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STRUCTURAL STABILITY OF SCHEELITE CATALYSTS IN THE REDUCTION-OXIDATION CYCLE

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Structural stability of scheelite catalysts, $Bi_{1-x/3}V_{1-x}Mo_xO_4$, in the reduction and reoxidation cycle increases with an increase of the mobility of the lattice oxide ions in the catalysts.

Composite metal oxides containing V and VI group elements are widely used for the industrial catalytic oxidations, where the redox mechanism involving lattice oxide ions has been well established.1,2) Life of these redox catalysts, i.e. deactivation and decrease of selectivity with time, is closely associated with the decomposition of the composite structure of the catalyst by the partial reduction in the redox cycle. In this communication, we wish to report that the structural stability of scheelite catalysts, $Bi_{1-x/3}V_{1-x}Mo_xO_4$, in the redox cycle seriously depends on the mobility of the lattice oxide ions revealed by the $^{18}O_2$ tracer investigation.

Five scheelite catalysts having different composition were prepared from mixtures of ammonium metavanadate, ammonium heptamolybdate and bismuth nitrate solution.3,4) Each mixed slurry was solidified by evaporation of water at 80 °C, dried at 110 °C, and calcined for 4 h at 500 °C. $^{18}O_2$ tracer experiments, reduction of catalyst in hydrogen, and temperature-programmed reoxidation (TPRO) were carried out using a conventional closed circulating system. The rates of reduction and reoxidation of the catalysts were followed by monitoring the decrease of pressure of hydrogen and oxygen, respectively. Details of the experimental procedure for $^{18}O_2$ tracer measurement in the oxidation of propylene were the same as reported previously.5,6) Structural analysis of catalyst after the reduction and reoxidation was carried out by powder X-ray diffraction patterns which were recorded using an X-ray diffractometer with CuK_α radiation.

All catalysts tested in the present study show the scheelite structure but the symmetry varies from monoclinic to tetragonal at about X=0.12.4) Characteristics, reduction rates in hydrogen, and catalytic properties in the oxidation of propylene for each scheelite catalyst are summarized in Table 1. As already reported, specific activity of these catalysts increases with increasing the cation vacancies introduced by the substitution of V^{5+} for Mo^{6+} ($Bi_{1-x/3}V_{1-x}Mo_x\phi_{x/3}O_4$,

ϕ ; cation vacancy).7) On the other hand, the reduction rate in hydrogen at 450 °C was the highest on $BiVO_4$ and decreased by the substitution of vanadium for molybdenum. The comparison of the reduction rate in hydrogen with the surface content of bismuth determined by XPS analysis (Table 1) suggests that the reduction proceeds mainly on the bismuth site. Actually, metallic bismuth was detected by XRD analysis in the several catalysts.

The fraction of lattice oxide ion involved in the oxidation of propylene to the total lattice oxide ions in the catalyst was estimated from $^{18}O_2$ tracer measurement, and values are listed in the fourth column in Table 1. The fraction increased with increasing the content of molybdenum, and in the case of $Bi_{0.85}V_{0.55}Mo_{0.45}O_4$ the fraction reached to 100%, indicating that the whole of oxide ion participates in the redox cycle. Rapid diffusion of the lattice oxide ions in the bulk of catalyst seems to be assisted by cation vacancies.

Structural stability was evaluated by XRD method, and typical XRD patterns of the catalysts after the reduction and reoxidation are shown in Fig. 1 for $BiVO_4$, $Bi_{0.93}V_{0.79}Mo_{0.21}O_4$ and $Bi_{0.85}V_{0.55}Mo_{0.45}O_4$. The following features in the variation of XRD patterns with the molybdenum concentration are prominent:

1) Free bismuth metal was detected after the reduction on the catalysts having lower content of molybdenum. In the case of $Bi_{0.85}V_{0.55}Mo_{0.45}O_4$, no liberated bismuth metal was detected after the treatment.
2) Peak broadening in the XRD was prominent after the reduction for the catalysts having higher content of molybdenum. This suggests that the reduction is not limited to the surface and structural deformation spreads over to the whole of catalyst.
3) After the oxidation at 450 °C, XRD peaks of free bismuth disappeared and the XRD pattern of the catalyst completely coincided with that of the original one except in the case of $BiVO_4$, where several unidentified new peaks were detected.

Table 1. $^{18}O_2$ Tracer measurement and XRD analysis data of $Bi_{1-x/3}V_{1-x}Mo_xO_4$.

