View Article Online / Journal Homepage / Table of Contents for this issue

J. CHEM. SOC. FARADAY TRANS., 1990, 86(24), 4077–4081

# Kinetic Features and Lattice-oxygen Participation in Propene Oxidation over Bi–Mo Oxide and some Mo Oxide Catalysts

**Takehiko Ono,* Takahiko Nakajo† and Tatsuo Hironaka‡**
*Department of Applied Chemistry, University of Osaka Prefecture, 804 Mozu-umemachi 4-cho, Sakai, Osaka 591, Japan*

Published on 01 January 1990. Downloaded by Washington State University Libraries on 25/10/2014 08:23:40.

The rates of propene conversion in the absence of oxygen have been compared with those in the presence of oxygen at the same propene pressures. Over Bi–Mo oxides which are mainly composed of the $\beta$- or $\gamma$-phase, the rates for propenal formation were 3.5–4.5 times bigger in the presence of oxygen than in the absence of oxygen. In contrast, some Mo-containing oxide catalysts such as $MoO_3$, Co–Mo (1/1), Co–Te–Mo (1/1/1) and other Bi–Mo oxides exhibit little or no difference in the rates of propenal formation in the presence or absence of oxygen. In the case of but-1-ene and (*E*)-but-2-ene oxidation, both rates were nearly the same even on $\beta$- and $\gamma$-phase Bi–Mo oxides. Such a sensitive effect of oxygen on propenal formation over $\beta$- and $\gamma$-phase oxides seems to originate from an appreciable increase of active sites owing to a reoxidation step. Using $^{18}O$ tracer studies in propene oxidation, the extents of lattice-oxygen participation were determined over various Mo oxide catalysts. The number of active sites for propene oxidation was found to be closely related to the extent of lattice-oxygen participation. A modified redox mechanism was proposed on the basis of a different active site model for the reduction and reoxidation steps. The kinetic features were discussed using this model.

Bi–Mo oxide catalysts have been investigated by a great number of workers because of the important role of oxidation processes in the petrochemical industry and because of their interesting properties, for example, the kinetics, structures and synergy features in the oxidation and ammoxidation of olefins.[1–4] First-order kinetics in propene have been observed above 400 °C over these catalysts.[5] It is therefore expected that the initial rates of reduction of the oxides with olefins should be essentially the same as the rate of the corresponding catalytic oxidation. A number of workers have studied the oxidation of propene and butene over Bi–Mo oxide catalysts in the absence of oxygen.[6–11] According to the work of Batist *et al.*,[10] no difference is observed, at least in the initial stages, between the rates of oxidation over Bi–Mo oxide in the presence and absence of gaseous oxygen, although Peacock *et al.*,[11] have reported that the rate of reduction of Bi–Mo oxide with propene is lower than that of the corresponding catalytic oxidation. Brazdil *et al.*[12] have reported that a rapid decrease of rates was observed in the absence of oxygen for ammoxidation of propene over $Bi_2Mo_2O_9(\beta)$ and $Bi_2MoO_6(\gamma)$ but that no decrease was observed over multicomponent oxide catalysts.

In order to understand the participation of lattice oxygen, propene oxidation has been studied by many workers using $^{18}O$ tracer techniques.[13–20] Keulks and co-workers[14,16] have confirmed that the oxygen for propene oxidation comes from lattice oxygen in the bulk over Bi–Mo oxide catalysts. They also proposed an exponential dilution for estimation of the extent of lattice-oxygen participation in propene oxidation.

In this work, the reduction of Bi–Mo and Mo-containing oxide catalysts, over which the oxidation is first order in propene and zero order in oxygen, was investigated in detail. Then the rates in the presence and absence of oxygen were compared. An unexpectedly large difference over some Bi–Mo oxides for propene and 2-methylpropene oxidation has been discussed on the basis of a redox mechanism. In order to understand the character of the lattice oxygen of Bi–Mo and other Mo-containing oxide catalysts, propene oxidation using $^{18}O_2$ was studied at various temperatures. On the basis of a modified redox mechanism, the catalytic activity and the lattice-oxygen participation have been discussed.

## Experimental

### Catalysts

Bi–Mo [(Bi/Mo) = (2.5/1), (1/1) and (1/2.18)] oxides were prepared as follows: The solution containing desired quantities of ammonium heptamolybdate and bismuth nitrate was evaporated with constant stirring, dried and calcined in air at 450 °C. Bi–Mo (2/1) oxide was prepared from molybdic and bismuth nitrate as reported by Batist *et al.*[21] Bi–Mo (2/1.2) was obtained by calcination of Bi–Mo (2/1) and $MoO_3$ powders at 600 °C. $MoO_3$ was prepared by heating ammonium heptamolybdate at 450 °C for 14 h. Co–Mo (1/1) oxide was prepared from ammonium heptamolybdate and cobalt nitrate. Te–Mo (1/4) oxide was prepared from $TeO_2$ and ammonium heptamolybdate. Fe–Mo (2/3) oxide was prepared from ammonium heptamolybdate and ferric nitrate. The procedure of preparation of these three catalysts was the same as that for Bi–Mo (1/1). Co–Te–Mo (1/1/1) oxide catalyst was prepared by heating mixtures of equal amounts of $CoMoO_4$ and $TeO_2$ at 500 °C for 10 h. The structure of the catalysts determined by XRD and IR spectroscopy, as well as the surface area determined by the B.E.T. method, are shown in Table 1. The IR spectra were obtained by the KBr method at *ca.* 1 wt.%.

