CHEMISTRY LETTERS, pp. 483-486, 1982.

ROLE OF TRANSITION METAL ELEMENTS IN Te-Mo-M-O CATALYSTS AS REVEALED BY THE OXIDATION OF PROPYLENE TO ACROLEIN WITH $^{18}O_2$ TRACER

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Participation of the lattice oxide ions in various tellurium-based multicomponent oxide catalysts, Te-Mo-M-O (M = Co, Mn, Fe and Cu) was investigated using $^{18}O_2$ tracer in the selective oxidation of propylene to acrolein. High mobility of the lattice oxide ions in this system plays an important role in stabilizing the active site for the redox process and in suppressing the vaporization of tellurium metal from the catalyst during the reaction.

Recently, a number of tellurium-based oxides have been developed as active and selective catalyst for the catalytic oxidation of lower olefin. It has been also claimed that addition of a small amount of tellurium oxide to other oxide systems improves remarkably their catalytic properties in the oxidation of propylene or isobutylene. A characteristic feature of the catalyst systems containing tellurium is the deactivation of the catalyst due to the aggregation and vaporization of tellurium metal during the catalysis. In order to get over 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,[1-3] we tried to obtain an insight into the mechanistic role of the third metal component of Te-Mo-M-O catalyst in the oxidation of propylene to acrolein. In this communication, we report a clear evidence that the vaporization of tellurium is suppressed by the rapid diffusion of the bulk oxide ion to the active site and the third component plays an important role to activate the molecular oxygen and to keep the active components in the highly oxidized state.

Te-Mo-M-O (M = Co, Mn and Fe) catalysts were prepared by the solid state reactions of TeO_2 with binary oxides of molybdenum and transition metal elements at 500°C for 3 h after the pre-calcination at 300°C for 2 h.[4] Te-Mo-Cu-O catalyst was prepared by the coprecipitation from a basic solution of ammonium heptamolybdate and a mixed solution of telluric acid and cupric nitrate and the calcination in air at 450°C for 2 h.[5] Two Te-Mo-O catalysts were prepared by the solid state reactions of MoO_3 with TeO_2 and H_6TeO_6 at 500°C for 2 h, respectively.[6)] Characteristics of the catalysts used are summarized in Table 1. Catalytic activity for the oxidation of propylene to acrolein with the reaction time was determined using the conventional flow reactor at 450°C under an atmospheric pressure (C_3'; 0.08%, O_2; 0.16%, N_2; balance). As shown in Fig. 1, specific activity of TeO_3-$6MoO_3$ is fairly high in the first few hours but it decreases continuously with the reaction time. In addition, severe vaporization of tellurium metal was observed in the cases of both Te-Mo-O catalysts which include no third transition metal elements. Initial decrease of the specific activity was also observed for ternary component catalysts, Te-Mo-M-O (M = Co, Mn, Fe and Cu), but constant activity was obtained within a few hours. It is noteworthy that the vaporization of tellurium element was almost completely prevented for these ternary component catalysts.

$^{18}O_2$ Tracer experiments were carried out using the closed circulating system at 450°C under a reduced pressure [C_3'; 70 torr, $^{18}O_2$(99.1%); 70 torr]. A typical time cource of ^{18}O fraction of the reaction products is shown in Fig. 2 for Fe-Te-Mo-O (2:0.1:3) catalyst. As has been reported for several binary or multicomponent metal oxide catalysts,[1-3)] participation of the lattice oxide ions is quite profound for every catalyst tested. The ^{18}O content of acrolein coincided at every time with that of carbon dioxide and no evidence was obtained for the

Table 1. Characterization of the Catalysts Used

Catalyst	Surface area (m^2/g)	Phase determined by X-ray analysis	Vaporization of tellurium	Selectivity to acrolein (%)	Number of oxide ion layer involved in the oxidation[a)]
$CoTeMoO_6$	1.0	$CoTeMoO_6$	low	89	80
$MnTeMoO_6$	1.1	$MnTeMoO_6$	low	77	60
Fe-Te-Mo-O(2:1:1)	2.0	——[b)]	low	97	150
(2:0.1:3)	0.5	$Fe_2(MoO_4)_3$	low	96	150
CuO-TeO_3-$6MoO_3$	1.9	——[c)]	low	96	160
TeO_3-$6MoO_3$	3.9	Te_2MoO_7, MoO_3	high[d)]	97	50
TeO_2-$6MoO_3$	0.7	Te_2MoO_7, MoO_3	high	95	80

a) Values estimated by assuming the complete mixing model and 10^{19} of oxide ion per unit surface area(m^2) of catalyst.

b) Not identified.

c) Heteropoly structure, cupric hexamolybdotellurate ($H_4CuTeMo_6O_{24}$) which was decomposed at 500°C by the heat treatment in air. Structure after decomposition was not identified.

d) Formation of metallic tellurium mirror was detected during the reaction on the wall of the reactor outlet within 0.5 h at 450°C.

discrimination of the lattice oxide ion from adsorbed oxygen species to form the partially oxidized product. The arrow mark in the figure shows the point where $^{16}O^{2-}$ incorporated into the oxidized products reaches the same amount as oxide ions in TeO_2 in the catalyst. The ^{18}O content of the reaction products is much lower than that of gaseous molecular oxygen at this stage. Thus, it is difinite that lattice oxide ions not only in tellurium oxide but also in other metal oxide are involved in the redox cycle.

