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The Role of Active Oxygen Transfer through the Gas Phase in Propylene Oxidation over a Bismuth–Molybdenum Catalyst

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Abstract—The transfer of atomic oxygen from the surface of bismuth oxide onto molybdenum oxide through the gas phase, including the case when ozone was fed to the catalyst bed, is experimentally studied. It is found that the transfer of atomic oxygen through the gas phase only leads to the formation of the products of complete oxidation of propylene under conditions of heterogeneous propylene oxidation on the mixture of molybdenum and bismuth oxides. No new sites are formed on the surface of molybdenum oxide.

INTRODUCTION

The partial oxidation of hydrocarbons is one of the most important tasks in the chemical industry, which now uses widely multicomponent bismuth–molybdenum catalysts based on bismuth molybdates. These catalysts (and simpler model systems) often show the effect of synergism, which reveals itself in the form of a nonadditive increase in the conversion and selectivity in the partial oxidation reaction compared to the values observed on separate components of the catalyst. To explain this phenomenon, the model of remote control was proposed. According to this model, some phases in the catalyst composition (usually enriched in bismuth) are oxygen donors, which activate oxygen and supply it in the active form onto the acceptor phases (usually enriched in molybdenum). On the latter phase, active oxygen participates in propylene oxidation or creates new active oxidative sites. Usually, active oxygen is believed to transfer to the acceptor in the form of O^- or O^{2-} ions by spillover over the surface [1].

Baumgarten and Schnok [2] also considered the possibility for oxygen transfer to the acceptor phase in the form of atoms or ozone, which is formed in the gas phase from desorbing oxygen atoms and oxygen molecules:

$$O + 2O_2 \longrightarrow O_3 + O_2. \qquad (1)$$

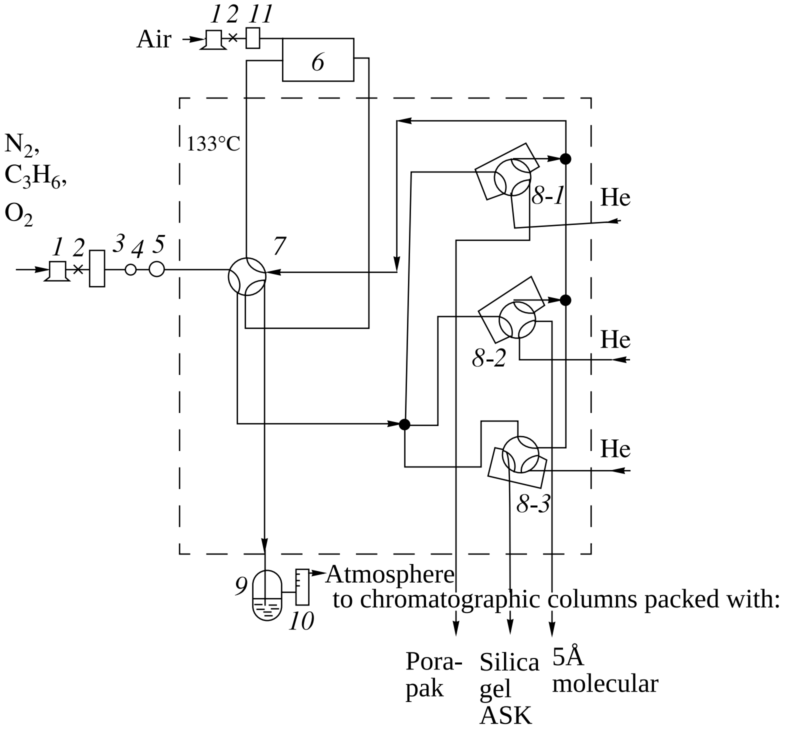
In our previous studies, we found that β-Bi_2O_3 (oxygen-donor phase prototype) generates atomic oxygen under certain conditions. This oxygen transforms into ozone by reaction (I) in the gas phase [3, 4]. The goal of this work is to elucidate the role of atomic oxygen transfer through the gas phase in the catalytic oxidation of propylene over a mechanical mixture of β-Bi_2O_3 and MoO_3. These oxides are model catalysts, one of which is oxygen donor (Bi_2O_3) and the other is oxygen acceptor.

