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NOTE

The Mechanism of Oxygen Atom Incorporation into the Products of Propylene Oxidation over Bismuth Molybdate*

INTRODUCTION

The catalytic oxidation of olefins, using bismuth molybdate catalysts, has received considerable attention during the past decade. Studies involving olefins have been principally concerned with the oxidation of propylene to form acrolein and with the oxidative dehydrogenation of *n*-butenes to form 1,3-butadiene.

The mechanism by which propylene reacts, at least initially, has been firmly established and has been extensively discussed in several recent reviews (*1–3*). The rate determining step in the oxidation is the abstraction of an allylic hydrogen atom by surface oxygen to form a symmetric allyl intermediate. A subsequent abstraction of a second hydrogen atom from either terminal carbon atom of the allyl intermediate followed by oxygen atom incorporation yields acrolein. Unfortunately this mechanism provides little or no information with regard to the pathway of the oxygen atom incorporation. In view of this uncertainty, it was decided to utilize isotopic oxygen ($^{18}O_2$) in an attempt to determine the mode of the oxygen atom incorporation into the oxygen containing products formed in the catalytic oxidation of propylene on bismuth molybdate.

EXPERIMENTAL METHODS

The reaction was studied in a recirculation reactor which was directly coupled to a Varian Quadrupole Residual Gas Analyzer (QRGA) and has been described earlier (*4*). The reactor portion containing the catalyst was fabricated out of quartz, while the rest of the system was constructed from Pyrex tubing. The catalyst tube was heated by a tubular furnace, whose temperature was controlled by a proportional temperature controller (Electronic Control Systems, Fairmont, W. Va.).

The bismuth molybdate catalyst used in the experiments was prepared by co-precipitation from solutions of bismuth nitrate and ammonium molybdate ($Bi/Mo = 1$), according to the method of Adams *et al.* (*5*). It had a surface area of 3.5 m^2/g, as determined by the BET method using nitrogen at $-195°$ as the adsorbate.

Before an experiment, the catalyst was outgassed at 425° for 8 hr. The pressure in the system at the end of this period normally was $<10^{-6}$ Torr. After the catalyst was isolated from the rest of the circulation loop, desired mixtures of propylene, oxygen, and neon, used as an internal standard, then were made by introducing these gases into the circulation loop. In order to achieve a homogeneous mixture, the gases were circulated through the loop for 30 min. The gas flow was then diverted over the heated catalyst, and the change in gas composition was followed by the QRGA using the neon as an internal standard.

The oxygen and neon were Baker Analyzed Research Grade supplied in 1-liter Pyrex bulbs. The oxygen-18 (99.3% ^{18}O, 0.3% ^{17}O) was obtained from Yeda Research and Development Co., Rehovoth, Israel. Propylene (Matheson, c.p. grade) was used without further purification.

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RESULTS AND DISCUSSION

*Heterophase Exchange Experiments**

Before studying the oxidation of propylene with $^{18}O_2$, it was important to establish the reactivity of the oxygen atoms of the bismuth molybdate catalyst with gaseous oxygen, i.e., heterophase exchange. To do so, experiments were conducted utilizing a mixture of 50% Ne and 50% $^{18}O_2$. No change in the gas phase composition was noted when this mixture was circulated over the catalyst for 2 hr at temperatures between 250 and 500°. Furthermore, a mixture of $^{16}O_2$ (25%), $^{18}O_2$ (25%), and Ne (50%) did not undergo the homophase equilibration reaction, i.e.,

$$^{16}O_2 + {}^{18}O_2 \rightleftarrows 2{}^{16}O^{18}O,$$

over the catalyst at these temperatures. The constancy of the gas phase composition also indicates that the chemisorption of oxygen on the bismuth molybdate catalyst, if it occurs at all, must be small. The lack of appreciable oxygen chemisorption at these temperatures was confirmed by a study in a conventional volumetric system using 6 g of catalyst.

Oxidation of Propylene

The oxidation of a 1.3:1:1 mixture of C_3H_6:$^{18}O_2$:Ne at 425° is shown in Fig. 1. In agreement with the work of Peacock *et al.* (*6*), the oxygen is removed from the gas phase faster than the propylene. In contrast to the heterophase exchange experiments, though, this experiment suggests that the oxygen is indeed reactive. However, it does not appear to be reacting with the adsorbed propylene because, very surprisingly, only a small fraction of the oxygen appearing in the products is ^{18}O. Analysis of the acrolein and the CO_2 (the two major components containing ^{18}O) indicates that 2–2.5% of the oxygen atoms in these products is ^{18}O. In addition, the species $^{16}O_2$ and $^{16}O^{18}O$ were not detected in the gas phase, indicating that the heterophase exchange and homophase equilibration reactions (several experiments were conducted with a mixture of $^{16}O_2$ and $^{18}O_2$) still are not occurring.

