	K_i(100°C), $m^3/(kg_{cat}\ h)$	E_i, kcal/mol	Constant no.	K_i(100°C), $m^3/(kg_{cat}\ h)$	E_i, kcal/mol
1	88.8	19.3	7	0.0295	20.4
2	14.9	18.1	8	27.7	19.7
3	15.3	23.7	9	0.0379	16.2
4	1.49	26.8	10	0.0433	18.3
5	0.45	10.6	11	0.0974	17.9
6	0.0782	13.8	12	0.0495	12.6
b_{ads}(100°C) = 0.248; Q_{ads} = 17.1 kcal/mol					

opinion, the simultaneous formation of all dimers is more probable. Therefore, to compose a scheme of the dimerization of AMS on a Y zeolite, two possible versions of the product formation were considered: at the beginning, all the three dimers (**1–3**) are simultaneously formed from a transient dimeric complex, or dimer (**1**) is formed first. A mathematical processing of experimental data showed that the first reaction path is the most probable. On the basis of the analysis of the literature and experimental data, a scheme of the chemical conversions of AMS on the $0.53HNaY_{6.0}$ zeolite was proposed; it comprises nine stages:

Scheme.

$$\begin{gathered} 1.\ 2C_1 \rightleftharpoons C_2;\quad 2.\ 2C_1 \rightleftharpoons C_3;\quad 3.\ 2C_1 \longrightarrow C_4, \\ 4.\ C_2 \rightleftharpoons C_3;\quad 5.\ C_2 \longrightarrow C_4;\quad 6.\ C_3 \longrightarrow C_4, \\ 7.\ C_1 + C_2 \longrightarrow C_5;\quad 8.\ C_1 + C_3 \longrightarrow C_5; \\ 9.\ C_1 + C_4 \longrightarrow C_5, \end{gathered} \tag{1}$$

where C_i is the concentrations of the components, $kmol/m^3$. Subscripting in (1) is as follows: 1 stands for AMS; 2, dimer (**1**); 3, dimer (**2**), 4, cyclic dimer (**3**); and 5, trimers.

The rate equations corresponding to conversion system (1) were analyzed in the form of two functional relationships: in terms of the mass action law (MAL) (2) and in the form of the Langmuir–Hinshelwood (L–H) relationships (3):

$$\begin{gathered} w_1 = K_1X_1^2 - K_{10}X_2;\quad w_2 = K_2X_1^2 - K_{11}X_3; \\ w_3 = K_3X_1^2;\quad w_4 = K_4X_2 - K_{12}X_3; \\ w_5 = K_5X_2;\quad w_6 = K_6X_3;\quad w_7 = K_7X_1X_2; \\ w_8 = K_8X_1X_3;\quad w_9 = K_9X_1X_4, \end{gathered} \tag{2}$$

$$\begin{gathered} w = (K_1X_1^2 - K_{10}X_2)/(1 + bX_1); \\ w_2 = (K_2X_1^2 - K_{11}X_3)/(1 + bX_1); \\ w_3 = K_3X_1^2/(1 + bX_1); \\ w_4 = (K_4X_2 - K_{12}X_3)/(1 + bX_1); \\ w_5 = K_5X_2/(1 + bX_1);\quad w_6 = K_6X_3/(1 + bX_1); \\ w_7 = K_7X_1X_2/(1 + bX_1);\quad w_8 = K_8X_1X_3/(1 + bX_1); \\ w_9 = K_9X_1X_4/(1 + bX_1), \end{gathered} \tag{3}$$

where X_i is the concentrations of the components, mole fractions.

It is assumed that the limiting stage of the process is the adsorption of original AMS; that is, a linear deceleration of the reactions takes place, which is shown by the denominator of equations in the L–H rate equations $1 + bX_1$, which indicates the fact of deceleration of the reactions by original component (3).

All the experimental data were obtained under isothermal conditions in a batch reactor with a stirrer. Heterogeneous catalytic processes in this reactor can be quite correctly described in an ideal-mixing approximation. To develop a mathematical description, it was also taken into account that the reactions occur with a significant decrease in the number of moles of the reaction gas mixture (or the reaction volume). In this case, the mathematical description of the oligomerization of AMS in an isothermal ideal-mixing reactor is represented through a system of equations (4)–(5):

$$\frac{dN}{dt} = \frac{G_k}{V_p}\sum_{j=1}^{9}\delta_j\frac{W_j}{C_o} = F_N,\quad \delta_j = \sum_{i=1}^{5}\nu_{ij} \tag{4}$$

$$\frac{dX_i}{dt} = \frac{F_i - X_iF_N}{N},\quad F_i = \frac{G_k}{V_p}\sum_{j=1}^{9}\nu_{ij}\frac{W_j}{C_o} \tag{5}$$

the initial conditions: $t = 0$; $X_i = X_i^0$ $N = 1$, where W_j is the chemical reaction rates, $kmol/(kg_{cat}\ h)$;ν_{ij} is the stoichiometric coefficients determined by conversion scheme (1), $N = C/C_0$ is the relative change in the number of moles of the reaction mixture; C and C_0 are the molar density of the reaction mixture and its initial value ($kmol/m^3$); $X_i = C_i/C$; G_k is the catalyst weight

