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Catalytic Properties of Tricomponent Metal Oxides Having the Scheelite Structure

II. Structural Stability in the Reduction–Oxidation Cycle

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Structural stability of complex metal oxide catalysts having the scheelite structure, $Bi_{1-x/3}V_{1-x}Mo_xO_4$, in the reduction–oxidation cycle is discussed on the basis of the mobility of lattice oxide ions determined by $^{18}O_2$ tracer measurements. Reduction of $BiVO_4$ and Bi–V–Mo–O with a lower content of molybdenum, where the mobilities of lattice oxide ions are low, takes place in the vicinity of the surface layer of oxide, so that the surface structure is significantly changed after the reduction–oxidation cycle. The catalysts which contain the higher amounts of molybdenum are found to be stable during the reduction–oxidation process because rapid migration of lattice oxide ions prevents the local reduction of the catalysts. © 1986 Academic Press, Inc.

INTRODUCTION

Complex metal oxides containing group V and/or VI elements as the main constituents are widely used for the industrial catalytic oxidation of olefins (*1*), where the redox mechanism, the so-called Mars and van Krevelen mechanism, has been well established (*2, 3*). One of the serious problems concerning the complex metal oxide systems is the decomposition of the active phase, which results in the deactivation of the catalyst system. The active composite oxide phase in the redox catalyst system is stable only when the reoxidation rate is balanced with the reduction rate. When the balance is lost, the active site may be deformed in the reduced state by the elimination of coordinated oxygen. Finally, the composite structure of the catalyst decomposed by changing into different phases or releasing the active element with the decay of catalytic activity and selectivity. Oxidation catalysts, therefore, are usually prepared by the combination of various metal oxides in order to obtain the higher structural stability.

We recently tried to obtain an insight into the role of the metal component of multicomponent oxidation catalysts in the redox mechanism on the basis of $^{18}O_2$ tracer measurements (*4, 5*). In a previous investigation of tellurium-based oxide catalysts, we obtained a good correlation between the degree of tellurium vaporization during the reaction and the number of oxide ion layers involved in the oxidation (*6*). This result suggested that the high mobility of the lattice oxide ions in the catalyst system plays an important role in sustaining the oxidation state of the active site from deep reduction and suppressing the vaporization of tellurium from the catalyst.

In our continuing study of complex metal oxide catalysts having the scheelite structure, $Bi_{1-x/3}V_{1-x}Mo_xO_4$ (*7*), we further report that the structural stability in the redox cycle depends strongly on the mobility of the lattice oxide ions.

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TABLE 1

Characterization of $Bi_{1-x/3}V_{1-x}Mo_xO_4$ Catalysts

X	Surface area (m^2/g)	Surface concentration of bismuth[a] (atom %)	Reduction rate in hydrogen[b] (10^{-6} mol H_2/min · m^2)	Mobility of lattice oxide ion[c] (%)
0.00	1.8	20.6	12.1	37.0
0.09	1.4	14.6	8.7	57.4
0.21	2.4	15.1	7.8	75.1
0.27	2.4	14.6	7.6	72.2
0.45	2.6	14.0	6.4	100

[a] Bi/(Bi + V + Mo + O).

[b] Rate of catalyst reduction by hydrogen at 5.8% reduction (450°C). Initial pressure of hydrogen: 200 Torr.

[c] Fraction of lattice oxide ions involved in the oxidation to the total lattice oxide ions in the catalyst. Values are taken from Ref. (*7*).

EXPERIMENTAL

Five scheelite oxide catalysts having different compositions, $Bi_{1-x/3}V_{1-x}Mo_xO_4$ ($X = 0, 0.09, 0.21, 0.27$, and 0.45), were examined in the present investigation. The preparation method was reported in the accompanying paper (*7*). Reduction of the catalysts in hydrogen and temperature-programmed reoxidation (TPRO) was carried out using a conventional closed circulating system. The rates of reduction and reoxidation of the catalysts were followed by monitoring the decrease in pressure of hydrogen and oxygen. TPRO spectra of partially reduced catalysts (6%) were obtained under oxygen in increasing temperature (9°C/min). Structural analysis of the catalysts after the reduction and reoxidation was carried out by powder X-ray diffraction patterns which were recorded using an X-ray diffractometer with CuKα radiation.

