

KINETICS OF OXIDATIVE DEHYDROGENATION OF ISOBUTYRIC ACID OVER $K_2HPMo_{12}O_{40}$ CATALYST

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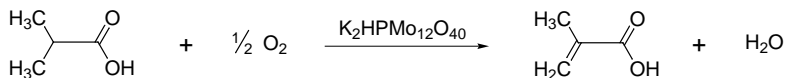
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The kinetics of oxidative dehydrogenation of isobutyric acid has been studied in gas phase over the $K_2HPMo_{12}O_{40}$ catalyst. The rate of consumption of isobutyric acid and of formation of methacrylic acid and acetone depending on the degree of conversion of isobutyric acid indicated an autocatalytic reaction mechanism. A model of $Mo^{VI}-O-Mo^V$ site has been suggested and the autocatalytic process to be due to formation of this site.

Keywords: Oxidations; Isobutyric acid; Methacrylic acid; Oxidative dehydrogenation; Heteropoly acid; Phosphomolybdates; Heterogeneous catalysis.

Oxidative dehydrogenation of isobutyric acid is one of the perspective ways of preparation of methacrylic acid. Among catalysts, which are in the center of interest of both academic and industrial research, are salts of phosphomolybdic acid with the Keggin structure. Reactivity of various compositions of Keggin structures have been analyzed, including determination of acid-base and redox properties¹. On the other hand, information on the kinetics and reaction mechanism of oxidative dehydrogenation of isobutyric acid (Scheme 1) are missing. Otahe *et al.*² have assumed that the first step of the reaction is a hydrolytic splitting of hydrogen from tertiary



SCHEME 1

carbon of adsorbed isobutyric acid with formation of an intermediate carbanion complex. Terminal oxygen of $Mo=O$ species have been suggested to be involved in the first step, and during hydrolytic splitting of the second

hydrogen from the methyl group of isobutyric acid Mo^{VI} has been suggested to be reduced to Mo^{IV} via a redox mechanism. According to Akimoto *et al.*³, the adsorbed isobutyric acid forms propene on the Brønsted acid site, or homolytic splitting of hydrogen from the tertiary carbon with formation of a reaction intermediate takes place. This intermediate is either transformed by homolytic splitting of the second hydrogen from the methyl group with formation of methacrylic acid or it is transformed to acetone. In both cases, the nucleophilic framework oxygen of the catalyst takes part in the reaction. The suggested reaction scheme also includes total combustion of adsorbed isobutyric acid by electrophilic oxygen. In simultaneous formation of methacrylic acid and acetone, both acid and basic centers are involved.

The results available at present, as obtained from the skeletal IR vibrations of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, isotopic exchange of framework oxygen, electrochemical methods and quantum chemical calculations¹⁻⁴, conclude that reduction of the catalyst with hydrogen occurs in the material bulk in several steps. First, reduction of the bridging oxygen ($\text{Mo}-\text{O}-\text{Mo}$) of the catalyst takes place. This is a two-electron process and removal of one framework oxygen results in formation of two Mo^{V} ions. In the final reduction step, terminal oxygens are involved and further reduction of molybdenum leads to its tetravalent state.

Systematic studies of oxidative dehydrogenation of isobutyric acid on catalysts based on cesium salts of $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ have been made by Haeberle *et al.*^{5,6}. They suggested rate equations for isobutyric acid consumption and acetone formation based on a two-step redox mechanism according to Mars and van Krevelen⁷. They found that formation of propene occurs via a different reaction mechanism from that of formation of methacrylic acid and acetone. Formation of propene, due to acid-base catalysis, is described using a power rate law equation. The study of Akimoto *et al.*³ indicates that at temperature of 530 K, the slowest reaction step of the catalytic cycle is reoxidation of the catalyst with molecular oxygen from gaseous phase, while above 570 K, it is the removal of framework oxygen from the catalyst.

The present study deals with the kinetics of oxidative dehydrogenation of isobutyric acid over a $\text{K}_2\text{HPMo}_{12}\text{O}_{40}$ catalyst to contribute to the better knowledge of the reaction mechanism, as it is available from formal kinetics studies.

