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REACTIVE LATTICE OXYGEN IN MULTICOMPONENT BISMUTH MOLYBDATE CATALYST FOR OLEFIN OXIDATION

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Position of the reactive lattice oxygen in the multicomponent bismuth molybdate catalyst was determined based on the isotope shift in Mo - O stretching vibration by measuring infrared and Raman spectra of the ^{18}O-substituted catalyst with propylene oxidation using $^{18}O_2$ tracer. It was proven that the oxidation reaction of olefin proceeds in accordance with the "water tank model" proposed by Moro-oka.

Oxidation reaction of olefins on bismuth molybdate catalyst is considered as a function of Redox mechanism which is controlled by lattice oxygen in the catalyst. Keulks[1)] and Wragg et al.[2)] examined the oxidation reaction of propylene using $^{18}O_2$ tracer on bismuth molybdate catalyst and found that lattice oxygen in the catalyst was incorporated in the products, acrolein and carbon dioxide. Moro-oka et al.[3)] have reported that, in many bismuth molybdate system catalysts, the participation of lattice oxygen for olefin oxidation came to over a few hundred layers depth inside the catalyst. One of us[4)] has found that, in multicomponent bismuth molybdate catalysts, the oxidation reaction of olefin proceeded on the surface layer of bismuth molybdate of the catalyst, but the oxygen used for the reaction was supplied from $M^{2+}MoO_4$ which constructed the core of the catalyst.

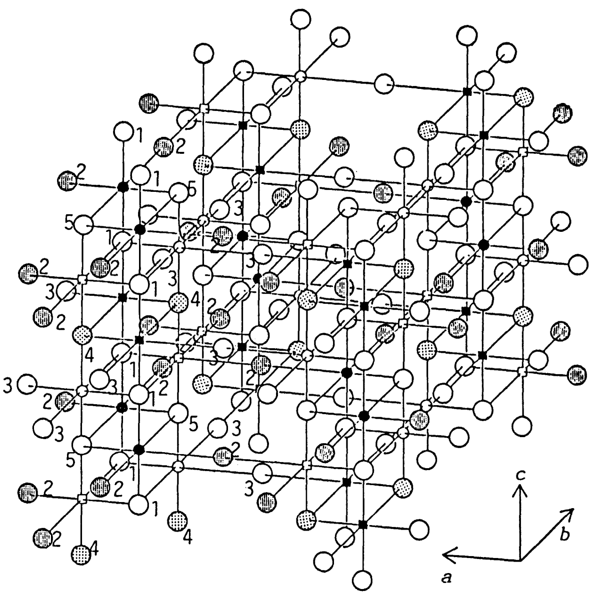
The present study was performed aiming at clarifying the reactive lattice oxygen in $M^{2+}MoO_4$ which constructs the core of multicomponent bismuth molybdate catalysts. As a model catalyst of multicomponent bismuth molybdate catalysts, we used α-$CoMoO_4$ and α-$MnMOO_4$ with 1% Bi and 3% Fe. The method of preparation of the model catalysts was given elsewhere.[4)] Propylene oxidation using $^{18}O_2$ tracer was carried out on the catalyst at 460 °C, according to the method of Moro-oka et al.,[3)] in order to replace ^{18}O for lattice oxygen in $M^{2+}MoO_4$ which participates in the oxidation reaction. The position of the reactive lattice oxygen in the core of catalyst was determined based on the isotope shift of Mo-O stretching vibration by measuring infrared and Raman spectra of the ^{18}O-substituted catalyst. Transferring process of oxygen in the core of catalyst during the oxidation reaction was also discussed.

The crystallographic data of α-$CoMoO_4$ and α-$MnMoO_4$ reported by Smith and Ibers[5)] and Abrahams and Reddy[6)] are shown in Table 1. The both structures are basically the same. A simplified structure of α-$CoMoO_4$ is shown in Fig. 1. Table 2 shows the assignment of the Mo-O stretching vibration of the $M^{2+}MoO_4$ on

