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Isotopic Exchange of Oxygen-18 of Carbon Dioxide with Lattice Oxygen of Bismuth Molybdate

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The isotopic oxygen exchange reaction of bismuth molybdate was found, to proceed very easily with oxygen-18-labelled carbon dioxide, though this does not proceed with gaseous oxygen-18. Moreover, all oxygen in the catalyst has been found to be replaced with oxygen-18 from carbon dioxide. It was thus proven that the bismuth molybdates have high diffusivility of oxide ions through their crystal lattice without any oxygen vacancies at temperatures above 220 °C.

It is known that the olefin oxidation occurring on bismuth molybdate catalysts proceeds by the so-called Redox mechanism, where the lattice oxygen in the catalyst is preferentially taken into the products. Moro-oka et al.1) deduced, from the quantity of lattice oxygen-16 of the catalyst which was taken into the products of the reaction $C_3H_8 + {}^{18}O_2$, that in many bismuth molybdate-based catalysts, the lattice oxygen existing in a few hundred layers in the catalyst participated in the olefin oxidation reaction. Keulks and Krenzke,2) in a similar experiment with bismuth molybdate catalysts, reported that all the lattice oxygen in the active catalysts, γ-Bi_2MoO_6 and β-$Bi_2Mo_2O_9$, took part in the propylene oxidation reaction, while a part of the lattice oxygen participated in the reaction in the case of the less active catalyst, α-$Bi_2Mo_3O_{12}$. They suggested that the catalytic activity would be dominantly affected by the rate of diffusion of the oxide ions through the lattice in the crystal. However, no experimental data have been obtained with regard to oxygen self-diffusion in bismuth molybdate catalysts. The reason is that these catalysts have no capability to allowing any appreciable oxygen-exchange reaction to occur between gaseous oxygen and lattice oxygen at temperatures up to 500 °C. Hence, we herein report the results of an experiment in which we attempted to measure the oxygen-exchange reaction between a catalyst using carbon dioxide labelled with oxygen-18 instead of gaseous oxygen-18.

In the work reported here we studied the reaction of isotopic exchange of oxygen-18 of carbon dioxide with the lattice oxygen of α- , β- , and γ- bismuth molybdate (with stoichiometric and 4% excess MoO_3). The catalyst were prepared according to a method proposed by Batist et al.3) X-ray analysis showed only the expected phase in the γ- and α-compounds. For compound β , small amount of γ and α were present. The surface areas and the particle sizes of these catalysts are given in Table 1. All the catalysts were tested for their activity and selectivity in the 1-butene oxidation to butadiene with a single-path flow reactor. The constant flow rates were 20 cm^3 min^{-1} of 1-butene and 100 cm^3 min^{-1} of artificial air over 1 g of catalyst. The catalytic activity for bismuth molybdate catalysts decreased in the following order;

$$\beta\text{-}Bi_2Mo_2O_9 \gtrapprox \gamma\text{-}Bi_2MoO_6(+4\%\ MoO_3) > \alpha\text{-}Bi_2Mo_3O_{12} \gg \gamma\text{-}Bi_2MoO_6$$

The isotopic exchange reaction of oxygen-18 of carbon dioxide and lattice oxygen of the catalysts was carried out in a static system at temperatures between 220 and 540 °C. The amount of each catalyst placed in the reactor was 0.06 g. Carbon dioxide labelled with oxygen-18 (purity 99.4% as atomic concentration of oxygen-18 supplied from CEA-ORIS) was admitted to the reaction system at a pressure between 12 to 16 kPa. The amount of oxygen-18 in the carbon dioxide used was equal to three times of the amount of oxide ions present in the catalyst. Periodic analysis of the gaseous isotopic mixture of carbon dioxide was performed with a quadropole spectrometer.

Figure 1 shows the typical oxygen exchange reaction of $C^{18}O_2$ with $\gamma\text{-}Bi_2MoO_6$ at 260 °C in term of the composition ratio of isotopic carbon dioxide, $C^{18}O_2$, $C^{18}O^{16}O$ and $C^{16}O_2$, against the reaction time . After a reaction of 12 hours, the exchange reaction was finished, indicating that more than 90% of the oxide ions in $\gamma\text{-}Bi_2MoO_6$ were replaced with oxygen-18. Figure 1 also gives the isotopic equilibrium of the carbon dioxide,

$$K = (C^{18}O^{16}O)^2/(C^{18}O_2)(C^{16}O_2),$$

where K reached its true equilibrium constant around 3.8 after 1 hour.