EXPERIMENTAL

The $K_2HPMo_{12}O_{40}$ catalyst was prepared by neutralization of phosphomolybdic acid (Fluka, grade puriss) with potassium carbonate. After concentrating the mixture at 350 K, the paste obtained was dried at 390 K overnight, followed by calcination at 450 K and annealing at 570 K, in both cases for 6 h. The specific surface area, determined by the BET method from nitrogen adsorption at 80 K, was $4.95 \text{ m}^2 \text{ g}^{-1}$. X-Ray diffraction and IR spectra of skeletal vibrations, measured by the KBr technique, proved the existence of a Keggin structure⁸. ESR spectra of the catalyst after the reaction, treated at 535 K in a stream of the reaction mixture (5 mole % O_2 , 5 mole % isobutyric acid (IBA) in nitrogen, $5 \text{ dm}^3 \text{ h}^{-1}$ STP) for 8 h, followed by cooling in a nitrogen stream, were recorded in a X-band ESR-220 spectrometer (DAW, Berlin) to indicate presence of Mo^V ions.

Kinetic data were obtained using a through-flow microreactor. Concentration of isobutyric acid (3, 5 and 7 vol.%) in the feed was attained by saturation of a nitrogen stream in a saturator. The reaction temperature (540 K) was kept with accuracy ± 3 K. Each experiment of conversion vs the time factor w/F (w , weight of the catalyst; F , total flow of the reaction mixture) was carried out with a fresh catalyst. The reproducibility of determination of conversion of isobutyric acid and yields of products varied up to 5 rel.%. To comply with a kinetic region for the catalytic reaction, the following conditions were used: catalyst grains 0.3–0.5 mm, total flow $5 \text{ dm}^3 \text{ h}^{-1}$ and the catalyst bed length 1 cm. The catalyst was diluted with silicon carbide. Concentration and temperature gradients across the catalyst bed were eliminated using the diameter of catalyst bed diameter of catalyst grains ratio equal to 10. The reactants and products were analyzed on-line by a gas chromatograph CHROM 5, using Valco dosing six-port valves, and equipped with TCD and FID detectors. A stainless-steel packed chromatographic column of 2.5 m length filled with Chromosorb 100 AW, 80/100 mesh was used with a heating program up to 470 K and the carrier gas was helium ($40 \text{ cm}^3 \text{ min}^{-1}$). CO, CO_2 and isobutyric acid were detected with an TCD detector; for analysis of propene, acetone, isobutyric acid and methacrylic acid, an FID detector was employed.

The experiments with empty reactor and those under conditions of variable volume after the catalytic bed evidenced that the catalytic reaction was not accompanied by a homogeneous radical reaction in the gaseous phase. The degree of conversion of isobutyric acid (X_{IBA}) and yields of methacrylic acid (Y_{MAA}), acetone (Y_A) and propene (Y_P) were calculated from Eqs (1) and (2)

$$X_{IBA} = \frac{\dot{n}_{IBA}^0 - \dot{n}_{IBA}}{\dot{n}_{IBA}^0}, \quad (1)$$

$$Y_j = \frac{\dot{n}_j}{\dot{n}_{IBA}^0}, \quad (2)$$

where \dot{n}_{IBA}^0 is initial molar flow of isobutyric acid, whereas \dot{n}_{IBA} and \dot{n}_j are outlet molar flows of components of the reaction mixture.

RESULTS AND DISCUSSION

Conversion of isobutyric acid and yields to methacrylic acid, acetone and propene depending on contact time and composition of the feed are given in Table I. Illustration of these dependences is given in Fig. 1. The dependence of isobutyric acid conversion exhibits a s-shaped character, which indicates that the catalytic reaction has an autocatalytic character. As the similar shape is obtained also for the reaction products, *i.e.* methacrylic acid and acetone, it indicates that both these products are formed from the similar reaction intermediate produced by the autocatalytic reaction and that their formation from the reaction intermediate is much faster compared to intermediate formation.

The experimental data showed a positive effect of the increasing concentration of isobutyric acid and oxygen on the reaction rate. Likewise, it is obvious that increasing oxygen content in the reaction feed supported formation of methacrylic acid to acetone.