### Apparatus and Procedure

A conventional closed-circulation system (310 cm$^3$) was used for the reduction and catalytic oxidation reactions. 1–2 g of oxide catalyst were used in each case for both reactions. After a desired reaction time, ranging from 0.5 to several minutes, the reactor was cooled quickly to stop the reaction. The oxidation products such as propenal, $CO_2$ and CO were analysed by gas chromatography. In order to obtain the initial rate, the conversion was kept below 5%. The percentage of $^{18}O$ in the reaction products was determined using a Hitachi mass spectrometer at an ionization voltage of 80 V for CO and $CO_2$ and 15 V for propenal. The $^{18}O_2$ (98.6%) was obtained from MSD Canada Co. Limited.

---

† Present address: Sakai's Intermediate School, Sakai, Osaka, Japan.

‡ Present address: Hyogo Prefectural Office, Kobe, Hyougo, Japan.

View Article Online

Published on 01 January 1990. Downloaded by Washington State University Libraries on 25/10/2014 08:23:40.

**Table 1** Catalyst properties

| catalyst (atomic ratio) | surface area /$m^2$ $g^{-1}$ | phase[a] | IR spectra/$cm^{-1}$ |
|---|---|---|---|
| $MoO_3$ | 1.1 | $MoO_3$ | 995 (vs), 880 (vs), 820 |
| Te–Mo (1/4) | 2.0 | $MoO_3$ | 998 (vs), 950 (w), 862 (vs) |
| Co–Mo (1/1)[b] | 7.9 | a- and b-$CoMoO_4$ | |
| Co–Te–Mo (1/1/1) | 0.94 | unknown ($2\theta$ = 26.5, 30, 31.8, 48.5, 55°) | 955 (vs), 905 (s), 780 (s)<br>670 (vs) |
| Fe–Mo (2/3) | 0.72 | $Fe_2(MoO_4)_3$ | 995 (w), 965 (s). 850 (vs) |
| Bi–Mo (1/2.18) | 1.9 | $\alpha$-$Bi_2Mo_3O_{12}$ (90%)<br>+ $MoO_3$ | 990 (w), 952 (s), 936 (s), 906 (s)<br>862, 848, 830, 720, 665 |
| Bi–Mo (1/1)[c] | 0.94 | $\beta$-$Bi_2Mo_2O_9$ (major)<br>+ $Bi_2Mo_3O_{12}$ | 952 (w), 925 (vs), 896 (vs), 835<br>795, 760, 715 |
| Bi–Mo (2/1.2) | 2.8 | $\gamma$-$Bi_2MoO_6$ | 910 (vw), 857 (s), 815 (s), 750 (vs) |
| Bi–Mo (2/1)[c] | 2.8 | $Bi_2MoO_6$ (80%)<br>+ $Bi_2Mo_3O_{12}$ | 932 (w), 905 (w), 855 (s)<br>810 (s), 750 (vs) |
| Bi–Mo (2.5/1) | 2.9 | $Bi_2MoO_6$ + $Bi_2O_3$ | 855 (s), 810 (s), 750 (vs) |

[a] Determined by XRD or IR spectroscopy. [b] See ref. 22. [c] See ref. 15, 21 and 23. vs, very strong; s, strong; w, weak; vw, very weak.

## Results and Discussion

### Comparison of the Rates of Propene Oxidation in the Presence and Absence of Oxygen over various Catalysts

The rate of propene oxidation was examined in the pressure range 0.8–8 kPa of propene and $O_2$ over the catalysts. The oxidation was first order with respect to $C_3H_6$ and zero order with respect to $O_2$ on all of the catalysts except for Fe–Mo (2/3). With Fe–Mo (2/3), the rate showed an $O_2$ pressure dependence between 0 and 2.7 kPa, and then no dependence around 3–7.8 kPa. Using the rate equation $R = k_{cat} P_{C_3H_6}$ where $R$ is the amount of propene reacted in μmol $m^{-2}$ $min^{-1}$, the rate constant $k_{cat}$ at 400 °C is calculated for some Mo-containing catalysts as shown in the Table 2.