RESULTS AND DISCUSSION

Reduction of the Catalysts

All catalysts tested in the present study have the scheelite structure but the symmetry varies from monoclinic to tetragonal with increasing molybdenum content (*8*). Every catalyst tested shows activity for the selective oxidation of propylene to acrolein as already reported (*9*). Mobility of the lattice oxide ions in the bulk of the catalysts is also high, especially at $X = 0.45$, where complete mixing of all lattice oxide ions is attained at the reaction conditions of propylene (*7*).

The reduction rate of each catalyst in hydrogen at 450°C and the surface content of bismuth determined by XPS are summarized in Table 1. The surface area of each catalyst is also listed in Table 1. The surface area of each catalyst did not change significantly after the reduction and the reoxidation adopted in these experiments.

The reduction rate in hydrogen at the initial stage was the highest on $BiVO_4$ and decreased with the substitution of vanadium by molybdenum in the catalyst system. It is noteworthy that the change in reduction rate as a function of molybdenum content is the reverse of that in the catalytic activity for the propylene oxidation. Since the catalytic activity of the scheelite catalysts parallels the reduction rate by propylene, the reversed dependency of the reduction rate by hydrogen on the molybdenum content suggests that the reducibility of the catalysts changes strongly depending on the reactant, propylene or hydrogen. Strong dependency of the reduction rates on the reductant was also observed in the reduction of Bi_2MoO_6 reported previously (*10*). Since the catalyst reduction is first-order to both hydrogen and propylene, the difference may be ascribed to the difference of the active site. Catalyst reduction may take place on the surface bismuth site because the reduction rate increased with increased surface concentration of bismuth cation (Table 1).

The reduction rate in hydrogen changes slightly with the degree of reduction. The dependency of the reduction rate on the degree of reduction is shown in Fig. 1. The degree of reduction on the abscissa is defined as $100y/4$ when the stoichiometry of the reduced oxide is $Bi_{1-x/3}V_{1-x}Mo_xO_{4-y}$. In the case of $BiVO_4$, the reduction rate decreased as the reduction proceeded,

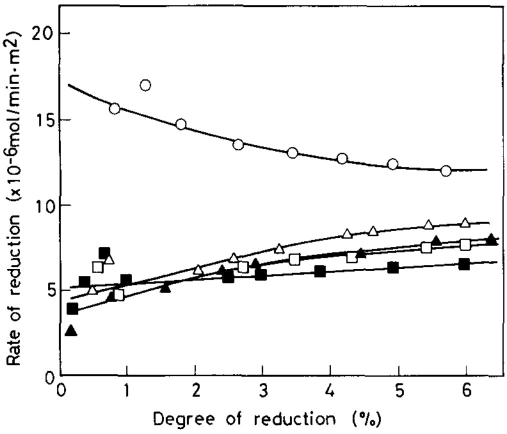

FIG. 1. Changes of the reduction rates of catalysts in hydrogen with the degree of reduction. Reduction temperature: 450°C. ○, $BiVO_4$; △, $Bi_{0.97}V_{0.91}Mo_{0.09}O_4$; ▲, $Bi_{0.93}V_{0.79}Mo_{0.21}O_4$; □, $Bi_{0.91}V_{0.73}Mo_{0.27}O_4$; ■, $Bi_{0.85}V_{0.55}Mo_{0.45}O_4$.

whereas the rates of the reduction of other catalysts increased with increased degree of reduction.