The obtained integral data were fitted to the following exponential equation (3)

$$X_{\text{IBA}} \text{ or } Y_j = a + be^{p_1\left(\frac{w}{F}\right)} + ce^{p_2\left(\frac{w}{F}\right)^2} + d\left(\frac{w}{F}\right)e^{p_3\left(\frac{w}{F}\right)} \quad (3)$$

with a condition that $a + b + c = 0$.

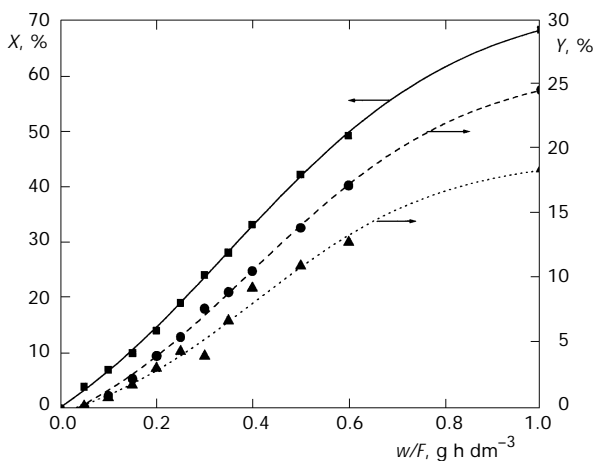


FIG. 1

Dependence of conversion of isobutyric acid (■) and yields of methacrylic acid (●) and acetone (▲) on contact time for $\text{K}_2\text{HPMo}_{12}\text{O}_{40}$ catalyst at molar ratio of oxygen : isobutyric acid = 5 : 3, at temperature 540 K

TABLE I
Kinetic data for different initial composition of the reaction mixture

w/F g h dm^{-3}	X_{IBA} %	Yield, %				$r \cdot 10^{10}, \text{mol s}^{-1} \text{g}^{-1}$		
		MAA	Acetone	Propene	IBA	MAA	Acetone	Propene
Initial molar ratio $\text{O}_2 : \text{IBA} = 5 : 3$								
0.00	0	0.00	0.00	0.00	2.115	0.000	0.000	0.000
0.05	4	0.08	0.20	0.20	2.471	0.508	0.314	0.132
0.10	7	0.98	0.84	0.42	2.810	0.754	0.606	0.193
0.15	10	2.30	1.80	0.60	3.105	0.969	0.844	0.233
0.20	14	4.06	3.08	0.84	3.332	1.144	1.010	0.250
0.25	19	5.51	4.37	1.14	3.477	1.269	1.100	0.248
0.30	24	7.68	4.00	1.68	3.533	1.344	1.117	0.231
0.35	28	8.96	6.72	1.96	3.504	1.369	1.073	0.209
0.40	33	10.56	9.24	2.31	3.398	1.351	0.988	0.187
0.50	42	13.86	10.92	2.52	3.018	1.217	0.767	0.157
0.60	49	17.15	12.74	2.94	2.533	1.017	0.579	0.149
1.00	68	24.48	18.36	4.76	2.253	0.498	0.279	0.140
Initial molar ratio $\text{O}_2 : \text{IBA} = 3 : 5$								
0.00	0	0.00	0.00	0.00	2.483	0.000	0.000	0.000
0.05	3	0.15	0.39	0.12	4.358	0.360	0.574	0.238
0.10	7	0.70	1.05	0.35	5.717	1.045	1.314	0.351
0.15	11	1.65	2.09	0.66	6.240	1.542	1.872	0.442
0.20	16	2.72	3.36	1.12	5.938	1.811	2.204	0.503
0.25	21	4.41	5.46	1.47	5.074	1.858	2.301	0.532
0.30	25	6.00	7.50	2.00	4.033	1.727	2.195	0.531
0.35	27	7.29	9.18	2.16	3.014	1.485	1.937	0.505
0.40	29	8.12	10.44	2.61	2.256	1.198	1.595	0.463
0.50	32	9.60	12.48	3.52	1.458	0.694	0.890	0.358
0.60	34	10.54	13.26	3.74	1.227	0.432	0.412	0.266
1.00	42	13.84	17.22	5.04	1.223	0.413	0.398	0.261
Initial molar ratio $\text{O}_2 : \text{IBA} = 5 : 5$								
0.00	0	0.00	0.00	0.00	3.673	0.000	0.000	0.000
0.05	4	0.04	0.48	0.08	5.059	1.126	1.468	0.192
0.10	8	1.12	1.76	0.40	6.073	2.050	2.372	0.457
0.15	12	2.88	3.96	0.48	6.475	2.653	2.829	0.573
0.20	18	6.30	6.84	1.08	6.254	2.887	2.829	0.571
0.25	23	8.97	9.23	1.61	5.583	2.792	2.498	0.508

