JOURNAL OF CATALYSIS 71, 405–410 (1981)

Modification of a Magnesium–Molybdenum Olefin Oxidation Catalyst by Alkali Additives

G. A. VOROB'EVA, B. V. ROZENTULLER, YU. V. MAKSIMOV, M. YU. KUTYREV, AND L. YA. MARGOLIS

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow

Received April 14, 1980; revised October 31, 1980

The effect of alkali elements incorporated into a magnesium–molybdenum system containing iron and bismuth ions on the structure and catalytic activity in isobutylene oxidation to methylacrolein was studied. It was found by Mössbauer spectroscopy and EPR that potassium and cesium ions are capable of rearranging the iron molybdate structure to form a substituted garnet, whereas the lithium and sodium ions exhibit no such effect. The iron ions were found to interact in the modified system. Comparison of data on structure with the catalysis results revealed that the structural rearrangement of iron molybdate in a complex oxide catalyst increases the process selectivity, due to changes in the lattice oxygen state.

INTRODUCTION

Much information has been published on the oxidation of olefins to unsaturated aldehydes on molybdates of various metals (*1*, *2*). The most effective catalysts for propylene and isobutylene oxidation were found to be the multicomponent oxide systems containing magnesium (or cobalt), iron, and bismuth molybdates (*3*). To increase the selectivity of olefin oxidation, alkali metal ions were introduced into the catalysts (*4*).

The alkali metals in oxide catalysts are claimed to alter the surface basicity and thus to act on the rate of propylene and isobutylene conversions (*5*). Taking into account the small concentrations of the species added and the complicated structure of the basic matrix, such a suggestion seems to be very debatable.

The given research consisted in a systematic study of the alkali metal effects on the structure and catalytic activity of a complex magnesium–molybdenum–bismuth–iron catalyst for selective oxidation of isobutylene.

METHODS

The catalysts of a general composition $Mg_6Mo_{12}Bi_{0.5}Fe_{0.75}R\frac{1}{2}x$ (R = Li, Na, K, Cs, and $x = 0.05$–0.04) were prepared by coprecipitation of metal nitrates and of ammonium paramolybdate with subsequent drying and sintering in air at 500°C.

Isobutylene oxidation was studied in a flow gradientless reactor at 300–410°C and contact time 1.5 s with chromatographic analysis of products. The initial gas mixture composition was 6% isobutylene, 20% oxygen, and 74% nitrogen.

It has been shown earlier (*6*) by X-ray phase analysis and GR spectroscopy that the alkali additives change the structure of iron molybdate only, leaving the other components intact. Therefore further study dealt with iron molybdate, using EPR, X-ray photoelectron spectroscopy (XPS), and Mössbauer methods.

The XPS spectra (ESCA) were obtained by a Varian instrument of Type VIEE-15.

The EPR spectra were obtained by an EPR instrument with a 3.2-cm wavelength. The linewidth accuracy was ±5 Oe, that of thermostating ±1°C.

The Mössbauer spectra were obtained at 20°C by an electrodynamic instrument with a ^{57}Co source in chromium. The isomer shifts were referred to the doublet center of sodium nitroprusside.

0021-9517/81/100405-06$02.00/0

The catalyst was restored in a static vacuum apparatus at 400°C after training under vacuum and treating with oxygen at the same temperature.

RESULTS AND DISCUSSION

Figure 1 presents a characteristic Mössbauer spectrum of a magnesium–molybdenum system containing no alkali metal ions. The spectrum exhibited a narrow singlet line due to octahedral coordination of tervalent ion in the garnet structure of iron molybdate (form I). Upon addition of alkali metal ions into the catalyst the intensity and position of certain reflexes of phase 1 suffered a change and there appeared a doublet with parameters characteristic of octahedrally coordinated Fe^{3+} ions in substituted garnets (form II) (Fig. 1b). With increasing alkali metal concentration the singlet component of form I disappeared and only the form II doublet remained (Fig. 1b). Table 1 lists the parameters of GR spectra of iron molybdate of different structures. The alkali metal ions seem to localize in the dodecahedral lattice of iron molybdate (Fig. 2). Depending on the concentration and radius of alkali metal ions in the bulk of the iron molybdate phase, there might be formation of nonstoichiometric garnet clusters

