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Role of Sorbed and Lattice Oxygen in Propylene Oxidation Catalyzed by Silica-Supported Bismuth Molybdate[1]

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By using gaseous oxygen-18, the oxidation of propylene on a bismuth molybdate catalyst has been shown to include sorbed oxygen at low catalyst temperatures and predominantly oxygen from the lattice at higher temperatures at which oxygen-ion mobility in the lattice becomes appreciable. The oxygen atoms of oxygen-18-enriched carbon dioxide exchanged very rapidly with lattice oxygen and participated in oxidation of propylene to labeled acrolein. In the heterogeneous oxidation of allyl alcohol, the original oxygen in allyl alcohol is found in the acrolein product.

INTRODUCTION

The heterogeneous oxidation of propylene in the presence of gaseous oxygen may involve oxygen from two sources: gas-phase oxygen that has sorbed on the catalyst surface, and lattice oxygen that has diffused from the bulk to the surface. Recently, Keulks (*1*) and Wragg *et al.* (*2*) used isotopic oxygen to study this reaction. They concluded that lattice oxygen was the primary source of the oxygen incorporated into the products (acrolein) and that gaseous oxygen replenished the lattice oxygen consumed by propylene.

There is some question concerning the generality of their conclusions. In the work of Keulks (*1*), a highly reduced catalyst (evacuated 8 hr at 700 K) was used, with the consequence that gaseous oxygen was rapidly taken up by the oxygen vacancies of the lattice. In most of the work of Wragg *et al.* (*2*) the catalyst was prereduced (evacuated 15 min at 748–773 K); the reacting gas mixture (equal amounts of oxygen and propylene), which would tend to remove lattice oxygen, and the exchange reaction was conducted at temperatures at which bulk oxygen transport becomes significant.

In the present study, pure oxygen-18 was used to reexamine the relative roles of sorbed and lattice oxygen for propylene oxidation on a silica-supported bismuth molybdate catalyst (similar to that used commercially), over a larger temperature range than previously studied, and at oxygen/propylene ratios that were substantially oxidizing. The degree of reduction of the catalyst was monitored by electron spin resonance (ESR).

EXPERIMENTAL DETAILS

The schematic diagram of the apparatus is shown in Fig. 1. The catalyst (0.2 g) was located in a small quartz reactor that was situated in the temperature-controlled Dewar of an X-band ESR spectrometer, as described in detail elsewhere (*3*). A constant flow of helium (30 cc/min) was passed over the catalyst and then to a mass spectrometer (Finnigan 3000

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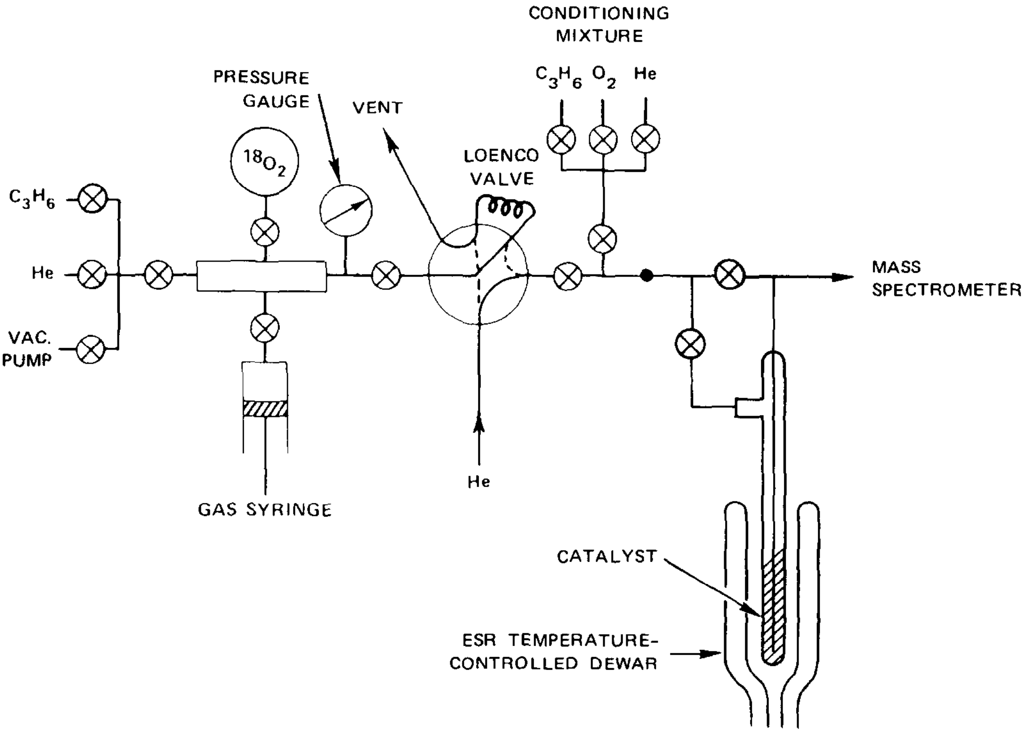

