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Kinetics of the Oxidation of Propene on MoO_3 Based Model Catalysts

Selective oxidation of olefins proceeds in a consecutive series of elementary steps of hydrogen abstraction and nucleophilic oxygen addition. The first step is activation of the hydrocarbon molecule by abstraction of an @-hydrogen and formation of the first allylic intermediate (*1–4*). Using model catalysts, composed of Bi^{3+} or Fe^{3+} ions supported on MoO_3 crystallites, it has recently been shown (*5*) that individual Bi^{3+}–oxygen polyhedra function as centers activating hydrocarbon molecules, the turnover frequency per Bi^{3+} ion being independent of their surface concentration, whereas it is the MoO_3 lattice which performs the nucleophilic addition of oxygen. The two operations take place at different sites which seem to be located at different crystal faces. On the other hand Fe^{3+} ions activate oxygen to its electrophilic form, responsible for total oxidation. It was established long ago that in the case of commercial bismuth molybdate catalysts the activation of the hydrocarbon molecule is the rate-determining step of the partial oxidation (*6*). It now seemed interesting to determine the kinetics of the oxidation of propene on model catalysts, composed of different transition metal ions supported on MoO_3 crystallites, and evaluate the contribution of various elementary steps to the overall kinetics of the reaction.

EXPERIMENTAL

Kinetics of the oxidation of propene were measured in a glass differential reactor. In the stationary state in a flow reactor the specific rate of the catalytic reaction may be expressed by the equation

$$r = \frac{(x_i - x_o)}{w \cdot A} \cdot \frac{p}{RT} \cdot \frac{V}{t},$$

where r is the specific rate in moles per square meter per second, w is the catalyst weight in grams, A is the specific surface area of the catalyst in square meters per gram, V/t is the flow rate in cubic meters per second, p is the total pressure of reactants in pascals, T is the temperature, and x_i and x_0 are the molar ratios of a given reactant at the inlet and outlet, respectively, of the reactor in the steady state.

Samples of 3–6 g of the catalyst with a grain size of 0.49–0.75 mm were placed in the reactor and preheated in air at 773 K for 5 hr. After attaining the reaction temperature a 1 : 1.2 mixture of propene and oxygen, diluted with nitrogen to obtain the appropriate pressure of propene in the reacting medium, was passed through the reactor at a flow rate of 15 $dm^3 \cdot hr^{-1}$. In order to determine the parameters of the rate equation the propene molar ratio was varied in the range 0.013–0.023 and that of oxygen in the range of 0.018–0.030.

Reaction products were analyzed using a Giede GChF 18.3 gas chromatograph with FID for the determination of hydrocarbons and their derivatives, and a TCD for the determination of carbon oxides. Steel columns of 3.6 mm diameter were used with 4% of carbowax 20M on Chromosorb G, AW, DMCS (80/100 mesh).

The catalysts were obtained by impregnation of MoO_3 supplied by Climax Molybdenum Co. with Bi^{3+}, Fe^{3+}, and Bi^{3+} + Fe^{3+} ions from the appropriate nitrate solutions (*5*). The following samples were prepared: Bi $1.0/MoO_3$, monolayer of Bi^{3+}

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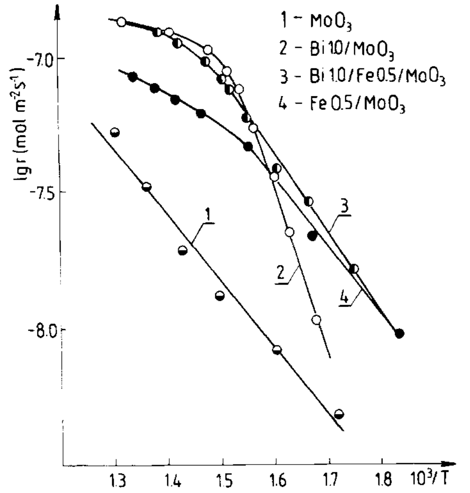


Fig. 1. Arrhenius plots of the oxidation of propene on MoO_3 (curve 1), Bi 1.0/MoO_3 (cuve 2), Bi 1.0 Fe 0.5/MoO_3 (curve 3), and Fe 0.5/MoO_3 (curve 4).

ions; Fe 0.5/MoO_3, half-monolayer of Fe^{3+} ions; Bi 1.0 Fe 0.5/MoO_3, monolayer of Bi^{3+} and half-monolayer of Fe^{3+} ions.

RESULTS AND DISCUSSION

Figure 1 shows the kinetic data of the oxidation of propene on Bi 1.0/MoO_3, Fe 0.5/MoO_3, Bi 1.0 Fe 0.5/MoO_3, and MoO_3 catalysts presented in the form of Arrhenius plots. In the case of the three supported catalysts which show high activity, two temperature ranges may be distinguished: a low temperature range below 650 K characterized by higher activation energy and high temperature range above 690 K where the activation energy drops to a much lower value. They clearly correspond to kinetic and diffusion-controlled ranges. In the case of pure MoO_3 of lower activity the reaction proceeds in the kinetic range in the whole temperature range studied.