$$\square_3{}^0Fe_2{}^{3+}[M_0{}^{6+}O_4]_3 \overset{+\mathrm{Me}^+}{\Theta\ \ 6} Me_y{}^+\square_{3-y}{}^0Fe_2{}^{3+}[Mo_y{}^{5+}Mo_{1-y}{}^{6+}O_4{}^{2-}]_3,$$

where □ is the vacancy and y is the nonstoichiometry coefficient.

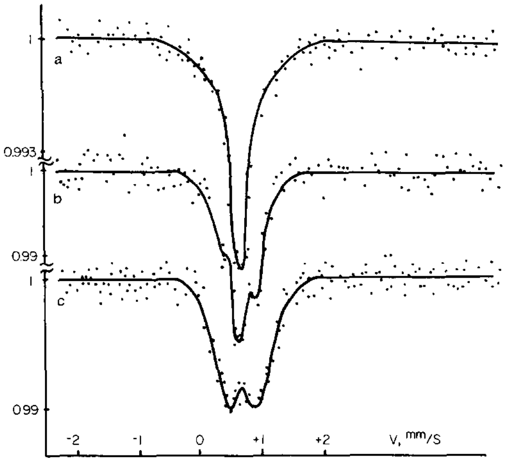


FIG. 1. GR spectrum of a magnesium–molybdenum catalyst. (a) Initial sample $Mg_6Mo_{12}Bi_{0.5}Fe_{0.75}O_x$; (b) $Mg_6Mo_{12}Bi_{0.5}Fe_{0.75}K_{0.1}O_x$; (c) $Mg_6Mo_{12}Bi_{0.5}Fe_{0.75}K_{0.4}O_x$.

Figure 3a presents the dependence of the iron ion fraction in the substituted garnet structure on the potassium ion concentration, obtained from the Mössbauer spectra.

The paramagnetic resonance technique was used to find out the nature of the interaction between iron ions. Since the resonant absorption line increases with temperature, the signal can be assigned to ferromagnetic resonance in garnet ferrites (*6*). The dependence of the linewidth on the K^+ concentration indicates that a more dense packing of iron molybdates occurs within the concentration range $x = 0.1$ to 0.2. A partial broadening of the resonance line by air oxygen indicates that $Fe_2(MoO_4)_3$ is localized in the near-to-surface layer accessible to oxygen.

TABLE 1

The Mössbauer Parameters of Iron Molybdates with Different Structures

Structure	Form of Fe ion	E_1 (mm/sec) (0.03)	ΔE (mm/sec) (0.03)	Coordination of Fe^{3+}
$Fe_2(MoO_4)_3$ garnet	I	0.70	0.15	O
$Me_y{}^+\square_{3-y}Fe_2{}^{3+}[Mo_y{}^{5+}Mo_{1-y}O_4]_3$	II	0.70	0.3–0.4[a]	O

[a] Increases with increasing y.

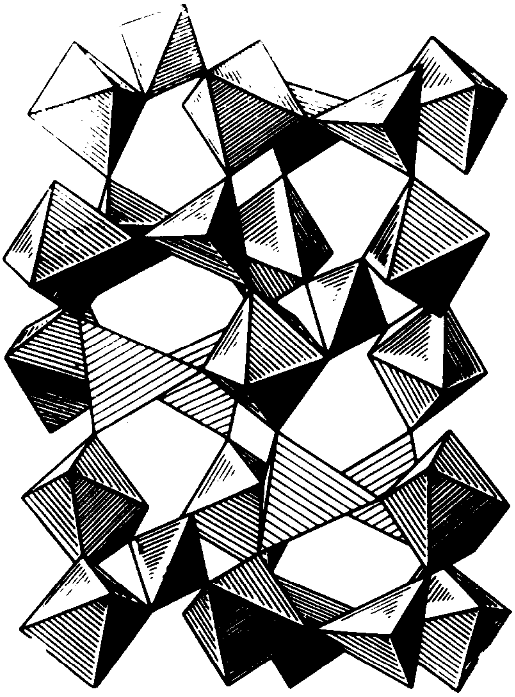


FIG. 2. Garnet structure of iron molybdate.