The reduced state of the scheelite catalysts at 6% reduction was investigated by using the XRD method. XRD patterns of the catalysts tested at the fresh state and after the reduction are shown in Fig. 2. The reduced samples were exposed in air at room temperature for the measurement of XRD but no appreciable change was observed for any catalyst. It was also confirmed by TPRO experiments which showed that the reoxidation of the reduced catalyst did not occur at room temperature. Two prominent features were revealed from the comparison of the XRD results for the catalysts having different compositions at the fresh state and at the reduced state:

1. Free bismuth metal was detected after reduction in catalysts having lower molybdenum contents, especially in $BiVO_4$. Relative XRD intensities of free bismuth metal decreased with increased content of molybdenum and no liberated bismuth metal was detected in the catalyst having the highest concentration of molybdenum.
2. All peaks of the fresh catalysts having higher concentrations of molybdenum were broadened after the reduction and the peak broadening became more prominent as the content of molybdenum was increased.

In the scheelite oxide, $Bi_{1-x/3}V_{1-x}Mo_xO_4$, V or Mo cation is tetrahedrally coordinated to oxygen with all V–O (or Mo–O) bonds being ideally equal in length, while the Bi cation is coordinated to eight oxygens from eight different tetrahedra. Simply, the structure may be considered as an assemblage of $[V(Mo)O_4]^{n-}$ anions and Bi cations. Since the $[V(Mo)O_4]^{n-}$ anions are not linked to each other and there is no oxygen bound exclusively to the bismuth cation, the elimination of lattice oxide ions by reduction may occur at tetrahedral sites, causing deformation of the tetrahedra, and the remaining electrons are trapped to the bismuth cations resulting in the reduced bismuth. The former may result in broadening of the XRD peaks and the latter forms free bismuth metal. The formed bismuth metal may aggregate in the oxide matrix by a thermal process giving larger particles which are detectable by XRD analysis. Since the degree of the reduction was restricted to only 6% of the total oxide ions, the metallic phase would be detected only when the reduction of the catalyst is localized in the vicinity of the oxide surface. On the other hand, when the reduction spreads to the whole oxide, peak broadening due to structural deformation is observed and no metallic bismuth phase is detected. As can be seen in Fig. 2, the typical former case is $BiVO_4$ and the latter case is the catalyst having the highest content of molybdenum ($X = 0.45$).

It is easily seen that migration of the lattice oxide ions during reduction plays an important role in the structural change of the scheelite catalysts. When oxides, such as $BiVO_4$, have low mobility of lattice oxide ions, the reduction takes place in a limited region, that is, in the vicinity of the oxide surface layer and not within the oxide bulk. Therefore, the surface structure may be changed considerably but the internal structure may remain unchanged. This results in

