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Synthesis of 2-Methoxy-3-pentene in a Liquid Phase over a Sulfoionite Catalyst: II. Kinetic Model of Reactions Occurring in the Synthesis

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Abstract—The kinetics of 2-methoxy-3-pentene synthesis from 1,3-pentadiene isomers and methanol was considered. Reaction rates were measured experimentally, and the compositions of reaction mixtures were determined by chromatography. Reaction rate constants and the activation energy of the main reaction were determined experimentally.

EXPERIMENTAL

The kinetics of *trans*-2-methoxy-3-pentene synthesis was experimentally studied by the sampling and analysis of liquid samples at regular intervals. The reaction was performed in the apparatus described previously [1] at a pressure of 0.5–0.8 MPa, which provided the liquid state of reactants.

The reaction temperature was maintained with an accuracy of ±0.5°C by circulating water through the reactor jacket, and the reaction mixture was vigorously stirred on a shaker (40 oscillations per minute) to eliminate the external diffusion effect. In our experiments, we used a commercial sample of the KIF sulfoionite catalyst, which was reduced in size to 1/16, to eliminate internal diffusion retardation.

The catalyst was preliminarily washed with distilled water to pH 5 to remove free sulfuric acid. Then, it was dried to constant weight at $T = 100$–$105°C$ for 4 to 5 h and left to swell in methanol for 2 h at room temperature. The total static exchange capacity of the KIF catalyst was 3.69 mg-equiv H^+ g^{-1} of dry catalyst.

The following reagents were used: methanol of 99.95 wt % (GOST 2222) purity containing less than 0.2 wt % water and a model fraction of 1,3-pentadienes containing 27.6 wt % *cis*-1,3-pentadiene, 48.8 wt % *trans*-1,3-pentadiene, 6.1 wt % 2-methyl-2-butene, and 17.55 wt % *n*-pentane. This fraction was purified of basic impurities, peroxide compounds, and moisture.

Reaction mixtures were analyzed by GLC using 6- and 8-m packed columns with PEG 1500 and PEG 3000 stationary phases on Tsvetokhrom 1K.

RESULTS AND DISCUSSION

The kinetics of the following reactions that took place during the synthesis of *trans*-2-methoxy-3-pentene from 1,3-pentadienes and methanol were considered:

$$trans\text{-}C_5H_8 + CH_3OH \rightleftharpoons trans\text{-}C_6H_{12}O, \qquad (I)$$

$$cis\text{-}C_5H_8 + CH_3OH \rightleftharpoons trans\text{-}C_6H_{12}O, \qquad (II)$$

$$iso\text{-}C_5H_{10} + CH_3OH \rightleftharpoons C_6H_{14}O, \qquad (III)$$

$$C_5H_8 + C_5H_8 \rightleftharpoons C_{10}H_{16}. \qquad (IV)$$

A series of experiments were carried out at 50, 70, and 90°C at different molar ratios between the reactants (0.3, 1.0, and 3.0) and at different concentrations of protons of the catalyst sulfo groups.

Figure 1 presents the 1,3-pentadiene conversion (α) into the *trans*-ether as a function of the conventional contact time τ (mg-equiv H^+ h l^{-1}), which was defined as the product of the real contact time (h) by the concentration of protons of the catalyst sulfo groups in a unit of the reaction volume (h mg-equiv H^+ l^{-1}), at different molar ratios between reactants and at different temperatures.

With an increase in temperature, a typical growth in the rate of the *trans*-ether synthesis was observed (Fig. 1). However, the experimental data showed that, at temperatures higher than ~75°C, the rate of the side reaction of 1,3-pentadiene dimerization drastically increased, corresponding to the high activation energy of this reaction. An increase in the concentration of dimers (C_{dim}) in the reaction mass was also facilitated by an increase in the conventional contact time (τ_{conv}) expressed in mg-equiv H^+ h g^{-1} dry catalyst and by a decrease in the molar ratio between reactants (Fig. 2).

An increase in the molar ratio between methanol and 1,3-pentadiene also resulted in the acceleration of the main reaction of ether formation. However, the rate of formation of dimethyl ether also increased because

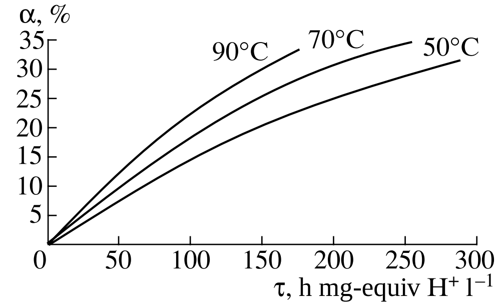

Fig. 1. Conversion of 1,3-pentadiene into *trans*-2-methoxy-3-pentene as a function of the conventional contact time τ at different temperatures.