Fig. 1A shows the amount of propene reacted as a function of reaction time in the absence of gaseous oxygen, *i.e.* in the reduction over Mo-containing catalysts. With the Bi–Mo (1/1) oxide catalyst, the amount of propene reacted increases linearly with time between 1 and 3 min. With some catalysts, there is no linearity, but the initial slope gives the rate of reduction. Using the equation $r = k_{red} P_{C_3H_6}$, the rate constants in the reduction have been determined and are given in Table 2. With $MoO_3$, $CoMoO_4$, Te–Mo (1/4) and Co–Te–Mo (1/1/1) catalysts, these rate constants in the presence and absence of oxygen are nearly equal. In contrast, with Bi–Mo (1/1) oxide, a large difference is observed unexpectedly. With Fe–Mo (2/3), there is a small difference between them. In the case of Bi–Mo (1/1), the zero-order dependence in $O_2$ was confirmed between 0.4 and 7.8 kPa. Thus, the rate enhancement in the presence of oxygen takes place at oxygen pressures between 0 and 0.4 kPa. The Fe–Mo (2/3) catalyst resembles Bi–Mo oxide catalysts as far as rate enhancement is concerned.

### Comparison of the Rates of Reduction and Catalytic Oxidation over various Bi–Mo Oxide Catalysts

It is well known that Bi–Mo oxide has three different phases, $\alpha$, $\beta$ and $\gamma$. In order to understand the role of gaseous oxygen on the rates, the same experiments were carried out on various Bi–Mo oxides which are mainly composed of these phases. The rates of reduction of various Bi–Mo oxides with $C_3H_6$ were obtained from the initial slopes of the plots of the amount of propene reacted *vs.* the reaction time (Fig. 1B). The rates ($C_3H_6$ reacted) and selectivities to propenal in the absence of oxygen are shown in Table 3 and the order of activity is as follows: Bi–Mo (1/1) > Bi–Mo (2/1) = Bi–Mo (2/1.2) > Bi–Mo (1/2.18) > Bi–Mo (2.5/1). From the results in Table 3, $k_{red}$ was determined. In catalytic oxidation, propene oxidation was first order in propene and zero order in $O_2$ over these Bi–Mo oxide catalysts. So the rate constants can be determined using the equation $r = k_{cat} P_{C_3H_6}$ as for the various Mo oxide catalysts described above. Table 2 also shows a comparison of the rate constants for propene oxidation in the presence ($k_{cat}$) and absence ($k_{red}$) of gaseous oxygen. The Bi–Mo (1/1, 2/1, 2/1.2) catalysts have high $k_{cat}/k_{red}$ values at around 3–5. In contrast, for Bi–Mo (2.5/1) and (1/2.18) $k_{cat}/k_{red} \approx 2$ or below. Thus, the rates of propene conversion are enhanced by the presence of oxygen over Bi–Mo oxides which contain the $\beta$- or $\gamma$-phases. On the other

**Table 2** Rate constants of propene oxidation in the absence ($k_{red}$) and presence ($k_{cat}$) of oxygen over Bi–Mo and Mo-containing oxide catalysts at $P_{C_3H_6}$ = 0.4–8 kPa, $P_{O_2}$ = 0.4–8 kPa and at 400 °C

| catalyst (atomic ratio) | $k_{red}$[a] | $k_{cat}$[a] | $k_{cat}/k_{red}$ | selectivity to $CH_2{=}CH{-}CHO$ (%) |
|---|---|---|---|---|
| $MoO_3$ | 0.11 | 0.11–0.19 | 1.0–1.7 | 50 |
| Co–Mo (1/1) | 0.15 | 0.16 | 1.1 | 80–90 |
| Te–Mo (1/4) | 0.36 | 0.37 | 1.0 | 95 |
| Co–Te–Mo (1/1/1) | 2.2 | 1.9–2.2 | 0.9–1.0 | 90 |
| Fe–Mo (2/3) | 1.1 | 2.5 | 2.2 | 30–50 |
| Bi–Mo (1/2.18) | 0.60 | 1.2 | 2.0 | |
| Bi–Mo (1/1) | 1.2 | 4.2–5.9 | 3.5–4.6 | |
| Bi–Mo (2/1.2) | 0.93 | 2.9 | 3.1 | [b] |
| Bi–Mo (2/1) | 0.93 | 2.9 | 3.1 | |
| Bi–Mo (2.5/1) | 0.21 | 0.31 | 1.5 | |

[a] Units: μmol $m^{-2}$ $min^{-1}$ $kPa^{-1}$. [b] See Table 3.

View Article Online

Published on 01 January 1990. Downloaded by Washington State University Libraries on 25/10/2014 08:23:40.

