reached with less water added to Catalyst B (containing a smaller number of active sites) than to Catalyst A. Once the critical pressure was reached every additional amount of water would cause hydration, were the active sites exactly identical. It was therefore possible to estimate the upper limit of number of active sites contained in each catalyst by calculating the amount of water necessary to reduce the original activity to zero, had the decrement of activity been equal to that of the maximum slope of the activity in the region of hydration. For a stoichiometry of 1:1 this value proved to be 30 μmole of active sites per gram of Catalyst A (i.e., 10% of the chromium content) and 8 μmole per gram of Catalyst B. These estimates were consistent with Ermakov's results (*3*) of 4 μmole of active sites per gram of catalyst, considering the higher polymerization temperatures he had to use in order to obtain similar reaction rates.

Similarly the oxidation of the catalyst by oxygen might also be preceded by adsorption, both processes resulting in deactivation. In that case the inception of oxidation occurred with smaller portions of added oxygen than added water and could not clearly be distinguished by inspection of Fig. 1. Such a hypothesis would find support from the previously published observations (*5*) that on addition of small amounts of oxygen the increase in the ESR signal, indicating oxidation to Cr^V was slight but increased considerably on further additions of oxygen.

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X-Ray Diffraction Studies of Mixed Oxide Catalysts

The importance of surface configuration in catalysis is recognized. The possibility of correlating surface catalysis with readily obtainable data such as lattice spacings in the solid has not been fully explored. To this end an X-ray diffraction (XRD) apparatus which allows measurements to be made under reaction conditions has been set up in our laboratory (*1*). Preliminary studies have indicated a possible relation between catalytic properties and XRD data (*1–3*). The work reported here represents qualitative studies of a large family of catalysts, the aim being to generalize on the relation of XRD data to catalytic properties.

The isomorphic family of compounds containing the molybdates, tungstates, and vanadates has been investigated. These catalysts have attracted considerable attention in the past due to their effectiveness in the selective oxidation of hydrocarbons. Detailed studies have determined the kinetics of catalytic oxidation (*4*), and postulated the reaction intermediate and the nature of the catalytic site (*5*) in one member of this family, bismuth molybdate. These studies do not, however, permit an *a priori* prediction of catalytic utility based on physical measurements on the catalyst. Our work is designed to test this possibility.

We here report on studies of phases and changes in phases of oxidation catalysts composed of binary mixtures of the oxides of Bi, Sb, Mo, W, and V, all of these binary compounds having successfully exhibited selective oxidation catalysis (*6*). The mixed oxide catalysts were prepared by mechanically mixing two from the group made up of bismuth nitrate, antimony oxalate, and ammonium paramolybdate, paratungstate, or metavanadate. The mixture was dehydrated, calcined at 525°C for about 20 hr, ground in a ball mill, and recalcined at 525°C for 20 hr. The sample to be analyzed was ground to pass a 297-μ mesh.

Spectra were taken in the standard XRD *in situ* configuration described previously (*3*). The Cu $K\alpha$ line was used. Spectra were first run in air at room temperature to investigate the formation of new phases. The samples were then heated to 500°C and subjected to a flow of propylene (Matheson CP) of 75 cc/min. After 5 min, the sample was quenched by rapidly reducing the temperature to 25°C and a scan of the XRD spectrum begun.

The dominant XRD peaks for the various unreacted mixed oxides are shown in Fig. 1. We have concentrated on the range of diffraction angles 22–36° 2θ (4.04–2.50 Å), these corresponding to oxygen–oxygen spacings in the lattice (*7*). Of the 18 samples observed, 11 indicated the formation of new phases (see Table 1). New phases have been reported in the literature in binary combinations represented by all of these 11 except Sb/W. Our *d*-spacing assignments agree with published values for Bi/Mo (*8*), Bi/W (*9*), and Bi/V (*10*). They disagree with published values on V/Mo (*11*) and Sb/V (*10*). The discrepancy is probably due to differing methods of preparation, previous work in our laboratory (*1*) and elsewhere (*12, 13*) indicating conclusively that this parameter is critical to the XRD spectrum.