FIG. 1. Experimental apparatus.

equipped with a helium separator). By means of a sampling valve (Loenco), a pulse of an $^{18}O_2/C_3H_6$ mixture could be carried over the catalyst (contact time 0.2 sec) and analyzed for products. The gas mixture was made by using a sensitive pressure gauge (22 cm Wallace Tiernan) and a gastight syringe (Hamilton 1050, 50 cc). The gases were thoroughly mixed by "pumping" the gas syringe about 20 times (the syringe displacement volume to total volume was about three). During this operation air leaks were not observed, but the possibility of such leaks was minimized by flooding the exterior of the syringe plunger with argon. Gas from the syringe was forced through the loop (0.3 cc) of the sampling valve, and this sample of gas was then carried by helium to the catalytic reactor. A bypass to the catalyst was provided to analyze the pulse mixture and to provide means of seasoning the catalyst with a flowing mixture of the same composition as the pulse but containing $^{16}O_2$. Unless otherwise specified, this composition was 20 Torr $^{18}O_2$, 7.0 Torr C_3H_6, and 733 Torr He. The ^{18}O-enriched oxygen (Miles Laboratory, Inc., Elkhart, IN) was reported to contain 98.837% $^{18}O_2$ and 0.0309% $^{17}O_2$, but our mass spectrometric analysis indicated that the gas also contained 2.1% $C^{18}O_2$, 0.6% $C^{18}O^{16}O$, and 0.18% $C^{16}O_2$. To remove residual carbon dioxide and water found in the enriched oxygen, small amounts of Ascarite and magnesium perchlorate were introduced into the syringe and permitted to remain in contact with the gas for several hours. By this means the carbon dioxide content of the gas was decreased by a factor of about 100. Propylene (CP), oxygen (99.95%), and helium (Grade A) gases were used as obtained from the Matheson Co.; acrolein, acetaldehyde, and allyl alcohol were used as received from Matheson Coleman & Bell, Inc.

The preparation of the silica-supported bismuth molybdate catalysts (50 wt%) designated as catalyst B/M-0.7 (1.25 $Bi_2O_3 \cdot 3\ MoO_3$) and catalyst M (MoO_3) have been described previously in detail (*3*).

RESULTS

The temperature dependence of acrolein production, as shown in Fig. 2, differed for mass 56 (acrolein-^{16}O) and mass 58 (acrolein-^{18}O). The product compositions were constant after the first pulse, and the results shown are the averages for several subsequent pulses. The overall activation energies for formation of acrolein-^{16}O and acrolein-^{18}O are 20 ± 0.4 and 13 ± 0.4 kcal mole^{-1}, respectively. For these data the relative intensities of the two major peaks at mass numbers 57 and 58 for acrolein-^{18}O corresponded with those of the cracking pattern for acrolein-^{16}O. Hence, there was no contamination at mass 58 as was noted by Wragg *et al.* (*2*). However, such contamination did appear when another cylinder of propylene was used to make up the reactant mixtures.

