Kinetics and Catalysis, Vol. 46, No. 4, 2005, pp. 535–544. Translated from Kinetika i Kataliz, Vol. 46, No. 4, 2005, pp. 569–579.
Original Russian Text Copyright © 2005 by Udalova, Shashkin, Shibanova, Krylov.

Action of Co–Mo–Bi–Fe–Sb–K Catalysts in the Partial Oxidation of Propylene to Acrolein: 1. The Composition Dependence of Activity and Selectivity

O. V. Udalova, D. P. Shashkin, M. D. Shibanova, and O. V. Krylov

Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, 117977 Russia

Received December 25, 2003

Abstract—The role of various components of a multiphase oxide catalytic system in the partial oxidation of propylene to acrolein is investigated. Catalytic activity is studied for the $Co_{6-8}Mo_{12}Fe_{2-3}Bi_{0.5-0.75}Sb_{0.1}K_{0.1}O_x$ catalyst, which is taken to be the reference, and for catalysts in which the amount of some component is progressively reduced down to zero. The results obtained provide insights into the role of the components of the catalyst. $CoMoO_4$ forms the structural framework of the catalyst. Iron molybdate can be stabilized on $CoMoO_4$ as β-phase. As its content is increased, the catalyst gains activity but its selectivity declines. Bismuth molybdate is responsible for the selectivity of the process. When present in small amounts, MoO_3 raises the selectivity, binds free oxides, and converts reduced molybdates into their oxidized forms. Excess molybdenum trioxide causes a dramatic fall in the catalytic activity. Potassium and antimony decrease the catalytic activity, but even small amounts of these elements raise the selectivity of the catalyst. Chromium can substitute for iron atoms in the multicomponent catalyst. Ni, Mn, and Mg substitute for Fe in iron molybdate to decrease the catalytic activity.

The most active and selective catalysts for the partial oxidation of olefins to unsaturated aldehydes and acids are multicomponent, generally molybdate-containing systems [1, 2]. The catalytic properties of bismuth molybdates in the partial oxidation and oxidative ammonolysis of olefins were discovered by Sohio Co. At present, the widest industrial use is found for oxide catalysts containing Ni, Co, Fe, Mg, K, and necessarily Bi and Mo [3]. The fundamental advantages offered by these multicomponent catalysts are a low percentage of bismuth (an expensive element), a high propylene conversion (up to 98%), a high acrolein yield (up to 90%), and a low optimal process temperature (330–350°C).

Although the phase composition of multicomponent molybdate catalysts has been the subject of numerous studies, the source of their high activity and selectivity is not known with certainty. The surface of these catalysts was considered as an $MMoO_4$ framework (M = Co, Ni, Mg, or Mn) covered with iron molybdate and an overlying layer of bismuth molybdate [4]. An *in situ* structural study demonstrated that the proportion of tetrahedrally coordinated Mo is correlated with the acrolein selectivity of propylene oxidation [5]. According to *in situ* Raman and IR spectroscopy data [6], the main phases of these catalysts, including α-$CoMoO_4$, $Fe_2(MoO_4)_3$, and bismuth molybdate, undergo transformations during the reaction. A band at 790 cm^{-1}, which is characteristic of β-$FeMoO_4$, appears in the spectrum, indicating that the catalyst undergoes reduction. Furthermore, the compound $Bi_nFe_mCo_pO$ forms upon long-term use of the catalyst.

The hypothesis that active bismuth molybdate exists on the surface of molybdate catalysts [4] is confirmed by the finding that $Bi_2Mo_3O_{12}/TiO_2$ affords 100% selectivity towards the oxidative dehydrogenation of butylene even when its supported phase is monolayer-thin [7]. By contrast, only deep oxidation takes place on unsupported α-$Bi_2Mo_3O_{12}$.

Researchers from the Institute of Chemical Physics (Russian Academy of Sciences, Moscow), based on X-ray powder diffraction and Mössbauer spectroscopic data [8], suggested a model for a partial propylene oxidation catalyst having the composition $Co_{6-8}Mo_{12}Fe_{0.5}O_{45}$ and consisting of β-$CoMoO_4$, $Fe_2(MoO_4)_3$, β-$FeMoO_4$, α-$Bi_2(MoO_4)_3$, β-$Bi_2O_3 \cdot 2MoO_3$, and MoO_3 phases. It is assumed that the reaction takes place at the iron molybdate/bismuth molybdate interface, because this is the place where the exchange of oxygen atoms and electrons is energetically most favorable. The oxygen and olefin activation sites are separated: dioxygen undergoes dissociative adsorption on $FeMoO_4$, and the resulting oxygen atoms diffuse to olefin activation sites. A very defective iron(III) molybdate phase forms under catalytic conditions. It serves to transport oxygen from β-$FeMoO_4$, which adsorbs dioxygen, to $Bi_2(MoO_4)_3$, which adsorbs propylene. Thus, different phases of this multicomponent system catalyze different steps of the process. MoO_3 is supposed to serve as a buffer. β-$CoMoO_4$ stabilizes β-$FeMoO_4$ owing to the coherence of their lattices.

A mechanical mixture of (α + β)-$CoMoO_4$ and MoO_3 produces a synergetic effect on the acrolein yield in propylene oxidation. Likewise, a mixture of $CoMoO_4$ and $Bi_2O_3 \cdot 2MoO_3$ exerts a synergetic effect on the CO_2 yield [9, 10]. Changing the order of these phases on the catalyst grain demonstrated that $CoMoO_4$ generates free (probably allyl) radicals, which leave the surface to carry out deep oxidation in the gas phase. Modifying the molybdate phase, e.g., with molybdenum trioxide leads to a dramatic reduction in the CO and CO_2 yields, indicating a decrease in the number of sites generating free radicals.

Synergetic effects of phases in multicomponent partial oxidation catalysts were also observed by other researchers. Catalytic activity in partial propylene oxidation was found to decrease in the following order: $CoMoO_4 + Bi_2Mo_3O_{12} + Fe_2Mo_3O_{12} > CoMoO_4 + Fe_2Mo_3O_{12} > CoMoO_4 + Bi_2Mo_3O_{12}$. A similar trend was reported in [12]. It was found in that study that the Bi–Mo–O phase coats $Fe_2(MoO_4)_3$ and $CoMoO_4$ particles and, in agreement with our results [8], iron molybdate serves to transfer oxygen and electrons.

An $Fe_xCo_{1-x}MoO_y$ solid solution mixed with $Bi_2Mo_3O_{12}$ is reported to form in Fe–Co–Bi–Mo–O catalysts [13]. In this solid solution, Fe^{3+} undergoes reduction to Fe^{2+}. At a high Fe content, excess iron molybdate appears and α-$FeMoO_4$ transforms into β-$FeMoO_4$. The simultaneous presence of Co and Bi stabilizes the active ion couple Fe^{3+}/Fe^{2+} at the interface.

