JOURNAL OF CATALYSIS 88, 214–221 (1984)

Study of Tellurium Oxide Catalysts by $^{18}O_2$ Tracer in the Oxidation of Propylene to Acrolein

WATARU UEDA, YOSHIHIKO MORO-OKA, AND TSUNEO IKAWA

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama, 227 Japan

Received December 9, 1983; revised February 22, 1984

Participation of the lattice oxide ions in various tellurium-based multicomponent oxide catalysts, M–Te–Mo–O (M = Co, Mn, Fe, and Cu) was investigated using the $^{18}O_2$ tracer in the selective oxidation of propylene to acrolein. The participation of the lattice oxide ions in the oxidation is quite prominent on every catalyst, beyond 100 layers of the lattice, and is comparable to that observed on bismuth molybdate catalyst system. The combination of the transition metal oxide as a third component with the binary oxide, Te–Mo–O increases the rate of diffusion of the lattice oxide ion. Clear correlation was observed between the degree of evaporation of tellurium element and the number of oxide ion layer involved in the oxidation. These results suggest that high mobility of the lattice oxide ions in this catalyst plays an important role in suppressing the vaporization of tellurium from the catalyst during oxidation.

INTRODUCTION

A number of tellurium-based oxides have been developed as active and selective catalysts for the oxidation of lower olefins (*1*). It has been also claimed that addition of a small amount of tellurium oxide to other metal oxides improves markedly their catalytic properties in the oxidation of propylene or isobutylene (*2*). In spite of the significant development of the catalyst systems containing tellurium, their catalytic behavior has not been clarified in comparison with the bismuth molybdate catalyst (*3–5*). Recently, Bart *et al.* studied the solid state chemistry of the binary tellurium–molybdenum oxide and identified Te_2MoO_7 as active phase for the selective oxidation of olefins (*6, 7*). They concluded that the high catalytic activity was explained both by the activation of propylene on Te sites and by the oxygen insertion at isolated and highly distorted MoO_6 octahedral sites.

A characteristic feature of catalyst systems containing tellurium is the deactivation of the catalyst due to the aggregation and vaporization of tellurium during the reaction. In order to avoid this difficulty, tellurium-based catalysts are usually prepared by combining tellurium oxide with various transition metal oxides, such as iron, cobalt, copper, and manganese, in addition to molybdenum trioxide. In our continuing investigation of multicomponent oxide catalysts using $^{18}O_2$ tracer (*8–10*), we tried to obtain an insight into the mechanistic role of the third metal component of M–Te–Mo–O catalysts in the oxidation of propylene to acrolein from the standpoint of the bulk diffusion of the lattice oxide ions.

The diffusion rate of the lattice oxide ions in the bulk of the catalyst was first determined by Keulks *et al.* for several single-phase bismuth molybdate catalysts and was discussed in connection with the catalytic activity and selectivity (*11–13*). Grasselli also estimated the rates of lattice oxide ion participation in the oxidation by a pulse reduction–reoxidation method for various bismuth molybdate catalysts (*14, 15*). On the other hand, the diffusion rates are not measurable precisely for the multiphase catalysts which are usually important for practical use. However, it is possible to estimate how many lattice oxide ions can take part in the redox cycle by using the $^{18}O_2$

0021-9517/84 $3.00

tracer method. This value seems to be quite an important factor for the activity and selectivity of the practical catalyst. In the present study, the stability of tellurium-based catalysts will be discussed in light of this parameter.

