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Tracer Studies of Catalytic Oxidation by Bismuth Molybdate

II. Propylene Reduction of Labeled Catalysts and Catalytic Oxidation of Propylene

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Differently ^{18}O-labeled bismuth molybdate catalysts were prepared by the solid-state reaction from ^{18}O-enriched bismuth and molybdenum oxides. The results of the propylene reduction of the catalysts and the catalytic oxidation of propylene clearly demonstrated that the oxygen atom in the acrolein formed comes from the $(Bi_2O_2)_n^{2+}$ layer whether or not the gaseous oxygen is present. During the catalytic oxidation, the oxide ions consumed by the reaction seem to be replenished by gaseous oxygen through the $(MoO_2)_n^{2+}$ layer.

INTRODUCTION

Batist *et al.* (*1*) suggested that the oxidizing species in the catalytic oxidation of butene over bismuth molybdate are the oxide ions of the catalyst lattice and that the gaseous oxygen replenishes the oxide ions consumed by the reaction. This is supported by the results of the catalytic oxidation of propylene obtained by Keulks (*2*), Wragg *et al.* (*3*), and Sancier *et al.* (*4*) using ^{18}O as a tracer. Schuit and his coworkers (*5, 6*) have further discussed the detailed mechanism of the incorporation of lattice oxygen into the reaction products in connection with the layered structure of bismuth molybdate which consists of $(Bi_2O_2)_n^{2+}$ and $(MoO_2)_n^{2+}$ layers interconnected by $(O)_n^{2-}$ layers.

Previously we obtained two kinds of γ-bismuth molybdate catalysts which were differently labeled with ^{18}O oxygen (*7*). One, designated as $\gamma\text{-}Bi_2{}^{18}O_3\cdot MoO_3$, was prepared by the solid-state reaction between ^{18}O-enriched bismuth oxide ($Bi_2{}^{18}O_3$) and molybdenum oxide (MoO_3). The other, designated as $\gamma\text{-}Bi_2O_3\cdot Mo^{18}O_3$, was prepared similarly but with Bi_2O_3 and $Mo^{18}O_3$. The results of the hydrogen reduction of these catalysts clearly demonstrated that $\gamma\text{-}Bi_2{}^{18}O_3\cdot MoO_3$ contained ^{18}O preferentially in the $(Bi_2O_2)_n^{2+}$ layers, while $\gamma\text{-}Bi_2O_3\cdot Mo^{18}O_3$ contained ^{18}O in the $(MoO_2)_n^{2+}$ layers. The results also revealed that hydrogen reacts with the oxide ions of the $(Bi_2O_2)_n^{2+}$ layers rather than with those of the $(MoO_2)_n^{2+}$ layers. This fact lead us to infer that the oxide ions of the $(Bi_2O_2)_n^{2+}$ layers would also be responsible for the oxidation of olefins. In order to prove this, we investigated the propylene reduction of ^{18}O-labeled catalysts and the catalytic oxidation of propylene over these catalysts. The results obtained are reported here.

EXPERIMENTAL METHODS

$\gamma\text{-}Bi_2{}^{18}O_3\cdot MoO_3$ and $\gamma\text{-}Bi_2O_3\cdot Mo^{18}O_3$ catalysts containing ^{18}O at 4.5% of the

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total oxide ions were prepared in the same way as reported previously (7). In addition, highly enriched catalysts (^{18}O 11%) were prepared similarly from either $Bi_2{}^{18}O_3$ (^{18}O 22%) or $Mo^{18}O_3$ (^{18}O 22%). $Bi_2{}^{18}O_3$ (^{18}O 22%) was obtained by the reoxidation of partially reduced Bi_2O_3 with ^{18}O oxygen (^{18}O 90%). MoO_3 was not easily reduced to the extent desired. Therefore, ammonium molybdate was decomposed in a hydrogen stream at 450°C and the MoO_2 produced was oxidized to $Mo^{18}O_3$ (^{18}O 30%) with ^{18}O oxygen at 550°C. $Mo^{18}O_3$ was next blended with $Mo^{16}O_3$ and the ^{18}O content was adjusted to 22%. The ^{18}O content of all oxides was calculated from the material balance for oxygen and no confirmation was made experimentally because of the difficulties. All catalysts were checked by means of X-ray diffraction. The structure of γ-bismuth molybdate was confirmed for all catalysts and no reaction residuals were detected within the detection limit.