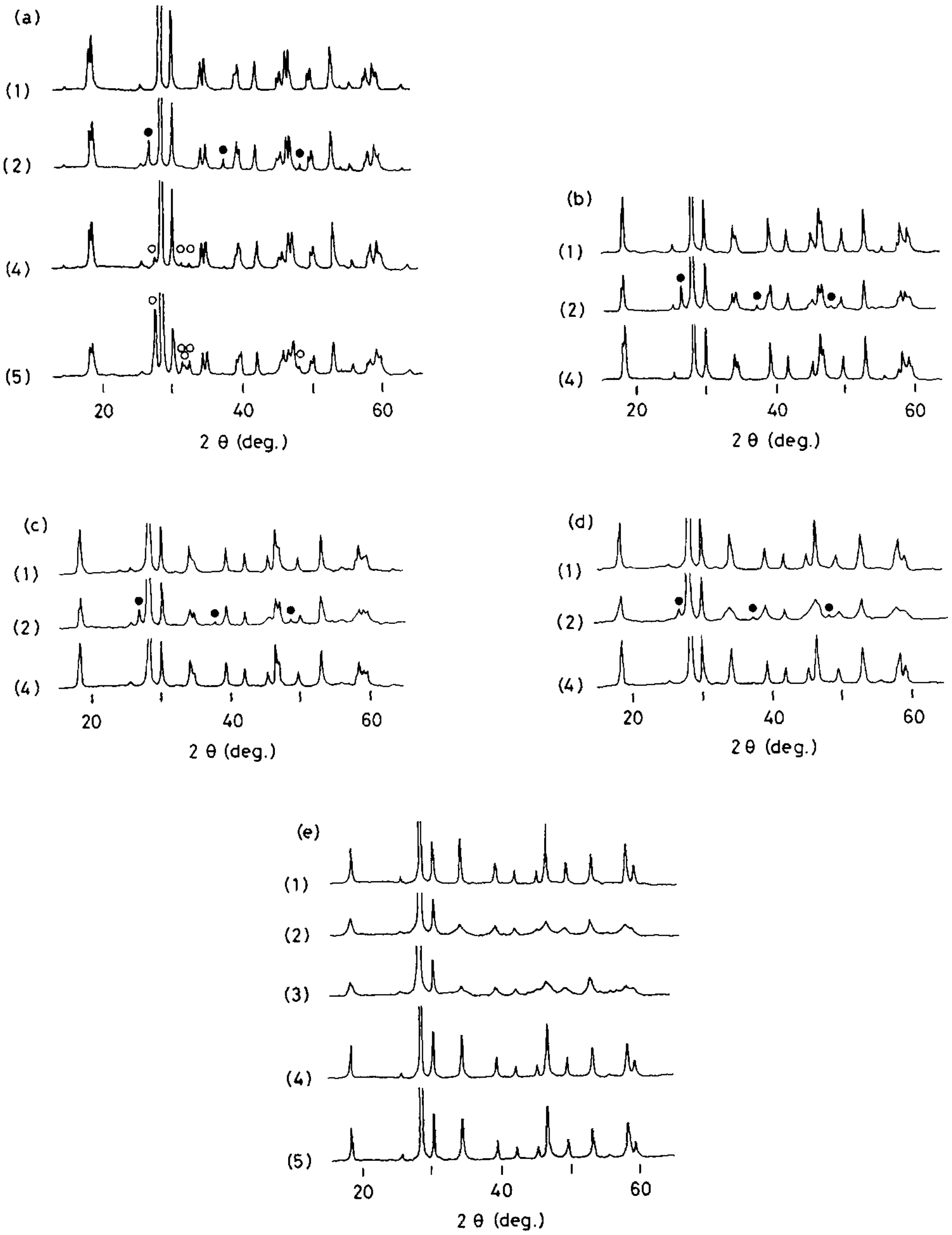

FIG. 2. XRD patterns of scheelite oxide catalysts, $Bi_{1-x/3}V_{1-x}Mo_xO_4$: (1) at fresh state; (2) after reduction in hydrogen (6%); (3) after temperature-programmed reoxidation up to 230°C; (4) after temperature-programmed reoxidation up to 450°C; (5) after four reduction (450°C, in H_2) and reoxidation (TPRO, up to 450°C) cycles. (a) $BiVO_4$; (b) $Bi_{0.97}V_{0.91}Mo_{0.09}O_4$; (c) $Bi_{0.93}V_{0.79}Mo_{0.21}O_4$; (d) $Bi_{0.91}V_{0.73}Mo_{0.27}O_4$; (e) $Bi_{0.85}V_{0.55}Mo_{0.45}O_4$. ●, Bi metal phase; ○, unidentified.

no peak broadening. When the diffusion of lattice oxide ions becomes rapid due to the combination of molybdenum (7), the reduction can proceed in the internal lattice by the transfer of reduced sites from the oxide surface to internal sites through the migration of electrons and lattice oxide ions. This results in a broadening of the XRD peaks. Reduced bismuth elements as well as oxide ion vacancies would be formed in these cat-