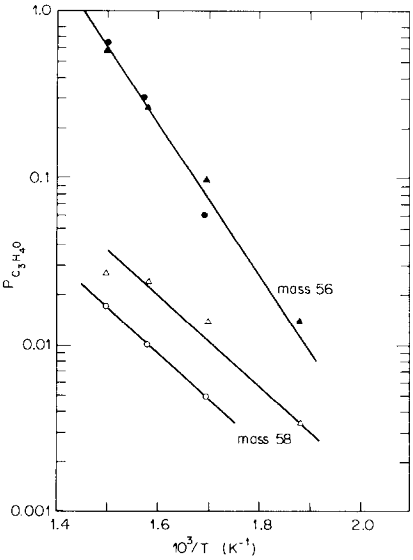

FIG. 2. Temperature effect of catalyst B/M-0.7 on oxidation of propylene to $C_3H_4{}^{16}O$ and $C_3H_4{}^{18}O$. (▲, △) 0.42 Torr $C^{18}O_2$ present; (●, ○) $C^{18}O_2$ removed by Ascarite.

The rates of formation of acrolein-^{16}O (r) and acrolein-^{18}O (r^*) were linearly dependent on propylene pressure when the oxygen^{-18} pressure was held constant at 20 Torr and the propylene pressure was raised to obtain O_2/C_3H_6 ratios in the range of 0.5 to 10 and for catalyst temperatures in the range of 590 to 670 K. This linear dependence confirms that the kinetics of the oxidation to acrolein is first order in propylene pressure.

The rates of formation of unlabeled and labeled acrolein, r and r^*, were also increased by raising the oxygen-18 pressure from 20 to 40 Torr at a given propylene pressure of 13 Torr and for catalyst temperatures in the range of 590–670 K. Upon doubling the oxygen-18 pressure, the ratio r^*/r increased by a factor of 1.5 ± 0.2. The magnitude of this increase indicates that the kinetics of the oxidation to acrolein is half-order in oxygen pressure, as reported earlier (*4*).

The results in Fig. 2 also show that the presence of 0.42 Torr of $C^{18}O_2$ (triangular points) in the reactant mixture increased the amount of acrolein-^{18}O produced by a factor of about two compared to when the $C^{18}O_2$ was removed (circular points), but did not affect the amount of acrolein-^{16}O. In these experiments, the maximum total conversion was about 5%, and the selectivity for acrolein formation was from 0.7 to 0.8.

The fate of the various isotopic carbon dioxide species in the $^{18}O_2$ as a result of their exchange with the catalyst in the presence of propylene is shown in Fig. 3 as a function of catalyst temperature. In each of the experiments [(a) and (b)], 20 Torr of $^{18}O_2$ and 7 Torr of propylene were used, but in (b) the initial carbon dioxide and water contents of the gas were greatly diminished by the Ascarite–magnesium perchlorate treatment. The initial pressures of the three carbon dioxide

