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The Mechanism of Action of a Multicomponent Co–Mo–Bi–Fe–Sb–K–O Catalyst for the Partial Oxidation of Propylene to Acrolein: II. Changes in the Phase Composition of the Catalyst under Reaction Conditions

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Abstract—The structures of a complex multicomponent Co–Mo–Fe–Bi–K–Sb–O catalyst for the oxidation of propylene to acrolein and simpler catalysts from which some catalyst components were absent were studied by X-ray diffraction analysis. The phases of α-$CoMoO_4$, β-$CoMoO_4$, $Fe_2(MoO_4)_3$, $Bi_2O_3 \cdot MoO_3$, $Bi_2O_3 \cdot 2MoO_3$, $Bi_2O_3 \cdot 3MoO_3$, oxidized molybdenum oxide, and reduced molybdenum oxide are the main components of the catalyst. Ternary compounds were not detected. Under catalytic reaction conditions, the relative amounts of the phases changed; this change suggests the occurrence of redox transformations with the participation of these phases, probably, at the interface.

INTRODUCTION

Multiphase catalysts for isobutylene oxidation to methacrolein were studied previously using X-ray diffraction (XRD) analysis and Mössbauer spectroscopy [1]. Structural transformations were studied in a $Co_8Mo_{12}Fe_3Bi_xSb_yK_{0.1}O_z$ catalyst, in which the values of x and y were varied over a range of 0–3. It was found that Co and Fe molybdate phases with different degrees of imperfection and the ternary compound $Bi_3FeMo_2O_{12}$ were present in the catalysts. In the course of a catalytic reaction, the conversion of $Fe_2(MoO_4)_3$ into β-$FeMoO_4$ accompanied by the release of oxygen from the solid lattice was observed; this oxygen was consumed in the elementary acts of catalysis. A nonstoichiometric oxide phase of MoO_{3-x} (probably, Mo_4O_{11}), which remained under reductive conditions and disappeared on reoxidation, was formed simultaneously.

Previously [2], we reported on the activity and selectivity of multicomponent Co–Mo–Fe–Bi–Sb–K–O catalysts and simpler systems from which one or more components were absent in another catalytic reaction of partial olefin reduction: the oxidation of propylene to acrolein. Multicomponent catalysts are at the same time multiphase catalysts. To confirm or refute conclusions reached on the role of particular components in catalysis, data on activity and selectivity should be compared with the concentrations of individual phases. In this work, we report the results of the XRD analysis of catalysts that were studied previously [2].

EXPERIMENTAL

Catalyst preparation methods were described elsewhere [2]. The XRD analysis of the test catalysts was performed on a DRON-3 diffractometer using CuK_α radiation. The accuracy of measurements was ±5%. The catalysts were tested before and after the reaction of propylene oxidation to acrolein. The reaction was performed for 10 h using a setup described elsewhere [2].

RESULTS AND DISCUSSION

The XRD analysis of the cobalt–molybdenum system modified with Bi and Fe ions before and after operation under reaction conditions demonstrated (see Fig. 1) that α-$CoMoO_4$, β-$CoMoO_4$, $Fe_2(MoO_4)_3$, MoO_3, and bismuth molybdate phases were present in the bulk of the catalyst. The ions of iron and bismuth can replace the ion of molybdenum to form a ternary compound [3]. However, we did not find this compound in a freshly prepared catalyst using XRD analysis (Fig. 1a). According to the diffraction pattern, a ternary compound was present in the sample only after a long operation of the catalyst in a flow of the reaction mixture.

The table summarizes data on the phase compositions of these catalysts. The specified line intensities are compared with the most intense line of the β-$CoMoO_4$ phase, as well as with the sum of intensities.