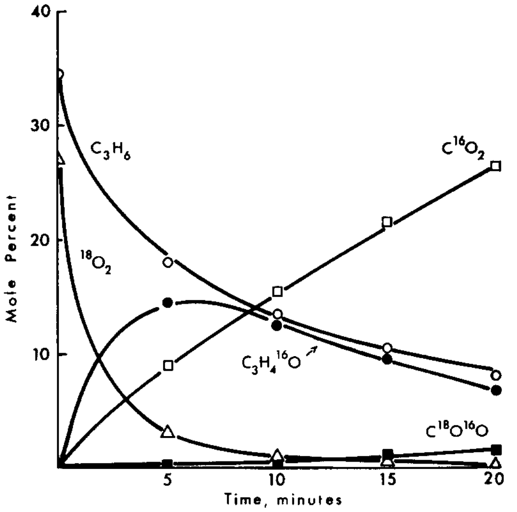

FIG. 1. Gas phase composition for the reaction of C_3H_6 with $^{18}O_2$ at 425°.

In view of the fact that the heterophase exchange reaction is not occurring, the lack of extensive incorporation of ^{18}O into the oxidation products strongly suggests that not only do oxide ions in the surface layer participate in the reaction, but also oxide ions in many subsurface layers. It also suggests that the diffusion of oxygen from the surface into the bulk and from the bulk to the surface must be rapid, and that the gaseous oxygen, once adsorbed, must be able to undergo this diffusion into the bulk. Such a process would allow the ^{18}O to become equilibrated throughout a number of layers before reaction. This point may be clarified by considering the following: if the oxidation proceeds through a chemisorbed layer of oxygen, then the products should have contained only ^{18}O because pure $^{18}O_2$ was used. Since only 2–2.5% of the oxygen atoms in the products contain ^{18}O, the number of layers participating in the reaction may be calculated by assuming that 1 m^2 of surface contains 6×10^{18} oxygen atoms, regardless of the crystallographic structure and the exact representation of the surface (*7*). Using this assump-

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* The nomenclature used in this article follows that suggested by Novakova, J., *Catal. Rev.* **4,** 77 (1970).

tion, it is found that approximately 500 layers, essentially all of the oxygen atoms of the bismuth molybdate, must participate in the reaction to give the observed ^{18}O content.

In order to confirm the reactivity of the surface and subsurface oxygen atoms of the bismuth molybdate catalyst, a subsequent reaction was conducted with a mixture of propylene and $^{16}O_2$. The only source of ^{18}O was now the ^{18}O which had become incorporated into the catalyst. As expected, the products contained some ^{18}O—approximately 2.5% in the CO_2 and 3% in the acrolein. The nearly identical ^{18}O content of the products in these two experiments suggests that the ^{18}O was able to essentially become equilibrated with the active oxygen atoms in the entire crystal lattice.

Oxidation of Carbon Monoxide

For comparison, the oxidation of CO was studied over the bismuth molybdate catalyst. It has been shown (*8,9*) that the oxidation of CO to CO_2 is very slow over this catalyst, but it still was the reaction of choice because of its simplicity. At 450° and with 1.2 g of the catalyst, the ^{18}O content of the CO_2 was 8% at 10% conversion (1.8 Torr $C^{16}O_2$ and 0.3 Torr $C^{16}O^{18}O$) and 5% at 80% conversion (13.2 Torr $C^{16}O_2$ and 1.5 Torr $C^{16}O^{18}O$). The amount of $C^{18}O_2$ detected was negligible. These results correspond to the participation of 60–100 oxide layers which again illustrates that the oxygen, once adsorbed on the catalyst surface, is able to interact with many oxygen ions in subsurface layers before reacting.

Mechanism

The mechanism for the incorporation of oxygen into the products observed in propylene oxidation, as well as its incorporation into the catayst, can be interpreted in terms of the layer structure for the bismuth molybdate catalyst as proposed by Batist *et al.* (*10*). As these workers suggest, all bismuth molybdate structures can be derived from layers of $(Bi_2O_2)_n^{2+}$ and $(MoO_2)_n^{2+}$, connected by layers of O^{2-}. For catalysts having Bi/Mo ratios of 2 or less, the oxygen-boundary layers occur on $(MoO_2)_n^{2+}$ layers which creates anion vacancies on molybdenum atoms.

The active sites for propylene reactivity are these anion vacancies in the oxygen-boundary layers (*11*). The oxygen-boundary layers, in addition, serve as the source of the oxygen that is incorporated into the products. The removal of oxygen from the boundary layers leaves the surface in a reduced state. Reoxidation of these layers by diffusion of O^{2-} ions from the bulk rather than by gas phase oxygen appears to be favored because of the very small ^{18}O content of the products. As indicated earlier, this also suggests that the bulk diffusion to the surface is rapid.

The adsorption of $^{18}O_2$ therefore occurs at some portion of the catalyst other than the site for propylene adsorption. One possibility suggested by Schuit (*11*) is crystal planes which contain the edges of the layers which make up the bismuth molybdate structure. The results reported herein indicate that once the oxygen becomes adsorbed, it rapidly diffuses through a great number of layers and thereby becomes equilibrated with the oxygen ions of the bulk. This interaction therefore greatly reduces the concentration of $^{18}O^{2-}$ available for reaction in the oxygen-boundary layers; hence, the observed small ^{18}O content in the products.

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George W. Keulks

Laboratory for Surface Studies,
Department of Chemistry
University of Wisconsin at Milwaukee
Milwaukee, Wisconsin 53201

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