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Selective Oxidation of Propene Over Bismuth Molybdate Catalysts: The Oxidation of Propene Using ^{18}O Labeled Oxygen and Catalyst

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Using ^{18}O-enriched gaseous oxygen and ^{18}O-enriched bismuth molybdate catalysts, it has been shown that the oxygen atom in the product acrolein is derived from the oxide ions of the catalyst in the early stages of the reaction at low pressures.

INTRODUCTION

Previous work has established that the oxidations of alkenes over bismuth molybdate are selective both in the presence (*1*, *2*) and absence (*3*, *4*) of gas-phase oxygen, although in the latter case the selectivity is maintained at a high level for a shorter period of the reaction. The initial rates of oxidation of butene to butadiene were found by Batist and his co-workers (*4*) to be virtually independent of the presence of oxygen in the gaseous mixtures, and they suggested that the oxidizing species in the system are the oxide ions of the catalyst. Thus gas-phase oxygen merely replenishes the anion vacancies created by reduction of the catalyst surface. This view of the function of gaseous oxygen in these oxidations is supported by measurements of the electrical conductance of bismuth molybdate catalysts in the presence of various reacting mixtures of propene and oxygen (*5*). The conductances could be predicted from separate measurements of the rates of conductance change of the catalyst in appropriate pressures of pure oxygen and pure propene, assuming that the reduction of the catalyst by hydrocarbon and reoxidation by oxygen are independent processes. This redox type of reaction has also been proposed for the ammoxidation of propene over similar catalysts (*6*).

The object of the present work was to provide a further experimental test of the proposed roles of oxide ions and gaseous oxygen in the selective oxidation of propene to acrolein over bismuth molybdate. This test involved the use of ^{18}O-enriched gaseous oxygen (indicated below as $^{18}O_2$) and ^{18}O-enriched catalyst (indicated as ^{18}oxide) to identify the source of the oxygen atom in the product acrolein molecule.

MATERIALS

Propene (C. P. Grade, Cambrian Chemicals) was subjected to three freeze–thaw and outgassing cycles before use. Gaseous acrolein was taken from a reservoir of quinol-stabilized liquid acrolein (AnalaR grade, B.D.H., saturated vapor pressure about 200 Torr at room temperature). $^{16}O_2$ (grade X Spec. Pure oxygen, B.O.C.) was used direct from the bulbs as supplied. ^{18}O-enriched oxygen (henceforth called $^{18}O_2$) was prepared from outgassed enriched water (Fluka A. G.) by electrolysis. The enrichment was such that 27% of the O_2 was present as $^{18}O^{16}O$ and 3.5% as $^{18}O^{18}O$.

The catalyst was basically the UBM 4 catalyst, prepared as described elsewhere

(*7*). It was activated so as to give two different forms. Activation at 500° or 475°C under a pressure of 50 Torr of $^{16}O_2$ for 15 min, followed by evacuation at 10^{-3} Torr for 15 min, yielded a catalyst containing only ^{16}O ions (indicated as ^{16}oxide). Reduction of the catalyst at 500° or 475°C by exposure to 50 Torr of propene for 15 min (*5*), with subsequent reactivation under 50 Torr of $^{18}O_2$, yielded a catalyst with oxide ions enriched in ^{18}O (indicated as ^{18}oxide).

EXPERIMENTAL METHODS

In all the experiments reported, the gas-phase mixture was analyzed continuously by the direct-inlet mass spectrometric method described previously (*8*), with the following modifications. The reaction vessel allowed the gas-phase mixtures to be sampled immediately above the catalyst bed. The connection between the reaction vessel and the spectrometer was heated to 250°C; this was found, by experiment, to minimize the response time of the analytical system. For acrolein the response time is longer than for other species; however, as the *ratios* of masses of each substituted and unsubstituted species is studied the effect of response time is removed.

For the tests on the labeling of the product acrolein (to give mass 58 instead of 56) to be valid, it was necessary to establish that the rates of exchange of (i) O_2 and catalyst oxygen, and (ii) acrolein and catalyst oxygen, were both very slow relative to any observed changes in the ratio $F =$ mass 58/mass 56 in the main test. In the course of the main and the control tests, it also became apparent that mass 58 was produced in small proportions during the oxidation of propene in the absence of ^{18}O, and the labeling results had to be corrected for this "impurity" of mass 58. The main tests then consisted of studies of changes in the ratio F for four combinations of reactants and catalysts, namely,

a. equimolar propene and $^{18}O_2$ with ^{18}oxide catalyst;
b. equimolar propene and $^{16}O_2$ with ^{18}oxide catalyst;
c. equimolar propene and $^{18}O_2$ with ^{16}oxide catalyst;
d. equimolar propene and $^{16}O_2$ with ^{16}oxide catalyst.