The ESCA technique was used for study of the surface condition. The additives had no effect on the binding energy of inner-shell electrons of Mg, Mo, and Bi ions. After addition of alkali only the Fe^{3+} ions were found in two forms with a different bond energy of $2P^{3/2}$ electrons. The ratio of these forms as a function of the potassium concentration is presented in Fig. 3c. The maximal ratio was observed for a potassium ion concentration of 0.1. The same figure shows the variations in selectivity of methylacrolein (MA) formation from isobutylene (Fig. 3d). The maximum is seen to correspond to the same concentration of potassium ions.

All the above show that the K^+ ions incorporated into the dodecahedral vacant sublattice of defectuous iron molybdate acquire the structure of substituted garnet, as observed by various spectroscopic methods. The number of dodecahedral vacancies represents one-fourth of the FeO_6 octahedrons. If the iron content in the catalyst is 0.75, complete occupation of all vacancies by potassium ions in this phase will correspond to a K^+ content of 0.15–0.2. Within the same range all curves show a bend and the highest selectivity of MA formation is observed.

Figure 4 presents the results obtained by the abovementioned methods depending upon the ionic radius of the species added. The potassium and cesium ions produce a higher amount of the substituted garnet (found from Mössbauer spectra) with a smaller linewidth of ferromagnetic resonance (Fig. 4) than do the sodium or lithium ions in the same concentration. As known from crystallography, the size of ions capable of occupying the dodecahedral vacancies in garnets is from 0.8 to 1.2 Å for ferrite and silicate systems. However, since the MoO_4 tetrahedron dimension is larger than

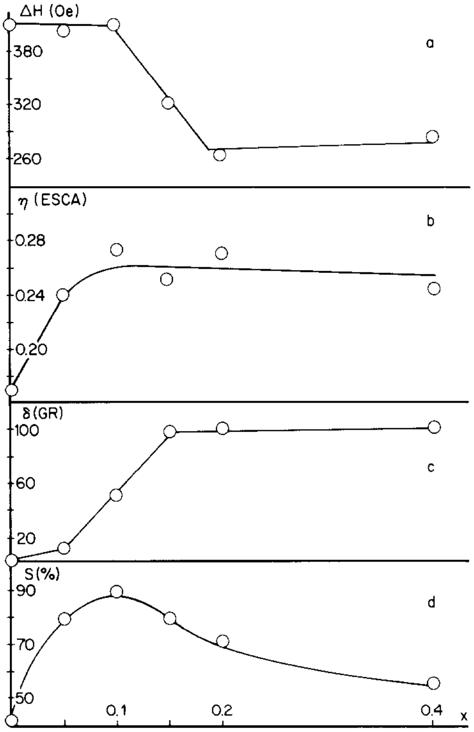


FIG. 3. Dependence of: (a) substituted garnet concentration (GRS data); (b) ferromagnetic resonance linewidth; (c) ratio of two iron forms (ESCA data); (d) selectivity of isobutylene oxidation to methylacrolein at t = 370°C on the potassium ion concentration in the catalyst.