The ^{18}O content in acrolein produced on each catalyst is plotted against the consumed gaseous oxygen per unit surface area of the catalyst (Fig. 3). Assuming 1×10^{19} of oxide ions per unit surface area(m^2) and the complete mixing model,[2] the number of the oxide ion layers involved in redox cycle is estimated for each catalyst and values are listed in the last column in Table 1. As shown in the table, more than 50 layers of the oxide ion participate in the reaction at the stationary state on every catalyst tested. The results show that the delivery of active oxygen to the reaction site is not achieved by the surface migration according to the Langmuir-Hinshellwood mechanism but by the bulk diffusion involving lattice oxide ions in the surface layer of the catalyst particles. Since rapid vaporization of tellurium element is observed only in its metallic state,[6] it is clear that the third transition metal component plays an important role to keep the tellurium element in highly oxidized state. It is easily estimated that activation of molecular oxygen is greatly facilitated by the third

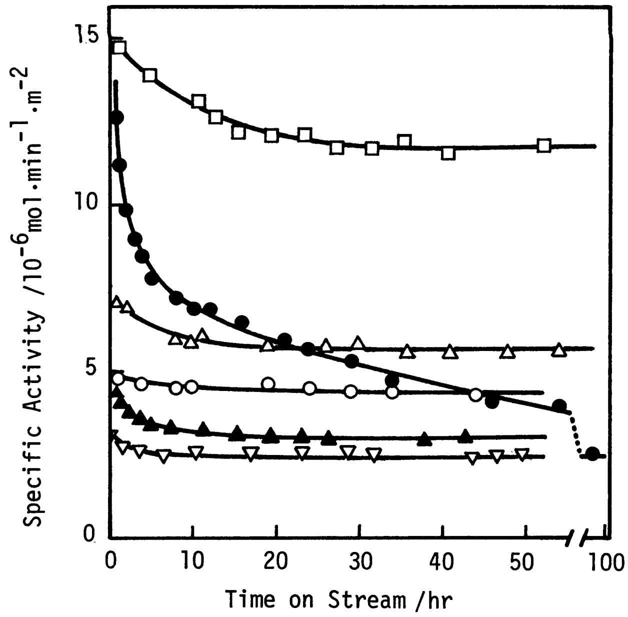

Fig. 1 Catalytic activity of tellurium-based catalysts for the oxidation of C_3H_6. ○ , $MnTeMoO_6$; △ , Fe-Te-Mo-O(2:1:1); □ , Fe-Te-Mo-O(2:0.1:3); ▲ , CuO-TeO_3-$6MoO_3$; ● , TeO_3-$6MoO_3$; ▽ , TeO_2-$6MoO_3$.

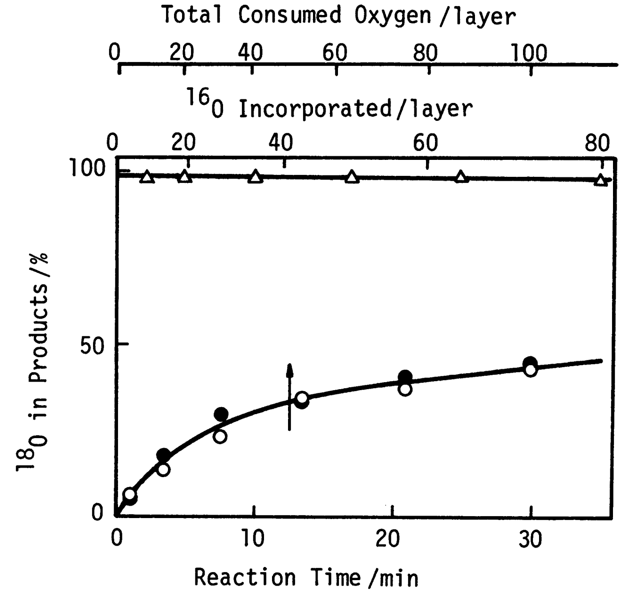

Fig. 2 ^{18}O Concentration of the oxidized products over Fe-Te-Mo-O(2:0.1:3) catalyst. ○ , Acrolein; ● , Carbon dioxide; △ , Gaseous oxygen. Arrow mark, see text.

transition metal elements. In addition, third transition metal element may accelerate the rate of the bulk diffusion of the lattice oxide ion in the catalyst. At this stage, it is not clear which role is more important to keep the tellurium element in highly oxidized state. Further investigation on the reduction and reoxidation of the catalysts is in underway to obtain the direct information concerning to the redox cycle.[7)]

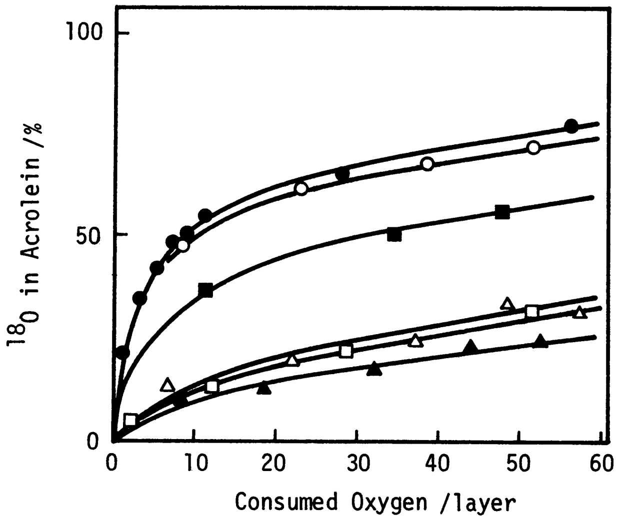

Fig. 3 Change of the ^{18}O fraction in acrolein against the total consumed oxygen in the oxidation of propylene. ■ , $CoTeMoO_6$; ○ , $MnTeMoO_6$; △ , Fe-Te-Mo-O(2:1:1); □ , Fe-Te-Mo-O(2:0.1:3); ▲ , $CuO-TeO_3-6MoO_3$; ● , TeO_3-6MoO_3.

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(Received January 20, 1982)