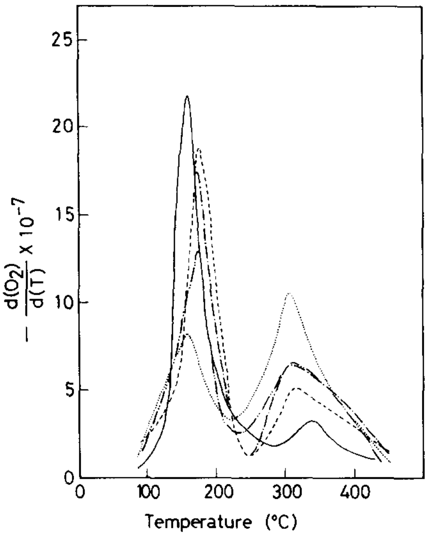

FIG. 3. Temperature-programmed reoxidation spectra of partially reduced catalysts (6%). —, $BiVO_4$; ---; $Bi_{0.97}V_{0.91}Mo_{0.09}O_4$; –·–, $Bi_{0.93}V_{0.79}Mo_{0.21}O_4$; –··–, $Bi_{0.91}V_{0.73}Mo_{0.27}O_4$; · · ·, $Bi_{0.85}V_{0.55}Mo_{0.45}O_4$.

alysts but are dispersed in the bulk of the oxide, so that no XRD patterns derived from metallic bismuth phase were detected.

Reoxidation of the Reduced Catalysts

The reduced state of the catalysts was further examined by using the TPRO technique. TPRO spectra were obtained for the partially reduced catalysts (6%) and are shown in Fig. 3. Two kinds of TPRO peak were observed for each catalyst. The first peak shows a maximum at about 180°C and the second at 230°C. The consumption of molecular oxygen at the first reoxidation step decreased with increasing molybdenum content in the catalyst, whereas the consumption of molecular oxygen in the second step increased with molybdenum concentration. The reoxidation temperature of the first step was independent of the catalyst composition. The second peak of TPRO shifts to the lower temperature with increase of the molybdenum concentration. XRD patterns of the catalysts were also measured after the TPRO up to 450°C (Fig. 2). All catalysts except $BiVO_4$ recovered their original patterns recorded before the reduction but several unidentified new peaks were detected in the case of $BiVO_4$ (Fig. 2a).

The first peak of TPRO is assigned to the reoxidation of the reduced bismuth because partially reduced bismuth oxide shows the same TPRO peak at 180°C. This assignment is supported by the fact that both the amount of the oxygen consumed in the first reoxidation step in the TPRO and the XRD peak intensity of the liberated bismuth metal show the same dependency on the molybdenum content of the catalyst. In addition, the XRD peaks below 230°C of bismuth metal in the reduced catalyst disappeared in the reoxidation. Thus, it seems reasonable that the first peak corresponds to the reoxidation of the reduced bismuth element.

The second reoxidation step is assumed to be the replenishing process of the oxygen to the oxide ion vacancies in the Bi–O–V(Mo) bond matrix in the bulk of the scheelite structure through the bulk diffusion of oxide ions. Since the reoxidation of partially reduced MoO_3 or V_2O_5 needs a higher temperature (ca. 450°C) than the second reoxidation step of the Bi–V–Mo–O system, the reduced element after the reduction seems to be bismuth rather than molybdenum or vanadium.

In order to justify the above assignments, especially for the second reoxidation step, further measurements of XRD and TPRO were carried out for the catalyst ($X = 0.45$). The XRD pattern of this catalyst after the reduction (6%) was compared to that obtained after the temperature-programmed reoxidation up to 230°C (Fig. 2e). Both XRD patterns showed similar peak broadening. The result indicates that the replenishing process of oxygen to the oxide ion vacancies from the surface to the inside of the bulk through the bulk diffusion of oxide ions does not proceed at a temperature below 230°C.

Figure 4 shows another TPRO spectrum and XRD pattern of the catalyst ($X = 0.45$) which reduced partially (6%) under hydro-

