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CHEMICAL REACTIVITY OF OXYGEN SPECIES ON γ-Bi_2MoO_6 STUDIED BY X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

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XPS studies of the reduction behavior of γ-Bi_2MoO_6 were carried out by using various reactants. It was found that in the initial reduction stage, H_2 reduced Mo alone, while allyl alcohol removed preferentially oxygen anions bound to Bi. With 1-butene, simultaneous reductions of Bi and Mo were observed. The reactivity and inter-layer diffusion of oxygen anions are discussed.

Bi-Mo binary oxides are excellent catalysts for the (amm)oxidations of propylene and butenes. It is well established that the lattice oxygen in the Bi-Mo catalysts participates in the oxidations via redox mechanism; lattice oxygen is removed by the oxidations of olefins and replenished by gaseous molecular oxygen.[1-8] In the case of γ-Bi_2MoO_6 catalyst, tracer experiments using $^{18}O_2$ indicated that many layers of lattice oxygen are used during the oxidations of olefins.[1-8] The structure of γ-Bi_2MoO_6 (koechlinite) consists of $(MoO_2)_n^{2+}$, O^{2-}, and $(Bi_2O_2)_n^{2+}$ layers.[9] The origin of the strong synergy between Mo and Bi oxides or the roles played by these individual layers during the oxidations are open to question.

Oxidations of various reactants in the absence of gaseous oxygen are considered to result in the removal of the lattice oxygen ions bound to Bi and/or Mo, depending on the reactivities of the oxygen anions for the reactants. In this study, the reactant-dependency of the reduction behavior of γ-Bi_2MoO_6 was investigated by XPS to reveal the differences in the reactivity of the individual lattice oxygen anions, which is affiliated to Bi, Mo, or both cations, for various reactants.

γ-Bi_2MoO_6 was prepared according to Batist et al.[10] A nitric acid solution of $Bi(NO_3)_3 \cdot 5H_2O$ was added to an aqueous solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and the pH of the mixture was adjusted to 5.2-5.4 by adding an aqueous ammonium solution. After filtration, the precipitate was dried at 110 °C for 16 h and then calcined at 550 °C for 5 h in air. The X-ray diffraction pattern of the catalyst was consistent with that reported for γ-Bi_2MoO_6 (koechlinite).

Reduction of the catalyst (reaction in the absence of gaseous oxygen) was carried out at 450 °C and an atmospheric pressure (total flow rate; ca. 60 ml/min/0.1 g-cat) by using a fixed bed flow reactor. The reactants used here and their

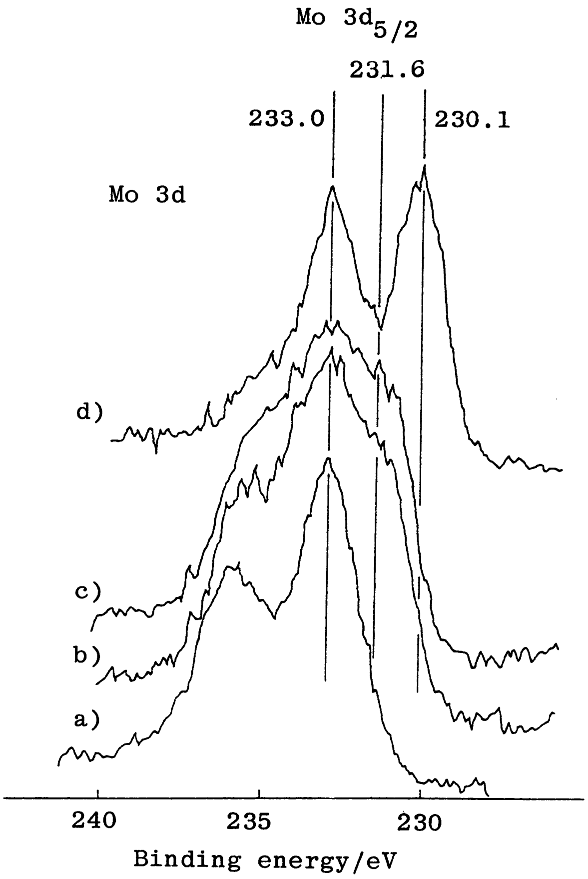

Fig. 1. Mo3d XP spectra of γ-Bi_2MoO_6 catalyst reduced by 1-butene at 450 °C. Partial pressure of 1-butene was a) 0.2, b) 0.3, c) 0.5, and d) 1.0 atm.