As is indicated in Table 1, new crystalline phases are inconsequential in the mixtures Sb/Mo, Mo/W, and V/W using our method of preparation. A substantial amorphous phase, however, is indicated by the absence of the complete XRD pattern for both single oxides.

TABLE 1
SUMMARY OF PHASES OBSERVED

No new phase	New phase	Change in C_3H_6 at 500°C
—	$BiMoO_x$	$BiMoO_x$
—	$Bi_2Mo_3O_x$	$Bi_2Mo_3O_x$
$SbMoO_x$	—	—
$Sb_2Mo_3O_x$	—	—
—	$VMoO_x$	$VMoO_x$
$V_3Mo_2O_x$	—	$V_3Mo_2O_x$
$V_3Mo_4O_x$	—	$V_3Mo_4O_x$
$MoWO_x$	—	—
$Mo_2W_3O_x$	—	—
VWO_x	—	—
—	$SbWO_x$	$SbWO_x$
—	$Sb_2W_3O_x$	—
—	$BiVO_x$	—
—	$Bi_4V_3O_x$	—
—	$SbVO_x$	—
—	$Sb_4V_3O_x$	—
—	$BiWO_x$	—
—	$Bi_2W_3O_x$	—

In an *air–propylene* mixture at 500°C, no changes in the XRD pattern were observed over a period of at least 15 min. This invariance is consistent with a prevalent hypothesis that the surface experiences practically simultaneous oxidation by air and reduction by hydrocarbon (*14*). Our experiments with *propylene alone* should thus give some measure of the reactivity between the surface and the hydrocarbon. We find varying reactivities as determined by the ease with which the XRD pattern changes. Thus, for example, Mo/V compounds undergo changes within 5 min at about 440°C, Bi/Mo only at 500°C or higher, and Bi/W at about 540°C. Furthermore, a number of compounds which show unchanged XRD spectra at 500°C do exhibit discoloration of the particle surface. These include $MoWO_x$, $Sb_2W_3O_x$, $BiVO_x$, and $SbVO_x$. Table 1 indicates those samples which react sufficiently to change the XRD pattern at $\leq$ 500°C in 5 min.