EXPERIMENTAL

Catalyst Preparation

Two tellurium compounds, TeO_2 and H_6TeO_6, were used for preparing the binary Te–Mo–O catalysts. TeO_2–$6MoO_3$ and TeO_2–MoO_3 were prepared by solid state reaction of tellurium oxide with molybdenum trioxide in the prescribed compositions at 500°C for 2 h. TeO_3–$6MoO_3$ was obtained by the crystallization from a mixed solution of telluric acid and ammonium heptamolybdate, followed by calcination at 500°C for 2 h. Ternary *M*–Te–Mo–O (*M* = Fe, Co, and Mn) catalysts were prepared by solid reactions of TeO_2 with binary oxides of molybdenum and transition metal elements. Binary Fe–Mo–O oxides were prepared by precipitation from an ammonium heptamolybdate solution and a ferric nitrate solution; calcination at 500°C for 3 h followed. The preparation methods for $CoMoO_4$ and $MnMoO_4$ have been reported elsewhere. CuO–TeO_3–$6MoO_3$ was prepared by the coprecipitation from a basic solution of ammonium heptamolybdate and a mixed solution of telluric acid and cupric nitrate, followed by calcination in an air stream at 450°C for 2 h.

Apparatus and Procedure

Propylene oxidation using $^{18}O_2$ gas was carried out in the same reactor systems as reported earlier (*8*). The catalyst was heated in gaseous oxygen at the reaction temperature for 1 h and then evacuated *in vacuo* for half an hour before reaction. The reaction gases, $^{18}O_2$ (British Oxygen Co., 99.1%) and propylene (Matheson CP Grade), were used without further purification. In the $^{18}O_2$ tracer experiment, results were obtained under the following standard conditions: initial pressure, $P_{C_3H_6} = P_{O_2} =$ 70 Torr; reaction temperature, 450°C. The condensable products, acrolein and water, were separated from the reaction gas by a cold trap at regular interval for gas chromatographic and mass spectrometric analysis. The reaction was followed by monitoring the decrease of the pressure and also by quantitative analysis of the gas phase and condensed products using gas chromatography (Porapak T, 3 m, 120°C; molecular sieve 5A, 0.5 m, 25°C). $^{18}O_2$ concentrations in gaseous oxygen, acrolein, and carbon dioxide were determined by mass spectrometry at 80 ionization voltage after the correction for natural isotopes, assuming the same ionization efficiency for both normal molecules and isomers containing ^{18}O. Reaction conditions for each $^{18}O_2$ tracer experiment, the catalytic activity for propylene oxidation and the selectivity to acrolein are summarized in Table 2. The catalytic activity was determined using a conventional flow reactor at 450°C at atmospheric pressure (propylene: 8%, oxygen: 16%, nitrogen: balance).

TABLE 1

Characterization of the Tellurium-Based Catalysts

Catalyst	Surface area (m^2/g)	Phase determined by X-ray diffraction analysis
$CoTeMoO_6$	1.0	$CoTeMoO_6$
$MnTeMoO_6$	1.1	$MnTeMoO_6$
Fe–Te–Mo–O		
2 : 3 : 3	0.8	$Fe_2(MoO_4)_3$, TeO_2
2 : 1 : 1	2.0	[a]
2 : 0.1 : 3	0.5	$Fe_2(MoO_4)_3$
CuO–TeO_3–$6MoO_3$	1.9	[a]
TeO_3–$6MoO_3$	3.9	Te_2MoO_7, MoO_3
TeO_2–$6MoO_3$	0.7	Te_2MoO_7, MoO_3
TeO_2–MoO_3	1.4	TeO_2, MoO_3

[a] Not identified.

Characterization of Catalyst

BET surface area by nitrogen adsorption and the structure of catalyst determined by powder X-ray diffraction patterns which were recorded using an X-ray diffractometer with Cu*Kα* radiation are listed in Table 1. Most of the sample showed complicated diffraction patterns, except for $CoTeMoO_6$

TABLE 2

Oxidation of Propylene on Tellurium-Based Oxide Catalysts and the Reaction Conditions for Tracer Experiment[a]