The apparatus was a closed recirculation system. An amount of 1.0 g of each catalyst was loaded in a U-tube-type reactor and evacuated at 500°C prior to reaction. The reduction of catalysts was carried out at 500°C with a mixture of 40 Torr of propylene and 100 Torr of helium. The acrolein and water produced were collected into a trap cooled at the melting point of methanol (−96°C) and taken in a sampling tube at intervals to analyze the isotopic concentration by mass spectroscopy. Two traps were installed in parallel and used alternately so that the reaction was carried out without interruption by sampling. Catalytic oxidation of propylene was conducted at 400°C by circulating a mixture of propylene (110 Torr), oxygen (100 Torr), and helium (250 Torr). The acrolein and water formed were trapped with a dry ice–methanol bath (−78°C).

The ^{18}O concentration in acrolein was carefully determined using a mass spectrometer (Hitachi RMU-5B). For some samples, several mass spectra were taken repeatedly and ^{18}O concentration was calculated from the spectra. The values of ^{18}O concentration showed good reproducibility on each sample and did not deviate more than ±0.1% from the average.

RESULTS AND DISCUSSION

The ^{18}O concentration in the acrolein produced by reduction of labeled catalysts was plotted against reaction time in Fig. 1. In the case of γ-$Bi_2{}^{18}O_3 \cdot MoO_3$, ^{18}O concentration was initially higher (12.0%) than ^{18}O content of the catalyst (11%) and gradually decreased to 10.1%. On the contrary, the ^{18}O concentration in the acrolein produced with γ-$Bi_2O_3 \cdot Mo^{18}O_3$ increased from the initial value of 9.3% which was lower than the ^{18}O content of the catalyst. These features were observed previously (7) when we studied hydrogen reduction of the labeled catalysts and concluded that the isotopic distribution is not uniform in the catalyst as prepared. This conclusion is also drawn from the present results. Similar time courses were obtained for the ^{18}O concentration in the water simultaneously produced with the acrolein, although the absolute value of ^{18}O concentration could not be determined exactly. The values calculated for water were always about 30% smaller than those for the acrolein. Water

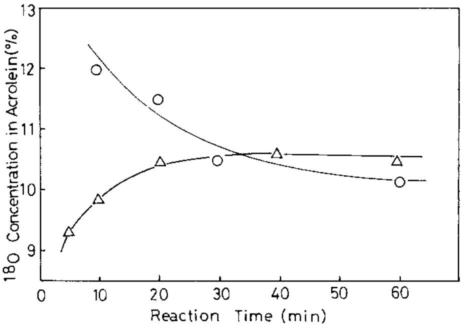

FIG. 1. Time course of ^{18}O concentration in the acrolein produced by the reduction of ^{18}O-labeled catalysts with propylene. (○) γ-$Bi_2{}^{18}O_3 \cdot MoO_3$; (△) γ-$Bi_2O_3 \cdot Mo^{18}O_3$.

seemed to exchange its oxygen easily with the other molecules (CO_2, H_2O, etc.) in the mass spectrometer during analysis.

The present results clearly indicate that the formation of acrolein involves the oxygen atoms of $(Bi_2O_2)_n^{2+}$ layers rather than those of $(MoO_2)_n^{2+}$ layers. Wragg *et al.* (*3*) have confirmed that no oxygen exchange occurs between acrolein and bismuth molybdate at 500°C. It is therefore concluded that the oxygen atom in the acrolein molecule is directly derived from $(Bi_2O_2)_n^{2+}$ layers by the reaction of propylene with the catalyst. Rapid oxygen exchange of water with bismuth molybdate has been suggested by Novâkovâ *et al.* (*8*). The results in Fig. 1 show, however, that the surface oxide ions are not scrambled extensively by the exchange reaction of water, at least in the initial stage of the reduction.

The results of the catalytic oxidation of propylene are shown in Fig. 2 where the ^{18}O concentration in the acrolein formed is plotted against reaction time. In an experiment, the oxidation was carried out with ^{18}O oxygen on an unlabeled catalyst which was prepared similarly to other catalysts from ordinary oxides. The results are shown by the darkened squares in Fig. 2 which show a montonous increase in ^{18}O concentration from 0%. Keulks (*2*) and Wragg *et al.* (*3*) observed the same results. It is likely, as they mentioned, that propylene is oxidized by the oxide ions in the catalyst whose ^{18}O content is almost 0% at first but increases as a result of scrambling of oxygen in the catalyst with ^{18}O oxygen. When propylene is oxidized with ^{16}O oxygen over ^{18}O-enriched catalyst, the reverse change in ^{18}O concentration would be expected. In fact, the time course of the ^{18}O concentration in the acrolein produced over γ-$Bi_2{}^{18}O_3 \cdot MoO_3$, shown by the blank circles in Fig. 2, decreased monotonously from the initial value of 4.1 to 2.4%. In the case of γ-$Bi_2O_3 \cdot Mo^{18}O_3$, however, the time course for ^{18}O concentration was not simple as shown by the blank triangles. It increased in the initial 10 min from 2.8% to the maximum value of 3.5% followed by a slow decrease. This feature was further confirmed by using a larger amount (3.0 g) of highly enriched γ-$Bi_2O_3 \cdot Mo^{18}O_3$ catalyst, the results of which were shown by the darkened triangles. The ^{18}O concentration started below 8% which was much lower than the ^{18}O content of the catalyst (11%) and, after abruptly reaching a maximum value of 11.1%, it started to decrease slowly. Since γ-$Bi_2O_3 \cdot Mo^{18}O_3$ contains most of ^{18}O oxygen in the $(MoO_2)_n^{2+}$ layers, the value of the initial ^{18}O concentration clearly indicates that the oxygen came from the $(Bi_2O_2)_n^{2+}$ layers rather than from the $(MoO_2)_n^{2+}$ layers. The participation of an undetectable amount of residual Bi_2O_3, if any, is definitely excluded because a bismuth oxide has no activity to produce acrolein under the reaction conditions employed here. The increase in ^{18}O concentration in the initial stage of the reaction may be explained by the scrambling of the oxide ions in the catalyst. The ^{18}O content of $(Bi_2O_2)_n^{2+}$ layers would increase