Table 1. Crystallographic data for $M^{2+}MoO_4$

	α-$CoMoO_4$	α-$MnMoO_4$
Crystal system	monoclinic	monoclinic
Space group	C2/m (C^3_{2h})	C2/m (C^3_{2h})
Coordination of M^{2+}	octahedral	octahedral
Coordination of Mo^{6+}	octahedral	tetrahedral
Mo - O bond length / A^o	Mo(1)-O(1) 2.314(2)	
	Mo(1)-O(3) 1.726(2)	Mo(1)-O(3) 1.724(2)
	Mo(1)-O(4) 1.891	Mo(1)-O(4) 1.851
	Mo(1)-O(5) 1.980	Mo(1)-O(5) 1.738
	Mo(2)-O(1) 1.928(2)	Mo(2)-O(1) 1.795(2)
	Mo(2)-O(2) 1.719(2)	Mo(2)-O(2) 1.731(2)
	Mo(2)-O(5) 2.328(2)	

the basis of normal coordinate analysis by use of a valence force field.$^{7)}$ This analysis was made based on the structural data of the crystals reported by Smith and Ibers$^{5)}$ and Abrahams and Reddy.$^{6)}$



○ ; Mo(1), □ ; M^{2+}(1), ◯ ; O^{2-}.
● ; Mo(2), ■ ; M^{2+}(2).

Fig. 1. Simplified structure of α-$CoMoO_4$.

Figures 2 and 3 show infrared and Raman spectra of the two catalysts before and after the oxidation reaction of propylene with $^{18}O_2$. In the case of α-$CoMoO_4$ after the oxidation, absorption bands in the infrared at 920 cm^{-1} and in Raman at 900 cm^{-1} strongly reduced and new bands were observed at 900 cm^{-1} and at 880 cm^{-1}, respectively. Absorption in infrared at 650 cm^{-1} was shifted to 630 cm^{-1}. For α-$MnMoO_4$, absorption band in infrared and Raman at 870 cm^{-1} was reduced and a new band was observed at 850 cm^{-1}. In addition a small shoulder was also observed at 690 cm^{-1} in infrared spectrum. Based on the results shown in Table 2, the new absorption bands at 900 cm^{-1} in infrared and at 880 cm^{-1} in Raman of α-$CoMoO_4$ and at around of 850 cm^{-1} of α-$MnMoO_4$ were ascribed to the isotope shift of Mo(2)-^{16}O(2) stretching vibration caused by the replacement of ^{18}O for ^{16}O. Other absorption bands newly observed were found to be a result of the isotope shift of Mo(1)-^{16}O(4) stretching vibration due to the ^{18}O-replacement. From these results, it was concluded that the oxidation reaction

Table 2. Mo - O stretching vibration of α-$CoMoO_4$ and α-$MnMoO_4$

α-$CoMoO_4$	ν / cm^{-1}	After reaction (new band)	α-$MnMoO_4$	ν / cm^{-1}	After reaction (new band)
Mo(1)-O(1)	600(IR)				
Mo(1)-O(3)	945(IR)		Mo(1)-O(3)	928(IR)	
	946(R)			933(R)	
Mo(1)-O(4)	650(IR)	630(IR)	Mo(1)-O(4)	726(IR)	690(IR)
Mo(1)-O(5)	600(IR)		Mo(1)-O(5)	945(IR)	
	620(R)			940(R)	
Mo(2)-O(1)	710(IR)		Mo(2)-O(1)	800(IR)	
	705(R)			821(R)	
Mo(2)-O(2)	920(IR)	900(IR)	Mo(2)-O(2)	870(IR)	845(IR)
	900(R)	880(R)		875(R)	850(R)
Mo(2)-O(5)	600(IR)				

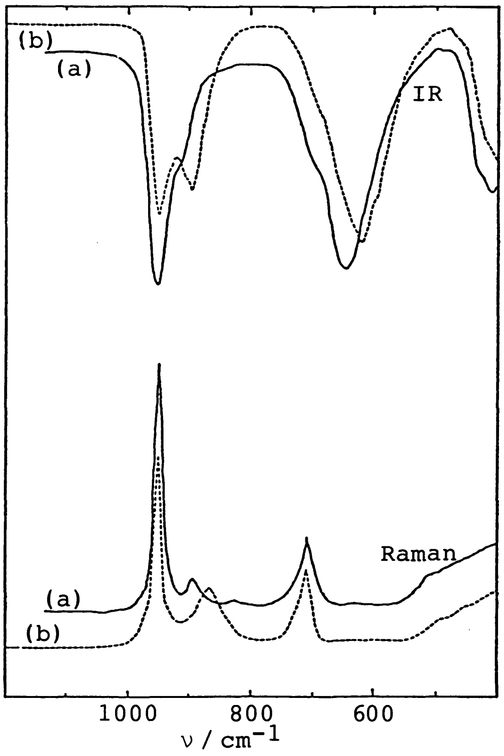


Fig. 2. IR and Raman spectra of α-$coMoO_4$ (a) before; (b) after C_3H_6 + $^{18}O_2$ reaction.

