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Mechanism of 1-Butene Oxidation in Connection with the Layered Structure of Bi_2MoO_6 Catalyst

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The oxidative dehydrogenation of 1-butene was studied over catalysts containing the same kind of layered structure as Bi_2MoO_6. BiOCl and BiOBr, which have $(Bi_2O_2^{2+})_n$ layers, are highly selective to butadiene, but are less active. Formation of 2-butene is negligibly small on these catalysts. La_2MoO_6, which has $MoO_4^{2-})_n$ layers, is active in isomerization, but is not selective in oxidation, forming considerable amounts of 2-butene and CO_2. It is suggested that 1-butene is first adsorbed on the Mo layers of Bi_2MoO_6, and then oxidized to form butadiene on the Bi layers using lattice oxygen from the Bi layers.

INTRODUCTION

In some cases binary oxides have catalytic properties which are strikingly different from those of the component single oxides. Bismuth molybdate represents a prime example of this type of catalytic behavior. Both bismuth oxide and molybdenum oxide show only poor activity and selectivity for the partial oxidation of olefins, whereas bismuth molybdate is an excellent catalyst for this reaction (*1*). Because of this remarkable synergistic effect, many efforts have been directed at studying and comparing the catalytic properties of bismuth molybdate to those of the single oxides, Bi_2O_3 and MoO_3. Unfortunately, bismuth molybdate is not a mixture of these oxides but consists of at least three different compounds—Bi_2MoO_6 (*2*), $Bi_2Mo_2O_9$ (*3*), and $Bi_2Mo_3O_{12}$ (*4*). Since the chemical environment surrounding each metal in the Bi–Mo oxide is different from that of the single oxides, a comparison of the catalytic activities and selectivities is very difficult.

γ-Bi_2MoO_6 appears to be one of the most effective oxidation catalysts of the Bi–Mo oxide system. It has been shown to have a layered type of crystal structure consisting of alternating $(Bi_2O_2^{2+})_n$ (abbreviation, Bi layers) and $(MoO_4^{2-})_n$ layers (Mo layers). The structure is shown in Fig. 1 (*2, 5*). If the catalytic properties of the Bi and Mo layers are examined separately, the relative catalytic functions of Bi^{3+} and Mo^{6+} can be brought into focus.

In this study, we have investigated the oxidative dehydrogenation of 1-butene over catalysts which contain either Bi or Mo layers. We have tested two bismuth oxyhalides (BiOX), BiOCl and BiOBr, as catalysts which contain only the Bi layers, and lanthanum molybdate, La_2MoO_6, which contains only Mo layers. In addition to the Bi layers, the BiOX catalysts also contain halide ion layers consisting of two-dimensional arrays of halid ions (*6*). La_2MoO_6 has a structure identical to that of Bi_2MoO_6 except that the Bi^{3+} ions are substituted by La^{3+} ions (*7*).

EXPERIMENTAL

Catalyst preparation. (a) BiOCl: 24 g of Bi_2O_3 (Made by pyrolysis of bismuth nitrate) was dissolved in 450 ml of 12% HCl, and NH_4OH was added until the final pH was 7. The white precipitate formed was filtered, washed with distilled water, and dried in air at 120°C for 20 hr. The dried powder was then calcined in air at 500°C for 5 hr. The formation of BiOCl was confirmed by X-ray diffraction analysis.

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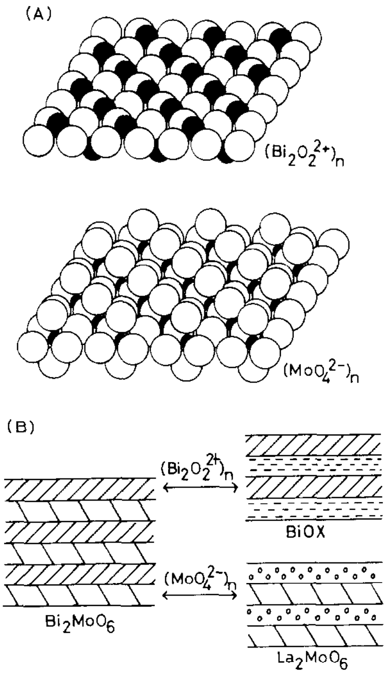

FIG. 1. Structure of the catalysts. (A) The Bi and Mo layers of γ-Bi_2MoO_6. (B) Illustration of the structural correspondence of the catalysts.