EXPERIMENTAL

The samples of β-Bi_2O_3 and MoO_3 were prepared using the following procedures: (1) heating basic bismuth carbonate (bismutite) at 380°C for 30 min and (2) rapid pouring of a small amount of slightly acidified bismuth nitrate (5 g) into a solution of NaOH (15 g per 100 ml) which is placed in a boiling-water bath. If the precipitate is filtered after 3–3.5 min, then the individual large-crystal phase of β-Bi_2O_3 is obtained. α-Bi_2O_3 was prepared by heating β-Bi_2O_3 at 500°C for 3 h. MoO_3 samples were obtained by heating ammonium paramolybdate at 590°C for 3 h. The phase compositions of the samples were examined by XRD using a Dron-3 instrument (CuK_α irradiation). X-ray diffraction patterns corresponded to reference data for Bi_2O_3 and MoO_3. The specific surface area was measured by the low-temperature argon adsorption method. The samples were pressed to pellets and then ground to a 0.5–1.0 mm fraction to be used in the preparation of the mechanical mixture (fraction B). Mechanical mixtures were also prepared from a 0.15–0.25 mm fraction, which was taken from nonpressed oxides (fraction A). Thus, experiments were carried out with two types of mechanical mixtures consisting of the grains of components with different sizes.

The formation of atomic oxygen from the phases of bismuth oxide was registered using chemiluminescence analysis [6].

The catalytic activity of the samples in propylene oxidation to acrolein was studied using a flow-type quartz reactor (20 cm^3) with a thermocouple well. The reactor diameter was 12 mm and the average length of the catalyst bed was ~1 cm. The thermocouple was placed in the middle of the catalyst bed. For the experiments with ozone, a reactor with a diameter of 20 mm was used. It had a special inlet for the ozone–oxygen mixture, which was immersed into the catalyst bed. The catalyst bed was placed onto the grid inside the reactor. The void volume after the catalyst in the reactor was



Schematic of the setup for propylene oxidation on mixed bismuth–molybdenum catalysts: (*1*) manostat, (*2*) fine-control valve, (*3*) rheometer, (*4*) mixer, (*5*) bubbler, (*6*) reactor, (*7*) six-way valve for the supply of the mixture to analysis before and after the reactor, (*8*) three six-way valves for sampling, (*9*) trap for condensate, (*10*) flow meter, and (*11*) ozonator.

packed with quartz wool. Initial reactants and reaction products were analyzed using gas chromatography. The schematic of the setup is shown in the figure. The initial mixture supplied to the reactor contained 1–2 vol % propylene in air. The products leaving the reactor passed right away into a chromatograph thermostat for analysis at 150°C. Hydrocarbons were analyzed using a column (length, 40 cm; diameter, 4 mm; packed with Porapak Q) and a flame-ionization detector. Carbon monoxide, N_2, and O_2 were analyzed using a column (length, 2 m; diameter, 3 mm) packed with a 5A molecular sieve (Linde). Carbon dioxide was analyzed using a column (length, 1 m; diameter, 3 mm) packed with large-pore silica gel. For these four gases, a thermal conductivity detector was used. The sensitivity of analyses was 0.1% or 2.5×10^{16} species. The main experimental error is due to the detection of the catalyst volume and may reach 10% according to our estimates.

RESULTS AND DISCUSSION

It has been shown earlier that overstoichiometric oxygen desorbs from the β-Bi_2O_3 phase in the atomic form at temperatures above 380°C [3]. In the thermal desorption, we registered $\sim 7 \times 10^{13}$ oxygen atoms without taking into account their decay on the reactor walls. Oxygen does not desorb from the α-Bi_2O_3 phase at temperatures below 500°C [3]. These findings were confirmed in this work.