According to Malakhov *et al.* [14], the action of the $Ni_{2.4}Co_{4.4}Fe_{2.9}Bi_{1.0}P_{0.57}K_{0.03}Mo_{12.3}$ oxide catalyst supported on SiO_2 is determined by the properties of one or a few phases combining all of the functions of an effective catalyst. Possible active phases are β-molybdates of divalent metals (Co, Ni, Fe) modified with all major elements, for example, cobalt molybdate modified with bismuth and iron oxides.

Modifiers affect the formation of new phases, increase the proportion of interfacial regions with a certain structure, and promote the growth of molybdate microcrystals in such a way that faces active in partial oxidation are in large excess [15]. Furthermore, modifiers can change the acid–base properties of the catalyst and the rate of electron and oxygen transfer. For example, addition of MoO_3 to $CoMoO_4$ increases the propylene selectivity of the latter [16]. Alkali metals reduce the acidity of the catalyst, thereby favoring olefin adsorption and product desorption. This is also true for propylene oxidation on $MnMoO_4$ [17, 18]. Pure manganese molybdate is a deep oxidation catalyst, but an MoO_3 addition makes it active and selective in partial oxidation. It is believed that MoO_3 inserts its oxygen into the hydrocarbon oxidized and $MnMoO_4$ gives O atoms for reoxidation by a spillover mechanism [19].

The $NiMoO_4 + MoO_3$ system was studied as a catalyst for the partial oxidation of C_3 and C_4 hydrocarbons [20–22]. Pure $NiMoO_4$ and MoO_3 show a low activity and a low selectivity. The selectivity of the mixed catalyst grows as the MoO_3 content increases up to $MoO_3/(MoO_3 + NiMoO_4) = 0.25$. The increase in selectivity is explained by MoO_3 blocking deep oxidation sites in $NiMoO_4$.

Alkali metals (Li, Na, K, Cs) added to a molybdate catalyst apparently do not form any new molybdate phases [23]. It was demonstrated that alkali metal atoms occupy dodecahedral holes in the $Fe_2(MoO_4)_3$ lattice, thereby increasing the reduction rate of the catalyst [24]. Cesium does not increase the capacity of $NiMoO_4$ for reduction [25].

Many authors consider the acrolein selectivity of a catalyst to be directly related to the diffusion rate of lattice oxygen. It is believed that the higher the concentration of defects the freer the ion diffusion. The behavior of oxygen was studied in a variety of multicomponent catalysts [26], and no correlation was observed between the diffusion rate of oxygen ions and the acrolein selectivity of the catalyst. Among the simple molybdates, the most selective are those in which the diffusion rate of lattice oxygen is the lowest [27].

Lattice oxygen, O^{2-}, is generally considered to be the active form of oxygen that is responsible for soft oxidation. For example, it was demonstrated that up to several hundreds of lattice oxygen layers may be taken out in the reduction of pure bismuth molybdate phases with a hydrocarbon [28]. On passing from bismuth molybdate to more complex, multiphase systems, lattice oxygen may become less significant than adsorbed oxygen [25]. Both electrophilic oxygen (O^-, O_2^-, and O_2^{2-}) and nucleophilic oxygen (O^{2-}) are readily adsorbed by the catalyst surface, and the latter is hardly distinguishable from lattice oxygen. Nucleophilic oxygen apparently plays a significant role in the selective oxidation of olefins.

Most of the above data refer to catalysts for propylene oxidation to acrolein. Similar findings were reported for the oxidation of isobutylene to methacrolein [29], the oxidation of butene-1 to maleic anhydride [21], the oxidative dehydrogenation of propane [22], and the oxidative dehydrogenation of *n*-butane into butenes [30].

The high activity and selectivity of the multiphase systems and the synergism of phases have been explained in the literature in the following ways:

(1) Two phases react to yield a more complex, more active, and more selective phase.

(2) The composite reaction involves a number of catalyst phases, each step being catalyzed by a particular phase.

(3) Catalyst phases do not interact chemically. They interact indirectly through gas-phase diffusion (spillover) or atom or ion transport through one of the solid phases.

(4) The active sites in the multiphase system are qualitatively the same as in the original single-phase catalyst, but their number depends on the modifiers added.

Note that these hypotheses are not necessarily conflicting.

Most of the data characterizing the composition dependence of the activity and selectivity of oxide catalysts refer to two-, three-, and four-component systems. The data concerning more complex systems are obviously scarce. The purpose of our study was to elucidate the path of action of the six-component catalytic system Co–Mo–Bi–Fe–Sb–K in the partial oxidation of propylene to acrolein. Here, we report the composition dependence of the activity and selectivity of this system.

EXPERIMENTAL

The catalytic partial oxidation of propylene was studied using a laboratory-scale setup including a quartz flow reactor 120 mm in length and 12 mm in diameter. A catalyst bed (1.5 cm^3, 1.02–1.12 g) was placed onto the reactor grid, and the free volume was filled with broken quartz. The reaction was carried out either on small pellets of size 0.5–1.0 mm or on large pellets of size ~5 mm. The catalyst temperature was measured with a Chromel–Copel thermocouple placed in a well 5 mm in diameter. The accuracy of temperature measurements was ±2 K. Furnace temperature was maintained using a temperature controller fitted with a Chromel–Copel thermocouple. The test temperature was 330°C unless otherwise specified, and the contact time was 3 s. Propylene and air were fed into a mixer. The resulting mixture (usually containing 5% propylene) was passed through a bubbler for saturation with water vapor and was then fed into the reactor. The reactor outlet was connected to a sampling and analysis system, which was arranged inside a chromatographic oven to prevent the condensation of reactants over 1 h.

The catalyst, in contact with a flowing reaction mixture, was heated to a preset temperature. Flow rates were controlled with metering valves and were measured with rheometers. After the prescribed regime was established (which usually took 1 h), the original mixture was sampled to ascertain that its composition was stable.

The kinetics of propylene and isobutylene oxidation on a multicomponent molybdate catalyst identical to ours were studied in earlier works [31, 32]. It was demonstrated that, at 290–360°C, the acrolein and methacrolein selectivities are still high and change little as the substrate conversion increases from 0 to 80%. This circumstance facilitates the analysis of data obtained at different conversions.

The chromatographic analysis was carried out on a Tsvet-100 chromatograph. The flow rate of the carrier gas (helium) was 50 cm^3/min. The analytical system included two thermal-conductivity detectors and a flame-ionization detector placed in parallel. The aldehydes and ketones resulting from the reaction were separated in a Teflon column of length 0.4 m and diameter 5 mm packed with Porapak Q (Anspec Company) and thermostated at 135°C. This column was connected to the flame-ionization detector. O_2, N_2, and CO were separated at 70°C in a stainless steel column of length 2 m and diameter 3 mm packed with a molecular sieve (Linde) pre-heat-treated at 300°C. This column was connected to a thermal-conductivity detector operating at a filament current of 200 mA. Carbon dioxide was detected using a column of length 1 m and diameter 3 mm packed with macroporous silica gel (Porasil) and thermostated at 30°C. Since samples for these analyses were taken separately, a trapping column with silica gel was placed upstream of the molecular sieve column to protect the latter from water, aldehydes, and ketones. The trapping column was occasionally regenerated. The accuracy of chromatographic analysis was ±1–2%.