Table 1 summarizes the selectivity data. Three main products were observed in all cases: acrolein, acetaldehyde, and carbon oxides. With Bi 1.0/MoO_3 catalyst practically only acrolein was formed, whereas on Fe 0.5/MoO_3, mainly carbon oxides. In the case of the Bi 1.0 Fe 0.5/MoO_3 catalyst, in addition to acrolein a considerable amount of CO + CO_2 is formed at lower temperatures, but the amount decreases with an increase in temperature. It is noteworthy that in the diffusion-controlled range the selectivity to acrolein on this catalyst attains almost 100%, similar to that observed on Bi 1.0/MoO_3 catalyst and remains independent of temperature. This fact indicates that the formation of CO + CO_2 is not due to the consecutive reaction of the oxidation of acrolein, but must be the result of parallel reaction of propene. In the case of a consecutive series of propene–acrolein–CO + CO_2 an increase in the amount of CO + CO_2 should be observed on an increase in the temperature in the diffusion-controlled

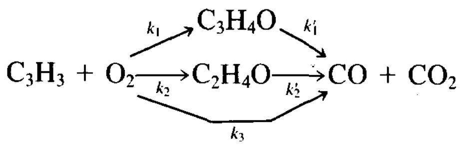
TABLE 1

Conversion and Selectivities to Different Products

Catalyst:	Bi 1.0/MoO_3				Bi 1.0 Fe 0.5/MoO_3				Fe 0.5/MoO_3				MoO_3			
Temp. (K)	Selectivity (%)			Conv. (%)	Selectivity (%)			Conv. (%)	Selectivity (%)			Conv. (%)	Selectivity (%)			Conv. (%)
	Acr.	A.ald.	CO + CO_2		Acr.	A.ald.	CO + CO_2		Acr.	A.ald.	CO + CO_2		Acr.	A.ald.	CO + CO_2	
570	96.1	3.9	—	2.0	55.9	15.8	28.3	6.7	—	—	—	—				
597	96.7	3.3	—	5.2	61.3	13.6	25.1	11.7	9.1	7.3	83.6	9.0	40.9	23.9	35.2	2.7
615	97.2	2.8	—	10.5	67.9	11.4	20.7	15.7	10.6	6.4	83.2	13.6	46.0	20.6	33.4	3.4
637	98.0	2.0	—	21.1	86.0	3.7	10.3	22.7	13.0	5.0	82.3	17.9	50.0	18.1	32.0	4.2
690	98.8	1.2	—	46.9	98.2	1.4	0.4	43.3	18.8	2.0	79.4	26.2	62.0	9.6	28.4	7.3
741	99.5	0.5	—	54.5	99.5	0.5	—	52.6	22.2	1.1	75.5	30.2	63.4	4.6	32.0	15.5

Note. Acr., acrolein; A.ald., acetaldehyde; Conv., conversion.

range. It may thus be concluded that the oxidation of propene may be described by the scheme



with $k_1' \ll k_1$, and $k_1' \ll k_2$, k_3. Under such conditions the rate of the formation of acrolein and $CO + CO_2$ may be calculated from the total rate of the reaction and the selectivity to these products. The results of such calculations indicate that the rate of acrolein formation on Bi 1.0 Fe 0.5/MoO_3 is in the whole temperature range similar to that observed with the Bi 1.0/MoO_3 catalyst. It may thus be concluded that in the former case it is only the Bi^{3+} ions which are responsible for the activation of propene molecules followed by nucleophilic addition of oxygen to form acrolein, and the properties of these ions remain unchanged upon addition of Fe^{3+} ions. The latter mainly perform the role of surface sites activating oxygen molecules to the reactive electrophilic forms, responsible for the total oxidation.

The Bi 1.0/MoO_3 catalyst gives in the kinetically controlled temperature range only acrolein; the measured activation energy amounting to 115 kJ·mole^{-1} may thus be taken as the value characterizing the activation of propene molecules on Bi^{3+} ions. With Fe^{3+}/MoO_3 total oxidation to carbon oxides is mainly observed, the activation energy of 48 kJ·mole^{-1} representing thus the value characteristic for activation of oxygen on Fe^{3+} ions. In the case of MoO_3 the selectivities to acrolein and carbon oxides are practically independent of temperature which indicates that both activation of propene and activation of oxygen have similar activation energies, amounting to 63 kJ·mole^{-1}. The activation energy observed in the diffusion-controlled range is equal to about 10 kJ·mole^{-1}.