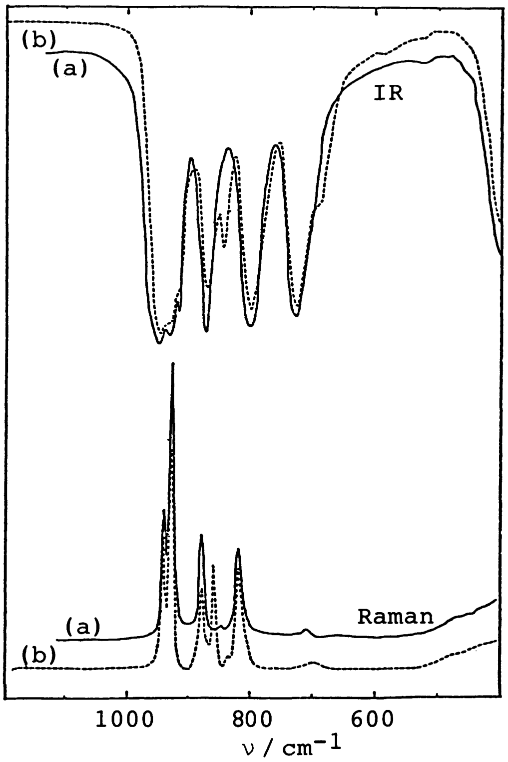


Fig. 3. IR and Raman spectra of α-$MnMoO_4$ (a) before; (b) after C_3H_6 + $^{18}O_2$ reaction.

of the olefin proceeded with the participation of lattice oxygen marked as O(2) and O(4) in the crystal of $M^{2+}MoO_4$ which constructed core of the catalyst.

Moro-oka8) has proposed a "water tank model" for the partial oxidation process of olefin oxidation on catalyst. According to his model, the catalyst contains a site for olefin oxidation and another site for oxygen adsorption, and the two sites are connected by a channel inside the catalyst. The oxidation reaction proceeds by the function of the channel and two sites. From the results obtained in this study using $M^{2+}MoO_4$ based catalyst, it was proven that the oxidation reaction of olefin proceeds in accordance with the "water tank model" of Moro-oka.

As can be seen in Fig. 1, $M^{2+}MoO_4$ which constructs the core of multicomponent bismuth molybdate catalyst is composed of columns made of $(M^{2+}_4Mo_4O_8)^{16+}_n$, and the crystal maintains its stable structure by connecting the columns each other through two oxygen ions marked as O(2) and O(3). In addition, the O(2) and O(3) ions form oxygen layers parallel to the a-c and b-c axes in the crystal. The O(2) ions which participate in the oxidation reaction of olefin are arranged stepwisely from (010) plane to (001) plane and from (100) plane to (001) plane in the oxygen layers. We already have reported that the (010) and (100) planes of $M^{2+}MoO_4$ were covered with bismuth molybdate.$^{9)}$ Consequently, it is concluded that bismuth molybdate on these two planes acts as the olefin oxidation site by connecting O(2) ions, which are arranged in the oxygen layer of $M^{2+}MoO_4$, and the (001) plane of $M^{2+}MoO_4$ which is not covered with bismuth molybdate acts as the oxygen adsorption site.

In this study, it was found that lattice oxygen marked as O(4) was also replaced partially by ^{18}O, in addition to the lattice oxygen marked as O(2) which was through to participate in the oxidation reaction in the $M^{2+}MoO_4$ crystal. This, however, will be explained as a result of the inter - exchanging reaction between O(2) and O(4) ions in the crystal, in view of the location of O(4) ions in the $M^{2+}MoO_4$ crystal.

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