The chromatograph was calibrated by absolute methods, except for acrolein, which is very volatile and prone to polymerization. For acrolein calibration, the reactor was charged with a catalyst selectively converting propylene into acrolein and the exit gas was analyzed. The volume of acrolein in the product mixture was derived from the amount of reacted propylene and was correlated with the corresponding chromatographic peak. As applied to acrolein, this calibration method is much more accurate than the absolute method. The peaks of acids were calibrated using aqueous solutions with known acid concentrations. The amount of water was determined by weighing the condensate collected from the product flow at the oven outlet over a certain time. Conversion (X), selectivity (S), and product yield (Y) data were rounded off to integers except in specified cases.

The reference catalyst in this study was $Co_{6-8}Mo_{12}Fe_{2-3}Bi_{0.5-0.75}Sb_{0.1}K_{0.1}O_x$, which shows a high activity and acrolein selectivity at 320–340°C. Hereafter, it is called IKhF-80. It was obtained using two solutions. To prepare the first solution, KNO_3 was added to a 2% tartaric acid solution in water and the mixture was stirred until all of the salt was dissolved. The resulting solution was brought to a boil, and Sb_2O_3 was added in small portions under continuous stirring. After the Sb_2O_3 was dissolved, the mixture was cooled to 40–50°C and iron, cobalt, and bismuth nitrates were added. Each new salt was added after the complete dissolution of the previous salt. The second solution was prepared by dissolving ammonium molybdate in water preheated to 70–80°C. The mixture was stirred up to the complete dissolution of the salt and was cooled to 25–30°C. For coprecipitation, the solution of the Sb, K, Fe, Co, and Bi salts was added to the ammonium molybdate solution. The mixture was stirred for 20–25 min to obtain a homogeneous suspension. The suspension was dried at 120–150°C for 5 h with intermediate stirrings. The dry material was ground to a particle size of ≤8 mm and heat-treated in a muffle furnace at 350°C for 1.5–2 h, until the evolution of nitrogen oxides ceased. The resulting substance was powdered, and aerosil-175 (10%) and water (20% of the weight of the solid) were

Table 1. Steady-state data for propylene oxidation at the optimum temperature T on catalysts based on various molybdate matrices

No.	Catalyst	T, °C	$X_{C_3H_6}$, %	Y_{acr}, %	S_{acr}, %	S_{sp}, m^2/g
1	$Co_6Mo_{12}Bi_{0.5}Fe_2K_{0.4}O_x$	350	72	64	88	3.0
2	$Ni_6Mo_{12}Bi_{0.5}Fe_2K_{0.4}O_x$	300	59	45	76	15
3	$Mg_6Mo_{12}Bi_{0.5}Fe_2K_{0.4}O_x$	380	32	29	93	1.8
4	$Mn_6Mo_{12}Bi_{0.5}Fe_2K_{0.4}O_x$	300	5	1.5	30	4.0
5	$Zn_6Mo_{12}Bi_{0.5}Fe_2K_{0.4}O_x$	280–490	0–0.6	0	0	0.9
6	$Cu_6Mo_{12}Bi_{0.5}Fe_2K_{0.4}O_x$	340–480	1–13	0	0	1.2

Note: $X_{C_3H_6}$ is propylene conversion, S_{acr} is acrolein selectivity, Y_{acr} is acrolein yield, and S_{sp} is specific surface area.

added. The mixture was stirred for 30 min to obtain a plastic paste, which was then extruded through a die with an orifice diameter of 4–6 mm. The extrudate was held in air for 30–40 min and cut into pellets. The pellets were dried in air at room temperature for 5–6 h and in a drying oven at 120–150°C for 2–3 h. Finally, they were calcined in a muffle furnace at 480–500°C for 2 h.

Furthermore, we tested catalysts in which one or several components were missing and the proportions of the other components were the same as in IKhF-80. In the preparation of catalysts containing equal amounts of antimony and potassium, these elements were introduced in another way, using a double salt of K and Sb.

Specific surface area was determined by the BET method from argon desorption data with an accuracy of ±20%.

RESULTS

The catalysts most active and selective in partial propylene oxidation are multicomponent scheelites with an $MMoO_4$ (M = Co, Ni, Mg, or Mn) framework. Other active components may be distributed in the $MMoO_4$ matrix. These molybdates can exist as two different phases. The high-temperature phase is β type, in which Mo has a tetrahedral coordination sphere. The low-temperature phase is α-$MnMoO_4$ type, in which Mo has an octahedral coordination sphere. The tetrahedral form of $MMoO_4$ is usually more active than the octahedral form.

In order to study the effect of the $MMoO_4$ matrix (main phase), we examined two groups of $M_6Mo_{12}Bi_{0.5}Fe_2K_{0.4}O_x$ catalysts (Table 1). In the first group, M was Co, Ni, Mg, or Mn; in the second, M was Cu or Zn. The groups are distinguished by the coordination sphere of the divalent cation M, while Mo is in a tetrahedral environment in both of them. The four catalysts of the first group have an α-$MnMoO_4$-type structure, with M in an octahedral environment. The two catalysts of the second group have an α-$ZnMoO_4$-type structure in which Zn or Cu cations occupy sites of three different types, namely, two octahedral and one tetragonal pyramidal. The data presented in Table 1 demonstrate that the first four catalysts are active in the allylic oxidation of propylene, the optimum temperature being 300–380°C, while the last two catalysts are inactive. Note that the freshly prepared magnesium catalyst is as active as the cobalt catalyst; however, it loses activity as it works.

Of the catalysts examined, the catalyst with the Co–Mo matrix is the most active and selective. This catalyst was selected to be modified with small amounts of various divalent metals (M). Activity and selectivity data for the modified catalysts are listed in Table 2.

Table 2. Oxidation of propylene to acrolein on $Co_6Mo_{12}Bi_{0.5}Fe_2M_{0.4}K_{0.4}O_x$ catalysts (M^{2+} is the modifying ion)

M^{2+}	T, °C	$X_{C_3H_6}$, %	Y_{acr}, %	S_{acr}, %	S_{sp}, m^2/g
No modifier	360	66	64	97	3.0
Ni	280–380	21–50	19–49	92–98	2.8
Mg	280–380	30–50	28–49	93–97	3.4
Mn	280–380	35–69	19–51	54–75	0.6
Zn	280–380	20–40	20–38	39–95	1.8
Cu	280–380	17–60	14–59	85–99	3.4

As is clear from the data presented in Table 2, the admixtures examined decrease the acrolein yield attainable with the original catalyst. According to X-ray diffraction data, M^{2+} ions only increase the β/α phase ratio in cobalt molybdate and do not generate any new phases. Because their molybdates are isostructural to cobalt molybdate, they are incorporated in the cobalt molybdate structure, as was also demonstrated in an earlier study [33].