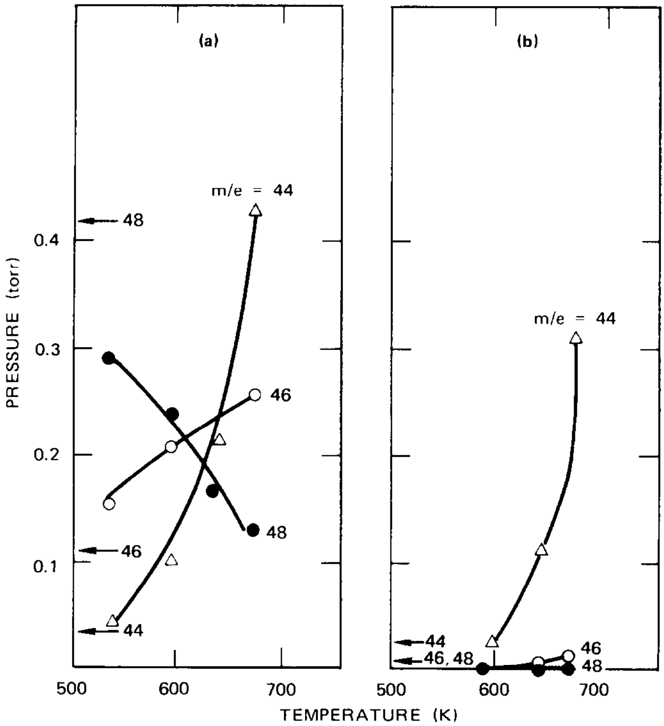

FIG. 3. The exchange of oxygen of carbon dioxide with catalyst B/M-0.7 in the presence of oxygen and propylene. (a) Initial partial pressures: 20 Torr O_2, 7 Torr C_3H_6, 733 Torr He, and those of CO_2 are indicated by arrows along left ordinate; (b) same partial pressures of reactants as in (a) but carbon dioxide content had been decreased by Ascarite.

species are indicated by arrows along the left ordinate. As the temperature was increased, the amount of $C^{18}O_2$ (mass 48) decreased, and the amounts of $C^{18}O^{16}$ (mass 46) and $C^{16}O_2$ (mass 44) increased. In these data, the contribution of acetaldehyde-^{16}O to the peak of mass 44 has been subtracted. The amount of acetaldehyde-^{18}O was insignificant. On the basis of these data the activation energy for the formation of $C^{16}O_2$ is 20 ± 0.4 kcal mole^{-1}, and the activation energy for the loss of $C^{18}O_2$ (mass 48) by exchange with the catalyst (taken from Fig. 3a) is about 4 kcal mole^{-1}.

The amount of $^{18}O_2$ removed from a pulse by the catalyst could not be measured adequately, because this amount was small compared to that originally present in the gas mixture. In the presence of propylene it is estimated from the 34 mass peak that at 670 K the catalyst caused about 0.4% exchange of $^{18}O_2$ to $^{18}O^{16}O$. This estimate was made by taking into account the exchange that occurred in the mass spectrometer.

By ESR measurements of the intensity of the signal due to Mo^{5+} it was shown that the state of reduction of the catalyst remained essentially unchanged during the operations of seasoning the catalyst with a given oxygen/propylene ratio, subsequently flushing with helium, and then injecting several pulses containing oxygen and propylene over the catalyst. By means of ESR it was also possible to evaluate the approximate ratio of surface and bulk resonance centers in the catalyst. To accomplish this, the catalyst, after having been exposed at 660 K to a steady-state concentration of oxygen and propylene (3 : 1) was cooled to room temperature.

Then a stream of 10% oxygen in helium or of helium was passed over the catalyst. In the presence of the oxygen, the intensities of the two resonances (at a *g* value of 1.93 due to Mo^{5+} and at a *g* value of 2.003 due to carbon or a radical) decreased, because the oxygen caused magnetic dipolar broadening of the surface species with which it could interact. When a helium gas was subsequently passed over the catalyst, the peak intensities of both resonances were reversibly and rapidly increased to the original values. By this means it was estimated that 25% of the Mo^{5+} centers and 90% of the carbon species are at the surface, where they can interact magnetically with gaseous oxygen.

In related experiments, we tested the hypothesis that allyl alcohol was a possible intermediate in the oxidation of propylene to acrolein over bismuth molybdate catalysts. Allyl alcohol can readily be oxidized over bismuth molybdate catalysts to acrolein, but it was not clear whether the dissociation occurs to form a hydroxyl group and an allyl radical which is oxidized, or the carbinol group is oxidized with retention of the oxygen and carbon identity (5). To elucidate the mechanism of the reaction, a mixture of oxygen-18 and allyl alcohol vapor in helium was pulsed over several catalysts (catalyst B/M-0.7, catalyst M, and TiO_2-supported bismuth molybdate) at temperatures in the range of 590–670 K. Products were analyzed by mass spectrometry, with a correction made to the mass 58 peak (acrolein-^{18}O) for unreacted allyl alcohol. Normal acrolein (mass 56) was found to desorb from the catalyst for periods up to 15 min, but no labeled product was observed. Even super-imposing a new pulse of allyl alcohol-$^{18}O_2$ on a catalyst that was desorbing acrolein at its maximum rate produced no labeling. Slow desorption of acrolein was not observed during the oxidation of propylene to acrolein.

