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Kinetics of Isobutylene Oxidation on a Mo–Sb–Te–O (1 : 0.6 : 0.06) Catalyst

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Abstract—Kinetics of isobutylene oxidation over a Mo–Sb–Te–O catalyst is studied in a flow–circulation system with the Korneichuk differential reactor. The reaction orders of methacrolein, acetic acid, acetone, and CO_2 formation, as well as the order of the overall reaction of isobutylene oxidation into methacrolein, with respect to oxygen and isobutylene are determined at 613–703 K and oxygen concentrations of $(0.33–13.05) \times 10^{-3}$ mol/l and isobutylene $(3.2–121.9) \times 10^{-4}$ mol/l. The activation energies of these reactions are determined.

In a study of Mo–Sb–O (Mo : Sb = 1 : 0.6) catalysts promoted with Sr, Pb, Se, Te, V, and W, we found that the highest methacrolein (MA) yield based on isobutylene is achieved in the Mo–Sb–Te (1 : 0.6 : 0.06) system [1, 2]. The maximal isobutylene conversion (76.5%) for the catalyst of this composition was obtained at 703 K and flow rates of oxygen of 2.8 cm^3/s and isobutylene of 0.17 cm^3/s. The maximal selectivity to MA was 85%. An even higher selectivity (88.1%) was observed over a catalyst promoted by tungsten, but all tungsten-containing catalysts were inactive. The conversion of isobutylene on a tungsten-containing catalyst under conditions similar to those used for tellurium-promoted catalysts was below 35.6%.

It was reasonable to carry out a kinetic study of isobutylene oxidation on the best catalyst with a Mo–Sb–Te (1 : 0.6 : 0.06) composition.

To construct a kinetic model, we used published data on isobutylene oxidation into MA via a redox mechanism [3, 4].

The first step is the reduction of the catalyst active site by isobutylene

$$\mathrm{RH} + \mathrm{ZO} \longrightarrow \mathrm{RHO} + \mathrm{Z}.$$

The second step is the re-oxidation of a reduced site by oxygen adsorbed on the surface

$$\mathrm{Z} + 0.5\mathrm{O}_2 \longrightarrow \mathrm{ZO}.$$

The results of kinetic studies are shown in Table 1. It is seen that, with an increase in the concentration of isobutylene [i-C_4], the formation rates of all products increase. When the concentration of one of the components was changed, the concentrations of other components were kept constant by dosing certain amounts of nitrogen.

Table 1. The effect of isobutylene and oxygen concentrations on the rate of oxidation product formation and isobutylene conversion over the Mo : Sb : Te (1 : 0.6 : 0.06) catalyst (the flow rate is 3.9 cm^3/s; the catalyst volume is 3.3 cm^3; temperature is 673 K)

$[O_2] \times 10^3$, mol/l	$[i\text{-}C_4] \times 10^3$, mol/l	Rate $\times 10^5$, mol l^{-1} s^{-1}				
		w_{AA}	$w_{acetone}$	w_{MA}	w_{CO_2}	$w_{i\text{-}C_4}$
6.70	0.32	1.48	0.43	21.92	9.70	25.14
6.70	0.68	1.87	0.87	26.88	11.96	30.88
6.70	1.27	2.48	1.43	33.10	14.88	38.54
6.70	3.02	3.17	2.04	40.71	14.79	47.54
6.70	6.00	3.61	5.83	42.11	16.27	52.37
6.70	12.19	4.18	12.64	60.9	20.88	72.25
0.33	6.20	1.65	1.48	13.01	3.61	16.09
0.67	6.20	2.00	2.00	16.96	4.44	20.92
1.68	6.20	2.57	3.04	24.32	7.31	29.84
3.36	6.20	2.91	4.52	32.80	10.92	40.41
6.71	6.20	3.61	5.83	41.85	16.44	52.37
13.05	6.20	4.31	7.44	52.07	20.97	65.12

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Table 2. The selectivity to isobutylene oxidation products on the Mo : Sb : Te (1 : 0.6 : 0.06) catalyst at different concentrations of isobutylene and oxygen (experimental conditions are shown in Table 1)

$[O_2] \times 10^3$, mol/l	$[i\text{-}C_4] \times 10^3$, mol/l	$x^*_{i\text{-}C_4}$, %	Selectivity, %			
			AA	acetone	MA	CO_2
6.70	0.32	66.6	2.9	0.1	87.3	9.7
6.70	0.68	39.0	3.0	0.2	97.1	9.7
6.70	1.27	26.0	3.2	1.3	85.9	9.6
6.70	3.02	15.8	3.3	3.2	85.7	7.7
6.70	6.00	7.5	3.5	8.4	80.4	7.8
6.70	12.19	5.1	2.9	12.1	77.8	7.2
0.33	6.20	2.4	5.2	8.4	80.8	5.6
0.67	6.20	3.0	4.8	8.8	81.8	5.3
1.68	6.20	3.4	4.3	7.7	81.8	6.2
3.36	6.20	4.8	3.6	8.4	81.2	6.8
6.71	6.20	7.5	3.5	8.4	80.4	7.8
13.05	6.20	8.9	3.3	8.7	79.9	8.1

* Isobutylene conversion.