Let us estimate the characteristic lifetimes of atomic oxygen in the gas phase under conditions of partial oxidation of propylene over the mechanical mixture of bismuth oxide and molybdenum oxide grains. Two reactions can contribute most significantly to the decay of atomic oxygen: the bimolecular reaction of atomic oxygen with propylene (with the rate constant equal to 3×10^{12} cm^3 mol^{-1} s^{-1} at 400°C [7]) and the termolecular reaction (I) (with the rate constant equal to 7×10^{13} cm^6 mol^{-2} s^{-1} at 400°C). Under our conditions (2% of propylene in air), we obtain the characteristic lifetime of atomic oxygen: $\tau \sim 10^{-6}$ s for the first reaction and $\tau \sim 10^{-4}$ s for reaction (I). It is clear that the main role in the decay of atomic oxygen belongs to the reaction of oxygen atoms with propylene, and ozone virtually is not formed in this case. If the diffusion coefficient of atomic oxygen is 1.4 cm^2/s [8] (air, 400°C, and atmospheric pressure), the diffusion radius of atomic oxygen calculated by the formula $R_{\text{diff}} = \sqrt{(D\tau)}$ (where D is the diffusion coefficient) is $\sim 10^{-2}$ mm. The catalyst bed is a space densely packed with the spherical 0.5-mm grains of two components in a 1 : 1 ratio. Therefore, ~15% of the grain surface of one component is at a distance shorter than R_{diff} from the grain surface of the other component. For the mechanical mixture with 0.15-mm grains, the fraction of such surface is ~50%. The efficiency of atomic oxygen transfer between grains through the gas phase should be of the same order. In the case of ozone formation by the interaction of gas-phase molecular oxygen and atomic oxygen on the surface of bismuth oxide and further ozone desorption, the diffusion radius stipulated by ozone consumption in the gas-phase reaction with propylene is a much higher value (0.7 mm), and the efficiency of transfer is much higher. Therefore, under the conditions of catalysis in our model system, atomic oxygen or ozone transfer from β-Bi_2O_3 through the gas phase is expectable for at least several tens of minutes up to the complete consumption of bulk overstoichiometric oxygen in β-Bi_2O_3. The possibility of replenishing β-Bi_2O_3 with oxygen by reoxidation remains uncertain. This amount of oxygen (which is two to three orders of magnitude greater than the amount of oxidized propylene molecules for the same time period) can substantially change the yield of reaction products only if atomic oxygen both participates in oxidation and creates new active sites for oxidation on the surface of molybdenum oxide. The possibility for the formation of such sites was considered by Weng and Delmon [1] as one of the possible remote control mechanisms. In the latter case, many propylene molecules can react on each site of this sort.

The following factors should be taken into account when comparing the catalytic activities of β- and α-Bi_2O_3 (measured as the conversions of propylene):

(1) The weights of catalyst samples of different fractions of the same volume may differ substantially since the larger fraction was pressed, and the finer fraction was not.

(2) The surface of β-Bi_2O_3 is twice as large as the surface of α-Bi_2O_3. Therefore, the conversion of propylene differs substantially over different fractions and phases of Bi_2O_3.

Table 1 shows the conversion of propylene on 1 cm^3 of the catalyst at different temperatures for two fractions (A and B) of individual oxides α-Bi_2O_3, β-Bi_2O_3, and MoO_3.

Before proceeding to the discussion of the catalytic tests of mechanical mixtures, it is necessary to make the following explanations. Experiments were carried out using 1 cm^3 mixture of the catalyst (0.5 cm^3 of each component). Therefore, the contact time of each component was preserved because a smaller amount of the catalyst was distributed over a volume of 1 cm^3. The second component can be considered as a diluent.

When calculating the additive value of the catalytic activity, we summed halves of the catalytic activities of separate components under their respective conditions. The value of the synergism was calculated using the formula [1]

$$\Delta Y = Y_{ij} - (W_i Y_i + W_j Y_j).$$

Here, Y_{ij} is the acrolein yield on the mechanical mixture of Bi_2O_3 and MoO_3, Y_i and Y_j are the yields of acrolein on individual components, and W_i and W_j are the fractions of the components of the mixture.