TABLE I
(Continued)

w/F g h dm^{-3}	X_{IBA} %	Yield, %				$r \cdot 10^{10}, \text{mol s}^{-1} \text{g}^{-1}$		
		MAA	Acetone	Propene	IBA	MAA	Acetone	Propene
0.30	27	10.26	10.80	2.16	4.716	2.467	2.017	0.440
0.35	30	11.40	11.40	2.40	3.875	2.033	1.546	0.394
0.40	33	12.87	12.54	2.31	3.193	1.596	1.179	0.375
0.50	37	14.80	14.06	2.96	2.394	0.956	0.822	0.389
0.60	41	17.22	16.40	4.10	2.102	0.697	0.794	0.426
1.00	54	21.60	22.14	7.02	2.079	0.602	0.633	0.401
Initial molar ratio O_2 : IBA = 7 : 5								
0.00	0	0.00	0.00	0.00	4.365	0.000	0.000	0.000
0.05	5	0.25	0.30	0.10	5.447	1.169	0.545	0.208
0.10	9	0.99	0.81	0.27	6.287	1.903	1.260	0.274
0.15	13	3.90	1.82	0.52	6.703	2.398	1.740	0.328
0.20	19	5.70	3.61	0.95	6.645	2.616	1.947	0.366
0.25	24	7.00	4.80	1.20	6.186	2.581	1.905	0.388
0.30	29	9.86	6.67	1.45	5.478	2.364	1.687	0.395
0.35	33	11.55	7.92	1.65	4.689	2.055	1.380	0.389
0.40	36	12.60	8.64	2.16	3.955	1.733	1.065	0.375
0.50	41	14.76	9.43	2.46	2.913	1.252	0.601	0.338
0.60	46	17.02	11.04	3.22	2.449	1.062	0.428	0.308
1.00	63	23.31	14.49	5.04	2.354	1.050	0.407	0.305
Initial molar ratio O_2 : IBA = 5 : 7								
0.00	0	0.00	0.00	0.00	4.792	0.000	0.000	0.000
0.05	4	0.16	0.32	0.12	7.955	1.391	1.428	0.296
0.10	8	1.44	1.12	0.32	9.262	1.911	2.220	0.436
0.15	14	2.94	3.08	0.56	8.386	2.187	2.683	0.487
0.20	18	3.96	4.68	0.90	6.432	2.204	2.788	0.468
0.25	21	5.25	6.09	1.05	4.635	2.020	2.601	0.412
0.30	23	6.21	7.36	1.38	3.490	1.727	2.241	0.353
0.35	25	6.75	8.25	1.50	2.903	1.417	1.833	0.308
0.40	27	7.56	9.18	1.62	2.618	1.149	1.469	0.281
0.50	29	8.70	10.73	2.03	2.349	0.821	1.021	0.259
0.60	32	9.92	12.16	2.24	2.234	0.697	0.895	0.253
1.00	42	12.60	16.38	3.36	2.192	0.587	0.819	0.233

Isobutyric acid conversion or yields of methacrylic acid, acetone and propene values were chosen as independent variables whereas dependent variables were values of the time factor (w/F). Fitting of the experimental data to Eq. (3) yielded equation parameters $a-d$, p_1-p_3 . The obtained dependences enabled transformation of integral kinetic data into their differential mode by differentiation with respect to the time factor.