Aerosil increases the specific surface area of the catalyst and, accordingly, catalytic activity per unit weight. Table 3 presents the catalytic properties of systems containing 10 wt % aerosil and equal amounts of Mn and K ions. Raising the K content in proportion to the Mn content is necessary to reduce the acidity induced by Mn^{2+} ions. The acidifying effect of manganese is due to Mn^{2+} ions passing to higher oxidation states under the action of oxygen and elevated temperatures. Introduction of K together with Mn has the most favorable effect on the selectivity of the catalyst.

In order to understand how the properties of the multicomponent catalyst depend on the MoO_3 content, we prepared two series of catalysts based on the Co–Mo–Bi–Fe–K system. In Table 4, we list activity and selectivity data for catalysts in which the amount of Co^{2+} is varied relative to the amounts of the other components. Passing from Co_4 to Co_8 reduces the amount of excess MoO_3. It is clear from Table 4 that catalytic activity grows with increasing Co^{2+} content (i.e., with decreasing amount of excess MoO_3). The selectivity of both catalysts is high. It was demonstrated by special experiments that further raising the Co^{2+} content dramatically decreases the activity of the catalyst.

In the other catalyst series (Table 5), we varied the Mo content at a fixed Co content. We list, in Table 5, selectivity data not only for acrolein (S_{Acr}) but also for acrylic acid (S_{HAcr}), carbon monoxide ($S_{\mathrm{CO}} = (Y_{\mathrm{CO}}/3)/(Y_{\mathrm{CO}}/3 + Y_{\mathrm{CO_2}}/3 + Y_{\mathrm{Acr}} + Y_{\mathrm{HAcr}})$), and carbon dioxide ($S_{\mathrm{CO_2}} = (Y_{\mathrm{CO_2}}/3)/(Y_{\mathrm{CO_2}}/3 + Y_{\mathrm{CO}} + Y_{\mathrm{Acr}} + Y_{\mathrm{HAcr}})$). The other reaction products are acetic acid (up to 4.5%), acetaldehyde, and small amounts of hydrocarbons. Oxygen conversion ($X_{\mathrm{O_2}}$) data are also listed in Table 5. The reproducibility of each catalytic test is illustrated by data collected in two independent runs. All data are accurate to 0.1%. For comparison, we present activity and selectivity data for Bi- and Fe-free and Sb- and K-containing catalysts.

Figure 1 demonstrates how the acrolein yield and selectivity at 350°C depend on the Mo content of the catalyst. A high catalytic activity (high C_3H_6 and O_2 conversion) are shown by Mo_{11}–Mo_{13} systems. The highest selectivity is observed for the Mo_{12} system, which is similar in composition to the active and selective catalyst IKhF-80. At the same time, the Mo_{12} catalyst is least selective with respect to deep-oxidation products. A still higher acrolein selectivity of about 98% is observed for the six-component catalyst Co–Mo–Bi–Fe–Sb–K–O. After passing through a maximum, the conversion and acrolein yield fall with increasing MoO_3 content, but the acrolein selectivity decreases only slightly. Thus, the correlation established for the first catalyst series (Table 4) is confirmed. Addition of Sb and K increases both the conversion and selectivity. Small amounts of acrylic acid (3–6%) form on all catalysts. The Fe-free catalyst has the drawback of a very low conversion, and the Bi-free catalyst suffers from a very low acrolein selectivity. The highest CO and CO_2 selectivities are observed for the Mo_9 and Mo_{11} catalysts. Removal of the entire Bi and Fe from the catalyst causes a further decrease in activity and selectivity.

Figure 2 plots propylene conversion and acrolein selectivity as a function of iron content (m) for

Table 3. Effect of equal amounts of Mn and K ions on the activity and selectivity of $Co_8Mo_{12}Bi_{0.5}Fe_2Mn_xK_xO_y$ catalysts at 320°C

x	$X_{\mathrm{C_3H_6}}$, %	Y_{acr}, %	S_{acr}, %	S_{sp}, m^2/g
0.1	68	63	92	4.0
0.3	92	78	85	7.0
0.6	65	55	86	5.0

Table 4. Effect of excess MoO_3 on the activity and selectivity of multicomponent catalysts at 320°C

Catalyst	$X_{\mathrm{C_3H_6}}$, %	Y_{acr}, %	S_{acr}, %	S_{sp}, m^2/g
$Co_4Mo_{12}Bi_{0.5}Fe_2K_{0.4}$	62	58	94	3.0
Co_8Mo_{12} $Bi_{0.5}Fe_2K_{0.5}$	85	75	93	7.0

$Co_8Mo_{12}Bi_{0.75}Fe_mSb_{0.15}K_{0.15}O_x$ catalysts. The catalyst with $m = 3$ affords the highest yield of the desired product, retaining a sufficiently high selectivity.

Chromium molybdate, like iron molybdate, is known to have dodecahedral holes that can accommodate potassium ions to change the oxidation and reduction rates of the molybdate ion and to increase the selectivity of the molybdate with respect to partial oxidation products [24]. Figure 3 plots activity and selectivity data as a function of chromium content (n) for $Co_8Mo_{12}Bi_{0.75}Fe_3Sb_{0.15}K_{0.1}Cr_nO_x$ catalysts. Introduction of Cr ions into the catalytic system at a fixed iron content ($m = 3$) affords high acrolein yields of 81% at $n = 0.5$ and 78% at $n = 1$.

Figure 4 plots propylene conversion and acrolein selectivity versus bismuth content for large pellets of the $Co_8Mo_{12}Bi_qSb_{0.3}K_{0.3}O_x$ catalyst containing 10% aerosil ($S_{\mathrm{sp}} = 20$–25 m^2/g). As the bismuth content of the catalyst is increased, the acrolein yield does not change, while the

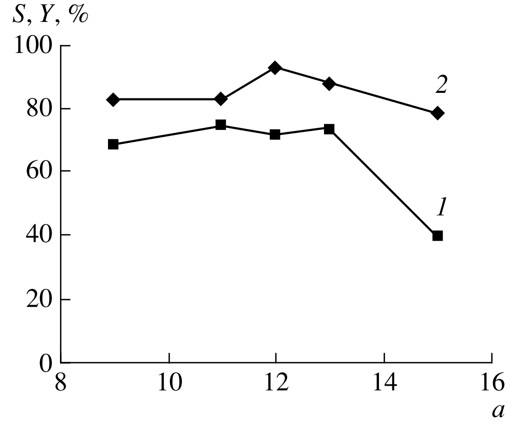

Fig. 1. (*1*) Acrolein yield and (*2*) acrolein selectivity S in propylene oxidation at 330°C as a function of the molybdenum content (a) of the $Co_8Mo_aFe_3Bi_{0.75}O_x$ catalyst.