(b) BiOBr: The procedure was identical to that used in the preparation of BiOCl except that HBr was used in place of HCl.

(c) La_2MoO_6: 23 g of $La(NO_3)_3 \cdot 6H_2O$ (reagent grade, Wako Pure Chem. Co.) was dissolved in 50 ml of distilled water. This was added to a solution prepared by adding 4.7 g of $(NH_4)_6Mo_7O_{24}$ (Climax Molybdenum Co.) to a 10% H_2O_2 solution. The resulting solution was heated and stirred vigorously to incipient gel formation. The gel was dried in an oven at 120°C for 20 hr, followed by calcination in air at 550°C for 5 hr. Formation of La_2MoO_6 was confirmed by X-ray diffraction analysis.

Activity measurements. The oxidative dehydrogenation of 1-butene was studied using a conventional pulse reactor. The gas mixture consisting of O_2 and 1-butene ($O_2/C_4H_8 = 1.6/1$) was stored in a vessel and 0.3 ml of the reactant gas was extracted using a syringe and injected into the reactor. The reaction products were analyzed using gas chromatography. Butene isomers, butadiene, and carbon dioxide were separated using a propylene carbonate column (4 m, 25°C), and O_2 and CO were separated using a molecular sieve 13X column (1 m, 25°C).

RESULTS

Catalytic activity and selectivity. The results of the reaction are shown in Table 1. Bi_2MoO_6 displayed a high activity and selectivity for butadiene formation; however, good yields of 2-butene were also obtained. Both BiOCl and BiOBr were also very

TABLE 1

Catalytic Activity and Selectivity for the Partial Oxidation of 1-Butene

Catalyst	Surface area (m^2/g)	Weight of catalyst (g)	Reaction temperature (°C)	Yield of 2-butene (%)	Yield of oxidation[a] (%)	Selectivity to butadiene[b] (%)
Bi_2MoO_6	5.2	0.20	350	27.6	49.8	97.1
			400	13.8	71.2	88.9
BiOCl	1.7	1.00	440	—	4.0	83.9
			500	—	11.2	89.0
BiOBr	19.1	0.20	400	—	7.4	92.7
			450	—	18.8	93.4
			500	—	50.8	92.6
La_2MoO_6	11.2	0.20	450	21.4	16.2	17.5
			500	28.6	35.9	33.6

[a] Yield of oxidation products, $\frac{1}{4}CO + \frac{1}{4}CO_2 + C_4H_6$.
[b] Selectivity to butadiene, $C_4H_6/(\frac{1}{4}CO + \frac{1}{4}CO_2 + C_4H_6)$.

selective catalysts for butadiene formation, although their activity was somewhat lower. In contrast to Bi_2MoO_6, only trace amounts of isomerization products were observed for both of the oxyhalides studied.

The activity of the La_2MoO_6 catalyst to form oxidation products was lower than that of BiOBr, although high yields of 2-butene were obtained. At 450°C, the 2-butene yield surpassed that of the oxidation products, indicating that La_2MoO_6 was superior in total activity (oxidation + isomerization) to BiOBr. The selectivity of La_2MoO_6 in the formation of butadiene, however, was inferior to that of BiOX and Bi_2MoO_6. Thus, La_2MoO_6 is active as an isomerization catalyst but poorly selective in the formation of butadiene.

In all cases, X-ray diffraction studies of spent catalysts showed no significant structural changes following reaction.