Catalyst	Used weight (g)	Reaction time (min)	Conversion (%)	Activity (10^{-5} mol/min · m^2)	Selectivity (%)
$CoTeMoO_6$	0.5	150	30	0.26	89
$MnTeMoO_6$	0.5	80	30	0.69	77
Fe–Te–Mo–O					
2:3:3	1.0	150	41	0.46	97
2:1:1	0.5	60	43	0.74	97
2:0.1:3	0.5	35	39	2.46	96
$CuO–TeO_3–6MoO_3$	0.5	110	43	0.41	96
$TeO_3–6MoO_3$	0.5	13	42	2.00	97
$TeO_2–6MoO_3$	1.0	200	29	0.32	95
$TeO_2–MoO_3$	1.0	240	32	0.16	93

[a] All runs were carried out at 450°C using the closed circulating system under a reduced pressure [$P_{C_3H_6} = P_{O_2}$ = 70 Torr].

and $MnTeMoO_6$ which have a single phase and are isomorphous to each other (*16*). The Te_2MoO_7 phase was detected in two binary oxides, TeO_3–$6MoO_3$ and TeO_2–$6MoO_3$, but not in TeO_2–MoO_3 where only TeO_2 and MoO_3 were observed. The CuO–TeO_3–$6MoO_3$ oxide before calcination showed heteropoly structure, but was decomposed by the heat treatment at 450°C in air. The structure after decomposition was not identified. No clear difference was detected in the X-ray diffraction patterns before and after use for the oxidation of propylene. The amounts of tellurium loss by the vaporization of tellurium during the propylene oxidation were determined by the thiourea method (*17*).

RESULTS

Catalytic Oxidation of Propylene

Specific activity and selectivity to acrolein in the oxidation of propylene are shown in Table 2 for the ternary oxide catalysts, *M*–Te–Mo–O (*M* = Co, Mn, Fe, and Cu) and for three binary Te–Mo–O oxide catalysts. Decay of catalytic activity for the oxidation of propylene to acrolein with the reaction time was also determined using the conventional flow reactor at 450°C. Results are shown in Fig. 1 for each catalyst.

Among the binary Te–Mo–O oxide catalysts, TeO_3–$6MoO_3$ was most active and selective to acrolein in the oxidation of pro-

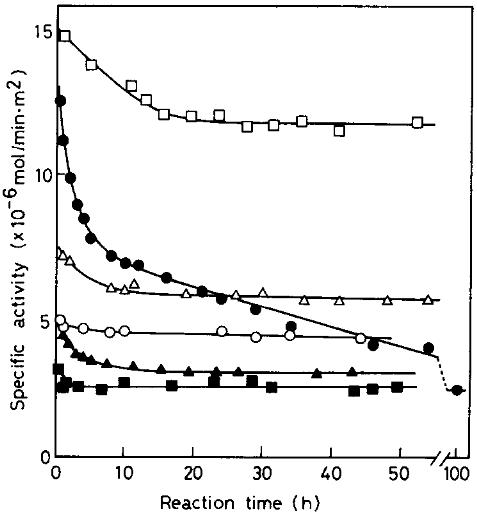

FIG. 1. Catalytic activity of tellurium-based catalysts for the oxidation of propylene to acrolein. ○, $MnTeMoO_6$; △, Fe–Te–Mo–O (2:1:1); □, Fe–Te–Mo–O (2:0.1:3); ▲, CuO–TeO_3–$6MoO_3$; ●, TeO_3–$6MoO_3$; ■, TeO_2–$6MoO_3$.

pylene. However, its high specific activity is only in the first few hours and decreases continuously with the reaction time. Its activity reaches finally to the same value of the TeO_2–$6MoO_3$ catalyst where the decrease in catalytic activity with time is not prominent because of its low activity. The high activity in TeO_3–$6MoO_3$ catalyst at initial stage of reaction may be attributed to the high concentration of the Te_2MoO_7 phase in the catalyst.