Table 5. Propylene oxidation on multicomponent catalysts containing various amounts of MoO_3*

Catalyst	T, °C	$X_{C_3H_6}$, %	S_{CO}, %	S_{CO_2}, %	S_{acr}, %	Y_{acr}, %	S_{HAcr}, %	X_{O_2}, %
$Co_8Mo_9Fe_3Bi_{0.75}O_x$	350	84.0	1.5	4.5	83.4	69.9	4.0	35.7
	350	82.9	1.5	4.5	83.2	69.1	3.7	35.7
	330	74.7	1.2	4.0	88.0	65.7	2.8	27.5
	330	73.5	1.2	4.1	88.9	65.4	2.6	27.5
	310	54.7	0.6	2.3	88.8	48.8	1.8	16.7
	310	47.6	0.7	2.7	87.5	41.6	1.3	16.7
	280	20.2	0.0	1.9	81.5	16.4	0.4	6.2
	280	18.3	0.0	2.2	76.3	14.0	0.3	6.2
$Co_8Mo_{11}Fe_3Bi_{0.75}O_x$	350	92.9	1.6	6.3	82.8	76.9	3.9	43.2
	350	93.5	1.6	6.3	76.7	73.6	3.9	43.2
	330	87.0	0.7	2.8	88.0	76.5	2.6	31.2
	330	85.3	0.7	2.9	85.5	72.9	2.2	31.2
	310	64.3	0.3	2.4	82.6	53.1	1.0	20.0
	310	55.3	0.3	2.8	87.8	47.8	0.9	20.0
$Co_8Mo_{12}Fe_3Bi_{0.75}O_x$	350	76.0	0.8	2.1	94.3	71.7	4.3	21.8
	350	76.8	0.8	2.0	92.1	70.7	4.5	21.9
	330	68.5	0.7	2.0	92.5	63.4	3.1	18.7
	330	63.5	0.7	2.1	95.8	61.1	2.7	18.7
	310	37.7	0.5	2.3	91.2	34.4	1.1	7.9
	310	38.5	0.5	2.2	86.6	33.4	1.5	7.9
$Co_8Mo_{13}Fe_3Bi_{0.75}O_x$	350	84.4	1.0	2.6	88.3	74.5	6.4	14.9
	350	84.4	1.0	2.6	87.9	74.2	6.3	14.9
	330	74.2	0.3	2.3	78.7	58.4	3.2	24.9
	330	71.5	0.3	2.4	89.4	63.9	3.3	24.9
	310	52.5	0.2	2.1	82.1	43.1	1.3	14.9
	310	48.8	0.2	2.3	77.5	37.8	1.2	14.9
$Co_8Mo_{15}Fe_3Bi_{0.75}O_x$	350	48.0	0.7	2.8	82.6	39.7	4.3	17.2
	350	48.5	0.7	2.8	76.5	37.1	4.2	17.2
	330	35.8	0.6	2.4	84.3	30.2	2.3	13.7
	330	35.8	0.6	2.4	89.3	32.0	2.3	13.7
	310	23.4	0.6	2.0	79.6	18.6	1.4	8.4
	310	23.3	0.6	2.0	71.6	16.7	1.5	8.4
$Co_8Mo_{12}Fe_3Bi_{0.75}O_x$ + Sb, K	350	87.2	0.1	0.8	96.8	84.3	2.3	24.5
	350	86.7	0.1	0.8	97.5	84.5	1.6	24.5
	330	81.2	0.4	0.8	97.3	79.0	1.5	21.3
	330	81.2	0.3	0.7	98.7	80.1	0.3	21.3
	310	64.8	0.0	0.8	94.2	61.1	2.3	15.2
	310	64.8	0.0	0.8	94.2	61.1	2.3	15.2
	290	31.3	0.0	0.9	94.9	29.7	–	12.2
	290	31.5	0.0	0.9	84.2	26.5	–	12.2
$Co_6Mo_{12}Fe_3O_x$	350	28.1	–	–	29.1	8.0	2.8	16.2
$Co_6Mo_{12}Bi_{0.75}O_x$	350	5.4	–	–	42.1	2.3	2.9	3.3

* The original mixture is 5% propylene + air.

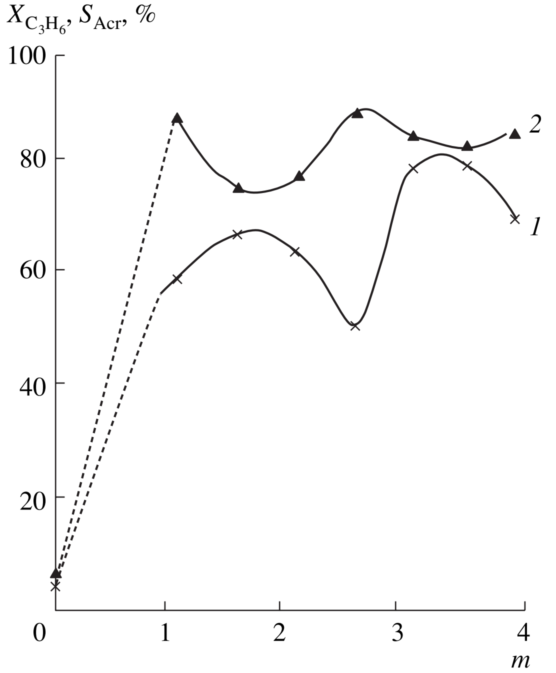

Fig. 2. (*1*) Propylene conversion and (*2*) acrolein selectivity at 330°C as a function of the iron content (*m*) of the $Co_8Mo_{12}Bi_{0.75}Fe_mSb_{0.15}K_{0.15}O_x$ + 10% SiO_2 catalyst.

acrolein selectivity grows to reach 86% at $q = 0.5$ and remains fairly high at larger q values.

Introduction of potassium into the multicomponent system containing coprecipitated Co, Bi, and Fe molybdates alters the redox and acid–base properties of this system. Figure 5 shows the plot of propylene conversion and acrolein selectivity versus potassium ion content for the $Co_8Mo_{12}Bi_{0.75}Fe_3K_yO_x$ (y = 0–0.8) system. As the K ion content is increased, the catalyst loses activity, retaining a rather high selectivity. A potassium addition as small as $y = 0.1$ raises the initial selectivity approximately by 15% through suppression of the deep oxidation reactions. X-ray powder diffraction examination of the resulting catalyst revealed no changes induced by potassium.

Sb(III) ions can substitute for Bi(III) ions in the bismuth molybdate structure. Because the radius of Sb^{3+} (0.9 Å) is smaller than the radius of Bi^{3+} (1.2 Å), antimony ions distort this structure considerably. In turn, this distortion affects the properties of catalysts containing bismuth molybdates. We found that introducing equal amounts of K and Sb has the most favorable effect on the selectivity of the catalyst. This effect is likely to be due to the fact that potassium reduces the antimony-induced acidity of the catalyst. Data characterizing the activity and selectivity of Co–Mo–Fe–Bi catalysts containing equal amounts of K and Sb are presented in Table 6.

