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Tracer Studies of Catalytic Oxidation by Bismuth Molybdate

I. Hydrogen Reduction of Labeled Catalysts

The incorporation of lattice oxygen of bismuth molybdate in the catalytic oxidation of propylene has been demonstrated both by Keulks (*1*) and Wragg, Ashmore and Hockey (*2*). The oxygen vacancy resulting from the reaction with propylene is supposed to be recovered by the gas phase oxygen. Furthermore it has been shown by Trifiro, Kubelkova and Pasquon (*3*) on the basis of an ir study that the double-bonded oxygen Mo═O is responsible for the propylene oxidation by $Bi_2O_3 \cdot MoO_3$. On the other hand, it has been deduced by Matsuura and Schuit (*4*) that the oxygen in the Bi_2O_2 layer of $Bi_2O_3 \cdot MoO_3$ is used for the oxidative dehydrogenation of 1-butene. There is, however, no direct evidence to decide which oxygen species is responsible for the oxidation of olefins.

γ-$Bi_2O_3 \cdot MoO_3$ is one of the active catalysts of various bismuth molybdates and its layered structure consists of Bi_2O_2, O and MoO_2 layers is well accepted (*5*). If the oxygen atoms in these layers could be individually distinguished by labeling with heavy oxygen ^{18}O, the olefin oxidation reaction over the labeled catalyst should give evidence for the reaction mechanism of oxidation, particularly the working species in the catalyst. We report an attempt to prepare ^{18}O-labeled γ-Bi_2MoO_6 catalyst samples and present evidence that the oxygen in Bi_2O_2 layer is responsible for the oxidation of olefin over γ-Bi_2MoO_6, with the MoO_2 layer acting as an oxygen supplier to the Bi_2O_2 layer.

PREPARATION OF CATALYST SAMPLES

γ-Bi_2MoO_6 was prepared by the solid state reaction, as shown in Eq. (*1*);

$$Bi_2O_3 + MoO_3 \rightarrow \gamma\text{-}Bi_2MoO_6. \quad (1)$$

First, $Bi_2{}^{18}O_3$ and $Mo^{18}O_3$ samples were separately prepared by decomposition of $Bi(NO_3)_3 \cdot 5H_2O$ and $(NH_4)_6Mo_7O_{24}$, respectively, at 550°C for 5 hr, followed by partial reduction with hydrogen (10% of total oxygen atoms) and reoxidation with $^{36}O_2$. The reduction and reoxidation were carried out at 300°C and 500°C, respectively. The $Bi_2{}^{18}O_3$ and $Mo^{18}O_3$ samples prepared as above contained ^{18}O in 9% of total oxygen atoms.

Second, two kinds of γ-Bi_2MoO_6 catalyst samples labeled with ^{18}O were prepared from the oxide samples by the solid state reaction (1) at 550°C for 20 hr in vacuum: one was obtained from the stoichiometric mixture of $Bi_2{}^{18}O_3$ and MoO_3, designated as γ-$Bi_2{}^{18}O_3 \cdot MoO_3$, and the other from Bi_2O_3 and $Mo^{18}O_3$, designated as γ-$Bi_2O_3 \cdot Mo^{18}O_3$. The typical X-ray diffraction patterns vs the time of the solid state reaction are shown in Fig. 1. It is seen that the solid state reaction is so fast as to give very little unreacted Bi_2O_3 and MoO_3 in 2 hr and is completed in 5 hr.

In addition to these two samples, another sample designated as γ-$Bi_2Mo^{18}O_6$ was prepared by reoxidizing the partially reduced (at 400°C) γ-Bi_2MoO_6 with $^{36}O_2$ at

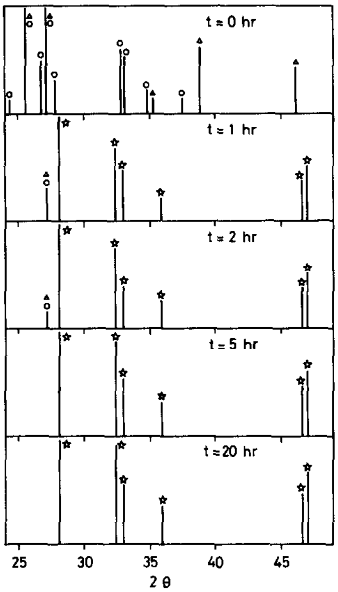

FIG. 1. X-Ray diffraction patterns vs the time of the solid state reaction (*t*). (○) Bi_2O_3; (△) MoO_3; (☆) γ-Bi_2MoO_6.

500°C. The structure of γ-Bi_2MoO_6 was unchanged after repeated reduction and reoxidation, which was confirmed by means of X-ray diffraction. All the catalyst samples used here contained ^{18}O in 4.5% of total oxygen atoms.

HYDROGEN REDUCTION OF THE CATALYST SAMPLES

Each catalyst sample was reduced by circulating hydrogen at 400°C. The water produced was collected at intervals into traps kept in dry-ice methanol bath, and analyzed for the isotopic concentration by mass spectrometry. The variation of ^{18}O concentration in water with the extent of reduction is shown in Fig. 2. In the case of γ-$Bi_2O_3 \cdot Mo^{18}O_3$, note that the ^{18}O concentration in water is, in initial stage, as low as 1%, which is substantially lower than the average value in the catalyst sample, 4.5%, and increases with the extent of reduction to a plateau value at 3.1%. However a completely opposite variation is observed in the case of γ-$Bi_2{}^{18}O_3 \cdot MoO_3$, where the initial value of ^{18}O concentration is higher than the average (4.5%) and decrease to the plateau value at 3.1%.