Reduction of the catalysts by 1-butene. Pulses containing only 1-butene were injected into the reactor in order to observe whether any reaction occurred when O_2 was excluded from the reaction system. Both BiOCl and BiOBr produce butadiene in the absence of O_2. Selectivities were increased (95–99% on BiOCl and 96–99% on BiOBr at 500°C) over those obtained in the presence of O_2. A slow decrease in the activity was observed when additional 1-butene pulses were added (Fig. 2). Following the addition of 100 pulses of 1-butene to the BiOBr catalyst, the deposition of yellow powder was observed in the glass tube downstream of the catalyst bed. The yellow powder was dissolved in HNO_3 and subsequently analyzed. The ratio of Bi : Br was found to be 1 : 3, strongly suggesting that the compound was $BiBr_3$. The used catalyst was submitted for X-ray diffraction analysis and the formation of metallic Bi was confirmed (Fig. 3c). It is clear that BiOBr was reduced to $BiBr_3$ and metallic Bi by 1-butene. It is also clear that the 1-butene was oxidized by the lattice oxygen of BiOBr from the Bi layers to form butadiene. Since BiOBr is not reduced when O_2 is present in the reaction mixture, it is apparent that oxygen from the gas phase can be incorporated into the BiOBr lattice. This result suggests that the actual working reaction mechanism for this catalyst is similar to the redox mechanism proposed for Bi_2MoO_6.

When 1-butene pulses were added to the La_2MoO_6 catalyst, a rapid decrease in the yield of oxidation products was observed for the first ten pulses. Following this initial decrease, the yield of oxidation products became very small. The lattice oxygen from La_2MoO_6 is not easily extracted by 1-butene; however, the 2-butene yield is independent of the number of 1-butene pulses

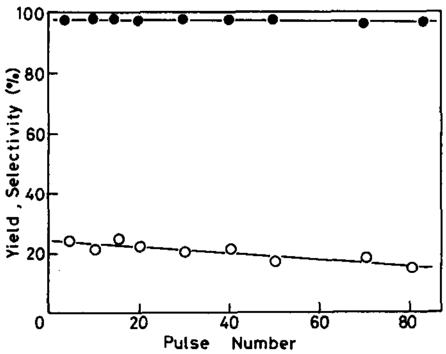

FIG. 2. Reaction of 1-butene on BiOBr in the absence of gaseous oxygen (500°C, W = 0.20 g). (○) Yield of C_4H_6; (●) selectivity to C_4H_6.

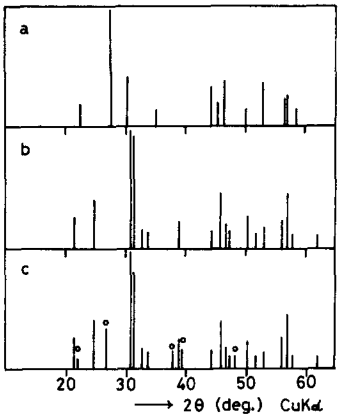

FIG. 3. X-Ray diffraction of La_2MoO_6 and BiOBr. (a) La_2MoO_6 (fresh); (b) BiOBr (fresh); (c) BiOBr after reduction by 1-butene pulses. (○) Metallic bismuth.

added. Following the injection of 80 1-butene pulses, no structural changes were observed for the La_2MoO_6 catalyst as determined by an X-ray diffraction study.

DISCUSSION

Our results are summarized as follows.

(i) The selectivity to butadiene formation for all the catalysts which contain the Bi layers (BiOCl, BiOBr, and Bi_2MoO_6) was about 90%. $Bi_4Ti_3O_{12}$, which also contains the Bi layers, was also reported to be a highly selective catalyst for butadiene formation (*8*). Thus, it appears that catalysts which contain bismuth layers are highly selective to the formation of butadiene.