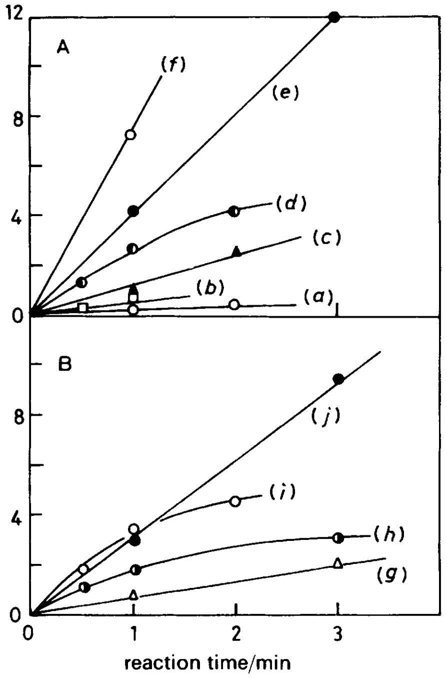

**Fig. 1** Amount of propene converted in the absence of oxygen as a function of time over various catalysts; $P_{C_3H_6}$ = 3.3 kPa, 400 °C. The selectivity to propenal is given in Tables 2 and 3. (A) (*a*) $MoO_3$, (*b*) Co–Mo (1/1), (*c*) Te–Mo (1/4), (*d*) Fe–Mo (2/3), (*e*) Bi–Mo (1/1) and (*f*) Co–Te–Mo (1/1/1). (B) (*g*) Bi–Mo (2.5/1), (*h*) Bi–Mo (1/2.18), (*i*) Bi–Mo (2/1) and (*j*) Bi–Mo (2/1.2)

**Table 3** Rate of propene conversion in the absence of oxygen over Bi–Mo oxide catalysts at $P_{C_3H_6}$ = 3.3 kPa and at 400 °C

| catalyst (atomic ratio) | rate /µmol m$^{-2}$ min$^{-1}$ | selectivity to $CH_2{=}CH{-}CHO$ (%) |
|---|---|---|
| Bi–Mo (1/2.18) | 2.0 | 90 |
| Bi–Mo (1/1) | 4.1 | 95 |
| Bi–Mo (2/1.2) | 3.1 | 90 |
| Bi–Mo (2/1) | 3.1 | 90 |
| Bi–Mo (2.5/1) | 0.71 | 15 |

hand, the rate of propene conversion over Bi–Mo (1/2.18), which consists mainly of α-phase, seems to be enhanced only very slightly. Anyway, the rate increase in the presence of oxygen is larger for Bi–Mo oxide catalysts than for other Mo-containing oxide catalysts.

The Bi–Mo (2.5/1) catalyst has a very low activity and selectivity to propenal despite the presence of γ-phase. According to Matsuura *et al.*,[23] pure γ-phase ($Bi_2MoO_6$) exhibited very low activity for butene oxidation. They also reported that the addition of 2–3 at.% of $MoO_3$ brings about very high activity and high selectivity, while the addition of 1–2 at.% of $Bi_2O_3$ brings about no promotion. They explained that surface composition (Bi/Mo ≈ 1) is closely related to high activity and selectivity. The low activity of Bi–Mo (2.5/1) in this work seems to arise from the difference in surface composition as described above. The Bi–Mo (2/1) in this work exhibited high activity and selectivity.

## Comparison of the Rates of Oxidation of various Alkenes in the Absence and Presence of Oxygen over Bi–Mo (1/1) Oxide Catalyst

Table 4 shows the results of various alkene oxidations in the presence and absence of gaseous oxygen. In the case of diene formation, such as oxidation of but-1-ene, (*E*)-but-2-ene and pent-1-ene, there appears to be only a small difference between the rates of reduction and catalytic oxidation, in spite of a lot of lattice oxygen consumption in the absence of oxygen. For 2-methylpropene, a large difference appears, as was found for propene oxidation, in spite of the small consumption of lattice oxygen occurring in the reduction. These features are confirmed at 450 and 370 °C. These results indicate that the rate enhancement by the presence of gaseous oxygen is closely related to the aldehyde formation, *i.e.* insertion of lattice oxygen after π-allyl formation.

**Table 4** Rate constants of oxidation of various alkenes in the absence ($k_{red}$) and presence ($k_{cat}$) of oxygen over the Bi–Mo (1/1) oxide catalyst

| alkene | temperature/°C | $k_{red}$[a] | $k_{cat}$[a] | $k_{cat}/k_{red}$ |
|---|---|---|---|---|
| propene | 450 | 3.76 | 17.2 | 4.5 |
| | 370 | 0.65 | 3.1 | 4.8 |
| 2-methylpropene[b] | 400 | 3.8 | 18.0 | 4.8 |
| | 370 | 2.15 | 10.5 | 4.8 |
| (*E*)-but-2-ene[c] | 450 | 4.3 | 6.2 | 1.4 |
| | 400 | 1.6 | 3.2 | 2.0 |
| but-1-ene[c] | 400 | 17.5 | 33.6 | 1.9 |
| pent-1-ene[d] | 400 | 39.0 | 75.3 | 1.9 |
| | 370 | 21.5 | 36.3 | 1.6 |

[a] Units: µmol m$^{-2}$ min$^{-1}$ kPa$^{-1}$;
[b] product: $CH_2{=}C(CH_3){-}CHO$, 90%;
[c] $CH_2{=}CH{-}CH{=}CH_2$, 99%;
[d] $CH_2{=}CH{-}CH{=}CH{-}CH_3$, 99% (*cis*/*trans* = 1).