	Propylene oxidation1)			Reduction	Surface	XRD analysis	
X	Activity ($\times10^{-4}$mol /min·m^2)	Sel. to acrolein (%)	Fraction2) (%)	rate3) ($\times10^{-6}$mol /min·m^2)	Bi4) (atom %)	Symmetry	Bi metal phase
0	0.08	75.6	37	12.1	20.6	monoclinic	d.5)
0.09	0.87	85.1	57	8.7	14.6	monoclinic	d.
0.21	1.43	93.7	75	7.8	15.1	tetragonal	d.
0.27	1.31	90.8	72	7.6	14.6	tetragonal	t6)
0.45	1.69	90.8	100	6.4	14.0	tetragonal	n.d.7)

1) All runs were carried out at 450 °C using 0.1 g of catalyst. Initial pressure: $P_{C_3H_6}=P_{O_2}=70$ Torr. 2) Values were estimated by assuming the complete mixing model. 3) Rates of catalyst reduction by hydrogen at 450 °C as the catalysts were partially reduced (5.8%). Initial pressure of hydrogen: 200 Torr. 4) Bi/Bi+V+Mo+O. 5) Detected. 6) Trace. 7) Not detected.

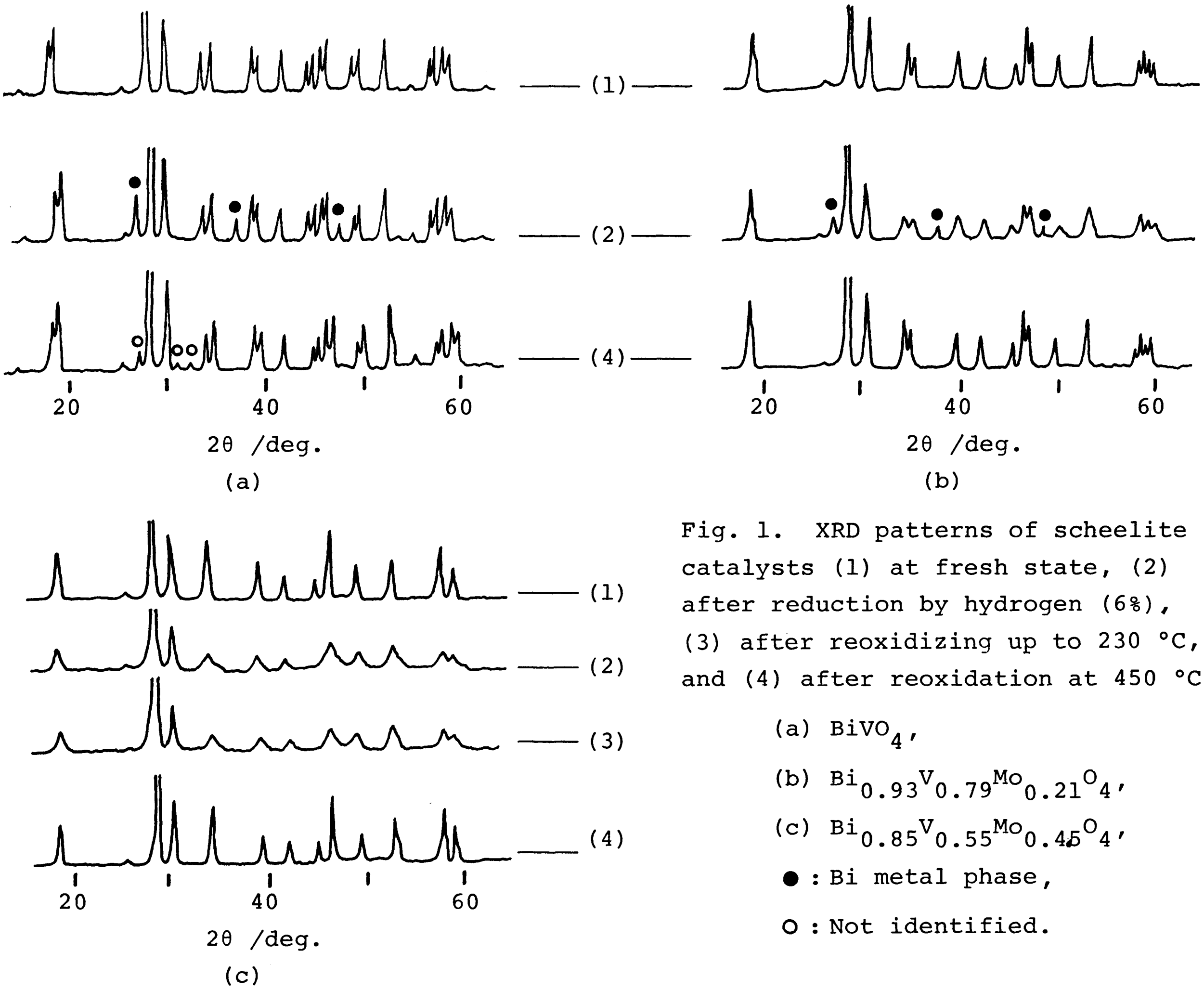

Fig. 1. XRD patterns of scheelite catalysts (1) at fresh state, (2) after reduction by hydrogen (6%), (3) after reoxidizing up to 230 °C, and (4) after reoxidation at 450 °C.

