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Exchange of Molecular Oxygen with the Oxygen of Some Metal Molybdates Used as Catalysts for Selective Oxidation

The activities and selectivities of simple metal oxide catalysts in redox reactions have often been correlated with their behavior in gas/solid oxygen exchange (*1–6*). There have been relatively few studies, however, on the more complex oxidation catalysts such as metal molybdates. In view of this, the oxygen exchange on MoO_3 and on Cu, Co, Mn, Ni, Cr, Fe, and Zn normal molybdates has been studied.

For the preparation of the molybdates solutions of metal nitrates and ammonium paramolybdate were used. The suspensions obtained during the precipitation were evaporated and the homogenized dry residues were calcined at 630°C for not less than 30 hr. Manganese molybdate was prepared according to a method described by Trifirò *et al.* (*7*). The high purity of the compounds obtained was confirmed by X-ray analysis, ir spectroscopy, and chemical analysis. BET surface areas determined by krypton adsorption were as follows (m^2 g^{-1}): MoO_3, −0.22; $CuMoO_4$, −0.48; $CoMoO_4$, −0.78; $MnMoO_4$, −0.23; $Fe_2(MoO_4)_3$, −0.42; $NiMoO_4$, −7.0; $Cr_2(MoO_4)_3$, −0.87; $ZnMoO_4$, −0.30.

The kinetic measurements were carried out by the static-circulation method (*8*), the influence of the external as well as the internal diffusion of the gaseous oxygen being eliminated. Fractions of the molybdates with 0.5 to 1 mm grain size were used. The periodic analysis of the gaseous isotopic mixture with an initial concentration of O^{18}–20%at was made with a Hitachi–Perkin–Elmer double focusing mass spectrometer.

The investigations were carried out under the conditions of adsorption equilibrium. The samples were first heat-treated at 630°C for 4 hr in vacuum (10^{-5} Torr) and then at a pressure of 10 Torr for 2 hr in spectroscopically pure oxygen with a natural isotopic composition. The specific rate of exchange was calculated from the equation:

$$R = -\frac{N_g}{(\lambda + 1)S}\frac{\ln H}{\tau} \qquad (1)$$

where $H = (\alpha - \gamma_0)/(\alpha_0 - \gamma_0)$, α_0 is the initial concentration of O^{18}, α is the concentration of O^{18} at time τ, and γ_0 is the equilibrium concentration of O^{18}. $\lambda = N_g/N_s$, where N_s is the number of exchangeable oxygen atoms in the molybdate sample and N_g is the number of oxygen atoms in the gaseous phase. S is the surface area of the sample in cm^2, R is the rate of exchange per unit surface area, in atoms $0/cm^2$-sec, and τ is the time of exchange (sec).

Figure 1 shows typical kinetic results for Cu, Mn, Fe molybdates and for MoO_3. The linear dependence of lg H on the time of exchange, τ, which was also observed for the other compounds studied, confirms the adherence to Eq. (1). It also shows that the surface oxygen in the molybdates studied behaves as energetically uniform with respect to the exchange. A linearity at

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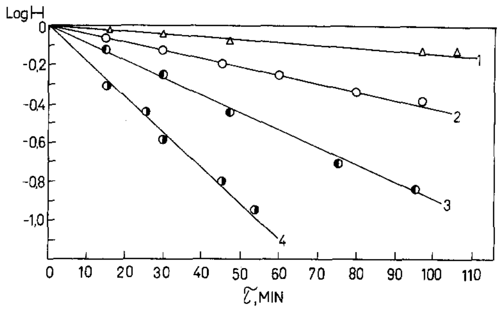

FIG. 1. Kinetic isotherms of the exchange of molecular oxygen with the oxygen of metal molybdates: (1) $CuMoO_4$ (522°C); (2) $MnMoO_4$ (573°C); (3) $Fe_2(MoO_4)_3$ (580°C); (4) MoO_3 (600°C).

degrees of exchange exceeding one monolayer of oxygen can be regarded as an indication for a rapid self-diffusion of oxygen in the molybdates under consideration. Occasional departure from linearity was observed, most noticeably with $CuMoO_4$ preheated above 750°C. As is known, however, this compound undergoes a measurable eutectoid decomposition to CuO and MoO_3 in this temperature region (*9*).

The temperature dependence of the specific rates of exchange is shown in Fig. 2.

Table 1 lists the activation energies E_e with results for simple oxides (*2*) for comparison. E_e for the simple oxides varies between 16 and 40 kcal mol^{-1} whereas the spread of E_e for the molybdates is much narrower, viz. 14 kcal mol^{-1}, or only 7 kcal mol^{-1} if the result for $CuMoO_4$, which has rather low thermal stability (*9*), is excepted.

Figure 3 shows a comparison of the specific rate of exchange of molecular oxygen with the molybdates (at 600°C) and with the simple oxides (at 300°C).

This shows the striking result that whereas the rates range over 5 orders of magnitude for the simple oxides, they lie within the narrow limits of one order of magnitude for the corresponding molybdates.