On the other hand, the ternary component catalysts, *M*–Te–Mo–O showed the stable activity for propylene oxidation, although the small decrease of the specific activity was observed for a few hours as shown in Fig. 1. The most active and stable catalyst was the ternary oxide containing iron as the third constituent, which was obtained by the combination of small amount of tellurium oxide with ferric molybdate, $Fe_2(MoO_4)_3$, in the atom ratio Fe–Te–Mo–O (2 : 0.1 : 3). Since only the $Fe_2(MoO_4)_3$ phase was detected by X-ray analysis in Fe–Te–Mo–O (2 : 0.1 : 3) catalyst and $Fe_2(MoO_4)_3$ is not active and has poor in selectivity to acrolein in the oxidation of propylene, it is obvious that the tellurium must have a pronounced effect on the catalytic activity and selectivity. In spite of low concentration of tellurium in this catalyst, the specific activity was higher than that of Fe–Te–Mo–O (2 : 3 : 3) which involved the larger amount of tellurium. The addition of a small amount of tellurium is sufficient for the improvement of catalytic activity and selectivity, and the excess addition rather suppresses them.

$CoTeMoO_6$ and $MnTeMoO_6$ which are composite oxides with the fixed chemical composition; $MTeMoO_6$ (M = Cd, Co, Mn, and Zn), were first demonstrated by Trifiro *et al.* as a new class of selective catalysts for the allylic oxidation of olefins (*16*). As can be seen in Table 2, these catalysts were active but the selectivity to acrolein was slightly low compared with the other tellurium-based catalysts in the present reaction conditions.

TABLE 3

Vaporization of Tellurium during the Oxidation of Propylene[a]

Catalyst	Amounts of vaporized tellurium metal	
	Weight (mg)	(%)
$CoTeMoO_6$	0.25	0.15
$MnTeMoO_6$	1.07	0.63
Fe–Te–Mo–O		
2 : 1 : 1	0	0
2 : 0.1 : 3	0	0
CuO–TeO_3–$6MoO_3$	Trace	Trace
TeO_3–$6MoO_3$	1.85	3.01
TeO_2–$6MoO_3$	0.75	1.20

[a] Reaction conditions; catalyst weight 0.5 g, reaction temperature 450°C, reaction time 1 h.

Vaporization of Tellurium

Stability of the tellurium-based catalysts was examined by measuring the amount of tellurium lost from the catalyst during the oxidation of propylene. The first column in Table 3 lists the weight of vaporized tellurium and the values in second column are the fraction of the amount of vaporized tellurium to that of tellurium in the original catalysts. As can be seen in Table 3, severe vaporization of tellurium metal from the catalyst was observed in the two binary Te–Mo–O catalysts, especially in TeO_3–$6MoO_3$ catalyst which showed the remarkable decrease of specific activity for propylene oxidation. On the other hand, it is noteworthy that the vaporization of tellurium was prevented on ternary component catalysts and in the case of the catalysts containing iron and/or copper, vaporization is almost suppressed. Thus, it is apparent that the third constituent plays an important role in suppressing the tendency of tellurium to become reduced to the metallic state during the catalytic oxidation.

$^{18}O_2$ Tracer Measurements

Typical changes of the ^{18}O concentration of the oxidized products are shown in Figs.

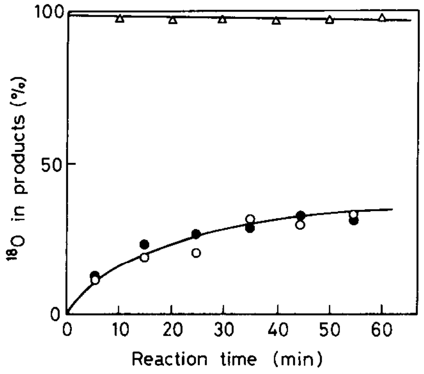

FIG. 2. Incorporation of ^{18}O into the oxidized products of propylene oxidation over Fe–Te–Mo–O (2 : 1 : 1) catalyst at 450°C. ○, Acrolein; ●, carbon dioxide; △, gaseous oxygen.