(a) $BiVO_4$,

(b) $Bi_{0.93}V_{0.79}Mo_{0.21}O_4$,

(c) $Bi_{0.85}V_{0.55}Mo_{0.45}O_4$,

● : Bi metal phase,

○ : Not identified.

These facts suggest that the scheelite catalysts with higher content of molybdenum are structurally stable in the redox cycle because the reduction of catalyst proceeds to the whole of oxide, whereas in the catalysts with lower content of molybdenum, especially in $BiVO_4$, the reduction is localized to the surface layer of oxide and thus its surface structure is fairly changed after the reduction and reoxidation.

We also evaluated the structural stability of scheelite catalysts using the TPRO technique, and TPRO spectra obtained for partially reduced catalysts (6%) are shown in Fig. 2. Reoxidation took place in two steps for every catalyst; first step at about 180 °C and second step at near 320 °C. The first step reoxidation may correspond to the oxidation of liberated metallic bismuth.8) The second step may correspond to the replenishing process of oxygen to the oxygen deficient site in Bi-O-V(Mo) bond matrix of scheelite structure.9) These assingments are justified by the XRD observation shown in Fig. 1 for $Bi_{0.85}V_{0.55}Mo_{0.45}O_4$, where the deformed scheelite structure of reduced oxide does not return to the original state by the reoxidation up to 230 °C but returns by the oxidation at 450 °C.

As can be seen in Fig. 2, the oxygen consumption at the second step reoxidation gradually increased with increasing the content of molybdenum in the catalyst.

This indicates that the reduction in the inside of bulk is predominant in the catalysts with higher content of molybdenum. The results are fairly consistent with XRD observation.

The results of XRD and TPRO measurements are explained on the basis of the mobility of lattice oxide ions revealed by $^{18}O_2$ tracer experiments. When the catalyst of which lattice oxide ion can diffuse rapidly is reduced, the reduced site on the vicinity of surface layer migrates to the inside of bulk and the reduction extends to the whole of catalyst. Consequently, the structural deformation caused by reduction spreads over the whole of oxide and the surface structure seems to be kept in constant state during the redox cycle.

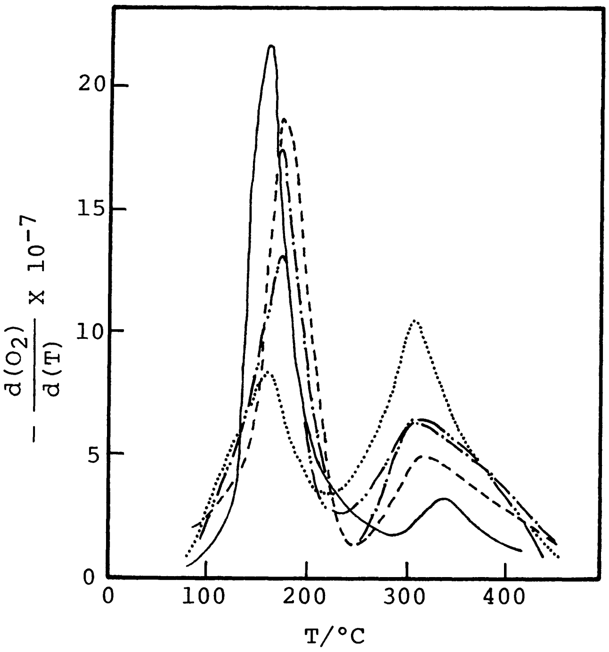

Fig. 2. Temperature-programmed reoxidation spectra of reduced catalysts.

—— : $BiVO_4$,
----- : $Bi_{0.97}V_{0.91}Mo_{0.09}O_4$,
—·— : $Bi_{0.93}V_{0.79}Mo_{0.21}O_4$,
—··— : $Bi_{0.91}V_{0.73}Mo_{0.27}O_4$,
……… : $Bi_{0.85}V_{0.55}Mo_{0.45}O_4$.

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9) Both reoxidation of slightly reduced MoO_3 and V_2O_5 needed higher temperature (near 450 °C) than the second step reoxidation of Bi-V-Mo-O oxide. It is obscure which metal element was reduced.

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