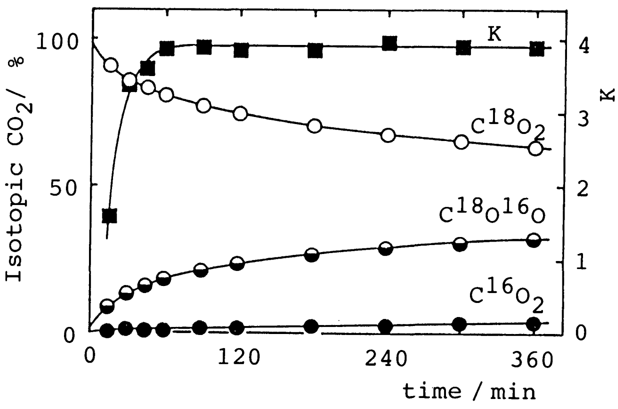

Fig. 1. Isotopic oxygen exchange of $C^{18}O_2$ with $\gamma\text{-}Bi_2MoO_6$ at 260 °C.

Table 1. Oxygen Diffusion Parameters of Bismuth Molybdate

Catalyst	Surface Area S/ m^2 g^{-1}	Particle Size 2r/ Å	pre-exponential factor $D_0/cm^2\ s^{-1}$	Activation Energy E/kJ mol^{-1}	Diffusion Coefficient at 380 °C D/cm^2 s^{-1}	Rate of C_4H_8 Oxidation at 380 °C k/s^{-1} m^{-2}
$\gamma\text{-}Bi_2MoO_6$	3.1	296	8.52×10^{-6}	123	1.38×10^{-15}	1.1×10^{-4}
$\gamma\text{-}Bi_2MoO_6$ (+4% MoO_3)	3.7	238	1.82×10^{-11}	67.5	3.10×10^{-16}	5.8×10^{-3}
$\beta\text{-}Bi_2Mo_2O_9$	2.6	240	7.77×10^{-12}	61.3	3.38×10^{-16}	6.6×10^{-3}
$\alpha\text{-}Bi_2Mo_3O_{12}$	2.7	296	3.22×10^{-8}	124	2.71×10^{-17}	1.6×10^{-3}

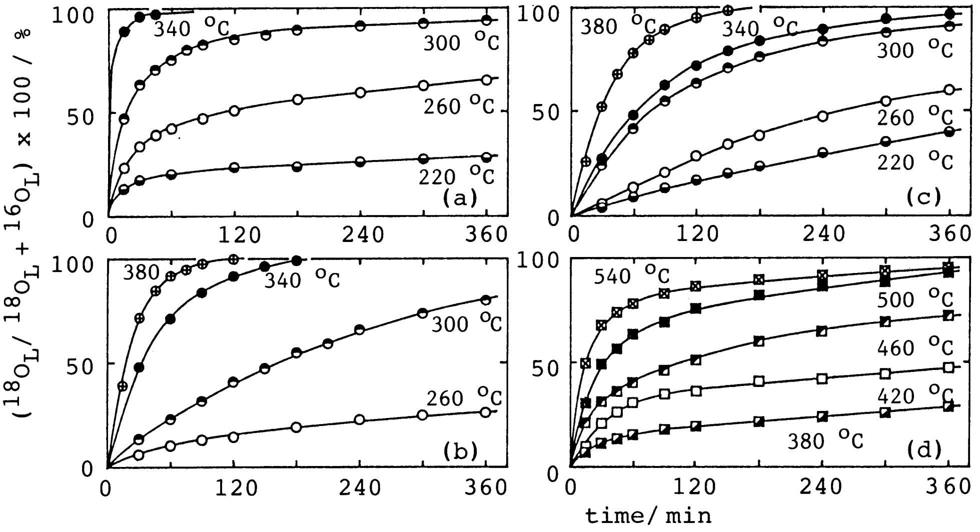

Fig. 2. Rate of oxygen exchange of bismuth molybdate with $C^{18}O_2$ as a function of time: (a) γ-Bi_2MoO_6, (b) γ-Bi_2MoO_6(+4% MoO_3). (c) β-$Bi_2Mo_2O_9$, (d) α-$Bi_2Mo_3O_{12}$