(ii) The isomerization to 2-butene, on the other hand, occurs preferentially on catalysts which contain the Mo layers. The ratio of *cis*- to *trans*-2-butene was nearly the same (0.78 on Bi_2MoO_6 and 0.82 on La_2MoO_6) on both catalysts. The formation of 2-butene was especially high on La_2MoO_6. On this catalyst, the yield of 2-butene was nearly equal to that of the oxidation products. The total activity (oxidation + isomerization) was higher on La_2MoO_6 than on BiOX.

(iii) In the absence of gaseous oxygen, 1-butene was oxidized by the lattice oxygen of BiOBr and BiOBr was reduced to $BiBr_3$ and metallic bismuth. It is well known that the lattice oxygen of Bi_2MoO_6 is available for oxidation, although the results of this study indicate that the lattice oxygen of La_2MoO_6 is not readily incorporated into the reaction. Thus, it is clear that the lattice oxygen of the Bi layers is available for the oxidation of 1-butene.

Such a difference in the availability of lattice oxygen for oxidation cannot be attributed to the mobility of lattice oxygen during the reaction. Miura *et al.* (*9*) have previously shown that the mobility of the lattice oxygen in both La_2MoO_6 and Bi_2MoO_6 is about the same during the oxidation of CO. The availability of lattice oxygen in this case appears to be related to the reducibility of La^{3+} or Bi^{3+}. The enthalpies of formation, ΔH_f°, for La_2O_3 and Bi_2O_3 are -428.5 and -137.2 kcal/mol, respectively (*10*), showing that Bi^{3+} is more easily reduced than La^{3+}.

(iv) In the presence of gaseous oxygen, BiOBr is not reduced; therefore the oxygen vacancy which remains following oxidation is readily filled by oxygen from the gas phase.

These results can be explained by the following mechanism.

(i) Bi_2MoO_6: 1-butene is initially absorbed on the Mo layers, probably as a σ-allyl intermediate. Isomerization proceeds via this intermediate on the Mo layers, but oxidation to butadiene takes place preferentially on the Bi layers using the lattice oxygen from the Bi layers which is readily available for reaction.

(ii) La_2MoO_6: The same intermediate, σ-allyl, is formed on the Mo layers, resulting in the formation of 2-butene; however, the activity for the oxidation to butadiene is inhibited due to the unavailability of lattice oxygen from the Bi layers. For this reason, the selectivity of La_2MoO_6 for butadiene is low and considerable amounts of 2-butene are formed.

(iii) BiOX: 1-butene can only be adsorbed on the Bi layers because the Mo layers are not present. Adsorbed species (most likely a π-allyl intermediate) are oxidized by the lattice oxygen in the Bi layers in a similar way to that found for Bi_2MoO_6, resulting in an enhanced selectivity for butadiene formation. Because the Mo layers are not present, isomerization does not occur.

Through the use of ^{18}O-labeled Bi_2MoO_6, Miura *et al.* (*11, 12*) have shown that the oxidation of both H_2 and C_3H_6 on Bi_2MoO_6 catalysts proceeds via the incorporation of lattice oxygen from the Bi layers into the reaction products.

The reported results in this study support these previous conclusions, because only those catalysts which contain the Bi layers are selective for butadiene formation. It is also clear that the lattice oxygen of the Bi layers plays a very important role in partial oxidation. Butadiene is also formed on La_2MoO_6; however, even though the rate of formation is somewhat higher than on BiOCl, the selectivity is much lower than that found for either Bi_2MoO_6 or BiOX. In addition to this, the rate of butadiene formation is much lower than that observed for Bi_2MoO_6 at the same temperature and it seems unlikely that the formation of butadiene on Bi_2MoO_6 occurs extensively on the Mo layers.

The existence of two different reaction intermediates is suggested. One of these intermediates is formed on the Mo layers resulting in the formation of 2-butene. The other is formed on the Bi layers and is a precursor to butadiene. Unfortunately, our data do not enable us to distinguish between these two intermediates, but the literature is useful in speculating as to the nature of their structure. Kondo *et al.* (*13*) have studied the isomerization of olefins on Bi_2MoO_6 in the presence of D_2O and have suggested that the adsorbed intermediate is a σ-allyl species. Consequently, the adsorbed species on the Mo layers is the σ-allyl intermediate. It is well established, on the other hand, that the oxidation of olefins over Bi_2MoO_6 proceeds via the formation of the symmetric π-allyl intermediate (*14*). This suggests that the symmetric π-allyl species is adsorbed on the Bi layers.