2 and 3 for Fe–Te–Mo–O (2 : 1 : 1) and CuO–TeO_3–$6MoO_3$, respectively. Heterophase exchange reaction between the gaseous oxygen and the lattice oxide ions under the reaction condition was not observed for all catalysts tested in the present study. As can be seen in the figures, ^{16}O from the bulk of the oxide catalyst based on tellurium oxide is clearly incorporated into both acrolein and carbon dioxide and exclusively participated in the selective oxidation of propylene, similarly to the other complex metal oxide containing V and VI group elements, such as bismuth molybdate (*8*).

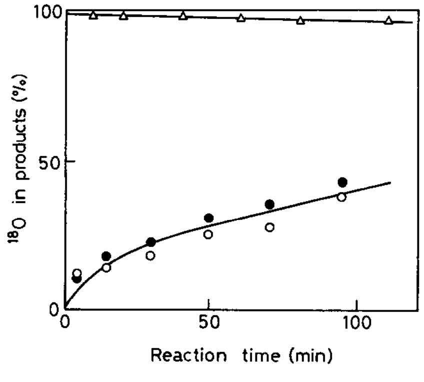

FIG. 3. Incorporation of ^{18}O into the oxidized products of propylene oxidation over CuO–TeO_3–$6MoO_3$ catalyst at 450°C. ○, Acrolein; ●, carbon dioxide; △, gaseous oxygen.

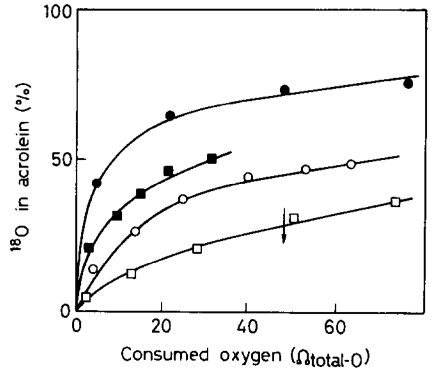

FIG. 4. Changes of ^{18}O concentration in acrolein against the total consumed oxygen in the oxidation of propylene. Arrow mark shows the point where the amounts of $^{16}O^{2-}$ incorporated into the oxidized products is equal to that of TeO_2 in the Fe–Te–Mo–O (2 : 0.1 : 3) catalyst. ○, Fe–Te–Mo–O (2 : 3 : 3); □, Fe–Te–Mo–O (2 : 0.1 : 3); ■, TeO_2–MoO_3 (1 : 1); ●, $Fe_2(MoO_4)_3$.

The results of the $^{18}O_2$ tracer measurement are shown in Figs. 4 and 5 for the Fe–Te–Mo–O catalysts having different compositions and for the ternary oxide catalysts containing copper, cobalt, and manganese together with the binary oxide catalysts, respectively. For comparing the catalysts with the extent of the participation of lattice oxide ion, ^{18}O concentration in acrolein is plotted against $\Omega_{total\text{-}O}$ in the figures (*8*). $\Omega_{total\text{-}O}$ which is expressed as the unit of ox-

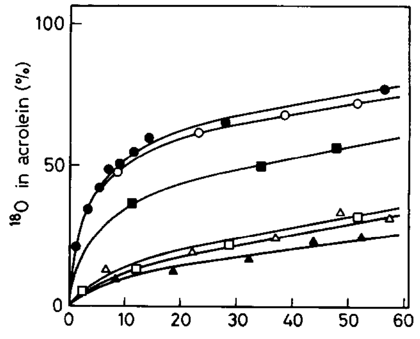

FIG. 5. Changes of ^{18}O concentration in acrolein against the total consumed oxygen in the oxidation of propylene. ■, $CoTeMoO_6$; ○, $MnTeMoO_6$; △, Fe–Te–Mo–O (2 : 1 : 1); □, Fe–Te–Mo–O (2 : 0.1 : 3); ▲, CuO–TeO_3–$6MoO_3$; ●, TeO_3–$6MoO_3$.