Table 3. Comparison of experimental and calculated data obtained using two versions of rate equations

Time, h	T_1			$T_2 + T_3$			T_4		
	experiment	MAL	L–H	experiment	MAL	L–H	experiment	MAL	L–H
80°C, 5 wt % catalyst									
0.5	58.6	68.7	69.1	35.5	28.3	28.3	2.0	1.6	2.0
1.0	51.1	51.9	52.5	42.2	42.5	42.0	2.4	2.5	3.1
2.0	41.0	34.5	35.3	51.1	56.3	56.4	3.1	3.4	4.3
3.0	31.1	25.8	26.5	59.6	62.8	63.1	3.1	3.9	5.0
80°C, 10 wt % catalyst									
0.5	39.2	46.3	44.4	50.3	51.6	50.3	3.2	3.1	3.0
1.0	30.1	26.8	28.1	58.6	64.3	63.5	4.0	4.0	3.9
2.0	17.3	15.2	15.8	70.5	72.5	71.9	4.6	4.7	4.7
3.0	10.0	10.5	10.8	77.3	75.3	74.3	5.1	5.0	5.1
90°C, 5 wt % catalyst									
0.5	38.7	40.9	43.8	49.8	52.3	50.2	6.5	5.3	5.0
1.0	27.5	25.5	26.4	60.1	65.0	64.7	6.6	6.6	6.5
2.0	14.4	14.4	14.1	73.2	73.2	73.9	7.1	7.6	7.6
3.0	7.8	9.8	9.4	78.0	75.9	76.8	8.0	8.0	8.1
90°C, 10 wt % catalyst									
0.5	35.3	35.5	35.9	50.8	50.8	54.7	6.9	5.8	4.7
1.0	23.1	21.3	21.4	64.4	64.9	65.9	7.2	7.7	6.2
2.0	11.5	11.5	11.5	70.3	70.3	70.3	7.8	8.7	7.9
3.0	5.1	7.7	7.6	74.7	71.3	70.1	9.2	9.1	9.2
100°C, 5 wt % catalyst									
0.5	29.1	24.7	29.1	59.8	64.7	62.2	6.6	7.7	7.2
1.0	12.4	13.8	12.2	72.1	72.4	75.6	8.9	8.9	8.9
2.0	2.0	7.1	4.3	80.6	75.8	80.2	10.1	9.8	9.8
3.0	1.0	4.6	2.3	80.6	76.0	80.4	11.2	10.4	10.1
100°C, 10 wt % catalyst									
0.5	9.0	9.6	9.0	75.2	75.0	75.2	10.2	11.3	12.6
1.0	5.1	4.8	4.6	77.5	76.6	76.4	11.7	13.9	14.3
2.0	3.2	2.3	2.3	73.0	74.7	74.2	17.1	16.3	16.8
3.0	1.0	1.5	1.4	72.3	72.0	71.5	18.9	18.5	18.9

(kg), V_p is the reactor volume (m^3); and t is the time (h).

In solving the inverse kinetic problem, the numerical values of the kinetic and adsorption constants, activation energies, and heats of adsorption were found; they are listed in Table 2 for rate equations in the form of the L–H relations.

A comparison of the calculated and experimental data for two versions of the rate equations is represented in Table 3. The accuracy of description of experimental data on the change in the component concentrations is within the error of a quantitative analysis for both the kinetic model with the MAL equations and the one with the L–H equations.

However, since with an increase in the catalyst concentration to 10 wt % and in temperature to 100°C, i.e., under the conditions of the assumed practical implementation of the process, the L–H rate equations more accurately describe the experimental data, it is these equations that will be used in the subsequent modeling of the process.

Thus, these kinetic studies of the dimerization of AMS in the presence of a new high-performance $0.53HNaY_{6.0}$ zeolite catalyst have made it possible to propose a nine-stage system of the conversion of AMS, which gives the possibility to describe all the chemical conversions of the observed components of the reaction mixture. A discrimination of the kinetic models of the dimerization of AMS has been performed, and it has been shown that the kinetic equations in the form of the L–H relations more adequately describe the experimental data. The inverse kinetic problem has been solved, and the numerical values of kinetic and adsorption parameters have been found.

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