## $^{18}O$ Tracer Study over Mo-containing Oxide Catalysts

Propene oxidation was performed using an $^{18}O_2$ tracer (98.6 at.%) in order to obtain information concerning the extent of lattice-oxygen participation. As shown in Fig. 2, in spite of using 98% $^{18}O_2$ as a reactant, the products are diluted with lattice oxygen ($^{16}O$). The dilution is larger for the high-activity catalysts than for the low-activity ones. Following Keulks *et al.*,[14,16] the extent of lattice-oxygen participation has been determined as shown in Table 5. The extents of lattice-oxygen participation range from *ca.* 5 layers for $MoO_3$ to *ca.* 140 for Bi–Mo (1/1). The higher the oxidation rates, the more lattice oxygen participates. With Bi–Mo (1/1), the percentages of $^{18}O$ consumed at different temperatures are

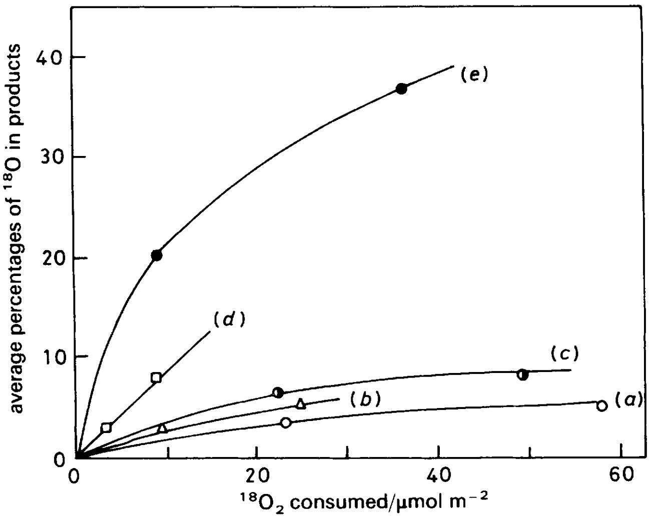

**Fig. 2** Plots of the average percentages of $^{18}O$ in the products *vs.* the amount of $^{18}O_2$ consumed in propene oxidation; 400 °C, $P_{C_3H_6}$ = 3.3 kPa, $P_{^{18}O_2}$ = 1.0 kPa. The average percentage of $^{18}O$ was obtained from those of propenal, $CO_2$, CO and $H_2O$. (*a*) Bi–Mo (1/1), (*b*) Co–Te–Mo (1/1/1), (*c*) Fe–Mo (2/3), (*d*) Te–Mo (1/4) and (*e*) $MoO_3$

View Article Online

Published on 01 January 1990. Downloaded by Washington State University Libraries on 25/10/2014 08:23:40.

**Table 5** The extent of lattice-oxygen participation and the activation energy for propene oxidation on some Mo-containing catalysts

| catalyst (atomic ratio) | lattice-oxygen participation at 400 °C (layers)[a] | activation energy /kJ mol$^{-1}$ |
|---|---|---|
| $MoO_3$ | 5–8 | 54[b] |
| Co–Mo (1/1) | — | 54[b] |
| Te–Mo (1/4) | 10 | 54 |
| Co–Te–Mo (1/1/1) | 40–50 | 63 |
| Fe–Mo (2/3) | 40–60 | 63 |
| Bi–Mo (1/1) | 140 | 84 |

[a] Calculated from the equation, (percentage of $^{18}O$ in products)/(percentage of $^{18}O$ in $O_2$) = $1 - \exp(-Ft/V)$, where $F$ is the flow of oxygen into and out of the catalyst (μmol min$^{-1}$), $t$ is the reaction time (min) and $V$ is the amount of catalyst oxygen (μmol) participating.[14,16] The number of layers were calculated assuming *ca.* 15 μmol of O for one layer. [b] From ref. 25.