Introduction of antimony into the system reduces the initial optimum process temperature (350°C) by 10–20°C, without changing any other process parameters. The activity of the catalyst decreases with increasing Sb and K contents, while its selectivity changes little. It is clear from Table 6 that adding minor amounts of K and Sb results in an active and selective catalyst.

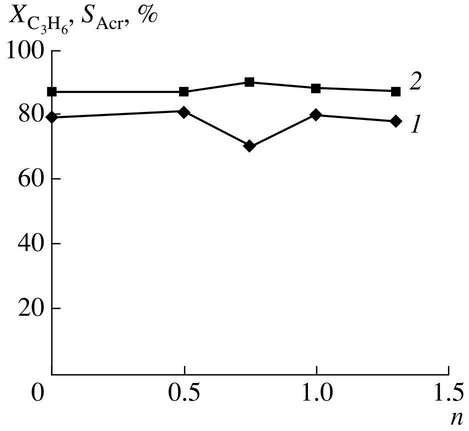

Fig. 3. (*1*) Propylene conversion and (*2*) acrolein selectivity at 330°C as a function of the chromium content (*n*) of the $Co_8Mo_{12}Bi_{0.75}Fe_3Cr_nSb_{0.15}K_{0.15}O_x$ + 10% SiO_2 catalyst.

The main phases of this multicomponent catalyst are much less active than the catalyst itself under the same conditions. Moreover, their activity shows up only starting at 400–440°C. Propylene conversion at 440°C was found to decrease in the order

$$Fe_2(MoO_4)_3(48\%) > CoMoO_4(26\%)$$
$$> Bi_2O_3 \cdot 2MoO_3(6\%) > MoO_3(0.2\%).$$

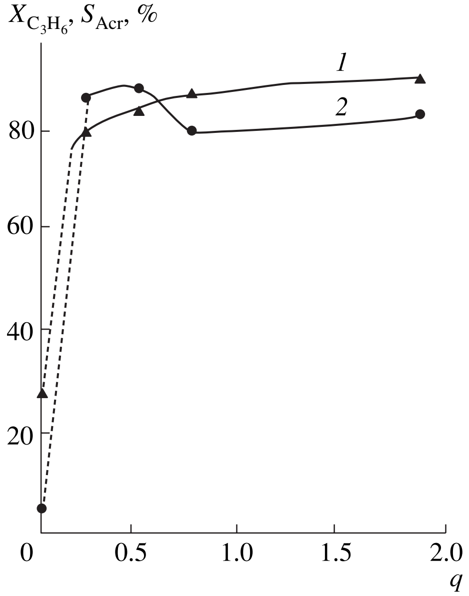

Fig. 4. (*1*) Propylene conversion and (*2*) acrolein selectivity at 330°C as a function of the bismuth content (*q*) of the $Co_8Mo_{12}Bi_qFe_3Sb_{0.3}K_{0.3}O_x$ catalyst.

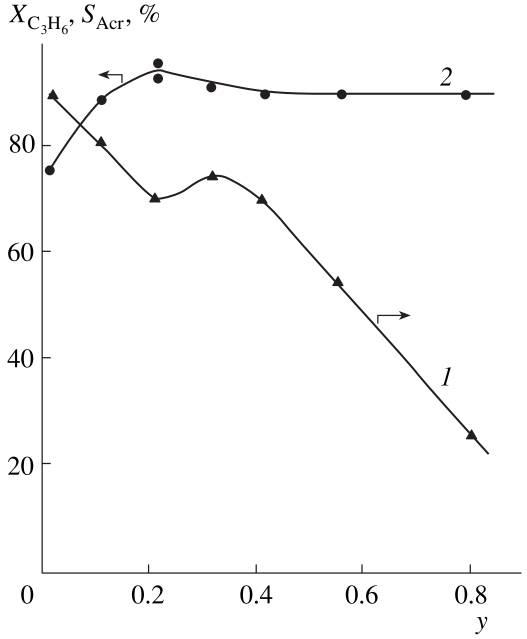

Fig. 5. (*1*) Propylene conversion and (*2*) acrolein selectivity at 330°C as a function of the potassium content (*y*) of the $Co_8Mo_{12}Bi_{0.75}Fe_3K_yO_x$ catalyst.

For acrolein selectivity,

$$Bi_2O_3 \cdot 2MoO_3(100\%) > CoMoO_4(7\%)$$
$$> Fe_2(MoO_4)_3, \quad MoO_3(0\%).$$

For CO_2 + CO yield,

$$Fe_2(MoO_4)_3(48\%) > CoMoO_4(24\%)$$
$$> MoO_3(0.2\%) > Bi_2O_3 \cdot 2MoO_3(0\%).$$

Thus, we confirmed the results of the numerous earlier studies that demonstrated that bismuth molybdate is selective in partial oxidation, iron and cobalt molybdates are active in deep oxidation, and pure MoO_3 shows a low activity and a low selectivity.

We examined potassium-modified pure phases and their mixtures. Very small amounts of potassium (one K^+ ion per 20–120 Mo atoms) were introduced into the structure. Special experiments were performed to determine the phase whose potassium modification is responsible for the changes in the activity and selectivity (Table 7). Minor amounts of potassium did not cause any considerable changes in the specific surface area of the catalyst.

It was found that only the introduction of potassium into bismuth molybdate (β-phase) results in an appreciable increase in the activity along with a slight decrease in the selectivity. Adding K to other phases diminishes their activity only through the suppression of deep oxidation. For example, iron molybdate is an active catalyst for deep oxidation, but it is much less active when modified with potassium. It was demonstrated that alkali metal ions occupy dodecahedral holes in the $Fe_2(MoO_4)_3$ lattice [24], thereby making it difficult to detach more than one oxygen atom from this structure. It was demonstrated in the same work that alkali metal ions increase the reduction rate of multiphase catalysts. Furthermore, alkaline additives reduce the acidity of a number of phases. This affects the aldehyde adsorption capacity of the catalyst and causes aldehyde desorption into the gas phase.

The decrease in the rate of deep oxidation is probably due to the fact that potassium ions change the rate of electron transfer to adsorbed oxygen, thus shortening the lifetime of electrophilic oxygen species. Some mechanical mixtures of K-free components show nonadditive catalytic properties ($CoMoO_4$ + MoO_3, $CoMoO_4$ + $Bi_2O_3 \cdot 2MoO_3$) [9, 10], while no such effect is observed for the same phases modified with potassium.

DISCUSSION

This study supports our model of the multicomponent oxide catalyst for partial oxidation of propylene to acrolein [2, 8]. Furthermore, the second of the hypotheses formulated in the introductory part of the article is valid. An active and selective catalyst must necessarily be multiphase. Among the systems examined here, all pure phases and their simple combinations are less active and less selective than multiphase catalysts. Varying the proportion of a selected component in the optimal catalyst $Co_8Mo_{12}Fe_3Bi_{0.75}Sb_{0.1}K_{0.1}O_x$, we arrived at the following conclusions.