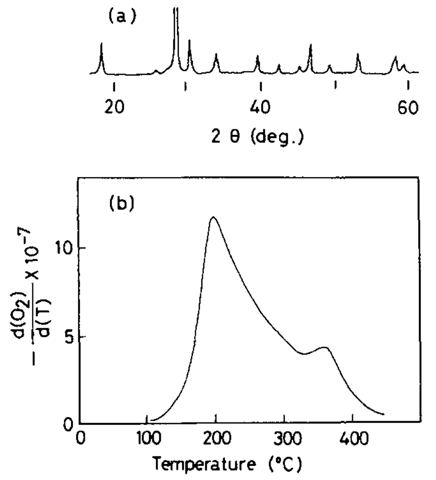

FIG. 4. XRD pattern (a) and temperature-programmed reoxidation spectrum (b) of the partially reduced (6%) $Bi_{0.85}V_{0.55}Mo_{0.45}O_4$ catalyst in hydrogen at 350°C.

gen at 350°C. Interestingly, the TPRO spectrum was quite different from that obtained on the same catalyst reduced at 450°C. The reoxidation took place mainly in the first step. No peak broadening was observed in the XRD pattern. This result is quite similar to that obtained on $BiVO_4$ and may be attributable to the low diffusion rate of lattice oxide ions at 350°C. All the results suggest that our assignments with regard to the two steps of the reoxidation are reasonable and that the mobility of the oxide ions affects the redox properties of oxide catalysts.

On the basis of the above assignments of the reoxidation steps, it can be expected that the second reoxidation step should start at the lower temperature for the higher molybdenum content catalysts because the bulk diffusion rate increases with the increase in molybdenum content. In fact, the shift of the second TPRO peak to the lower temperature was observed with increased molybdenum content.

Structural Stability of the Multicomponent Catalysts in the Redox Cycle

It is well known that a number of multicomponent transition metal oxide catalysts, such as multicomponent bismuth molybdates, modified iron antimonates, and scheelite type oxides, are utilized widely in the industrial oxidation of lower hydrocarbons. One of the serious problems regarding the practical use of these multicomponent catalysts is the deactivation of the catalysts due to the decomposition of the active composite oxides. The results obtained in this study may throw light on the problem.

The structural stability of two typical catalysts, $BiVO_4$ and $Bi_{0.85}V_{0.55}Mo_{0.55}O_4$, were further examined by XRD measurements after the repeated redox cycles (Figs. 2a and 2e). In the $BiVO_4$ catalyst, which has the lowest mobility of lattice oxide ions among catalysts having the $Bi_{1-x/3}V_{1-x}Mo_xO_4$ structure, a significantly changed XRD pattern was observed after four cycles of reduction (450°C, under hydrogen) and reoxidation (TPRO, up to 450°C). Since the lattice oxide ions in $BiVO_4$ could not diffuse rapidly during the reduction, the catalyst was reduced mainly in the vicinity of the surface oxide layer and was destroyed completely after repeating the redox cycle. On the other hand, $Bi_{0.85}V_{0.55}Mo_{0.45}O_4$ has the highest mobility of the lattice oxide ions, so that the reduction was not limited to the vicinity of the surface oxide layers but could spread into the bulk of the catalyst. The structural deformation caused by the reduction would be mild compared to that of $BiVO_4$ and the surface structure seems to be unimpaired during the reduction and reoxidation. In fact, no unidentified peaks or peaks assigned to the metallic bismuth were detected at any time during the redox cycle. The original XRD pattern was completely recovered after four redox cycles as shown in Fig. 2e and the catalysts showed high structural stability during the redox cycle long after the experiment.

The structure of the composite oxide catalysts for the oxidation of hydrocarbons changes dynamically under the reaction conditions according to the Mars and van Krevelen mechanism. The structural changes of the catalysts result in changes of the catalytic properties. Formation of different metal oxide phases, growth of larger crystals which decrease the surface area, transformation of amorphous states to crystals, liberation of active elements, and losses of a particular element due to vaporization, all these changes result in the deactivation of the catalyst. In order to diminish the change in catalytic properties, it seems to be important to suppress the structural deformation. The present study reveals clearly that the structural deformation during catalysis would be minimized by the rapid diffusion of the lattice oxide ions. In fact, most of the excellent practical catalysts show high mobility of the lattice oxide ions and the combination of various metal elements to form highly active and selective catalysts is done for the purpose of improving the mobility of the lattice oxide ions.

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