RESULTS AND DISCUSSION

Control Experiments

(i) The rate of exchange between gaseous oxygen and oxide ions was examined by exposing 20 Torr of $^{18}O_2$ to ^{16}oxide and continuously monitoring masses 32 and 34. It was found that the concentration of $^{16}O^{18}O$ remained virtually constant for periods greatly exceeding the duration of the main tests. Moreover, regular checks on masses 32 and 34 during the main tests showed that their ratio remained constant, so that propene and the products of its oxidation do not induce the exchange between gaseous O_2 and oxide ions in the catalyst. These results are entirely in keeping with experiments of Winter (*9*), who showed that the exchange between gaseous oxygen and a bismuth molybdate catalyst, of similar composition and surface area to the catalyst used in this work, was very slow in the temperature range 560–610°C with an activation energy of about 56 kcal $mole^{-1}$. Incidentally these results seem to show that a measurably *reversible* chemisorption of gaseous oxygen to give O or O^- or O^{2-} does not occur at these temperatures (475–500°C) on the fully oxidized catalyst, nor during the oxidation reactions, as this should readily produce exchange.

(ii) To test the possibility of exchange between acrolein and oxide ions in the catalyst, 20 Torr of normal acrolein was exposed to ^{18}oxide and the ratio $F =$ mass 58/mass 56 was found to have a finite value which changed only slowly with time. However, a further control using normal acrolein and ^{16}oxide showed that mass 58 was produced and F again slowly increased with time, indicating the formation of some "impurity" of mass 58 by the reactions of the acrolein. Comparison of the

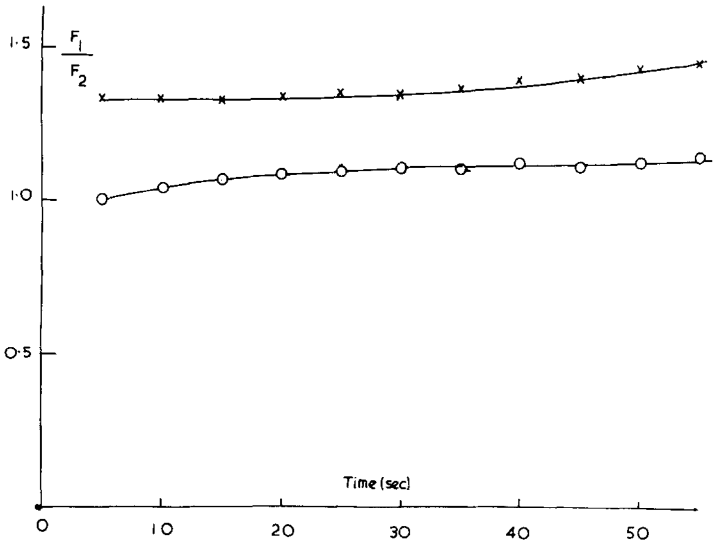

FIG. 1. F_1/F_2 as a function of time for the oxidation of 20 Torr of acrolein over UBM 4: ×, T = 475°C; ○, T = 500°C.

two sets of results for 500°C showed that the ratio of the two F values remained very close to unity over the duration of the experiments (see Fig. 1). This seems to indicate that the ratio 58:56 is not enhanced by the presence of ^{18}O in the oxide, and hence no detectable exchange occurs. The results for 475°C were similar, the ratio of the F values remaining constant but higher than unity. This higher ratio might appear to indicate a very rapid "scrambling" between acrolein and oxide ions, but later results show that the ratio would have to be about 3–5 for scrambling to have occurred.

Oxidation of Propene in ^{18}O-Labeled Systems

The results of the experiments with the four combinations (a) to (d) of labeled oxygen and catalyst are typified by the plots in Fig. 2. These plots were perfectly reproducible. The results with $^{16}O_2$/^{16}oxide demonstrates that, as with acrolein, an "impurity" species of mass 58 is produced in the absence of ^{18}O, and allowance must be made for its presence when ^{18}O is present. Assuming from the reproducibility of the results that it is produced in identical fashion in the presence or absence of ^{18}O,

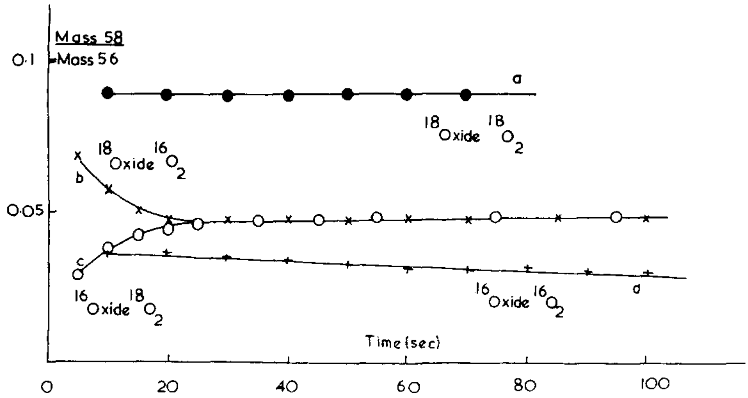

FIG. 2. F as a function of time for mixtures of 20 Torr oxygen and 20 Torr C_3H_6 over UBM 4: T = 500°C.