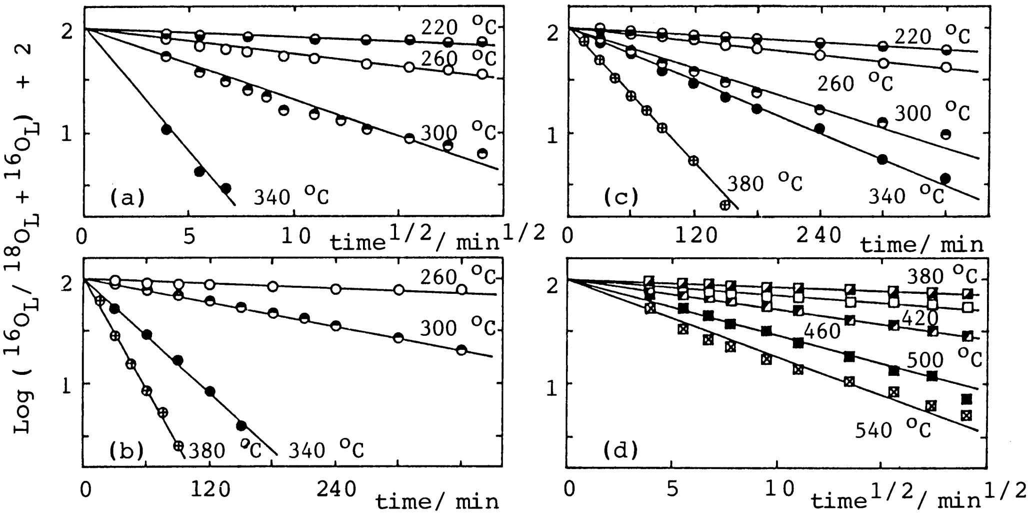

Fig. 3. Plots of the logarithms of oxygen exchange fraction versus time or root time: (a) γ-Bi_2MoO_6, (b) γ-Bi_2MoO_6(+4%MoO_3), (c) β-$Bi_2Mo_2O_9$, (d) α-$Bi_2Mo_3O_{12}$.

Figure 2 shows the isotopic oxygen fraction ($^{18}O_L$/ $^{16}O_L$ + $^{18}O_L$), where ($^{18}O_L$ + $^{16}O_L$) is equal to the oxide ions in the lattice oxygen of bismuth molybdates, against the reaction time . As shown in this figure, the exchange reaction of total oxygen in γ-Bi_2MoO_6 and β-$Bi_2Mo_2O_9$ progressed very fast, while that of α-$Bi_2Mo_3O_{12}$ was not so fast as those of the other two catalysts. This fact suggested that the oxide ions can migrate very easily through their crystal lattices.

The solid-gas exchange technique using oxygen-18 as a tracer has been used to study the oxygen diffusion in many single crystals and poltcrystalline oxides.[4)] The oxygen diffusion coefficient in bismuth molybdate can be estimated from the data obtained by measuring the exchange reaction of oxygen between carbon dioxide and the catalysts. In general, in the case of a small sphere, Crank's relation is used for calculating the diffusion coefficient D:

$$\frac{M_t}{M_\infty} = 1 - \frac{6\alpha(\alpha + 1)}{9 + 9\alpha + q^2\alpha^2} \exp(-Dq^2 t / r^2)$$

where q is the non-zero root of $\tan q = 3q / 3 + \alpha q$, r is the sphere radius, α is the gram atom ratio of oxygen present in the solid particles to that in the gas phase, and M_t is the total amount of tracer in the solid at time t as a function of the amount M_∞ after infinite time.5) For the mutual diffusion, Teichner et al.6) described the following equation,

$$\mathrm{Log} \frac{(a_t - a_\infty)}{(a_o - a_\infty)} = \rho S / n_g \sqrt{4D/\pi}\sqrt{t}$$

where S is the surface area, ρ is the number of oxygen ions in a unit volume of the solid, n_g is the number of oxygen atoms in the gas phase, and a_o, a_t, and a_∞ are the concentration of oxygen-18 in the carbon dioxide at time zero, t and infinity, respectively. Figure 3 shows the plot of the logarithms of the oxygen fraction ($^{16}O_L / ^{16}O_L + ^{18}O_L$) in the lattice oxygen against the reaction time for α - and γ - bismuth molybdate and the root of the reaction time for β - and 4% excess MoO_3 γ- bismuth molybdate. These plots are represented by straight lines which agree satisfactorily with either Crank's or Teichner's equation. Table 1 shows the thus-determined diffusion coefficients and activation energies as expressed in the formula $D = D_o \exp(-E / RT)$. In addition, the oxygen diffusion coefficient of these catalysts at 380 °C are indicated in Table 1, in order to compare them with those of the rate constants of 1-butene oxidation appearing in the same table. Except for inactive γ-Bi_2MoO_6, a correlation between the catalytic activity and the diffusivity of oxide ions could be recognized, as suggested by Keulks and Krenzke.2)

One of us has already reported that when a small amount of MoO_3 is added to inactive γ-Bi_2MoO_6 it becomes an active catalyst, because oxidation reaction sites are formed at the outer surface layer.7) Therefore, from the capability of γ-Bi_2MoO_6 to induce easy migration of oxide ions in the crystal, even though γ-Bi_2MoO_6 itself has no activity in oxidation reactions, we infer that the catalytic activity for oxidation is determined by mutual cooperation between the diffusibility of oxide ions inside a catalyst and the oxidation power of the reaction sites in the outer surface layer.

References

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