It is unclear whether the initial reaction

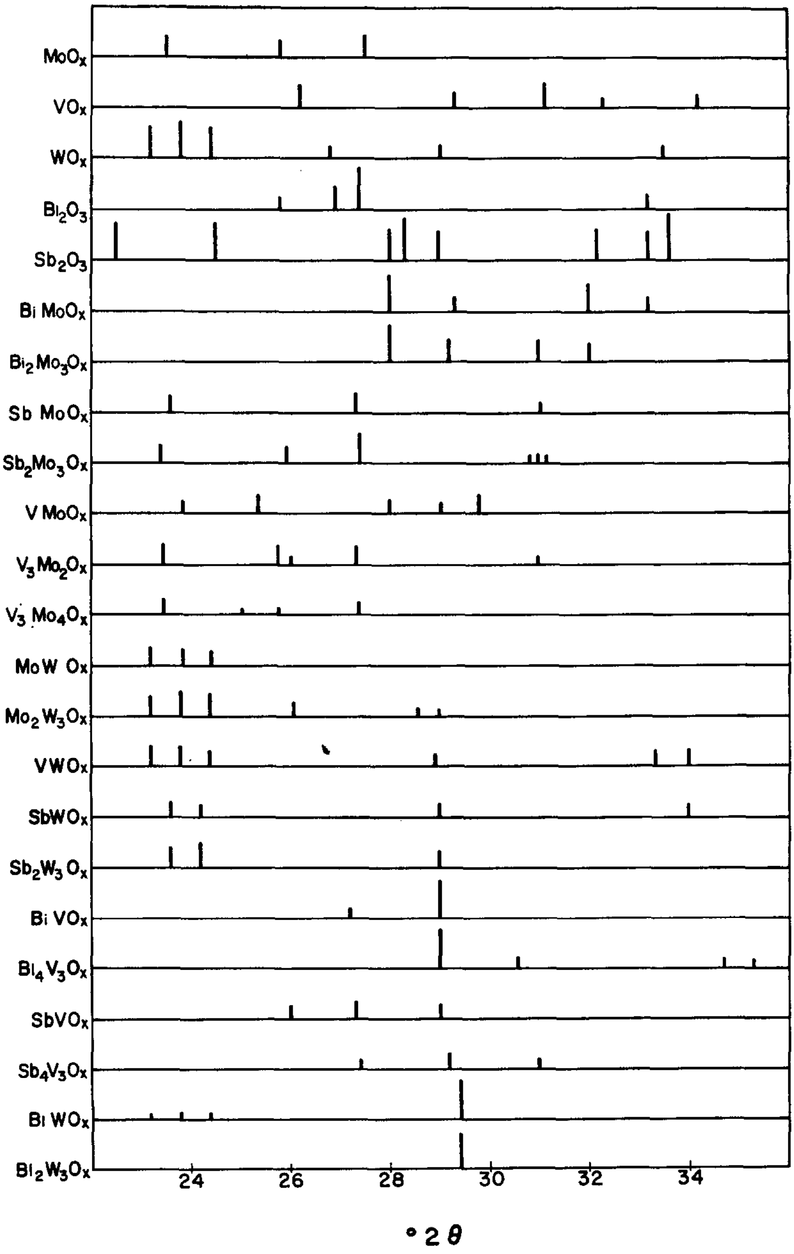

FIG. 1. X-Ray diffraction lines observed at room temperature in air.

starting at the surface is one of reduction of the cation or of the reorganization of defects or dislocations which are typical in this class of compounds (*15*). Reduced species have been identified in the past, and after more severe treatments (i.e., temperature above 550°C) we indeed see both Bi^0 and MoO_2 appearing in the Bi/Mo samples. However, under the mild conditions in these runs, those samples which react exhibit a time-dependent growth and decay of diffraction lines corresponding to no known species. A careful analysis of these lines has not been performed.

The evidence accumulated to date indicates that such an analysis may give little information of import to catalysis. Gorokhovatskii *et al.* have found that the yield in the propylene-to-acrolein reaction is virtually independent of the phase relations in a $CuO/Cu_2O/Cu^0$ catalyst system (*16*). The data we have reported indicate that crystal structure alone cannot be used as a criterion for the reactivity of the surface with propylene. For example, we find that of the six species investigated which react readily with propylene at $\leq 500°C$, four contain a new phase and two do not. Even within a binary family, variation occurs. All three V/Mo samples react readily with propylene although one exhibits a new phase and two do not. These factors, plus others demonstrated in this work—the dependence of crystal structure on method of preparation and the complicated nature of the *reacted* mixed oxide—make any effort to relate crystal structure and catalytic properties extremely tenuous.

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Catalytic Hydrogen Transfer between Cyclohexane and Benzene

In an effort to establish conditions for the study of hydrogen transfer at catalytic surfaces under conditions of thermodynamic equilibrium, we have found that the reaction

$$^*C_6H_6(g) + C_6H_{12}(g) \rightarrow C_6H_6(g) + {}^*C_6H_{12}(g) \quad (1)$$

where $^*C$ is an isotopically tagged carbon atom, occurs readily on a variety of catalysts, including transition and nontransition metals, supported and nonsupported.

The experiments were conducted by flowing a mixture of benzene and cyclohexane, containing radioactive benzene, in a stream of purified He over a fixed catalytic bed. The reactor outlet was fractionated by gas chromatography, the fractions collected by freezing at liquid N_2 temperature, and