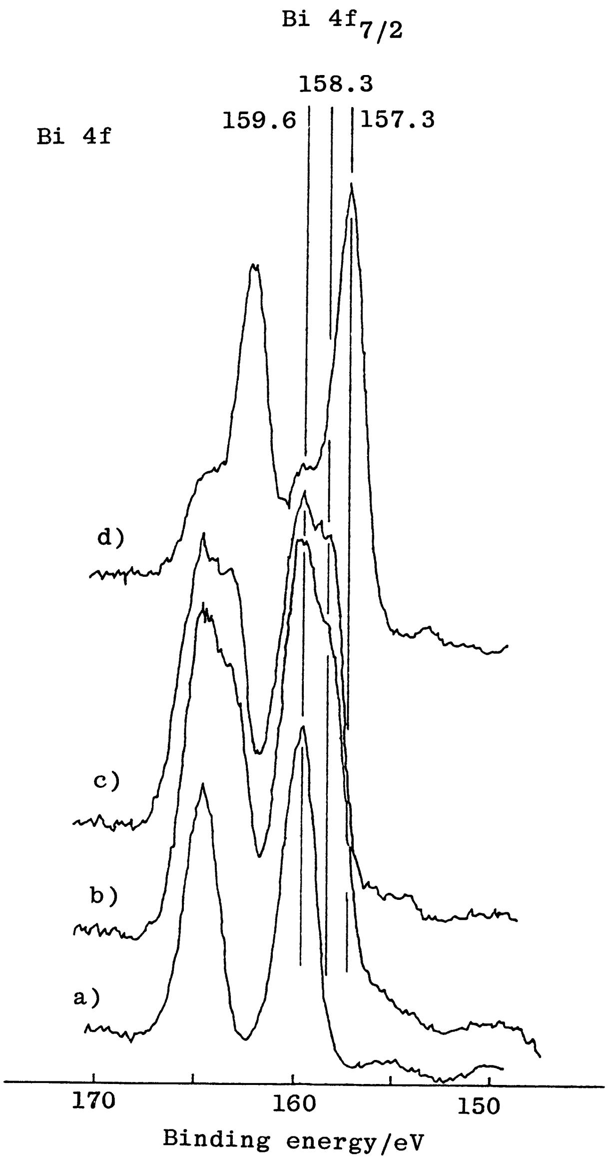

Fig. 2. Bi4f XP spectra of γ-Bi_2MoO_6 catalyst reduced by 1-butene at 450 °C. See the legend in Fig. 1 for a) - d).

partial pressures (balance; N_2 or He) were 1-butene (0.2 - 1.0 atm), allyl alcohol (0.3 atm), and H_2 (1.0 atm). The main products were butadiene from 1-butene and acrolein from allyl alcohol in addition to small amounts of CO, CO_2, and decomposed products. The reduction degree of the catalyst was not accurately measured in the present study. After being cooled gradually in a N_2 or He stream to room temperature, the reduced catalyst was transferred, without being exposed to air, to a N_2-filled glovebox attached to a X-ray photoelectron spectrometer (Hitachi 507, Al anode) and mounted on a double-sided adhesive tape. Binding energies were referenced to the Cls band at 285.0 eV due to contaminants. The surface composition of the catalyst was calculated from the area intensities of the Mo3d and Bi4f spectra by using a relative atomic sensitivity factor (Mo3d/Bi4f =

2.75/7.4) reported by Wagner et al.11)

The surface analysis of the γ-Bi_2MoO_6 catalyst indicated that Mo(VI) ($Mo3d_{5/2}$; 233.0 eV) and Bi(III) ($Bi4f_{7/2}$; 159.6 eV) species were present and that the surface Mo/(Mo + Bi) atomic ratio was 0.35 ± 0.01 which was very close to the nominal bulk composition of the catalyst (0.33). When the catalyst was contacted with 1-butene of various pressures at 450 °C for 2 h, the Mo3d and Bi4f XP spectra indicated partial reduction of both Mo(VI) and Bi(III), as shown in Figs. 1 and 2, respectively. The new peaks in the Mo3d spectra are ascribable to Mo(V) ($Mo3d_{5/2}$; 231.6 eV) and Mo(IV) (230.1 eV).12) The $Bi4f_{7/2}$ peak at 157.3 eV is attributable to Bi metal. An additional band observed at 158.3 eV is considered to be assigned to Bi(I) species on the basis of the binding energy. With increasing the partial pressure of 1-butene, the reduction degrees of Bi and Mo increased. Although the Bi-Mo catalyst was reduced by 0.2 atm of 1-butene as evidenced by the production of butadiene and by the color change of the catalyst from yellow to dark green or gray, the XP spectra a) in Figs. 1 and 2 showed no detectable reductions of Mo(VI) and Bi(III) species. Similar phenomena were also observed when the catalyst was reduced for shorter periods (less than 1 h at 450 °C and 1 atm). In our reduction conditions, the surface reductions were detected at the bulk reduction of > 10 %, which was estimated from the amount of butadiene produced. These findings are surmised to be due to a rapid surface reoxidation by the lattice oxygen anions in the bulk.