The reaction rates r were determined from relationships (4) and (5)

$$r = c_{\text{IBA}}^0 \frac{dX_{\text{IBA}}}{d\left(\frac{w}{F}\right)} \quad (4)$$

or

$$r = c_{\text{IBA}}^0 \frac{dY_j}{d\left(\frac{w}{F}\right)}, \quad (5)$$

where c_{IBA}^0 stands for molar concentration of isobutyric acid in the starting reaction mixture.

The obtained values of the rate of the decrease in concentration of isobutyric acid depending on its conversion are given in Fig. 2. The observed maxima in the dependences of the reaction rate vs isobutyric acid

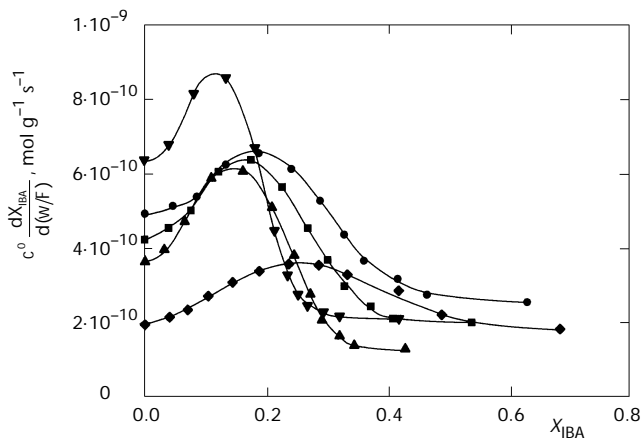


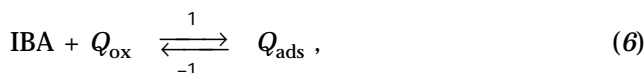
FIG. 2

Dependence of the reaction rate r on conversion of isobutyric acid for different initial composition of the reaction mixture. \blacktriangledown $p_{\text{O}_2}^0 = 5$ kPa, $p_{\text{IBA}}^0 = 7$ kPa; \blacklozenge $p_{\text{O}_2}^0 = 5$ kPa, $p_{\text{IBA}}^0 = 3$ kPa; \bullet $p_{\text{O}_2}^0 = 7$ kPa, $p_{\text{IBA}}^0 = 5$ kPa; \blacksquare $p_{\text{O}_2}^0 = 5$ kPa, $p_{\text{IBA}}^0 = 5$ kPa; \blacktriangle $p_{\text{O}_2}^0 = 3$ kPa, $p_{\text{IBA}}^0 = 5$ kPa

conversion clearly indicate an autocatalytic course of the reaction. The same feature is observed for the rates of formation of methacrylic acid and acetone as it is obvious from data given in Table I and Fig. 1. Independent measurements of the oxidation of methacrylic acid on the catalyst in a steady state proved that it does not participate in other reactions.

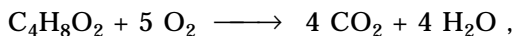
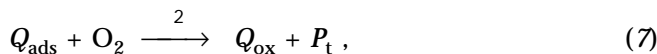
Autocatalytic transformation of isobutyric acid to methacrylic acid and acetone, and the appearance of Mo^{V} signal at $g = 1.94$ in the ESR spectrum of the catalyst after the reaction support the suggestion that the reaction follows a redox mechanism *via* $\text{Mo}^{\text{VI}}\text{--}\text{Mo}^{\text{V}}$ redox cycle. According to the literature^{3,5,6}, the first step of the reaction is formation of the reaction intermediate which is common for methacrylic acid and acetone. As the formation of methacrylic acid and acetone proceeds by an autocatalytic mechanism *via* the common reaction intermediate, which transformations to these products cannot be analyzed based on the experimental data, the kinetic equations are analyzed only for the first step of the reaction, the autocatalytic one. The following reaction mechanism consisting of the individual steps was suggested:

1. Equilibrium adsorption of isobutyric acid takes place on oxidized form of the catalyst



where Q_{ox} and Q_{ads} stand for a part of the catalyst in an oxidized form (Mo^{VI}), which is unoccupied and occupied by adsorbed isobutyric acid, respectively.