As can be seen from the results of experiments, the individual phases of β-Bi_2O_3 and α-Bi_2O_3 are not responsible for the partial oxidation of propylene. On bismuth oxide, we observed only the complete oxidation of the hydrocarbon, while molybdenum oxide contributed slightly to the acrolein yield, but the selectivity was very low.

Analysis of the data presented in Table 1 shows that, contrary to expectations, the large-grain fraction of the β-Bi_2O_3 phase (B) is more active in propylene oxidation than the fine-grain fraction (A). The higher weight and specific surface area of the sample can explain this. The finer fraction of α-Bi_2O_3 is more active. The activity of molybdenum oxide is higher in the case of the larger-grain fraction. Note that, according to TPD data [9], the desorption of atomic oxygen from β-Bi_2O_3 is completed below 420°C. XRD data show that, in the course of the reaction, β-Bi_2O_3 transforms into α-Bi_2O_3. Nevertheless, the activity of the catalyst does

Table 1. Propylene oxidation on individual oxides (2% propylene in air; catalyst volume, 1 cm^3; contact time, 1 s; grain size 0.15–0.25 mm (A) and 0.5–1 mm (B))

Catalyst, surface area	T, °C	Fraction*	Propylene conversion, %	Acrolein yield, %
β-Bi_2O_3 0.7 m^2/g	380	A	2.9	0
		B	8.8	0
	400	A	3.5	0
		B	14.4	0
	420	A	5.4	0
		B	18.8	0
	440	A	7.7	0
		B	23.6	0
α-Bi_2O_3 0.4 m^2/g	380	A	2.2	0
		B	–**	–**
	400	A	2.9	0
		B	–**	–**
	420	A	3.8	0
		B	2.9	0
	440	A	4.3	0
		B	4.1	0
MoO_3 1.8 m^2/g	380	A	1.0	0.2
		B	2.75	0.6
	400	A	1.1	0.3
		B	2.7	1.0
	420	A	1.5	0.4
		B	3.5	1.5
	440	A	1.8	0.5
		B	4.4	2.7

* Sample weight, g: β-Bi_2O_3, 0.8 (A) and 2.3 (B); α-Bi_2O_3, 0.79 (A) and 1.34 (B); and MoO_3, 1.44 (A) and 1.80 (B).

** No data.

Table 2. Propylene oxidation on mechanical mixtures of oxides (2% propylene in air; catalyst volume, 1 cm^3; contact time, 1 s; ratio of components, 1 : 1)

Catalyst	*T*, °C	Fraction	Conversion, %	Acrolein yield, %	Additive acrolein yield, %	Δ*Y*
β-Bi_2O_3 + MoO_3 (1 : 1)	380	A	3.3	2.8	0.1	2.7
		B	7.1	6.2	0.3	5.9
	400	A	3.6	2.8	0.15	2.65
		B	10.1	9.8	0.5	9.3
	420	A	4.5	3.8	0.2	3.6
		B	11.6	11.5	0.75	10.75
	440	A	5.4	4.0	0.25	3.75
		B	12.9	11.7	1.35	10.35
α-Bi_2O_3 + MoO_3 (1 : 1)	380	A	5.7	4.7	0.1	4.6
		B	14.6	7.1	0.3	6.8
	400	A	7.2	6.6	0.15	6.45
		B	20.8	9.0	0.5	8.5
	420	A	8.5	6.7	0.2	6.5
		B	34.2	9.5	0.75	8.75
	440	A	9.4	7.5	0.25	7.25
		B	36.1	8.1	1.35	6.75

not change noticeably at temperatures higher than 420°C. Table 1 shows that on average the β-Bi_2O_3 phase is more active in complete oxidation, and this fact can be explained by the presence of excess mobile oxygen.

Data on the catalytic activity of the mechanical mixtures of Bi_2O_3 and MoO_3 are presented in Table 2. Based on these data we conclude that

(1) The fine fraction of the β-Bi_2O_3 + MoO_3 mixture (fraction A), for which the effect of desorbing atomic oxygen on the catalytic process (when it does occur) should be maximal, is less active than the finer fraction of the α-Bi_2O_3 + MoO_3 mixture.