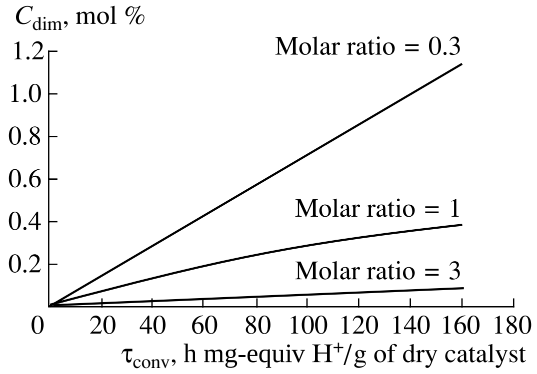

Fig. 2. Kinetic curves of the accumulation of 1,3-pentadiene dimers at 90°C.

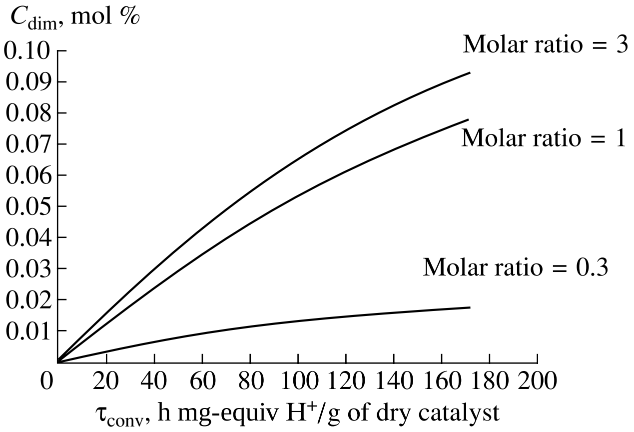

Fig. 3. Kinetic curves of the accumulation of dimethyl ether (DME) at 90°C.

of a stoichiometric excess of methanol in the reaction mass.

Figure 3 demonstrates the kinetic curves of dimethyl ether buildup during the synthesis of *trans*-2-methoxy-3-pentene.

Thus, the optimal molar ratio between methanol and 1,3-pentadiene in the initial mixture lies in the range 1.5–2.0.

MATHEMATICAL DESCRIPTION OF KINETIC DATA

The kinetic data were described mathematically, using equations proposed in [2, 3]. These equations, as well as the widely known Langmuir–Hinshelwood equations [4], accounted for the differences in the sorption of substances on active sites of a solid catalyst.

We overcame the restriction that did not allow the Langmuir–Hinshelwood equation to be used for the description of liquid-phase reactions. It is known that these equations were derived by Langmuir and Hinshelwood to describe gas-phase reactions providing that part of catalyst active sites remained vacant, that is, bore no sorbed molecules. In liquid-phase reactions, virtually the entire catalyst surface is filled with a liquid.

In the derivation of Eqs. (1) and (2), the concept of local concentrations was used. According to this concept, local concentrations of components in the layer adjacent to catalyst active sites were determined by the relationship

$$\zeta_i = \frac{a_i\rho_i}{\sum\limits_j a_j\rho_j} = \frac{x_i\gamma\rho_i}{\sum\limits_j x_j\gamma\rho_j}, \qquad (1)$$

where ζ_i are the local concentrations, a_i and a_j are the activities, x_i and x_j are the mole fractions, γ_i and γ_j are the activity coefficients of *i*th and *j*th components in the external solution, and ρ_i and ρ_j are the coefficients that take into account the sorption of components on the surface (on active sites) of catalyst.

The use of Eq. (1) instead of the relationship

$$\zeta_i = \frac{x_i\rho_i}{1 + \sum\limits_j x_j\rho_j} \qquad (2)$$

in a procedure (for the derivation of kinetic equations) similar to that described in [4] and the introduction of the factor $[H^+]^n$ that allowed for the concentration of proton active sites of the catalyst gave the equation

$$w = \frac{k[H^+]^n a_n a_m \beta_m}{\left(\sum\limits_j a_j\beta_j\right)^2}\left[1 - \frac{a_e}{\kappa_a a_n a_m}\right] \qquad (3)$$

for reversible bimolecular reactions (including the synthesis of *trans*-2-methoxy-3-pentene and methyl *tert*-amyl ether) and the equation

$$w = \frac{k[H^+]^n a_\kappa^2}{\left(\sum\limits_j a_j\beta_j\right)^2} \qquad (4)$$

for irreversible bimolecular reactions (in particular, the dimerization of 1,3-pentadiene). In Eqs. (3) and (4), Parameters of rate equations for the description of the reactions proceeding during the synthesis of *trans*-2-methoxy-3-pentene over the KIF catalyst