The selectivity to MA formation passes through a maximum at an isobutylene concentration of 6.8 mol/l. The selectivities to acetic acid (AA) and CO_2 do not depend on the concentration of isobutylene. A change in the oxygen concentration within the interval (3.3–130) × 10^{-4} mol/l does not affect the selectivities to acetone and MA, although it favors the selectivity to CO_2 and disfavors the selectivity to acetic acid (Table 2).

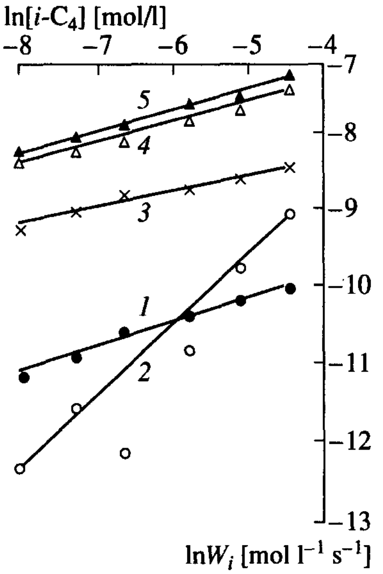

Fig. 1. Dependence of the rate of product formation and the overall rate of reaction on the isobutylene concentration: (*1*) acetic acid, (2) acetone; (*3*) CO_2; (*4*) MA; and (*5*) overall reaction.

The orders of product formation were determined by constructing the plots of $\ln w_i$ vs. $\ln C_i$ (Figs. 1 and 2). The orders are summarized below.

Reaction	MA	AA	Acetone	CO_2	Σ
Order in i-C_4	0.4	0.3	0.8	0.4	0.4
Order in O_2	0.4	0.2	0.4	0.4	0.4

These values of reaction orders confirm that, with an increase in the isobutylene concentration, the selectivity to acetone will increase (the reaction order with respect to the olefin is higher than for other reactions). The concentration of oxygen should not affect the selectivity to MA, and this agrees with experimental observations (Table 2).

The effect of product concentrations on the rates of their formation was studied by changing the contact time (Table 3). We assume that the concentration of MA exerts the strongest effect on the rate of product formation because MA may compete with isobutylene for the active catalyst surface. Under our experimental conditions, the concentration of MA changes by more than an order of magnitude.

Analysis of the $\ln w_i$–ln[MA] dependence, changes in isobutylene and oxygen concentrations, and the orders with respect to each product suggested that the rate of MA and CO_2 formation is virtually independent of the concentration of carbonyl compounds (MA and acetone), and reactions of acetone and acetic acid formation are retarded by MA. The rate orders of the two last reactions with respect to MA are −0.4 and −1.0, respectively. Table 3 shows that the selectivity to MA

Table 3. Effect of the contact time (the concentration of reaction products) on the rate of isobutylene oxidation product formation on the Mo : Sb : Te (1 : 0.6 : 0.06) catalyst. (The composition of the mixture at the reactor inlet, mol/l: isobutylene, 4.3×10^{-3}; oxygen, 8.4×10^{-3}. The reaction temperature is 673 K, $S_{sp} = 2.9$ m^2/g)

Contact time, s	[MA] × 10^4, mol/l	S_{MA}, %	Rate × 10^5, mol l^{-1} s^{-1}					
			w_{AA}	$w_{acetone}$	w_{MA}	w_{CO_2}	w_{CO}	w_{Σ}
0.18	1.0	74.7	11.5	25.01	94.0	30.9	–	136.1
0.36	1.8	72.5	12.2	24.88	83.7	28.5	–	115.6
0.72	3.3	80.8	6.1	12.61	75.9	22.2	–	94.0
1.80	6.2	87.0	3.0	3.31	57.2	14.7	3.7	65.6
3.60	9.4	84.1	3.7	1.61	43.1	12.8	7.7	51.3
7.20	10.8	75.2	2.6	1.04	24.9	10.0	14.3	33.1

Table 4. The effect of temperature on the rate of butylene oxidation product formation on the Mo : Sb : Te (1 : 0.6 : 0.06) catalyst

T, K	[MA] × 10^4, mol/l	$[O_2] \times 10^3$, mol/l	$[i\text{-}C_4] \times 10^3$, mol/l	Rate × 10^4, mol l^{-1} s^{-1}					
				w_{AA}	$w_{acetone}$	w_{MA}	w_{CO_2}	w_{CO}	w_{Σ}
613	1.1	7.4	4.0	0.09	0.13	0.97	0.43	–	1.21
643	2.4	7.2	3.3	0.23	0.16	2.26	0.64	–	2.66
673	6.2	6.8	3.1	0.32	0.32	5.70	1.43	0.37	6.56
703	11.8	6.1	2.9	0.46	0.46	10.83	2.76	2.64	10.6