(2) A decline in the synergism at 440°C for fraction B is explained by the partial oxidation of acrolein. When the catalyst beds and contact times were longer, this effect was even more pronounced.

We can estimate the probability of the participation of excess oxygen desorbed from β-Bi_2O_3. It is known that the maximal amount of excess oxygen in β-Bi_2O_3 corresponding to the formula $BiO_{1.75}$ [10] is 6×10^{20} atoms of oxygen per 1 g of β-Bi_2O_3. On the other hand, the real amount of oxygen desorbed from β-Bi_2O_3 at the temperature of catalysis is ~10^{14} atoms (judging from the amount of ozone formed). The difference in these concentrations is explained by the decay of atoms both on the sample and on the reactor walls. One should take into account that excess oxygen of the β-Bi_2O_3 phase can also desorb molecularly. Our measurements [9] showed that, at the maximum of the thermal desorption peak of atomic oxygen, the amount of desorbed O_2 is ~500 times higher than the amount of desorbed oxygen atoms. On the mixed β-Bi_2O_3 + MoO_3 catalysts, a portion of oxygen atoms that hit upon MoO_3 can stimulate catalytic activity. The absence of a noticeable effect of excess oxygen on the catalytic properties of β-Bi_2O_3 + MoO_3 compared with α-Bi_2O_3 + MoO_3 points to the fact that it does not participate in the selective oxidation of propylene. A higher activity of α-Bi_2O_3 in the mixed catalysts led us to assume that excess oxygen in β-Bi_2O_3 only participates in the complete oxidation of propylene. The mechanism of the selective oxidation of propylene apparently is not associated with the transfer of atomic oxygen through the gas phase. Data presented in Table 3 provide additional arguments in favor of the above assumption. These data concern propylene oxidation over molybdenum oxide under conditions when ozone-rich oxygen is added to the catalyst layer. These experiments model the process of active oxygen transfer from β-Bi_2O_3 through the gas phase. Furthermore, ozone is much less reactive toward propylene, and the average radius of its diffusion under the reaction conditions is $R_{\text{diff}} = 0.7$ mm. This removes barriers to reaching the grain surfaces and penetrating inside them, in which case oxygen transfer affects a larger surface area of molybdenum oxide than in the case of atomic oxygen. The ozonizer makes it possible to create substantial ozone concentrations in the reaction layer to compensate for ozone decay in the pores of grains. Under conditions of catalysis, ozone decay is a purely heterogeneous process. Therefore, we can consider that ozone transfers to the surface without loss, while homogeneous oxidation processes are minor.

Table 3. Propylene oxidation on MoO_3 by air enriched in ozone (T = 360°C; contact time, 2 s; 1.4% propylene in air)

Amount of ozone supplied onto the catalyst, molecule/s	Propylene conversion, %	Acrolein yield, %	Selectivity to acrolein, %	Yield of complete oxidation products, %	Selectivity to complete oxidation products*, %	Amount of complete oxidation products, molecule/s
0	1.1	0	0	0.5	45	0.14×10^{16}
10^{16}	1.2	0	0	0.8	67	0.22×10^{16}
3×10^{16}	5.5	0	0	4.8	87	1.3×10^{16}

* Determined from CO_2.

Experimental results show that there is some increase in the propylene conversion, which is basically due to complete oxidation. The ratio of the amount of reacted propylene to the amount of ozone introduced into the catalyst layer is lower than unity. This fact supports the above conclusion that atomic oxygen does not create new oxidation sites on the surface of molybdenum oxide. Thus, the transfer of active oxygen through the gas phase on multicomponent catalysts for partial oxidation, if it is possible, leads to the complete oxidation of propylene. The possibility for creating new oxidation sites is excluded according to this mechanism. Synergism in the partial oxidation of propylene cannot be explained by remote control via the transfer of active oxygen through the gas phase.

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