The determination of the kinetic equation of the partial oxidation of propene to acrolein was carried out for the Bi 1.0/MoO_3 catalyst, which was characterized by a very high selectivity of acrolein formation amounting to 98% and the influence of the side reactions could be neglected with a good approximation. The temperature of 617 K, well below the transition between kinetic and diffusion-controlled ranges, was selected and measurements of the reaction rate at constant stationary oxygen concentration $x_{O_2} = 0.023$ and changing propene concentration $x_{C_3H_6}$ as well as at constant stationary propene concentration $x_{C_3H_6} = 0.019$ and changing oxygen concentration x_{O_2} were carried out. Similarly parameters of the rate equation of the parallel reaction of total oxidation of propene to $CO + CO_2$ were determined for the Fe 0.5/MoO_3 catalyst, on which formation of $CO + CO_2$ prevailed. The measurements were carried out at 643 K at a constant oxygen concentration of $x_{O_2} = 0.018$ and varying propene concentration, and at a constant propene concentration $x_{C_3H_6} = 0.019$ by changing oxygen pressure.

Results are illustrated in Fig. 2, in which curves 1A and 1B represent the dependence of the reaction rate on the concentration of propylene in the case of Bi 1.0/MoO_3 and Fe 0.5/MoO_3 catalysts, respectively, and curves 2A and 2B, on that of oxygen. They show that the rate of the reaction may be expressed by

$$r = k \cdot p_{C_3H_6}^{\beta_1} \cdot p_{O_2}^{\beta_2}$$

in which the exponents β assume the values $\beta_1 = 1$ and $\beta_2 = 0$ in the case of selective oxidation of propene to acrolein on Bi 1.0/MoO_3 catalyst, and the values $\beta_1 = 0.17$ and $\beta_2 = 0.58$ for the prevailing total oxidation on Fe 0.5/MoO_3 catalyst. The partial oxidation of propene on the model catalysts used in this study is thus of first order in propene and of zero order in oxygen. This is in full agreement with earlier results obtained with the industrial bismuth molybdate catalysts (*6*) which showed that adsorption of propene is the rate-determining step in its oxidation to acrolein. It seems plausible to assume that the reaction of total oxidation of propene is of the order 0 in propene and 1 in oxygen, the deviation

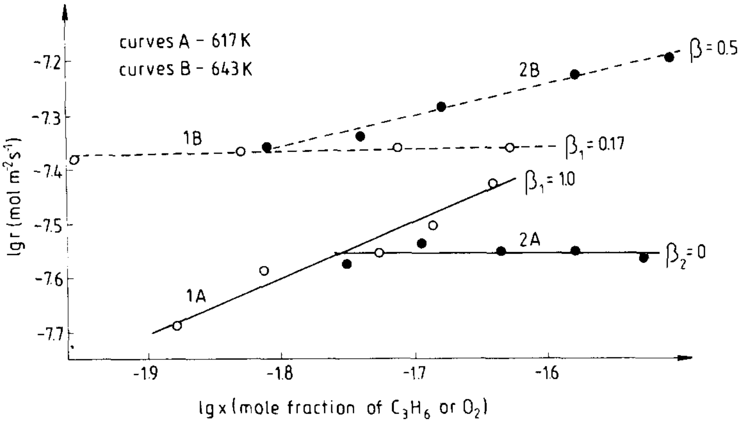


Fig. 2. Rate of the oxidation of propene to acrolein on Bi 1.0/MoO_3 (solid lines A) and Fe 0.5/MoO_3 (dotted lines B) catalysts as functions of the concentration of propene (curves 1) and oxygen (curves 2).

from these numbers in the case of the reaction on Fe 0.5/MoO_3 catalyst being due to the fact that for this catalyst parallel selective oxidation also takes place to some extent. It should also be borne in mind that a number of parasite reactions may simultaneously take place and the rate constant k'_1 of the total oxidation of acrolein in the reaction network (*1*) may not be negligible on Fe 0.5/MoO_3 catalyst. This would result in a dependence, albeit a weak one, of the rate on propene pressure.

Results of the kinetic studies are thus consistent with the model of the reaction, in which propene molecules are activated on Bi^{3+} sites and then transformed by nucleophilic oxygen addition into acrolein, the first step being rate determining. When Fe^{3+} ions are present at the surface, activation of oxygen to its electrophilic forms takes place, which react with propene in a parallel reaction of total oxidation, activation of oxygen being here the rate-determining step. The presence of isolated Fe^{3+} ions does not influence the activity of Bi^{3+} ions, the promoting effect of iron molybdate on the performance of multicomponent molybdate catalysts being due to the facility of phase transformations of Fe(III) into Fe(II) molybdate in the presence of the isomorphic bismuth molybdate on the one hand, and cobalt molybdate on the other hand, as postulated in (*7*).

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