Cobalt molybdenum serves as a matrix (framework) for the formation of the other phases of the multiphase catalyst. Oxygen tetrahedrally coordinated to molybdenum is involved in partial oxidation. Substitution of magnesium and nickel molybdates for cobalt molyb-

Table 6. Oxidation of propylene to acrolein on a Co–Mo–Bi–Fe catalyst modified with K and Sb

Catalyst	T_{opt}, °C	$X_{C_3H_6}$, %	Y_{acr}, %	S_{acr}, %
$Co_8Mo_{12}Bi_{0.75}Fe_3Sb_{0.15}K_{0.15}O_x$	335	81	70	86
$Co_8Mo_{12}Bi_{0.75}Fe_3Sb_{0.3}K_{0.3}O_x$	335	79	68	86
$Co_8Mo_{12}Bi_{0.75}Fe_3Sb_{0.6}K_{0.6}O_x$	330	78	67	86
$Co_8Mo_{12}Bi_{0.75}Fe_3Sb_{0.9}K_{0.9}O_x$	335	53	47	89
$Co_8Mo_{12}Bi_{0.75}Fe_3Sb_{1.2}K_{1.2}O_x$	350	25	22	87

date causes no changes in the acrolein selectivity and decreases the propylene conversion and the stability of the catalyst.

Iron molybdate is active but not selective. Reduced β-$FeMoO_4$ is stabilized on β-$CoMoO_4$, since these phases are coherent. It activates dioxygen by converting it to O^{2-}, and this species enters into the partial oxidation reaction. Part of the iron molybdate stays in the oxidized state as $Fe_2(MoO_4)_3$. Chromium additions act like iron.

Bismuth molybdate is the key component since it makes the partial oxidation reaction selective. Even a catalyst with a very low Bi content is highly selective. This finding supports the opinion of those researchers who believe that bismuth molybdate is located in the surface layer of the multiphase catalyst considered. As the Bi content is raised, the selectivity of the catalyst gradually declines.

The role of MoO_3 in the multiphase catalyst is less clear [1, 2, 8]. Pure molybdenum trioxide is neither active nor selective. As the MoO_3 content of the multiphase catalyst is increased, the acrolein yield and selectivity pass through a maximum. The initial rise of the activity and selectivity can be explained by the fact that buffer MoO_3 binds free oxides and reduced molybdate species, converting them into oxidized species, and thus maintains an appropriate degree of oxidation of the catalyst. After the maximum is passed, free MoO_3 appears, which decreases both the activity and selectivity of the catalyst.

The role of MoO_3 has received little attention in the studies devoted to the catalytic properties of multiphase molybdate systems (see, e.g., [1, 2, 8]). The activity of the above MoO_3-containing multiphase catalysts varies widely. It is likely that the activity of a catalyst is decreased by excess MoO_3 blocking part of the active surface. During the catalytic process, MoO_3 can result from the reactions

$$Fe_2(MoO_4)_3 \longrightarrow 2FeMoO_4 + MoO_3 + 1/2O_2,$$

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

$$Bi_2(MoO_4)_3 + Fe_2(MoO_4)_3$$
$$\longrightarrow Bi_2Fe_2Mo_2O_{12} + 4MoO_3$$

which yield ternary compounds as well. However, it was demonstrated that the activity of these ternary compounds is not very high [29]. Furthermore, MoO_3 sublimation takes place during long-term processes. This increases the formation rates of the products owing to the surface getting free of the low-activity MoO_3. At the same time, MoO_3 will be very active if it is in contact with a phase capabale of giving it lattice oxygen. If this is the case, its catalytic activity will exceed the activity of the β-phase of bismuth molybdate.

An enhanced catalytic activity and selectivity will be shown by MoO_3 in contact with a phase capable of activating gas-phase dioxygen by reducing it, e.g., to O^{2-}. According to the literature, this phase may be Sb_2O_4, $BiPO_4$, or $FeSbO_4$ [34, 35]. In the catalysts considered here, dioxygen can be activated by iron(II) molybdate.

Table 7. Effect of potassium on the catalytic properties of separate phases ($T = 440°C$)

Catalyst	$X_{C_3H_6}$, %	Y_{acr}, %	S_{acr}, %	Y_{CO+CO_2}, %
MoO_3	0.2	0	0	0.2
$(MoO_3)_{12} + K_{0.1}$	0.4	0	0	0.3
$CoMoO_4$	26	1.8	7.0	24
$(CoMoO_4)_6 + K_{0.1}$	1.5	1.2	80	0.1
$Bi_2O_3 \cdot 2MoO_3$	6.0	6.0	100	0
$Bi_2O_3 \cdot 2MoO_3 + K_{0.1}$	15	13	87	2.1
$Fe_2(MoO_4)_3$	48	0	0	48
$Fe_2(MoO_4)_3 + K_{0.1}$	3.0	1.0	33	2.0

As regards modified cobalt molybdate, note that Fe and Bi ions might substitute for molybdenum in the $CoMoO_4$ lattice to yield a ternary compound [29]. However, no such compound was detected in a freshly prepared catalyst. X-ray diffraction revealed a ternary compound only in a catalyst sample that had long worked in a flowing reaction mixture. The formation of this compound is believed to be responsible for the enhancement of catalytic activity during the service of the catalyst [36]. However, it was demonstrated that the catalytic activity of the individual compounds is insufficient to account for the high activity and selectivity of the multicomponent catalyst [37]. Furthermore, reduced iron molybdate in the form of β-$FeMoO_4$ is isostructural to β-$CoMoO_4$; as a consequence, it is readily stabilized by the coherent phase $CoMoO_4$ in the course of the catalytic process and persists even after the propylene flow is turned off. This is confirmed by Mössbauer spectroscopic data for similar systems [8].

A dramatic decrease in catalytic activity caused by potassium and other alkali metals (Li, Na, Cs) has also been observed for other molybdate systems. For example, there have been reports on the effect of sodium on scheelite-type bismuth molybdate (α-phase) catalyzing the oxidative ammonolysis of propylene [38, 39]. It was demonstrated that the double salt $NaBi(MoO_4)_2$ forms in this system. This salt is catalytically active; however, being nonselective, it diminishes the acrylonitrile yield. According to our data, potassium enhances only the activity of $Bi_2O_3 \cdot 2MoO_3$ and reduces the activity of the other phases (Table 7). The marked adverse effect of potassium ions on the activity of the Co–Mo–Bi–Fe system is possibly due to the formation of similar double salts.

The variable-composition compound $Bi_nSb_mFe_pMo_2O_{12}$, in which $n = m = 3$ or 2 and $p = 1$ or 2, was identified by X-ray diffraction and Mössbauer spectroscopy in molybdate catalysts containing Sb and K [29]. It is believed that the active sites of these catalysts are interfaces between $Fe_2(MoO_4)_3$, the variable-composition compound, and β-$CoMoO_4$.