TABLE 4

Participation of Lattice Oxide Ions in the Oxidation of Propylene

Catalyst	Number of oxide ion layer involved in the oxidation	^{18}O fraction in acrolein (%)
$CoTeMoO_6$	80	44
$MnTeMoO_6$	60	57
Fe–Te–Mo–O		
2:3:3	100	35
2:1:1	150	22
2:0.1:3	150	21
$CuO–TeO_3–6MoO_3$	160	20
$TeO_3–6MoO_3$	50	60
$TeO_2–6MoO_3$	80	41
$TeO_2–MoO_3$	70	47

ide ion layer assuming 1 × 10^{19} oxygen atoms/m^2-surface area (*12*), is the total amount of oxygen consumed in the oxidation. Further assuming the complete mixing model for the diffusion process of the lattice oxide ion in the bulk of oxide catalyst during the oxidation of propylene, the hypothetical number of the lattice oxide ion layers involved in the reduction–oxidation cycle is estimated for each catalyst from the results shown in Figs. 4 and 5. Values based on the above assumption do not have precise physical meanings in the case of multiphase catalysts but can be used as measure of the diffusion rate of lattice oxide ions. Obtained values are listed in the first column in Table 4 together with the ^{18}O fraction in acrolein at the time when the consumed oxygen corresponded to 20 layers of lattice oxide ion in each catalyst. Since the vaporization of tellurium occurred during the $^{18}O_2$ tracer measurement for binary oxide catalysts, the values in Table 4 for these catalysts must be reduced to some extent.

In Fe–Te–Mo–O catalyst system, tellurium content was varied from 0 to 3 with the fixed ratio of iron to molybdenum (= 2:3). As can be seen in Fig. 4, the extent of participation of the lattice oxide ions in the propylene oxidation was changed according to the composition of catalyst in the order $Fe_2(MoO_4)_3$ < $TeO_2–MoO_3$ < Fe–Te–Mo–O (2:3:3) < Fe–Te–Mo–O (2:0.1:3). Although the participation of the lattice oxide ions in $Fe_2(MoO_4)_3$ catalyst is limited in the vicinity of surface layer (about 30 layers), the extent of participation increases markedly only by the combination of $Fe_2(MoO_4)_3$ with small amount of tellurium oxide and exceeds that of the $TeO_2–MoO_3$ catalyst. The same result was also observed on $CuO–TeO_3–6MoO_3$ catalyst as shown in Fig. 5. These results, however, contrasted with that of $CoTeMoO_6$ and $MnTeMoO_6$ catalysts, where the combination effect of transition metal element on the participation of lattice oxide ion was not appreciable.

DISCUSSION

Participation of the Lattice Oxide Ion in the Oxidation of Propylene

As revealed by the results of $^{18}O_2$ tracer experiments shown in Table 4, participation of the lattice oxide ion in the oxidation of propylene is profound on every tellurium-based catalyst, and is comparable to that observed in bismuth molybdate and/or scheelite type oxide catalyst (*18*). It may be noted that every catalyst which shows high participation of lattice oxide ions contains molybdenum oxide as an essential constituent, along with another metal oxide belonging to group V and VI element such as Te and Bi; that is, mobile behavior of the lattice oxide ion is a common characteristic of complex metal oxides consisting of molybdenum oxide. These facts clearly show that the lattice oxide ion is active for allylic oxidation of olefins and that migration of active oxygen to active sites occurs through their bulk diffusion.

Diffusion of the lattice oxide ions during catalytic oxidation is important in determining which phase in the multicomponent oxide catalyst system is catalytically active. As already reported in a previous paper (*8*), the participation of the lattice oxide ions varies with the kind of constituent, composition, and structure of oxide catalyst. In the case of tellurium-based catalysts, these variations were revealed in the results shown in Fig. 4 for Fe–Te–Mo–O catalysts having different composition. Since the participation of lattice oxide ions both in $Fe_2(MoO_4)_3$ and TeO_2–MoO_3 were limited to the vicinity of surface layers, it appears that an appreciable increase of participation is only obtained in the combination of three elements, Fe, Te, and Mo.