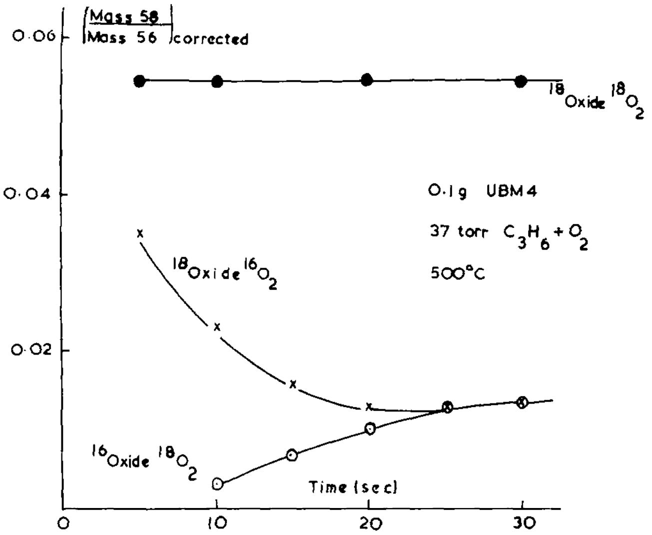

FIG. 3. $F_{\mathrm{corrected}}$ as a function of time for mixtures of 20 Torr oxygen and 20 Torr C_3H_6 over UBM 4: $T = 500°C$.

the impurity F values have been subtracted from each F value for plots (a), (b), and (c) to give the corrected results shown in Fig. 3. Very similar results were obtained at 475°C, as shown in Fig. 4, although the F levels are rather different. The conversion is of course low, being around 2% when the curves coincide at 500° and at 475°C, with a selectivity of 95–100% in both cases.

The crucial point of each diagram is that with curves (b) and (c) the labeling of the product acrolein corresponds in the earliest stages of each reaction to the labeling of the *catalyst oxygen,* and not to the labeling of the *gaseous oxygen.* As the reaction proceeds the F ratio changes in the direction expected if oxide ions are being replaced by gas-phase oxygen. We might expect the F values to trend towards the gas-phase labeling. However, the F values for (b) and (c) reach common levels, independent of initial labeling, which remain nearly constant and different from

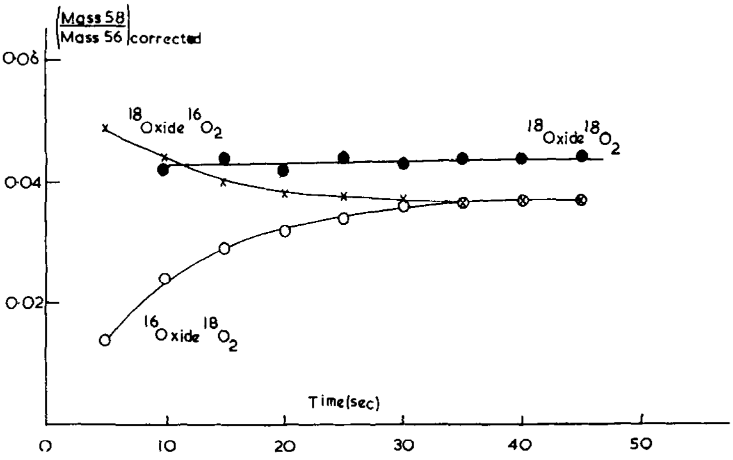

FIG. 4. $F_{\mathrm{corrected}}$ as a function of time for mixtures of 20 Torr oxygen and 20 Torr C_3H_6 over UBM 4: $T = 475°C$.

(a) and (d) for much longer than shown in Figs. 2–4. This would seem to indicate that the oxide ions around the active sites on the catalyst and the gas-phase oxygen scramble in about 30 sec at 500° and 40 sec at 475°C. Nevertheless, as explained previously, the gas-phase oxygen does not appear to be scrambled. Possibly very few active sites are involved; this would account for the absence of appreciable change in $^{16}O^{18}O$, but to scramble the oxide ions around the active sites would apparently require high mobility of oxide ions. Thus the attainment of a common level for F, irrespective of the relative gas-phase composition, remains puzzling. The possibility of scrambling through reactions with product carbon monoxide or carbon dioxide was studied, using pressures of these gases well in excess of the pressures formed in the reaction time. The exchange between carbon monoxide and oxide ions was negligible; that between carbon dioxide and oxide ions was faster, having an apparent first order rate constant of about 1.5×10^{-1} min^{-1} at 500°C with an activation energy of about 11 kcal mole^{-1}, but this is not fast enough to explain scrambling in 30–40 sec. An untested possibility is that the scrambling requires vacant sites which might occur during the oxidation reactions but not with the separate products CO and CO_2, although they would be expected with acrolein, which reduces the surface and produces CO and CO_2. We have not been able to test the exchange between water vapor and oxide ions.

We have not been able to identify the "impurity" formed from propene or acrolein. Propene oxide and acetone are possibilities, and could be formed, in the very small amounts required, in the gas phase or on the catalyst.

In spite of some unexplained features, the results shown in Fig. 3 and 4 do strongly support the view that in these selective oxidations the oxidizing species is the oxide ion in the catalyst, and not gas phase or chemisorbed oxygen.*

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* After this study was completed, Keulks informed us that he had carried out a similar study *(10)*, the results of which are in broad agreement with our own.