DISCUSSION

The results show that both sorbed and lattice oxygen of the catalyst can be incorporated into the product gases. The relative amounts of oxygen from these two sources depend on the rate of oxygen chemisorption and on the mobility of oxygen or of oxygen ion vacancies through the lattice. At low temperatures lattice oxygen mobility is low and propylene can capture an oxygen sorbed on the catalyst surface. At higher temperatures, where lattice oxygen mobility is greater, scrambling of oxygen from the lattice with that at the surface becomes more rapid, and the probability increases the propylene will react with an oxygen originating from the lattice. Also, at higher oxygen-18 pressure, an oxygen-18 surface atom will have a greater chance to react with propylene before being scrambled with lattice oxygen.

The competitive oxidation by sorbed and lattice oxygen can be expressed by the following kinetic analysis. Consider that the oxidation of propylene (R) to acrolein (RO) occurs by the following sequence of steps:

$$O_2 \rightleftarrows 2\ O_a, \tag{1}$$

$$O_a \underset{k_2}{\overset{k_1}{\rightleftarrows}} O_a', \tag{2}$$

$$O_a' \underset{k_4}{\overset{k_3}{\rightleftarrows}} O_b', \tag{3}$$

$$R + O_a' \overset{k_5}{\rightleftarrows} RO, \tag{4}$$

where the subscript a refers to surface oxygen atoms, the subscript b refers to bulk oxygen atoms, and the primes denote charged oxygen species (e.g., O^{2-} or O^-) formed by electron transfer from the solid. Reaction (1) can be represented in terms of the equilibrium constant *K*:

$$[O_a] = K^{1/2}\ [O_2]^{1/2}. \tag{5}$$

Under steady-state conditions the concentration of reactive oxygen-16 ions $[O_a']$ is

$$[O_a'] = \frac{k_1 K^{1/2}[O_2]^{1/2} + k_4[O_b']}{k_2 + k_3 + k_5[R]}. \quad (6)$$

A similar equation can be used to express the steady-state concentration of reactive oxygen-18 ions $[O_a^{*\prime}]$.

In accordance with the kinetic analysis the rate of formation of acrolein-^{16}O (RO) and the rate of formation of acrolein-^{18}O (RO*) depend on the surface concentration of oxygen-16 $[O_a']$ ions and oxygen-18 $[O_a^{*\prime}]$ ions and on the propylene pressure. Accordingly,

$$r = \frac{d[RO]}{dt} = k_5\,[R][O_a'], \quad (7)$$

$$r^* = \frac{d[RO^*]}{dt} = k_5\,[R][O_a^{*\prime}]. \quad (8)$$

By dividing Eqs. (8) and (7) and substituting the appropriate values of O_a' and $O_a^{*\prime}$, we obtain

$$\frac{r^*}{r} = \frac{k_1 K^{1/2}[O_2^*]^{1/2} + k_4[O_b^{*\prime}]}{k_1 K^{1/2}[O_2]^{1/2} + k_4[O_b']}. \quad (9)$$

Under our experimental conditions $[O_2] = 0$ (since only $^{18}O_2$ is being used in the gas) and $[O_b^{*\prime}] \approx 0$. Then Eq. (9) reduces to

$$\frac{r^*}{r} = \frac{k_1 K^{1/2}[O_2^*]^{1/2}}{k_4[O_b']}. \quad (10)$$

This equation indicates that the ratio of the rates r^*/r is proportional to the square root of the oxygen-18 pressure. Thus, the theoretical model is in agreement with the experimental observations referred to earlier. At constant oxygen pressure this ratio is proportional to the ratio of the rate constants k_1/k_4, which expresses the ratio of the rate of oxygen chemisorption to that of bulk oxygen diffusion.