shown in Fig. 3. The percentage values of $^{18}O$ for the initial stages of the reaction do not lie on the same line. However, such a difference becomes smaller as the reaction proceeds and the plots tend to lie on the same line. The extent of lattice-oxygen participation is 50–60 layers during the initial stages of reaction and 140–150 layers after sufficient reaction time. This indicates that the rapid diffusion of lattice oxygen is affected by the concentration of anion vacancies. Fig. 4 shows the results on the Te–Mo (1/4) catalyst. In this case, the percentage of $^{18}O$ in the propenal formed depends on the temperature as well. The ratio of the number of layers in which lattice oxygen participates in the reaction at 370, 400 and 430 °C is calculated to be 7 : 10 : 18. The catalytic-activity ratio was obtained as 0.3 : 1.0 : 1.8, which is nearly the same as the layer ratio. In the case of the Te–Mo (1/4) catalyst, lattice-oxygen participation seems to be accompanied by reduction and reoxidation at the surface sites. The temperature dependence of the rate over this catalyst can be explained from the increase in the rate of the first hydrogen abstraction, since the rate-determining step will not have changed. On the other hand, in the case of Bi–Mo (1/1), the extent of lattice-oxygen participation is remarkably large, indicating that the oxygen which reacts with propene comes from the bulk, even from more than 100 layers deep. This indicates that the sites of reduction are different from those of reoxidation and that the lattice oxygens are transferred rapidly along the molybdenum shear planes.[1–4,12] It has been accepted that the rate-determining step is the first hydrogen (allyl hydrogen) abstraction even in such a case.[1–4]

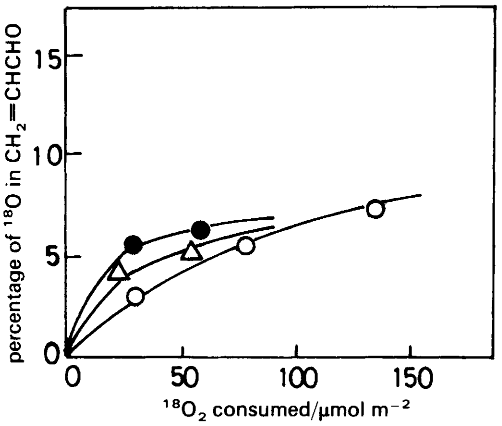

**Fig. 3** Plots of the percentages of $^{18}O$ in the propenal formed *vs.* the amount of $^{18}O_2$ consumed at various temperatures over the Bi–Mo (1/1) oxide catalyst: (●) 370 °C, (△) 400 °C and (○) 430 °C; $P_{C_3H_6}$ = 3.2 kPa and $P_{^{18}O_2}$ = 1.0 kPa

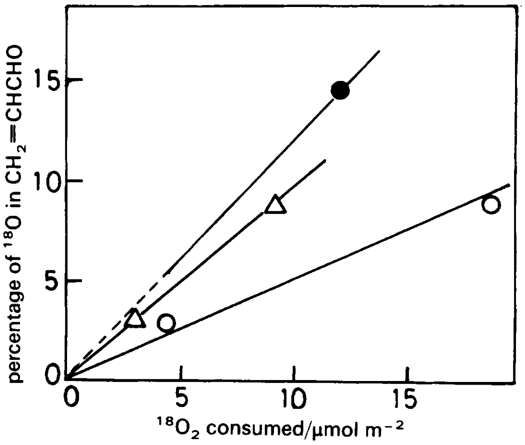

**Fig. 4** Plots of the percentages of $^{18}O$ in the propenal formed *vs.* the amount of $^{18}O_2$ consumed at various temperatures over the Te–Mo (1/4) oxide catalyst: (●) 370 °C, (△) 400 °C, (○) 430 °C; $P_{C_3H_6}$ = 3.2 kPa and $P_{^{18}O_2}$ = 1.0 kPa

### Nature of the Active Sites in the Oxidation of Propene over β- and γ-phase Bi–Mo Oxide Catalysts

As shown in Tables 2 and 4, the differences in reaction rates in the absence and presence of oxygen are particularly evident for aldehyde formation rather than diene formation over Bi–Mo (1/1) and Bi–Mo (2/1.2–2/1) catalysts. From the results described above, *ca.* 2–1 molecules of propene reacted per 100 Å$^2$ of catalyst surface per min in the absence of oxygen at 400 °C (Fig. 1), but during the catalytic oxidation 9–5 molecules per 100 Å$^2$ reacted on these catalysts in the same time interval. The activation energies of propene oxidation are listed in Table 6, taken from previous work and this work over Bi–Mo oxide catalysts. There seems to be a very small difference in activation energy between the reactions in the presence and absence of gaseous oxygen. These facts indicate that the active sites for the first hydrogen abstraction step are more plentiful in the presence than in the absence of oxygen. Several mechanisms have been proposed for propene oxidation over Bi–Mo oxides.[1–4] Recently, it has been accepted that the allylic hydrogen is abstracted by the oxygen of Bi oxide and that the second hydrogen abstraction and