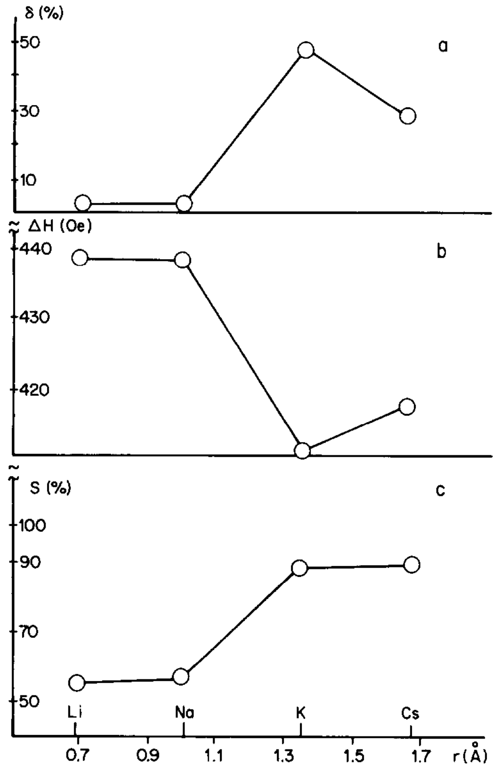


FIG. 4. Dependence of: (a) substituted garnet concentration (GRS data); (b) ferromagnetic resonance linewidth; (c) selectivity of isobutylene oxidation to methylacrolein at 370°C on the radius of alkali metal ions.

those of FeO_4 and SiO_4 the minimal radius is also accordingly larger. Therefore the vacancies are best occupied by K^+ and $C_3{}^+$ ions in small concentrations, and the sodium and lithium ions form no substituted garnet structures. The ferromagnetic resonance theory states that the more perfect the structure is, the narrower the ferromagnetic resonance line (*7*) is and this supports the model described above. It will be seen from Fig. 4a that the formation of a substituted garnet favors the selectivity of MA formation.

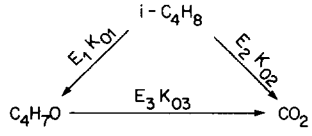
The effect of the substituted garnet structure on the rate of a catalytic reaction is due to the following. The kinetic data indicate unambiguously that for a catalyst containing no substituted garnet the rate of MA formation is independent of the oxygen concentration in the reactant system, and the activation energy of this process is 155 kJ/mole. For a catalyst containing K^+ and Cs^+ ions and, consequently a substituted garnet, the reaction is first order in oxygen and the activation energy is 92 kJ/mole. Table 2 lists the kinetic data for initial and alkali-modified catalysts. The ions added increase the rate of MA formation and decrease the formation of CO_2. Special experiments showed that the rate of MA total oxidation is much faster than direct oxidation of olefins. Comparison of kinetic data leads to the conclusion that the modified catalyst suppresses the parallel pathway of CO_2 formation from isobutylene. This can be due to a change in the interaction both of olefin and of oxygen with the catalyst. However, it was found by programmed thermodesorption that the surface forms and energies of olefins do not change in the presence of the alkali additive. Thus it remains to suggest that the additive ions decrease the amount of active mobile oxygen and thus suppress the parallel reaction path.

To verify this suggestion the rate of the catalyst reduction with hydrogen was studied at the catalysis temperature. The reduction rate was found to drop with increasing radius of the alkali metal ions, similar to the selectivity of MA formation (Fig. 5).

TABLE 2

The Effect of K^+-Ions on the Kinetic Parameters of Isobutylene Oxidation

Catalyst	Formation rate ($W \cdot 10^5$ mole/m² sec)		K_{03}/K_{02}	ΔE^a kJ/mole
	iC_4H_7O	CO_2		
Mg–Mo–Bi–Fe–O	2.8	1.6	10^{-4}	−62.7
Mg–Mo–Bi–Fe–K–O	7.2	0.5	10^2	4.17



[a] $\Delta E = E_3 - E_2$.

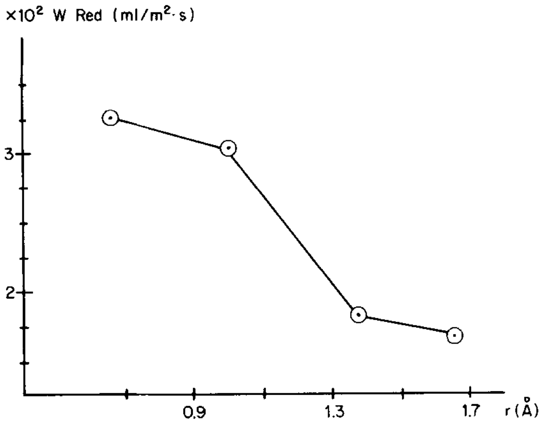


FIG. 5. The rate of catalyst reduction with hydrogen (400°C, 15–20% of monolayer) as a function of the radius of alkali ions.