The arrow mark in Fig. 4 shows the point where the total amount of lattice oxide ion incorporated into the oxidation products reaches the amount of lattice oxide ion in TeO_2 phase of Fe–Te–Mo–O (2 : 0.1 : 3) catalyst. Since TeO_2 phase was not detected in this catalyst, the amount of lattice oxide ion was calculated from the tellurium content by assuming that tellurium is present in a state of TeO_2. At this point, ^{16}O of original lattice oxide ion of catalyst are still incorporated into the reaction products. This result clearly shows that the lattice oxide ions not only in tellurium oxide but also in other metal oxides are active for the oxidation of propylene. Estimated value of oxide involved in the oxidation for this catalyst exceeds 150 layers as shown in Table 4. Thus, it is definite that the addition of small amounts of tellurium oxide is sufficient for the improvement of the extent of participation. Since tellurium oxide combines with molybdenum oxide to construct the active phase which is responsible for the enhanced activity and selectivity observed during oxidation of propylene, it is suggested that iron itself undergoes reduction and oxidation and assists the redox cycle of the active phase during the catalytic oxidation through the diffusion of lattice oxide ion. The same trend was observed in the ternary oxide catalysts containing copper as shown in Fig. 5. At this stage, however, it is impossible to pinpoint exactly the precise combination effect of the transition metal oxide on the participation of lattice oxide ion, such as the mechanism for the diffusion process of lattice oxide ion.

Stability of Tellurium-Based Catalysts

The loss of active metal components during catalytic oxidation is an important and common characteristic of allylic oxidation catalysts which consist of V and VI group of metal oxides; for example, molybdenum in various bismuth molybdate catalysts, antimony in uranium–antimony and/or iron–antimony catalysts, and tellurium in tellurium-based oxide systems. In particular, tellurium-based oxide catalysts are appreciably sensitive to the catalyst reduction compared with other catalyst systems because of the low sublimation temperature of metallic tellurium, so that the vaporization of tellurium from the catalyst occurs in its reduced state.

Metallic tellurium was detected in the outlet of the reactor after the reaction over the binary oxide catalysts, $CoTeMoO_6$ and $MnTeMoO_6$. As shown in Table 3, it is obvious from the analysis after the reaction that the tellurium vaporizes during the oxidation of propylene for these catalysts, while the vaporization is hardly detectable at the present reaction conditions for the ternary oxide catalysts; Fe–Te–Mo–O and CuO–TeO_3–$6MoO_3$. Thus, it is apparent that the third transition metal element supports the high oxidation state of tellurium during the catalytic oxidation.

The phenomenon of tellurium vaporization is discussed to relate with the mobility of the lattice oxide ions of catalyst as follows. The results in Table 4 show that the active surface oxygen is equivalent to lattice oxide ion in the bulk of the oxide catalyst. Delivery of this active oxygen to the reaction site is not achieved by the surface migration according to the Langmuir–Hinshelwood mechanism but by the bulk diffusion of lattice oxide ion in the surface layers of the catalyst particles. Furthermore, by comparing the amount of vaporized tellurium (Table 3) with the number of oxide ion layer involved in the oxidation (Table 4), one sees a clear correlation between these phenomena during the catalytic oxidation.

The catalysts which show a lower extent of the lattice oxide ion participation in the redox cycle easily convert tellurium into a metallic state, but addition of transition metal oxides markedly suppresses the vaporization of tellurium and increases the number of lattice oxide ion layers involved in the oxidation.

The active phase may be catalytically stable only when the reoxidation rate can be made to balance the reduction rate. When the diffusion rate of lattice oxide ions is slow such as in binary oxide catalysts, $CoTeMoO_6$ and $MnTeMoO_6$, the active sites might be deformed by the elimination of coordinated oxygen at reduction stage, so that these reduced sites easily release metallic tellurium during the oxidation (Table 3) with the decay of catalytic activity (Fig. 1). On the other hand, when a transition metal such as iron and/or copper is present in the tellurium-based catalyst, deformation of active sites at reduction stage is minimized because active oxygen is easily supplied to the oxygen deficient site formed by the reduction through the bulk diffusion of lattice oxide ion. Thus, the active site is held in the constant oxidation state and structure, and consequently the high stability of catalyst and high catalytic activity are achieved. It is concluded that the third transition metal component plays an important role to keep the tellurium element in highly oxidized state by supplying the lattice oxide ions from the bulk of oxide catalyst.