**Table 6** Activation energies in the absence ($E_{red}$) and presence ($E_{cat}$) of oxygen for the partial oxidation of propene over Bi–Mo oxides (from previous work)

| catalyst | $E_{red}$/kJ mol$^{-1}$ | $E_{cat}$/kJ mol$^{-1}$ | temperature/°C | ref. |
|---|---|---|---|---|
| $Bi_2MoO_6$ | 75 | 84 | 400–500 | 6 |
| $Bi_2MoO_6$ | 59 | 59 | 420–450; 350–420 | 7 |
| $Bi_2MoO_6$ | 67 | 71–59 | | 8 |
| $Bi_2Mo_2O_9$ | 67 | 75–63 | | 8 |
| $Bi_2Mo_3O_{12}$ | 67 | 71 | | 8 |
| Bi–Mo (1/1) ($Bi_2Mo_2O_9$) | 84 | 84 | 370–430 | this work |

View Article Online

Published on 01 January 1990. Downloaded by Washington State University Libraries on 25/10/2014 08:23:40.

oxygen insertion takes place on Mo ions, the former being rate-determining.[1] Two possibilities have been proposed for the reoxidation step, *i.e. via* Bi oxide vacancies or Mo oxide vacancies. Although details are still unclear at present, the rate increase caused by reoxidation on the Mo moiety seems to induce the appearance of the more active sites near the reoxidation sites. In other words, a smaller number of active sites in the absence of oxygen may cause the reduction of $Mo^{6+}$ to, for example, $Mo^{3+}$ or $Mo^{4+}$.[1] Rapid oxygen transfer from the Mo moiety to the Bi moiety under stationary-state conditions may be disturbed. In the case of oxidative dehydrogenation, *i.e.* diene formation from butenes, very small differences were observed between the rates of reaction in the presence and absence of oxygen. Such a small rate difference indicates the reduction of $Mo^{6+}$ to, for example, $Mo^{5+}$, with little or no disturbance caused by the rapid transfer of lattice oxygen. Ueda *et al.*[19] also reported that the lattice-oxygen species associated with oxygen insertion for propenal formation are different from those associated with hydrogen abstraction over Bi–Mo oxide catalyst using $^{18}O$ tracer studies.

With Fe–Mo (2/3) oxide catalyst, *ca.* 50 layers of lattice oxygen participate during the reaction at 400 °C. Furthermore, there is a small enhancement in the rate, caused by the presence of gaseous oxygen. As far as these facts are concerned, an explanation similar to that employed for Bi–Mo oxide as described above, may be applied to the Fe–Mo oxide catalyst.

## A Modified Redox Mechanism

As described above, the reduction of the oxides with propene and the oxidation of the latter by gaseous oxygen occur in different regions on the surface of the catalysts. The surface anion vacancies formed in region A are refilled by diffusion of the oxide ions from the bulk, which results in the formation of surface anion vacancies in region B. These B vacancies bring about oxygen uptake. In such a situation, the following equation holds for stationary-state conditions[24]

$$k_A N_A P_{C_3H_6} \theta_A = k_B N_B P_{O_2}^{1/2}(1 - \theta_B) \qquad (1)$$

where $\theta$ and $1 - \theta$ refer to the surface oxide ions and anion vacancies in regions A and B, respectively. $N_A$ and $N_B$ are the surface lattice-oxygen concentrations which participate in the oxidation. $k_A$ and $k_B$ are the rate constants for the reduction step in region A and for the reoxidation step in region B, respectively. If the diffusion of oxide ions from B to A is rapid compared with the surface reaction, there will be no marked difference between $\theta_A$ and $\theta_B$ ($\approx \theta$). Then, the rate is given by:

$$\begin{aligned} R &= k_A N_A P_{C_3H_6} \theta \\ &= k_A N_A k_B N_B P_{C_3H_6} P_{O_2}^{1/2} / (k_A N_A P_{C_3H_6} + k_B N_B P_{O_2}^{1/2}) \qquad (2) \end{aligned}$$

If $k_B \gg k_A$, eqn. 2 becomes:

$$R = k_A N_A P_{C_3H_6} \qquad (3)$$

The first-order kinetics over Bi–Mo oxide catalysts can be explained by this equation. The physical significance of the rate constant, $k$, in the reduction step is somewhat different from that given by a simple redox mechanism, *i.e.* $k_A N_A$ denotes the rate constant $k_{cat}$ or $k_{red}$ in region A. $R_{cat}/R_{red} = k_{cat}/k_{red}$ at the same propene pressure and temperature. With Bi–Mo (1/1) in this work, $k_{cat}/k_{red} = (k_A N_A)_{cat}/(k_A N_A)_{red} = N_{A,cat}/N_{A,red} \approx 4$, since the same activation energies for propene oxidation both in the presence and absence of oxygen are observed as described above. The difference in the number of active sites for propene oxidation in the presence and absence of oxygen can be expressed by this equation.