The high MoO_3 contents of all of the catalysts are the most unexpected results of XRD analysis (see the values of I_2 and I_3 in the table and Fig. 2a). As the concentration of molybdenum in the catalyst was increased, the concentration of the MoO_3 phase in the Mo_{11}–Mo_{12} systems initially decreased down to a min-

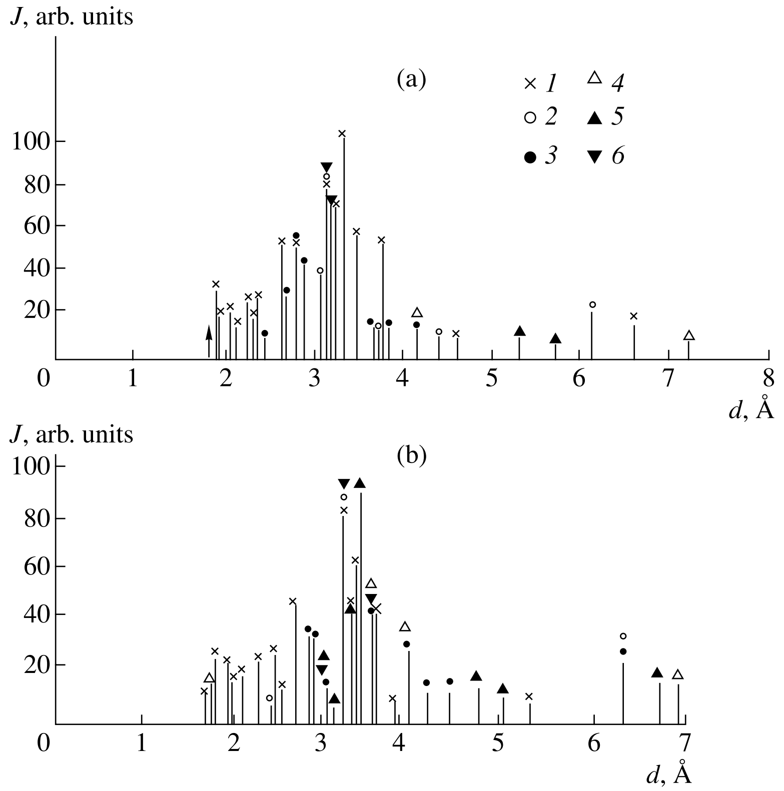

Fig. 1. X-ray diffraction analysis of (a) the initial $Co_8Mo_{12}Bi_{0.75}Fe_2O_x$ catalyst and (b) the above catalyst after operation under reaction conditions of propylene oxidation to acroleins: (*1*) β-$CoMoO_4$, (*2*) α-$CoMoO_4$, (*3*) $Fe_2(MoO_4)_3$, (*4*) MoO_3 (rhombic), (*5*) $Fe_2Bi_2Mo_2O_{12}$, and (*6*) $Bi_2O_3 \cdot 2MoO_3$.

imum. These systems are active and selective. The concentration of the MoO_3 phase further decreased under reaction conditions.

Under conditions of catalysis, MoO_3 can be reduced to MoO_2, and the latter can sublime on the interaction with water vapor [4]. As a result, the catalyst is depleted in molybdenum. A study of the process of reduction [5] demonstrated that intermediate oxide phases can be formed. XRD analysis exhibited only MoO_3 and MoO_2, whereas the formation of $Mo_{18}O_{52}$, that is, a crystallographic-shear structure [6], was observed using X-ray absorption spectroscopy (XAS). It is likely that the vacancies formed in this case are necessary for the interaction with an olefin.

It is likely that a portion of MoO_3 must leave the system and convert a reduced phase of Fe and Bi molybdates into an oxidized phase in order to develop active multiphase catalysts. In these Mo_{11}–Mo_{12} systems, an increased value of the lattice parameter of MoO_3 was observed (see Fig. 2b). The values of d = 3.29, 3.81, 3.46, and 4.00 Å [7] are the most characteristic maximums of MoO_3. The values of d = 3.93, 3.60, and 3.40 Å [8] are the most characteristic maximums of the reduced Mo_4O_{11} phase. It is likely that a less reduced phase of MoO_{3-x} ($0.3 > x > 0$), probably, with a crystallographic-shear structure, rather than the Mo_4O_{11} phase was formed under conditions of sample preparation and formation. The interplanar spacing (in angstrom units) varied through the following ranges depending on the degree of oxidation or reduction of the sample:

$$3.96\text{–}4.00\ (\text{ox.}) \rightleftharpoons 3.93\ (\text{red.})$$

$$\text{and } 3.46\ (\text{ox.}) \rightleftharpoons 3.40\ (\text{red.}).$$

It is believed that an active oxide with a smaller lattice parameter (a more reduced phase) interacts with molybdates by the reaction

$$2FeMoO_4 + MoO_{3-x} + (x + 1/2)O_2 \rightleftharpoons Fe_2(MoO_4)_3,$$

whereas the MoO_3 phase with a greater lattice parameter (a more oxidized phase) remained in excess. As the molybdenum concentration was further increased, a phase with d = 3.795 Å remained in excess. This phase did not participate in transformations under conditions of catalysis and did decrease activity and selectivity. This phase was present in the purest form in a sample of $Co_8Mo_{12}Bi_{0.75}O_x$, which is free of iron molybdate.

Thus, two molybdenum oxide phases occur in a complex catalyst. One of them is necessary for the generation of active centers and interfaces with iron molybdates at which oxygen exchange takes place. The other phase occurs in excess and does not participate in catalysis.

Phase composition of multicomponent catalysts for the oxidation of propylene to acrolein

Catalyst	Phase composition	Before the reaction			After the reaction		
		d, Å	I, %	I_2, %	d', Å	I_1, %	I_3, %
$Co_8Mo_9Fe_3Bi_{0.75}O_x$	α-$CoMoO_4$	3.130	55	21	3.134	55	21
	β-$CoMoO_4$	3.356	100	39	3.358	100	38
	$Fe_2(MoO_4)_3$	3.857	38	14	3.860	39	13
	$Bi_2O_3 \cdot MoO_3$	3.167	35	15	3.171	40	15
	MoO_3	3.805	30	11	3.811	34	13
$Co_8Mo_{10}Fe_3Bi_{0.75}O_x$	α-$CoMoO_4$	3.128	62	23	3.143	67	25
	β-$CoMoO_4$	3.368	100	37	3.373	100	37
	$Fe_2(MoO_4)_3$	3.870	32	12	3.870	38	14
	$Bi_2O_3 \cdot 2MoO_3$	3.178	52	19	3.173	39	15
	MoO_3	3.818	28	9	3.824	24	9
$Co_8Mo_{11}Fe_3Bi_{0.75}O_x$	α-$CoMoO_4$	3.127	79	27	3.145	54	22
	β-$CoMoO_4$	3.358	100	34	3.373	100	42
	$Fe_2(MoO_4)_3$	3.867	38	13	3.877	31	13
	$Bi_2O_3 \cdot MoO_3$	3.169	48	17	3.182	32	14
	$Bi_2O_3 \cdot 2MoO_3$	–	–	–	–	–	–
	MoO_3	3.831	25	9	3.831	25	10
$Co_8Mo_{12}Fe_3Bi_{0.75}O_x$	α-$CoMoO_4$	3.125	78	25	3.143	48	19
	β-$CoMoO_4$	3.358	100	31	3.378	100	41
	$Fe_2(MoO_4)_3$	3.863	60	19	3.877	41	17
	$Bi_2O_3 \cdot 3MoO_3$	3.180	55	17	3.195	35	14
	MoO_3	3.776	25	8	3.834	24	9
$Co_8Mo_{13}Fe_3Bi_{0.75}O_x$	α-$CoMoO_4$	3.132	57	22	3.143	42	18
	β-$CoMoO_4$	3.361	100	39	3.376	100	44
	$Fe_2(MoO_4)_3$	3.853	35	14	3.880	31	14
	$Bi_2O_3 \cdot 3MoO_3$	3.178	39	15	3.195	28	13
	MoO_3	3.818	26	10	3.837	24	11
$Co_8Mo_{15}Fe_3Bi_{0.75}O_x$	α-$CoMoO_4$	3.127	55	19	3.127	76	23
	β-$CoMoO_4$	3.361	100	35	3.361	100	30
	$Fe_2(MoO_4)_3$	3.870	45	16	3.857	64	19
	$Bi_2O_3 \cdot 3MoO_3$	3.182	49	17	3.184	57	17
	MoO_3	3.798	34	13	3.811	33	11
$Co_8Mo_{12}Fe_3Bi_{0.75}O_x$ + Sb, K	α-$CoMoO_4$	3.140	39	17	3.153	39	17
	β-$CoMoO_4$	3.358	100	43	3.376	100	47
	$Fe_2(MoO_4)_3$	3.857	34	15	3.880	28	13
	$Bi_2O_3 \cdot MoO_3$	3.171	31	13	3.189	25	12
	$Bi_2O_3 \cdot 3MoO_3$	–	–	–	–	–	–
	MoO_3	3.808	29	12	3.837	24	11
$Co_8Mo_{12}Fe_3O_x$	α-$CoMoO_4$	3.136	45	20	3.130	35	17
	β-$CoMoO_4$	3.366	100	45	3.356	100	49
	$Fe_2(MoO_4)_3$	3.870	46	21	3.853	35	17
	MoO_3	3.821	33	14	3.814	35	17
$Co_8Mo_{12}Bi_{0.75}O_x$	α-$CoMoO_4$	3.123	62	26	3.125	51	23
	β-$CoMoO_4$	3.356	100	40	3.356	100	44
	$Bi_2O_3 \cdot 3MoO_3$	3.178	48	20	3.180	43	19
	MoO_3	3.795	33	14	3.808	32	14