REFERENCES

1. (a) Fetterly, L. C. (Shell), Japan Patent 65-8,522 (1965); (b) Caporali, G., Ferlazzo, N., and Giordano, N. (Montercatini–Edison), U.S. Patent 3,691,244 (1972); (c) Takayama, Y., and Ikeda, T. (Mitsubishi Rayon), Japan Patent 86-13,139 (1968); (d) Grasselli, R. K. (Standard Oil, Ohio), Japan Patent 76-8,218 (1976).
2. Yoshino, T., Saito, S., and Sasaki, Y. (Nitto Chemicals), Japan Patent 71-03,564 (1971), 71-02,804 (1971).
3. Keulks, G. W., Krenzke, L. D., and Nottermann, T. M., "Advances in Catalysis" Vol. 27, p. 183. Academic Press, New York, 1978.
4. Grasselli, R. K., and Burrington, J. D., "Advances in Catalysis," Vol. 30, p. 133. Academic Press, New York, 1981.
5. (a) Andrushkevich, T. V., Boreskov, G. K., Kuznetsova, L. L., Plyasova, L. M., Tyurin, Y. N., and Shchekochikhin, Y. M., *Kinet. Katal.* **15,** 424 (1974); (b) Fedevich, E. V., Zhiznevskii, V. M., Nikipanchuk, M. V., Yakubovskaya, L. F., and Golub, I. M., *Kinet. Katal.* **15,** 1288 (1974); (c) Zhiznevskii, V. M., Fedevih, E. V., Pikulyk, O. M., Shipailo, V. Y., and Tolopko, D. K., *Kinet. Katal.* **13,** 1488 (1972).
6. Bart, J. C. J., Petrini, G., and Giordano, N., *Z. Anorg. Allg. Chem.* **412,** 258 (1975).
7. Bart, J. C. J., and Giordano, N., *J. Catal.* **64,** 356 (1980).
8. Moro-oka, Y., Ueda, W., Tanaka, S., and Ikawa, T., *in* "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980" (T. Seiyama and K. Tanabe, eds.), Part B, p. 1086. Kodansha, New York/Elsevier, Amsterdam, 1981.
9. Ueda, W., Moro-oka, Y., and Ikawa, T., *J. Catal.* **70,** 409 (1981).
10. Ueda, W., Moro-oka, Y., Ikawa, T., and Matsuura, I., *Chem. Lett.* 1365 (1982).
11. Keulks, G. W., *J. Catal.* **19,** 232 (1970).
12. Keulks, G. W., and Krenzke, L. D., in "Proceedings, 6th International Congress on Catalysis, London, 1976" (G. C. Bonds, P. B. Wells, and F. C. Tompkins, Eds.), Vol. 2, p. 806. The Chemical Society, London, 1977.
13. Krenzke, L. D., and Keulks, G. W., *J. Catal.* **61,** 316 (1980).
14. Brazdil, J. F., Suresh, D. D., and Grasselli, R. K., *J. Catal.* **66,** 347 (1980).
15. Grasselli, R. K., Burrington, J. D., and Brazdil, J. F., *Faraday Discuss. Chem. Soc.* **72,** 203 (1981).
16. Forzatti, P., Trifiro, F., and Villa, P. L., *J. Catal.* **55,** 52 (1978).
17. Boltz, D. F., "Colorimetric Determination of Nonmetals," 2nd ed., p. 380. Wiley, New York 1978.
18. Ueda, W., Chen, C. L., Asakawa, K., Moro-oka, Y., and Ikawa, T., *Chem. Lett.* 135 (1984).