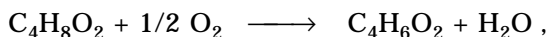
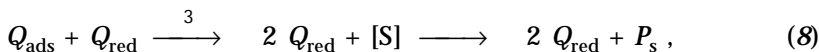
2. Oxidation of adsorbed isobutyric acid to the products of complete oxidation is supposed to occur by electrophilic oxygen *via* an associative mechanism



where P_{t} is carbon dioxide.

3. Parallel autocatalytic oxidation of the adsorbed isobutyric acid to acetone and methacrylic acid takes place *via* a common surface complex [S]

with participation of the nucleophilic oxygen of the catalyst and the reduced form of the catalyst *via* a redox mechanism

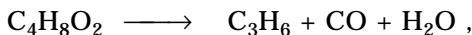
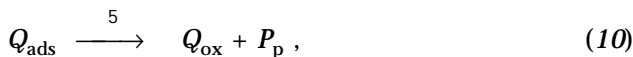


where Q_{red} indicates a part of the catalyst in a reduced form (Mo^V) and P_s is the sum of methacrylic acid and acetone.

4. The catalyst is reoxidized with oxygen from the gas phase.



5. Conversion of adsorbed isobutyric acid to propene proceeds *via* acid-base catalysis



where P_p is propene.

The suggested reaction scheme can be described by a system of rate equations in a differential mode

$$\frac{dp_{\text{IBA}}}{d\left(\frac{w}{F}\right)} = -k_1 p_{\text{IBA}} Q_{\text{ox}} + k_{-1} Q_{\text{ads}}, \quad (11)$$

$$p^0 \frac{dQ_{\text{ox}}}{d\left(\frac{w}{F}\right)} = -k_1 p_{\text{IBA}} Q_{\text{ox}} + k_{-1} Q_{\text{ads}} + k_2 Q_{\text{ads}} p_{O_2} + k_4 Q_{\text{red}} p_{O_2} + k_5 Q_{\text{ads}}, \quad (12)$$

$$p^0 \frac{dQ_{\text{ads}}}{d\left(\frac{w}{F}\right)} = k_1 p_{\text{IBA}} Q_{\text{ox}} - k_{-1} Q_{\text{ads}} - k_3 Q_{\text{ads}} Q_{\text{red}} - k_2 Q_{\text{ads}} p_{\text{O}_2} - k_5 Q_{\text{ads}}, \quad (13)$$

$$p^0 \frac{dQ_{\text{red}}}{d\left(\frac{w}{F}\right)} = k_3 Q_{\text{ads}} Q_{\text{red}} - k_4 Q_{\text{red}} p_{\text{O}_2}, \quad (14)$$

$$\frac{dp_{\text{O}_2}}{d\left(\frac{w}{F}\right)} = -k_2 Q_{\text{ads}} p_{\text{O}_2} - k_4 Q_{\text{red}} p_{\text{O}_2}, \quad (15)$$

where Q_i variables are dimensionless parameters represented by adsorbed isobutyric acid Q_{ads} , a part of the free surface of the catalyst in oxidized form Q_{ox} , and a part of the free surface of the catalyst in reduced form Q_{red} ; p_i is the actual partial pressure of a given component and w/F is the time factor in units ($\text{g dm}^{-3} \text{ h}$) and constant p^0 is taken at 1 kPa.

The system of differential equations was solved using the stiff embedded Runge–Kutta numeric method⁹. For optimization, the Levenberg–Marquart optimization algorithm¹⁰ was used. For all the data, values of the rate constants and initial relative concentration of reduced sites of the catalyst were optimized. Initial relative concentration of reduced sites is defined as

$$\frac{Q_{\text{red}}}{Q_{\text{ads}} + Q_{\text{ox}} + Q_{\text{red}}}$$

and its value was determined to be 0.024.

For optimization, the objective function was applied

$$\sum_{i=1}^n \left[p_{\text{IBA}} \left(\frac{w}{F} \right)_i - \hat{p}_{\text{IBA}} \left(\frac{w}{F} \right)_i \right]^2 \rightarrow \text{minimum}, \quad (16)$$

where p_{IBA} is the partial pressure of isobutyric acid for a given time factor, \hat{p}_{IBA} is the value of the same quantity obtained from solution of the system of differential equations. Table II presents the constants of rate equations obtained from the optimization procedure. Figures 3 and 4 confront the computed values of conversion of isobutyric acid with the experimental data.