Note: d and d' are the main lines before and after operation under reaction conditions, respectively; I and I_1 are the intensities of main lines with reference to the line intensity of β-$CoMoO_4$ before and after the reaction, respectively; I_2 and I_3 are the intensities of lines with reference to the total intensity before and after the reaction, respectively.

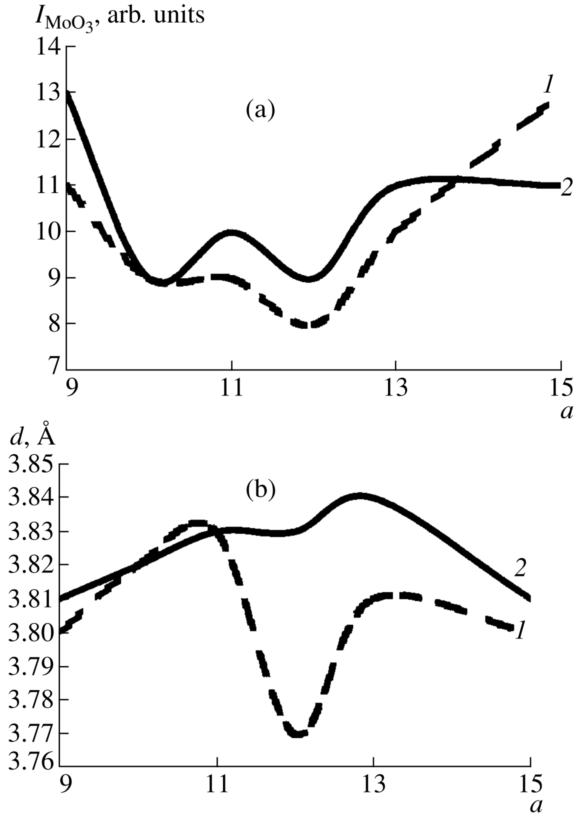

Fig. 2. Dependence of (a) the line intensities of the MoO_3 phase and (b) the interplanar spacing d in MoO_3 on the molybdenum content a of the $Co_8Mo_aFe_3Bi_{0.75}O_x$ catalyst (*1*) before and (*2*) after the reaction.