The addition of a charged alkali species would have to be compensated by the arising negative charges, and this would retain the lattice electroneutrality. Consequently Mo^{5+} and Fe^{2+} ions would have to appear accordingly in the catalyst. However, this was not found experimentally. These charge defects might localize on the interphase and might be screened by surface oxygen. Indeed this oxygen is loosely bound and is removed under vacuum at 100°C. The samples with high content of K and CS exhibit EPR signals due to Mo^{5+} ions ($g_{\perp} = 1.98$, $g_{\parallel} = 1.93$), and at 20 K there appear also signals due to Fe^{2+} in the g-factor range around 4.

After comparing the results obtained by structural methods (ir, uv spectroscopy, X-ray phase analysis) and also by X-ray photospectroscopy with the data on olefin adsorption, surface poisoning, and changes in catalytic activity with the catalyst modification and variations in content, it was suggested that the active centers in such multicomponent systems concentrate at the boundaries between individual crystallites. The transition metal ions in different coordinations existing at such sites increase the probability of electron transitions between the sites, and of active oxygen diffusion.

The catalyst $Mg_6Mo_{12}Bi_{0.5}O_x$ was found to contain three regularly crystallized phases β-$MgMoO_4$, $Bi_2(MoO_4)_3$, MoO_3 (Fig. 6) and also the phase $Fe_2(MoO_4)_3$ forming a defectuous garnet structure (Fig. 2).

The amount of iron ions in the near-to-surface layers of the sample corresponds to the maximal number of adsorption sites and to the amount of ions at the boundary regions (taking into account that the average size of crystallites is 1000 Å) (*8*).

Seemingly, the iron ions (3^+) in the very

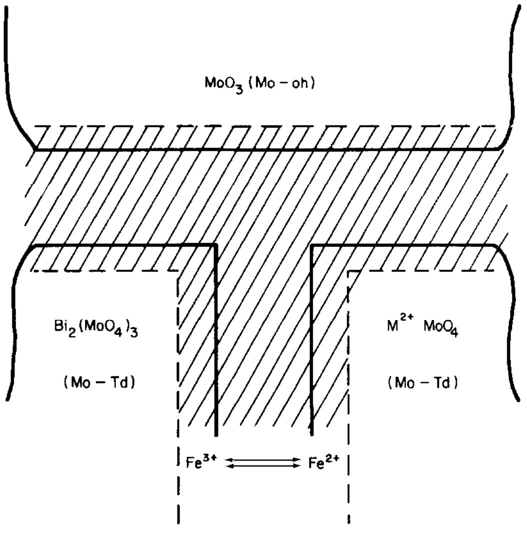


FIG. 6. Interaction model of individual phases in the $M_6^{2+}Mo_{12}Bi_{0.5}Fe_{0.75}O_x$ catalyst.

loose garnet lattice can readily capture electrons in the course of activated propylene and isobutylene adsorption to form a methallyl complex, and then can favor a faster reoxidation of the catalyst with the gas-phase oxygen.

Thus, the results obtained indicate that the alkali ions become incorporated into the iron molybdate structure, occupying a part of the dodecahedral vacancies and increasing the binding strength of the lattice oxygen. This decreases the rate of deep oxidation and increases accordingly the selectivity of isobutylene oxidation to methylacrolein.

ACKNOWLEDGMENTS

The research was carried out at the Institute of Chemical Physics in the Laboratory headed by Yu. G. Borod'ko.

The authors wish to thank T. N. Moravskaya and T. N. Ioffe for the ESCA measurements they carried out.

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