Evidently, the properties of the molybdates cannot be inferred from the properties of the simple oxides. While the specific rate of exchange, for instance, of molecular oxygen with the oxygen of cobaltous–cobaltic oxide is higher by several orders of magnitude than that for ferric oxide, with the corresponding molybdates the difference is negligible and even in favor of the ferric molybdate.

A general characteristic of the molybdates studied is that the reactivity of oxygen in the surface layer is very close to the reactivity of oxygen in the surface layer of MoO_3 and is influenced to a smaller extent by the presence of bivalent of trivalent cations of the second metal.

The investigations carried out up to now show a more general trend, namely, that the reactivity of oxygen in complex oxide catalysts, which can be regarded as consisting of two oxides, usually approaches the oxygen reactivity of the oxide forming the anionic component. Thus the reactivity is close to that of oxygen in MoO_3 in the case of molybdates, to that of V_2O_5 in the case of vanadates, etc.

The role of the oxygen reactivity and of the strength and type of the oxygen bonds in transition metal molybdates with respect to their properties as oxidation catalysts has been the subject of numerous discussions (*10–16*).

TABLE 1

Comparison between the Activation Energies of Exchange of Molecular Oxygen with the Oxygen of Metal Molybdates (E_e) and the Activation Energies of Exchange in Molecular Oxygen on the Corresponding Oxides (E^*_e)

Compound	E_e (kcal mol^{-1})	Compound	E^*_e (2) (kcal mol^{-1})
$CoMoO_4$	54	Co_3O_4	16
$MnMoO_4$	55	MnO_2	22
$NiMoO_4$	53	NiO	24
$CuMoO_4$	41	CuO	26
$Fe_2(MoO_4)_3$	52	Fe_2O_3	33
$Cr_2(MoO_4)_3$	53	Cr_2O_3	42
$ZnMoO_4$	48	ZnO	40

According to current views, there is a correlation between the rate and the activation energy of exchange of molecular oxygen with the oxygen of oxide catalysts and their activity and selectivity in a large group of reactions proceeding according to a redox mechanism (*1, 2, 4, 6*). As was shown in previous papers of ours (*4, 17*) in the cases of weakly bound and highly reactive oxygen in the surface layer of the catalysts the oxidation process leads mainly to products of complete oxidation. With lower reactivity of the surface oxygen, partial oxidation with an appropriate rate is more probable.

The values found for the activation energy and the rate of oxygen isotopic exchange permit the assumption that all of the molybdates studied will possess a low catalytic activity with respect to reactions of complete oxidation. They possess surface oxygen with a relatively low reactivity and thus satisfy a necessary condition for the heterogeneous selective oxidation for a series of reactions. It should be noted, however, that the selectivity with respect to a given reaction should also depend on the specific activation of the molecule to be oxidized, and on the surface acidity.

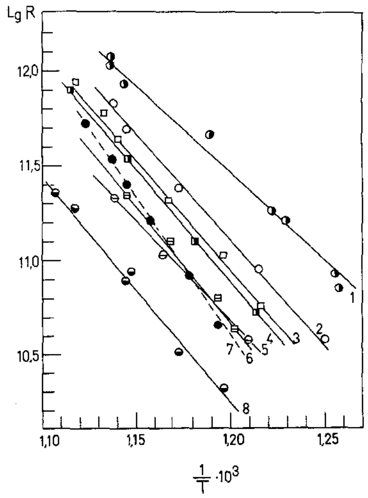

FIG. 2. Temperature dependence of the rate of exchange *R*: (1) $CuMoO_4$; (2) $Fe_2(MoO_4)_3$; (3) $MnMoO_4$; (4) $Cr_2(MoO_4)_3$; (5) $ZnMoO_4$; (6) $CoMoO_4$; (7) MoO_3; (8) $NiMoO_4$.

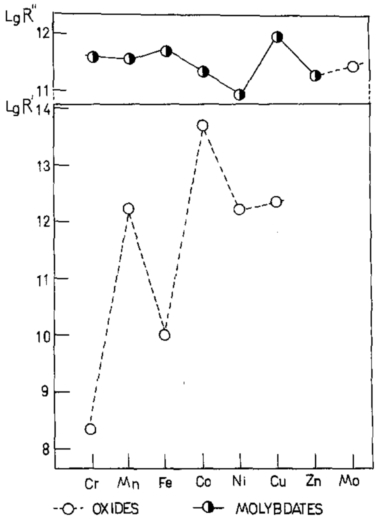

FIG. 3. Specific rates of exchange of molecular oxygen with the oxygen of metal oxides *R'*, in molecules $O_2/cm^2\cdot sec$ (300°C, P_{O_2} = 10 Torr) and with the oxygen of metal molybdates *R''* (600°C, P_{O_2} = 10 Torr) in atoms $O/m^2\cdot sec$.

The results of the present study have demonstrated relatively narrow limits of variation of the reactivity of surface oxygen in the molybdates studied. This fact shows the possibility of preparation of new selective catalysts by modification or combination of some transition metal molybdates which have not had wide application up to now, such as manganese, chromium, copper, and zinc molybdates.

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