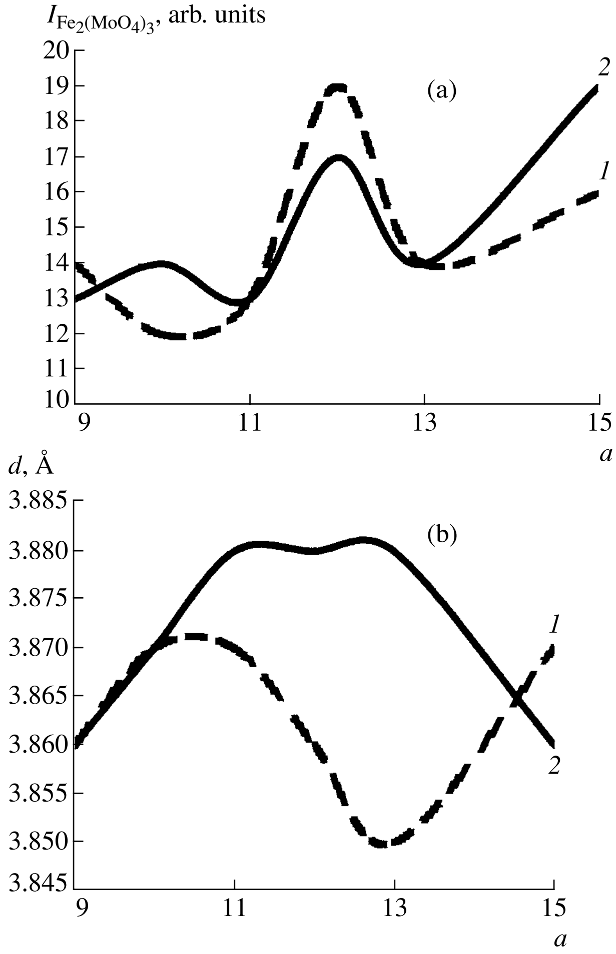

Fig. 3. Dependence of (a) the line intensities of the $Fe_2(MoO_4)_3$ phase and (b) the interplanar spacing d in $Fe_2(MoO_4)_3$ on the molybdenum content a of the $Co_8Mo_aFe_3Bi_{0.75}O_x$ catalyst (*1*) before and (*2*) after the reaction.

The total concentration of α-$CoMoO_4$ + β-$CoMoO_4$ did not significantly change depending on the amount of molybdenum in the catalyst, except the Mo_{15} system, in which the above value decreased. This may suggest that $CoMoO_4$ does not interact with MoO_3 or $Bi_2O_3 \cdot MoO_3$. However, $CoMoO_4$ is redistributed between the α and β phases. In the course of operation, the concentration of the β-$CoMoO_4$ phase with tetrahedrally coordinated molybdenum increased. The Mo_{11}–Mo_{12} systems exhibited the greatest changes: the concentration of the α phase before and after the reaction exhibited a maximum and a minimum, respectively. This can be explained by the interaction of β-$CoMoO_4$ with isomorphic β-$FeMoO_4$. It is likely that, under conditions of the redox process

$$\alpha\text{-}CoMoO_4 + Fe_2(MoO_4)_3$$
$$\rightleftharpoons \beta\text{-}CoMoO_4 + 2\beta\text{-}FeMoO_4 + MoO_3 + 1/2O_2$$

the total spectrum of Co and Fe β-molybdates changed. Consequently, a decrease in the concentration of α-$CoMoO_4$ in the region of Mo_{11}–Mo_{12} means an increase in the total concentration of β-$CoMoO_4$ + β-$FeMoO_4$. The value of d for β-$CoMoO_4$ before operation changed only slightly depending on the concentration of molybdenum (3.356–3.378 Å), whereas it passed through a maximum after the reaction in the Mo_{11}–Mo_{12} systems (3.378 Å). According to published data, the value of d for β-$FeMoO_4$ is 3.40 Å.

The concentration of $Fe_2(MoO_4)_3$ changed only slightly with molybdenum concentration both before and after operation. The maximum change (increase) was observed in the Mo_{12} system (Fig. 3a), that is, in a maximum of activity. A considerable increase in the value of d was observed under conditions of catalysis (see Fig. 3b). It is believed that a defect phase of $Fe_2(MoO_4)_3$ is formed in this case. Previously, we detected this phase in a multiphase catalyst by Mössbauer spectroscopy [9]. A small amount of bismuth can enter into the lattice of this phase under reaction conditions.