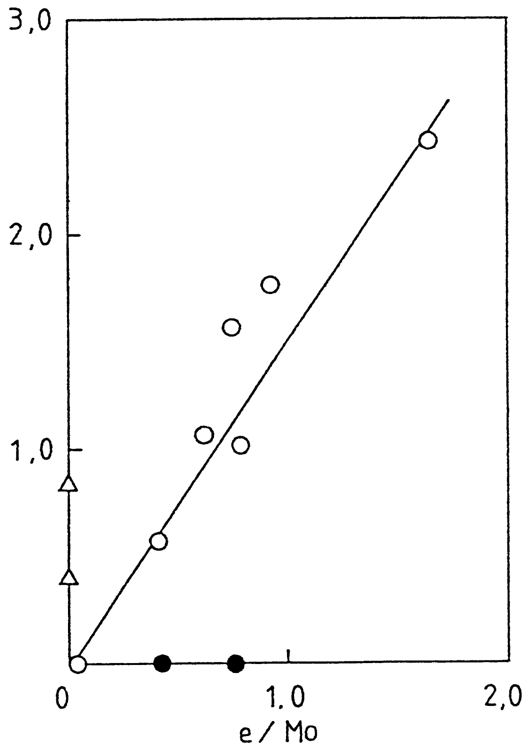

Fig. 3. Relations between e/Mo and e/Bi in the reductions of γ-Bi_2MoO_6 by 1-butene (○), H_2 (●), and allyl alcohol (△).

The reduction degrees of Mo and Bi were estimated by the resolutions of the Mo3d and Bi4f envelopes to Mo(VI), Mo(V), and Mo(IV) and to Bi(III), Bi(I), and Bi(0), respectively. Figure 3 shows a correlation between the reduction degree of Mo expressed by e/Mo and that of Bi (e/Bi), where e/Mo or e/Bi indicates the number of electrons transferred to Mo or Bi during the removal of the lattice oxygen. The accuracy in e/M was estimated to be ± 0.2. It is revealed that both Mo and Bi cations are simultaneously reduced by 1-butene when surface reductions are once observed by XPS. This may suggest a strong cooperating nature between Mo and Bi in γ-Bi_2MoO_6.

On the other hand, H_2-reductions of γ-Bi_2MoO_6 showed significantly different behaviors from those in the 1-butene-reductions. It was found that Mo was reduced, while Bi remained intact in an initial reduction stage. This is consistent with the observations by Grzybowska et al.13) Contrary to the H_2-reduction, only the reduction of Bi was observed at 450 °C by the contact with allyl alcohol. In both reductions with H_2 and allyl alcohol, e/Mo and e/Bi increased with the reduction time, contrary to the reduction by 1-butene. These reduction behaviors are shown in Fig. 3.

The above findings imply that there are at least two distinct types of lattice oxygen species with different chemical reactivities on the γ-Bi_2MoO_6 catalyst. Ueda et al.8) also demonstrated the participation of different lattice oxygen species in the oxidations of propylene and 1-butene. The oxygen species in $(MoO_2)_n^{2+}$ layer react with hydrogen, whereas the oxygen anions bound to $(Bi_2O_2)_n^{2+}$ layer play a decisive role in the oxidation of allyl alcohol. Both kinds of oxygen species and/or O^{2-} in the intermediate layer cooperate in the selective oxidation of 1-butene. It is demonstrated that the reduction behavior of γ-Bi_2MoO_6 depends strongly on the reactant, suggesting various interaction modes between γ-Bi_2MoO_6 and the reactant.

From the observations that the Mo- and Bi-layers are serarately reduced under certain conditions, it is considered that no significant inter-layer diffusion of the anions takes place when only the Mo- or Bi-layer participates in the reaction. It is well established that several hundred-layers of the bulk oxygen take part in the oxidations of 1-butene and propylene.3,6,7) The present results suggest that such complete mixing of oxygen anions is caused by simultaneous participation of the anions both in the $(MoO_2)_n^{2+}$ and $(Bi_2O_2)_n^{2+}$ layers and/or the O^{2-} layer.

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