In addition to being an intermediate in the isomerization reaction, the σ-allyl may also be a precursor to the formation of the π-allyl intermediate. This is in agreement with the experimental observation that Bi_2MoO_6 has a higher activity than BiOX even though both catalysts contain the Bi layers. On Bi_2MoO_6 the formation of the σ-allyl intermediate on the Mo layers may be followed by subsequent migration and rearrangement to the π-allyl species on the Bi layers, while on BiOX the π-allyl species must necessarily be formed on the Bi layers. The mechanism suggested here may very well lead to an enhanced activity due to a synergistic effect catalyzed by both the Mo and the Bi layers.

The mechanism suggested in this study proposes the migration of the adsorbed species from the Mo layers to the Bi layers. A similar mechanism has been proposed by Matsuura and Schuit (*15*), who measured the adsorption isotherms of several olefins on Bi_2MoO_6. They suggested that 1-butene is initially adsorbed on the B sites (present on the Mo layers) as a σ-allyl intermediate, and subsequently migrates to the A sites (present on the Bi layers) to form a symmetric π-allyl intermediate. The abstraction of a hydrogen atom from the intermediate leads to the formation of butadiene.

In their mechanism, the lattice oxygen of the B site accepts a H atom from the adsorbed intermediate. Our results show, however, that lattice oxygen from BiOBr can oxidize 1-butene even though only the Bi layers are present. Apparently, lattice oxygen from BiOBr can react with the intermediate.

Although the lattice oxygen of the Bi layers can oxidize 1-butene, BiOBr is not reduced if gaseous oxygen is present. This result suggests that the Bi layers can add oxygen to replace the lattice oxygen which has been depleted by reaction. This does not necessarily lead to the conclusion that oxygen is introduced into the catalyst lattice from the Bi layers in the case of Bi_2MoO_6. If an oxygen vacancy is present in either layer, reoxidation may occur in order to fill the vacancy. Dadyburjor and Ruckenstein (*16*) have suggested on the basis of calculations involving interaction potentials between an oxygen ion and either a bismuth or a molybdenum ion, that if an oxygen bound to bismuth is reduced during the oxidation, a lattice oxygen from a nearby molybdenum ion would occupy the vacancy near the bismuth, and that the vacancy created next to the molybdenum ion is filled by gaseous oxygen. Thus, our previous contention (*11*) that gaseous oxygen is introduced into the Mo layers appears to hold.

Recently, Matsuura *et al.* (*17*) have claimed that in the Bi–Mo–O system, only the β phase ($Bi_2Mo_2O_9$) is active in partial oxidation and that Bi_2MoO_6 is active only when an excess of Mo is introduced. Batist (*18*), however, has argued against this point of view and the subject is still under discussion. According to Matsuura *et al.*, the Bi layers become active only when the Mo^{6+} ions are incorporated into the layers together with cation vacancies, as is the case for the β phase. Our results show that the presence of the Bi layers is sufficient to enhance the activity for butadiene formation, and so we feel that Bi_2MoO_6 itself is a highly selective catalyst for the oxidative dehydrogenation of 1-butene. In addition, the presence of the Mo layers appears to improve the activity by enabling the formation of a new precursor, and it seems correct to consider that Bi_2MoO_6, which has both Bi and Mo layers, has both high activity and selectivity.

In conclusion, compounds which contain either Bi or Mo layers (BiOCl, BiOBr, and La_2MoO_6) illustrate the properties of the respective layers, and the catalytic properties of Bi_2MoO_6 can be understood from a knowledge of the properties of the separate layers.

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