The above results strongly suggest that the isotopic distribution is not uniform in the catalyst samples as prepared and the evolved water is largely produced from the adjacent oxygen to Bi at least in the initial stage of the reduction. However, it might be possible that there was a small amount of unreacted Bi_2O_3 which could not be detected by X-ray diffraction after the 20 hr of solid state reaction. If this was the case, and if the small amount of Bi_2O_3 is responsible for the oxidation of hydrogen, the variation in $H_2{}^{18}O$ concentration produced from γ-$Bi_2Mo^{18}O_6$ should show a feature similar to γ-$Bi_2{}^{18}O_3 \cdot MoO_3$, because ^{18}O in the γ-$Bi_2Mo^{18}O_6$ must be preferentially incorporated in the residual Bi_2O_3 during the preparation of γ-$Bi_2Mo^{18}O_6$. As shown

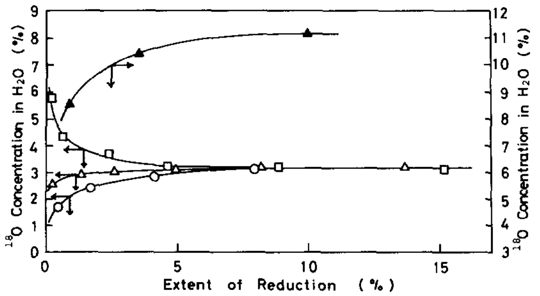

FIG. 2. Variation of ^{18}O concentration in water with extent of reduction. (○—) γ-$Bi_2O_3 \cdot Mo^{18}O_3$; (□—) γ-$Bi_2{}^{18}O_3 \cdot MoO_3$; (△—) γ-$Bi_2Mo^{18}O_6$; (▲—) γ-$Bi_2Mo^{18}O_6$.

in Fig. 2, however, this is not born out by the experimental result. The ^{18}O distribution in the γ-$Bi_2Mo^{18}O_6$ sample appears to be similar to that in γ-$Bi_2O_3 \cdot Mo^{18}O_3$. This feature was confirmed by the reduction of another γ-$Bi_2Mo^{18}O_6$ sample containing ^{18}O in 15% of total oxygen atoms, shown in Fig. 2 by (▲—).

DISCUSSION

It is generally accepted that some solid state reactions of metal compounds proceed through diffusion of metal cation. A typical example is the reaction between $Mg^{18}O$ and Al_2O_3, shown by Nakano, Yamaguchi and Saito (*6*) where the spinel structure is formed by the penetration of Mg^{2+} and Al^{3+} ions into the individual opponent O^{2-} lattice. Accordingly ^{18}O atoms remain enriched at the original position but bound to either of Mg^{2+} or Al^{3+} cation. Contrary to this, the results shown in Fig. 2 indicate that the ^{18}O in the labeled catalyst samples remains bound to the starting cations. In other words, the original Bi–O and Mo–O bonds seem to be retained in the product of the reaction (1), indicating that MoO_3 and Bi_2O_3 reacts with each other as groups without breaking Bi–O and Mo–O bonds. On the other hand, one of the reactant MoO_3 is known to be made up of a layer structure (*7*). Since this layer structure is retained in the product compound, γ-Bi_2MoO_6, the solid state reaction (1) seems to proceed by accommodation of Bi_2O_3 to MoO_3 layer matrix.

It is clearly demonstrated in the present result that γ-$Bi_2O_3 \cdot Mo^{18}O_3$ and γ-$Bi_2{}^{18}O_3 \cdot MoO_3$ exhibit the reverse distribution of ^{18}O, suggesting that the isotopic oxygen mixing hardly takes place between two species, Bi_2O_3 and MoO_3, under the reaction condition of 550°C and 20 hr. Such situation is changed by reduction. In fact, Fig. 2 shows that the hydrogen reduction of above samples up to 7% (attained in about 5 min at 450°C) and above renders the ^{18}O concentration in H_2O invariable, indicating that the ^{18}O distribution in the whole solid is homogenized within a shorter time under a milder condition than the solid state reaction. Presumably the anion vacancy formed by the reduction causes the transfer of oxygen atoms between MoO_2 and Bi_2O_2 layers.

The reduction of γ-Bi_2MoO_6 thus seems to proceed as follows: the first reduction by hydrogen takes place on Bi_2O_2 layer, resulting in anion vacancies in the layer, which causes the oxygen transfer from MoO_2 to Bi_2O_2 layer. In this way, the reduction takes place in both Bi_2O_3 and MoO_3 components. The ^{18}O distribution in the γ-$Bi_2Mo^{18}O_6$ sample which is prepared by hydrogen reduction of γ-Bi_2MoO_6 followed by reoxidation with $^{36}O_2$ is consistent with the view that the reoxidation takes place at MoO_2 layer, since it resembles with that of γ-$Bi_2O_3 \cdot Mo^{18}O_3$.

The mechanism of reduction of γ-Bi_2MoO_6 and of the following reoxidation seems to be explained as above. This mechanism is likely to be applicable for the oxidation of olefin over the composite oxide catalyst. Indeed a similar tracer study over the ^{18}O-enriched catalysts disclosed that propylene is oxidized by Bi_2O_2 layer and oxygen is supplied through MoO_2 layer from gas phase oxygen. The details of the results will be reported in a subsequent paper.

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