As the potassium content of the catalyst is increased, the catalytic activity falls sharply, while the selectivity remains almost invariable. Potassium located in the surface layer reduces the acidity of the surface, thereby facilitating the desorption of acidic products, including CO_2. According to our data, the introduction of potassium into all phases except bismuth molybdate greatly suppresses deep oxidation.

It is convenient to introduce antimony together with potassium. This ensures compensation of the charges of K^+ and Sb^{3+}. The antimony cation replaces a Bi^{3+} ion, distorting the structure, and can enhance the activity of the catalyst.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 03-03-32228.

REFERENCES

1. Krylov, O.V., *Vestn. Akad. Nauk SSSR*, 1983, no. 1, p. 10.
2. Krylov, O.V., *Kinet. Katal.*, 1999, vol. 40, p. 752.
3. Alkhazov, T.G. and Margolis, L.Ya., *Vysokoselektivnye katalizatory okisleniya uglevodorodov* (Highly Selective Catalysts for Hydrocarbon Oxidation), Moscow: Khimiya, 1988.
4. Matsuura, I. and Wolfs, M.W.I., *J. Catal.*, 1979, vol. 51, p. 174.
5. Che, M., Figueras, F., Forissier, M., *et al.*, *Proc. 6th Int. Cong. on Catalysis*, Amsterdam: Elsevier, 1976, vol. 1, p. 261.
6. Matsuura, I., Mizuno, S., and Hashiba, H., *Polyhedron*, 1986, vol. 5, p. 111.
7. Bhakoo, A., Bond, G., Rees, R.D., *et al.*, *Catal. Lett.*, 1999, vol. 57, p. 55.
8. Krylov, O.V., Maksimov, Yu.V., and Margolis, L.Ya., *J. Catal.*, 1985, vol. 95, p. 289.
9. Isaev, O.V., Udalova, O.V., and Krylov, O.V., *Kinet. Katal.*, 1984, vol. 25, p. 1016.
10. Orel, L.I., Udalova, O.V., Korchak, V.N., *et al.*, *Kinet. Katal.*, 1992, vol. 33, p. 1162.
11. Legendre, O., Jaeger, P., and Brunelle, J.P., *New Developments in Selective Oxidation*, Studies in Surface Science and Catalysis, Ruiz, P. and Delmon, B., Eds., Amsterdam: Elsevier, 1992, vol. 72, p. 1992.
12. Poncellet, H., Miller, I.W.M., Coudurrier, G., *et al.*, *J. Catal.*, 1993, vol. 142, p. 373.
13. Benaichouba, B., Bussiere, P., and Vedrine, J.C., *Appl. Catal.*, 1995, vol. A130, p. 31.
14. Malakhov, V.V., Vlasov, A.A., Boldyreva, N.N., *et al.*, *Kinet. Katal.*, 1996, vol. 37, p. 457.
15. Volta, J.C. and Portaifaix, J.L., *Appl. Catal.*, 1985, vol. 18, p. 1.
16. Andrushkevich, T.V., Popova, G.Ya., Boreskov, G.K., *et al.*, *Kinet. Katal.,* 1976, vol. 19, p. 184.
17. Ozkan, U.S., Smith, M.R., and Driscoll, S.A., *J. Catal.*, 1990, vol. 123, p. 173.
18. Ozcan, U.S., Driscoll, S.A., Zhang, L., and Ault, K.-L., *J. Catal.*, 1992, vol. 124, p. 189.
19. Ozcan, U.S., Smith, M.R., and Driscoll, S.A., *J. Catal.*, 1992, vol. 134, p. 24.
20. Madeira, L.M., Portela, M.F., and Mazzocchia, C., *Catal. Rev.*, 2004, vol. 46, p. 53.
21. Ozcan, U.S. and Schrader, G.L., *J. Catal.*, 1985, vol. 95, p. 120.
22. Barrault, J., Batiot, C., Magaud, L., and Genue, M., *Proc. 3rd World Cong. on Catalytic Oxidation*, Amsterdam: Elsevier, 1997, p. 375.
23. Martin-Arranda, L.M., Portela, M.F., Madeira, L.M., *et al.*, *Appl. Catal.*, 1995, vol. A127, p. 201.
24. Vorob'eva, G.A., *Cand. Sci. (Chem.) Dissertation*, Moscow: Inst. of Chemical Physics, 1985.
25. Madeina, L.M., Portela, M.F., Mazzocchia, C., *et al.*, *Catal. Today*, 1998, vol. 40, p. 229.
26. Moro-Oka, Y., Ueda, W., Tanaka, S., and Ikawa, T., *Proc. 7th Int. Cong. on Catalysis*, Tokyo, 1980, p. B-30.
27. Krenzke, L.D. and Keulks, G.W., *J. Catal.*, 1980, vol. 61, p. 316.
28. Noller, H. and Vinek, H., *J. Mol. Catal.*, 1980, vol. 51, p. 289.
29. Maksimov, Yu.V., Firsova, A.A., Lubentsov, V.Z., *et al.*, *Kinet. Katal.*, 1983, vol. 24, p. 460.
30. Vieira-Soares, A.P., Dimitrov, L.D., Oliveira, M., Portela, M.F., *et al.*, *Proc. 4th World Cong. on Catalytic Oxidation*, Potsdam, 2001, vol. 1, p. 179.
31. Vazhnova, T.G., Korchak, V.N., Timoshenko, V.I., *et al.*, *Kinet. Katal.*, 1986, vol. 26, p. 1378.
32. Korchak, V.N. and Udalova, O.A., *Kinet. Katal.*, 1993, vol. 37, p. 258.
33. Isaev, O.V. and Spiridonov, K.N., in *Khimicheskaya kinetika i kataliz* (Chemical Kinetics and Catalysis), Moscow: Nauka, 1979, p. 153.
34. Jamal, M.El., Forissier, M., Courdurier, G., and Vedrine, J.C., *Proc. 9th Int. Cong. on Catalysis*, Amsterdam: Elsevier, 1988, vol. 4, p. 1617.
35. Delmon, B. and Ruiz, P., *React. Kinet. Catal. Lett.*, 1987, vol. 35, p. 369.
36. Umemura, S., Odan, K., and Asada, S., *Trudy 5-go sovetsko-yaponskogo seminara po katalizu* (Proc. 5th USSR–Japanese Workshop on Catalysis), Tashkent, 1979, p. 63.
37. Lo Jacono, M., Noteman, T.M., and Keulks, G.W., *J. Catal.*, 1979, vol. 40, p. 19.
38. Michalchenko, E.L., Tarasova, D.V., and Nikoro, T.A., *React. Kinet. Catal. Lett.*, 1979, vol. 12, p. 327.
39. Hayakawa, T., Tsunoda, T., Orita, H., *et al.*, *Chem. Commun.*, 1987, vol. 10, p. 780.