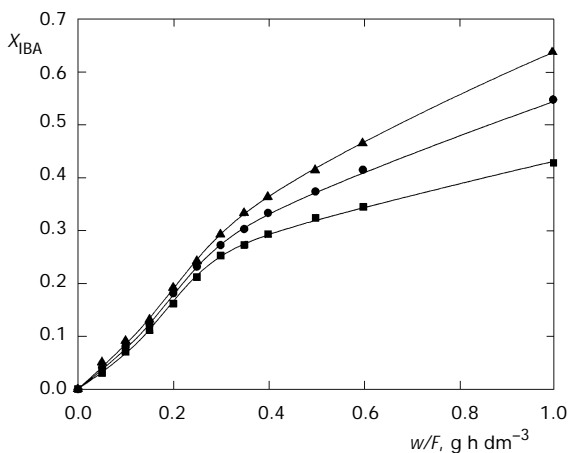


FIG. 3

Experimental and calculated conversions of isobutyric acid for \blacksquare $p_{O_2}^0 = 3 \text{ kPa}$, \bullet $p_{O_2}^0 = 5 \text{ kPa}$, \blacktriangle $p_{O_2}^0 = 7 \text{ kPa}$; p_{IBA}^0 of 5 kPa (lines represent calculated values)

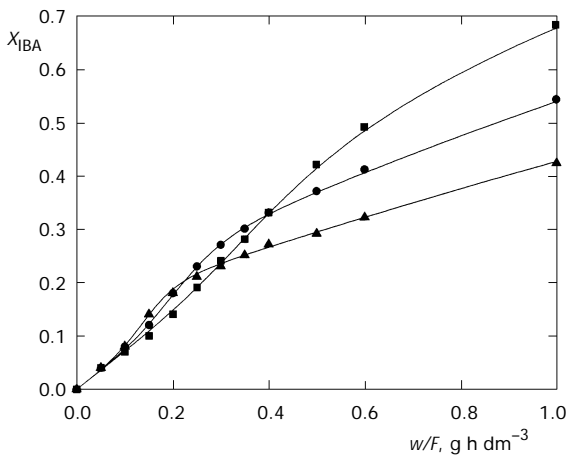


FIG. 4

Experimental and calculated conversions of the isobutyric acid for \blacksquare $p_{IBA}^0 = 3 \text{ kPa}$, \bullet $p_{IBA}^0 = 5 \text{ kPa}$, \blacktriangle $p_{IBA}^0 = 7 \text{ kPa}$; $p_{O_2}^0$ of 5 kPa (lines represent calculated values)

TABLE II
Results of verification of the suggested reaction mechanism

Reaction step	Rate constant	Value	Dimension
Adsorption	k_1	29	$\text{dm}^3 \text{g}^{-1} \text{h}^{-1}$
Desorption	k_{-1}	1760	$\text{kPa dm}^3 \text{g}^{-1} \text{h}^{-1}$
Associative mechanism	k_2	298	$\text{dm}^3 \text{g}^{-1} \text{h}^{-1}$
Redox mechanism	k_3	0.51	$\text{kPa dm}^3 \text{g}^{-1} \text{h}^{-1}$
Reoxidation of catalyst	k_4	4.3	$\text{dm}^3 \text{g}^{-1} \text{h}^{-1}$
Acidobasic catalysis	k_5	2.3	$\text{kPa dm}^3 \text{g}^{-1} \text{h}^{-1}$

CONCLUSION

The suggested autocatalytic reaction mechanism is in a good agreement with the experimental data of conversion of isobutyric acid. The related rate equation describes quantitatively well the kinetics of oxidative dehydrogenation of isobutyric acid. The satisfactory description of the experimental data by the proposed model and the appearance of the Mo^{V} signal in ESR spectra of the catalyst after the reaction can be taken as a support of the hypothesis that the $\text{Mo}^{\text{VI}}\text{-O-Mo}^{\text{V}}$ structure plays the role in the oxidative dehydrogenation of isobutyric acid to methacrylic acid on heteropoly acid based catalysts.

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