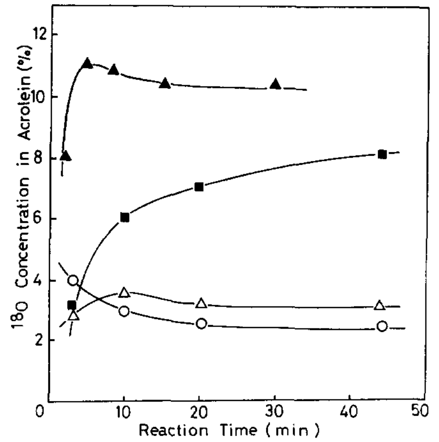

FIG. 2. Time course of ^{18}O concentration in the acrolein produced by the oxidation of propylene with $^{16}O_2$ over (○) γ-$Bi_2{}^{18}O_3 \cdot MoO_3$ (^{18}O 4.5%); (△) γ-$Bi_2O_3 \cdot Mo{}^{18}O_3$ (^{18}O 4.5%); and (▲) γ-$Bi_2O_3 \cdot Mo^{18}O_3$ (^{18}O 11%). (■) On unlabeled catalyst with ^{18}O-enriched oxygen.

if scrambling with ^{18}O-enriched oxygen in the $(MoO_2)_n^{2+}$ layers occurred. The slow decrease in ^{18}O concentration at the later stage results from the dilution of ^{18}O in the catalyst with ^{16}O taken from the gas phase. This dilution effect is seen in the run with γ-$Bi_2{}^{18}O_3 \cdot MoO_3$ in Fig. 2.

The present study strongly supports the mechanism of lattice oxygen incorporation proposed by Matsuura *et al.* (*6*) for the oxidation of butene. The results clearly demonstrate that propylene is selectively oxidized to acrolein by the oxide ions of $(Bi_2O_2)_n^{2+}$ layers whether or not gaseous oxygen is present. These particular oxide ions consumed by the reaction might be immediately replenished by subsurface oxide ions. High mobility of the oxide ions from the bulk to the surface and from the surface into the bulk has been shown by Keulks (*2*). From his estimation, the oxygen adsorbed on the catalyst surface scrambles with 500 oxide layers and 60 to 100 oxide layers before reacting with propylene and carbon monoxide, respectively. We (*9*) investigated the oxidation of carbon monoxide over various molybdate catalysts using ^{18}O-enriched oxygen and found that the oxide ions in β- and γ-bismuth molybdate and lanthanum molybdate are more mobile than those in α-bismuth molybdate, nickel molybdate, and calcium molybdate by a factor of 10. The former group has metal oxide layer, $(Bi_2O_2)_n^{2+}$ or $(La_2O_2)_n^{2+}$, sandwiched by $(MoO_2)_n^{2+}$ layers. On the other hand, the corresponding layer in the latter group consists of only metal ions, that is, Bi_n^{3+}, Ni_n^{2+}, and Ca_n^{2+}. The $(Bi_2O_2)_n^{2+}$ layer seems not only to act as a source of the reactive oxygen favorable to selective oxidation of olefins but also to facilitate the interlayer transfer of oxide ions.

It is likely that the oxide ions are replenished by the gaseous oxygen through the $(MoO_2)_n^{2+}$ layer during catalytic oxidation, because the catalyst with a ^{18}O distribution similar to that of γ-$Bi_2O_3 \cdot Mo^{18}O_3$ has been obtained (*7*) by reoxidation of partially reduced γ-bismuth molybdate with ^{18}O oxygen.

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