## A Correlation between the Catalytic Activity and the Extent of Lattice-oxygen Participation

The order of oxidation activities ($k_{cat}$, Table 2) is as follows: $MoO_3$ < Co–Mo (1/1) < Te–Mo (1/4) < Co–Te–Mo (1/1/1) < Fe–Mo (2/3) < Bi–Mo (1/1). The order of activation energies for propene oxidation on these catalysts is as follows (Table 5); $MoO_3$ = Co–Mo (1/1) = Te–Mo (1/4) < Co–Te–Mo (1/1/1) < Fe–Mo (2/3) < Bi–Mo (1/1). The catalysts which exhibit high activities have high activation energies. On the other hand, the order of the extent of lattice-oxygen participation runs parallel with the catalytic activity (Table 5). $k_{cat}$ is given by $k_A N_A$ according to the eqn. 3. Thus, the high activities of Co–Te–Mo (1/1/1), Fe–Mo (2/3) and Bi–Mo (1/1) oxide catalysts come from the greater number of active sites ($N_A$) for the first hydrogen abstraction rather than from the lowering of the activation energy in $k_A$. In this sense, the extent of lattice-oxygen participation is closely related to the number of active sites. As described above, high values of the extent of lattice-oxygen participation are explained by the separation of active sites between the reduction and reoxidation steps and by the rapid transfer of lattice oxygen. These characteristics seem to maintain the number of active sites in spite of the rising activation energy.

## References

1 T. P. Snyder and C. G. Hill Jr., *Catal. Rev. Sci. Eng.*, 1989, **31**, 43.
2 R. K. Grasselli and J. D. Burrington, *Adv. Catal.*, 1981, **30**, 133.
3 D. B. Dadyburjor, S. S. Jewur and E. Ruckenstein, *Catal. Rev. Sci. Eng.*, 1979, **19**, 293.
4 G. W. Keulks, L. D. Krenzke and T. M. Notermann, *Adv. Catal.*, 1978, **27**, 183.
5 J. R. Monnier and G. W. Keulks, *J. Catal.*, 1981, **68**, 51; L. D. Krenzke and G. W. Keulks, *J. Catal.*, 1980, **64**, 295.
6 R. D. Wragg, P. G. Ashmore and J. A. Hockey, *J. Catal.*, 1973, **31**, 293.
7 L. D. Krenzke and G. W. Keulks, *J. Catal.*, 1980, **64**, 295.
8 J. Haber, *Int. Chem. Eng.*, 1976, **15**, 21; J. Haber and B. Gryzbowska, *J. Catal.*, 1973, **28**, 489.
9 M. Egashira, H. Sumie, T. Sakamoto and T. Seiyama, *Kogyo Kagaku Zasshi*, 1970, **73**, 860.
10 Ph. A. Batist, H. J. Prette and G. C. A. Schuit, *J. Catal.*, 1969, **15**, 267.
11 J. M. Peacock, A. J. Parker, P. G. Ashmore and J. A. Hockey, *J. Catal.*, 1969, **15**, 398.
12 J. F. Brazdil, D. D. Suresh and R. K. Grasselli, *J. Catal.*, 1980, **66**, 347.
13 G. W. Keulks, *J. Catal.*, 1970, **19**, 232.
14 G. W. Keulks and L. D. Krenzke, *Proc. 6th International Congress on Catalysis, London*, ed. G. C. Bond, P. B. Wells and F. C. Tompkins, The Chemical Society, London, 1976, p. 806.
15 E. V. Hoefs, J. R. Monnier and G. W. Keulks, *J. Catal.*, 1979, **57**, 331.
16 L. D. Krenzke and G. W. Keulks, *J. Catal.*, 1980, **61**, 316.
17 T. Otsubo, H. Miura, Y. Morikawa and T. Shirasaki, *J. Catal.*, 1975, **36**, 240.
18 H. Miura, T. Otsubo, T. Shirasaki and Y. Morikawa, *J. Catal.*, 1979, **56**, 84.
19 W. Ueda, Y. Morooka and T. Ikawa, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 495.
20 R. K. Grasselli, *Appl. Catal.*, 1985, **15**, 127.
21 Ph. A. Batist, H. J. Prette and G. C. A. Schuit, *J. Catal.*, 1972, **25**, 1.
22 T. G. Alkhazov, K. Ku. Adzamov and N. Kh. Allakhrevdova, *Kinet. Catal.*, 1974, **15**, 1319.
23 I. Matsuura, R. Schut and K. Hirakawa, *J. Catal.*, 1980, **63**, 152.
24 T. Ono and Y. Kubokawa, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 1748; T. Ono, M. Kiryu, M. Komiyama and R. L. Kuczkowski, *J. Catal.*, in press.
25 Y. Morooka, S. Tan and A. Ozaki, *J. Catal.*, 1970, **17**, 125.

*Paper* 0/02102D; *Received* 14*th May*, 1990