(S_{MA} passes through a maximum (87%) at a contact time of 1.8. This can be associated with the effect of MA on the rate of acetone and acetic acid formation. At longer contact times (>1.8 s), CO appears in the reaction products, which is probably formed by the decomposition of carbonyl compounds. To determine the reaction order of CO formation with respect to MA, a plot of $\ln w_{CO}$ vs. $\ln C_{MA}$ was constructed at constant concentrations of oxygen and isobutylene. Under these conditions, the reaction is first-order with respect to MA.

Thus, the rate of CO formation can be approximated by the equation $w_{CO} = k_{CO}$ [MA].

The study of the effect of temperature on the formation of reaction products (Table 4) allowed us to determine the rate constants at different temperatures. The dependence of $\ln k_i$ on $1/T$ was used to calculate the activation energies of reactions and preexponential factors k_0 (Table 5).

A comparison of the activation energies shows that with an increase in temperature, the selectivity to acetone should grow faster than other selectivities. The results of experiments at different temperatures shows that isobutylene oxidation over an Mo–Sb–Te–O catalyst should be carried out at about 673 K, when the decomposition of MA to yield CO does not yet occur.

Vazhnova et al [5] studied the kinetics of isobutylene oxidation over a complex Bi–Co–Fe–Mo catalyst. The proposed kinetic model of the process assumes that oxygen and isobutylene adsorption occurs on different surface sites. At high isobutylene concentrations (>8 vol %), the catalyst surface is reduced, and its activity and selectivity decrease. The maximal yield of MA (74%) is achieved at an isobutylene concentration

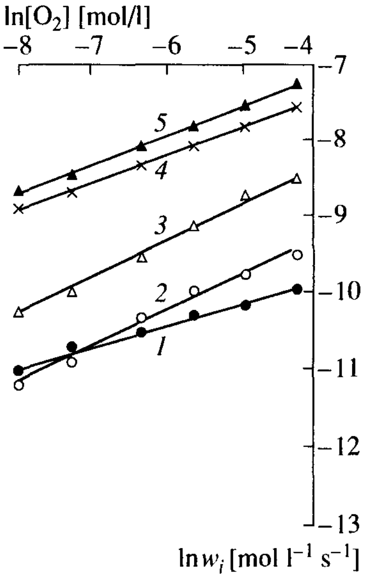

Fig. 2. Dependence of the rate of product formation and the overall rate of reaction on the oxygen concentration: (*1*) acetic acid, (*2*) acetone; (*3*) CO_2; (*4*) MA; and (*5*) overall reaction.

Table 5. Preexponential factors and activation energies of reactions of isobutylene oxidation product formation on the Mo : Sb : Te (1 : 0.6 : 0.06) catalyst

Product	$k_0 \times 10^{-6}$	Activation energy, kJ/mol
Methacrolein	4.20 $\text{mol}^{0.2}\,\text{l}^{-0.2}\,\text{s}^{-1}$	103
Acetone	7.30 $\text{mol}^{0.2}\,\text{l}^{-0.2}\,\text{s}^{-1}$	150
Acetic acid	0.34 $\text{mol}^{1.5}\,\text{l}^{-1.5}\,\text{s}^{-1}$	131
CO_2	0.03 $\text{mol}^{0.2}\,\text{l}^{-0.2}\,\text{s}^{-1}$	83

of 7.5 vol % and 603 K. At 623–653 K, the order of the overall reaction with respect to isobutylene is close to the first. At a high concentration of oxygen starting from $P_{O_2}/P_{i\text{-}C_4} > 3.0$, the order with respect to oxygen is zero.

In our case, on the catalyst with a different composition, the orders with respect to oxygen and isobutylene are fractional over the whole interval of temperatures and concentrations of initial reactants.

REFERENCES

1. Zhiznevskii, V.M., Shipailo, V.Ya., and Bazhan, L.V., *Dokl. Akad. Nauk Ukr.*, 1994, no. 7, p. 139.
2. Zhiznevskii, V.M., Shipailo, V.Ya., Bazhan, L.V., and Mokryi, E.N., *Dokl. Akad. Nauk Ukr.*, 1994, no. 10, p. 123.
3. Boreskov, G.K., *Zh. Fiz. Khim.*, 1958, vol. 32, no. 12, p. 2739.
4. Zhiznevskii, V.M., *Cand. Sci. (Chem.) Dissertation*, Moscow, 1982.
5. Vazhnova, T.G., Korchak, V.N., Timoshenko, V.I., and Krylov, O.V., *Kinet. Katal.*, 1985, vol. 26, no. 6, p. 1378.