Reaction	$k \times 10^{-5}$, mol (mg-equiv $H^+)^{-1}$ h^{-1}			Parameters of equation	
	323 K	343 K	363 K	k_0, mol (mg-equiv $H^+)^{-1}$ h^{-1}	E, kJ/mol
Synthesis of *trans*-2-methoxy-3-pentene	3.58	22.9	119.3	2.37×10^{-9}	85.46
Synthesis of methyl *tert*-amyl ether	8.7	47.6	216.1	4.00×10^{-8}	78.30
Formation of 1,3-pentadiene dimers	0.8	6.9	469.0	8.93×10^{-10}	99.23

w is the reaction rate, mol l^{-1} h^{-1}; k is the reaction rate constant, mol (mg-equiv $H^+)^{-1}$ h^{-1}; $[H^+]$ is the concentration of proton active sites of the catalyst in volume unit, mg-equiv H^+ l^{-1}; β_i and β_j are the relative sorption coefficients of the ith and jth components with respect to the κth component κ; a_κ and $\left(\beta_i = \frac{\rho_i}{\rho_\kappa}; \beta_j = \frac{\rho_j}{\rho_\kappa}\right)$; a_κ is the activity of the κth component in solution, mole fraction; K_a is the reaction equilibrium constant in terms of activities of components; n is the numerical coefficient (in the reactions under consideration, $n = 1$); and subscripts κ, i, and j denote 1,3-pentadiene, methanol, and any component (including 1,3-pentadiene and methanol).

The calculated constants $K_a = 2.83$, 1.99, and 1.43 at 50, 70, and 90°C, respectively [1], were used as equilibrium constants for the synthesis of *trans*-2-methoxy-3-pentene. For the synthesis of methyl *tert*-amyl ether, the constants in terms of activities $K_a = 5.32$, 2.90, and 1.71 at 50, 70, and 90°C, respectively [3], were used.

Activity coefficients of components were calculated from the Wilson equation [5] in the form

$$\ln\gamma_\kappa = -\ln\left[\sum_j x_j \Lambda_{\kappa j}\right] + 1 - \sum_i \frac{x_i \Lambda_{i\kappa}}{\sum_j x_j \Lambda_{ij}}, \qquad (5)$$

where $\Lambda_{\kappa j}$, $\Lambda_{i\kappa}$, and Λ_{ij} are the numerical parameters that take into account differences in the intermolecular attraction of components; subscript κ refers to the component for which γ is being calculated; and subscripts i and j refer to all components present.

The experimental data were most accurately described when the relative sorption coefficients β for methanol, hydrocarbons (1,3-pentadiene and isoamylenes), and ethers (*trans*-2-methoxy-3-pentene and methyl *tert*-amyl ether) were equal to 80, 1.0, and 1.2, respectively.

Reaction rate constants and averaged relative sorption coefficients of components were determined by the statistical processing of the kinetic data at a minimum value of function F, as determined by the relation

$$F = \frac{1}{n}\sum_i \sum_j \left(\frac{x_{ij}^{\text{exp}} - x_{ij}^{\text{calcd}}}{x_{ij}}\right)^2, \qquad (6)$$

where n is the number of experimental points and x_{ij}^{exp} and x_{ij}^{calcd} are the experimental and calculated molar concentrations of components, respectively.

The summation was taken over all components (index i) and all experimental points of every run (index j).

The dependence of the logarithms of reaction rate constants $\ln k$ on $1/T$ (K) was linear. The preexponential factor k_0 and the activation energy E in the equation

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \qquad (7)$$

were calculated.

The results of the mathematical treatment of the kinetic data are summarized in the table.

REFERENCES

1. Kotel'nikov, N.G., Voronenkov, V.V., Pavlov, O.S., and Pavlova, I.P., *Kinet. Katal.*, 2001, vol. 42, no. 6, p. 771.
2. Pavlov, O.S., Bubenkov, V.P., and Pavlov, S.Yu., in *Issledovanie i razrabotka tekhnologii proizvodstva monomerov, katalizatorov, sinteticheskikh kauchukov* (Research and Development in the Synthesis of Monomers, Catalysts, and Synthetic Rubber), 1997, p. 178.
3. Pavlov, O.S., *Cand. Sci. (Eng.) Dissertation*, Yaroslavl: Yaroslavl State Univ., 1997.
4. Bremer, H. and Wendland, K., *Heterogene Katalyse: Eine Einfuhrung*, Berlin: Academie, 1978, p. 54.
5. Reid, R.C., Prausnitz, Y.M., and Sherwood, T.K., *The Properties of Gases and Liquids*, New York: McGraw–Hill, 1987.