The above theory and the rate data indicate that under certain conditions the rate of acrolein formation involving oxygen species originating from the gas phase becomes competitive with that involving lattice oxygen. Thus, the operating conditions for acrolein formation can be adjusted to favor the reaction with surface oxygen from the gas; for example, by increasing the oxygen pressure in the feed gas.

The measured activation energy of 20 ± 0.4 kcal mole^{-1} for formation of acrolein-^{16}O as well as of $C^{16}O_2$ compares to a value of 18–23 kcal mole^{-1} derived from charge transfer studies (*4*), and of 19–21 kcal mole^{-1} for propylene oxidation on various bismuth molybdates (*7*). Most likely this activation energy reflects diffusive transport of lattice oxygen, in line with activation energies for diffusion reported (*6*) in the range from 20–29 kcal mole^{-1}. The lower activation energy, 13 ± 0.4 kcal mole^{-1}, for formation of acrolein-^{18}O is ascribed to a process involving sorbed oxygen rather than oxygen originating from the lattice.

The role of temperature in the inclusion of sorbed or lattice oxygen in the acrolein is apparent from the data in Fig. 4, in which our results are combined with those of Keulks (*1*) and of Wragg *et al.* (*2*). As shown, the data are mutually consistent, considering the differences in the experimental procedure, contact time, measure-

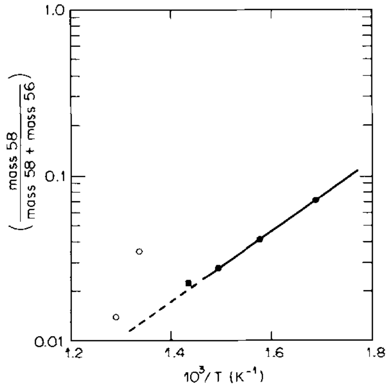

FIG. 4. Temperature effect of catalyst B/M-0.7 on mole fraction of oxygen-18 enriched acrolein. Feed gas: 20 Torr $^{18}O_2$ (purified), 7 Torr C_3H_6, and 733 Torr He. (●) Present study; (■) Keulks; (○) Wragg *et al.*

ment techniques, and the fact that our catalysts were silica-supported whereas the others were not.

The role of carbon dioxide in oxygen exchange was explored to some extent by Wragg *et al.* (*2*), who reported the reaction to be first order, with an activation energy of 11 kcal mole^{-1}. This value was considered too high to account for the rapid scrambling of oxygen species. Our results indicate an activation energy of 4 kcal mole^{-1}, which could account for the rapid exchange of $C^{18}O_2$ with lattice oxygen. Also, such fast scrambling could explain the inability of Keulks (*1*) to oxidize CO with $^{18}O_2$ to $C^{18}O_2$.

It is probable that exchange of oxygen between the lattice and carbon dioxide occurs by means of a carbonate surface complex in which the oxygen atoms can rearrange before the carbon dioxide molecule leaves the surface. The fact that greater amounts of acrolein-^{18}O are produced in the presence of $C^{18}O_2$ (Fig. 2) strongly indicates that the oxygen-18 from $C^{18}O_2$ is available at the surface for reaction with propylene. These results suggest that carbon dioxide provides a mechanism for oxygen scrambling at the surface and an alternative mechanism to that ascribed to water (*8*, *9*).

The layer structure of bismuth molybdate catalysts was discussed by Batist *et al.* (*6*) to account for the unusual oxygen transfer properties of the catalysts. According to their model, oxygen enters at one face and transfers through the bulk to another face where oxidation occurs. Our investigation shows that, while such a mechanism may apply at high temperatures where bulk mobility of oxygen may be high, it need not be invoked at low temperatures where sorbed oxygen seems adequate to oxidize the propylene.

The heterogeneous reaction of allyl alcohol to form acrolein indicates that the original oxygen of the allyl alcohol is retained in the product acrolein molecule and that the reaction is one of dehydrogenation. If the allyl radical were formed as an intermediate, we would have seen labeled acrolein, as in our propylene oxidation experiment, in the presence of gaseous $^{18}O_2$.

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