For this reason, in the case of bismuth molybdates, a small decrease in their concentration was observed after the reaction. The lattice parameter increased with the concentration of molybdenum; this increase was most significant after operation. This can be explained by a transition from $Bi_2O_3 \cdot MoO_3$ (d = 3.15–3.17 Å) to $Bi_2O_3 \cdot 2MoO_3$ (d = 3.17–3.18 Å) and further to $Bi_2O_3 \cdot 3MoO_3$ (d = 3.18–3.195 Å). A transition between $Bi_2O_3 \cdot 2MoO_3$ and $Bi_2O_3 \cdot 3MoO_3$ occurs at a composition that corresponds to the most active catalyst, near Mo_{12}. It is likely that these phase transitions are of importance for catalysis, because the reaction

$$Bi_2(MoO_4)_3 \rightleftharpoons Bi_2O_3 \cdot 2MoO_3 + MoO_3$$

results in the formation of interfaces between MoO_3 and bismuth molybdates or, in other words, active centers for the catalytic reaction.

Bismuth molybdates can also interact with iron molybdate by the reaction

$$3Bi_2(MoO_4)_3 + Fe_2(MoO_4)_3 \rightleftharpoons 2Bi_3FeMo_2O_{12} + 8MoO_3$$

to form the ternary compound $Bi_3FeMo_2O_{12}$ with d = 3.18 Å. This compound was detected in a study of a multiphase catalyst for the partial oxidation of isobutylene to methacrolein [1]. It is unclear why this compound was not detected in this work. It was difficult to determine the crystal structure of the ternary compound in this work because the main lines of $Bi_3FeMo_2O_{12}$ (d = 3.18, 3.14, and 3.15 Å) and other Bi and Co molybdates [5] occurred in the same region of reflection angles. It is likely that the formation of this compound can be attributed to the fact that the precalcination temperatures (550–600°C) in the previous study [1] were higher than those in this work (480–500°C). We noted [2] that, in accordance with published data [10], the individual catalytic activity of ternary compounds is insufficient to explain the high activity and selectivity of a complex catalyst.

In general, a multicomponent catalyst containing Sb and K is similar to the Mo_{12} system in term of its properties; however, the intensity (concentration) of a β-$CoMoO_4$ or α-$CoMoO_4$ phase was even higher or lower, respectively. It is evident that the presence of K and Sb in a complex catalyst is favorable for the above phase transitions, which are effective for the formation of an active and selective catalyst.

An increased concentration of α-$CoMoO_4$ was characteristic of a bismuth-free catalyst (hence, the concentrations of β-$CoMoO_4$ and β-$FeMoO_4$ were decreased). The lattice parameter of phases changed only slightly; this is indicative of a weak interaction of bismuth molybdate with other phases.

An increased concentration of MoO_3 and α-$CoMoO_4$ at a reduced lattice parameter was characteristic of an iron-free catalyst. It is likely that MoO_3 in this catalyst is a ballast component that is ineffective for catalysis.

CONCLUSIONS

This study provided support to our conclusions drawn previously [2] and allowed us to refine the roles of individual phases in a complex Co–Mo–Fe–Bi–Sb–K–O catalyst for the partial oxidation of propylene to acrolein. Of the two α and β cobalt molybdate phases, the β-$CoMoO_4$ phase participates in catalysis. The main role of this phase consists in the development of a common catalyst framework and in a shift of equilibrium between oxidized and reduced iron molybdates toward β-$FeMoO_4$. This iron molybdate, on the one hand, forms an interface with MoO_3, at which oxygen is activated, and, on the other hand, comes into contact with the $Fe_2(MoO_4)_3$ phase (and forms this phase), which transfers this oxygen to bismuth molybdates for the interaction with propylene. Bismuth molybdates not only activate propylene but also participate in phase transformations to facilitate the formation of an interface between MoO_3 and iron molybdates. MoO_3 is formed as two phases, a more oxidized phase and a more reduced phase. The former phase participates in the formation of active centers, and the latter phase is a ballast component that is ineffective (or even harmful) in catalysis.

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