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Reaction of Mo^{5+} Formed on Supported Molybdena Catalysts with Oxygen or Water

Masamichi AKIMOTO and Etsuro ECHIGOYA

Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

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Reactivity of Mo^{5+} formed on supported molybdena catalysts with oxygen or water was investigated by means of ESR spectroscopy. Mo^{5+} formed on the alumina carrier could not be oxidized with gaseous oxygen even at 450 °C and was poisoned by water at 200 °C losing its ESR signal. The Mo^{5+} formed on the titania carrier disappeared by reaction with either oxygen or water. The mechanism for the reactions was investigated and the different reactivities of Mo^{5+} with oxygen as regards carrier effect on the structure were discussed.

The surface area of a catalyst determined by the BET method has long been used as a measure of catalytic activity. However, in the case of supported catalysts, the surface area also contains that of carrier and does not give the actual surface area of the active site. The need to determine this area increases particularly in the case where catalysts of the same or similar compositions show different activity and selectivity. Various methods have been presented to determine the number of active sites. As an example, adsorption of hydrogen or carbon monoxide was used to estimate the active surface area of platinum supported on alumina. Carbon monoxide was also utilized in the analysis of real surface area of supported nickel catalyst. For the case of supported metal oxide catalysts, the actual surface area of chromic oxide[1] supported on either alumina, silica or silica-alumina and of bismuth molybdate[2] on silica was estimated by reducing these catalysts with hydrogen followed by the determination of the amount of oxygen required for reoxidation.

We observed Mo^{5+} which cannot be oxidized even at 450 °C, denoted as Mo^{5+} (A), in molybdena catalysts supported on alumina and magnesia.[3] Mo^{5+} formed on silica and zinc oxide carrier, denoted as Mo^{5+} (B), was easily oxidized and showed good selectivity for maleic anhydride in the vapor phase oxidation of butadiene. Both Mo^{5+} (A) and Mo^{5+} (B) appeared in titania supported molybdena catalyst. In order to investigate the mechanism for carbon dioxide and maleic anhydride formation during the course of oxidation of butadiene, a method is desirable for estimating the amount of Mo^{5+} on the surface of supported molybdena catalysts. Thus, the reaction of Mo^{5+} formed in supported molybdena catalysts with oxygen or water was investigated by means of ESR, their structure being discussed with respect to different reactivities.

Amounts of Mo^{5+} (A) and Mo^{5+} (B) formed in MoO_3–TiO_2 catalyst and their distribution on the surface and in bulk were also determined.

Experimental

The reactivity of Mo^{5+} formed in a supported molybdena catalyst was investigated by means of ESR with a glass instrument consisting of a 5 mm o.d. quartz tube, 150 mm long with a glass cock. The amount of catalyst was 0.100 g. Evacuation was carried out with a conventional apparatus consisting of an oil diffusion pump. Heating was carried out by means of a cylindrical thermal air bath. Oxygen was introduced into the reaction vessel from a reservoir connected with the evacuation apparatus and water as saturated vapor at room temperature. First, the catalyst was evacuated for 30 min at 10^{-4}—10^{-5} mmHg and the Mo^{5+} was determined at room temperature by means of ESR using Mn^{2+} as an internal standard. Oxygen or water was then introduced into the vessel at room temperature and the vessel was heated to start the reaction. After the elapse of a certain time, the reaction mixture was cooled to room temperature and evacuated for 30 min. The amount of decreased Mo^{5+} was also determined by ESR at room temperature. The effect of temperature on the amount of

1) H. Charcossett, A. Revillon, and A. Guyot, *J. Catal.*, **8**, 334 (1967).

2) E. H. Lee, *ibid.*, **12**, 314 (1968).

3) M. Akimoto and E. Echigoya, *Chem. Lett.*, **1972**, 305.

adsorbed oxygen species was also measured by a similar method to that described above. However, in this case the catalyst (50 mg) was evacuated at 540 °C for 1 hr, and oxygen was introduced at a pressure of 5 mmHg at about −100 °C. A temperature-programmed cavity was used for ESR studies at −100—+250 °C. For temperatures above 250 °C, the vessel was heated at various temperatures for a fixed time followed by the determination of the amount of adsorbed oxygen species at room temperature. The catalysts were prepared by wet mixing of alumina sol or titania gel with an aqueous solution of ammonium paramolybdate.[3]

The surface area of the catalysts was determined by the BET method using nitrogen adsorbate. The structure of these catalysts was investigated by X-ray diffraction using nickel-filtered Cu$K\alpha$ radiation. It was found that molybdena can dissolve in anatase titania to the extent of 25—30 mol% and MoO_3–Al_2O_3 catalyst is amorphous within a 66.7 mol% molybdena content.

Results and Discussion

Reaction of Mo^{5+} with Oxygen or Water. Figure 1 shows the effect of reaction temperature and time on the amount of Mo^{5+} decreased as a result of the reaction. Mo^{5+} was formed by the evacuation of MoO_3–TiO_2 (1 : 3) catalyst at 365 °C for 30 min and then reacted. The same result was previously obtained for oxygen pressures of 20 and 200 mmHg. Therefore, gaseous oxygen of 20 mmHg was used in all experiments. We see that water does not react with Mo^{5+} at 100 °C but easily does so at 200 °C. Mo^{5+} is oxidized rapidly with oxygen at 200 °C in contrast with the case at 100 °C.

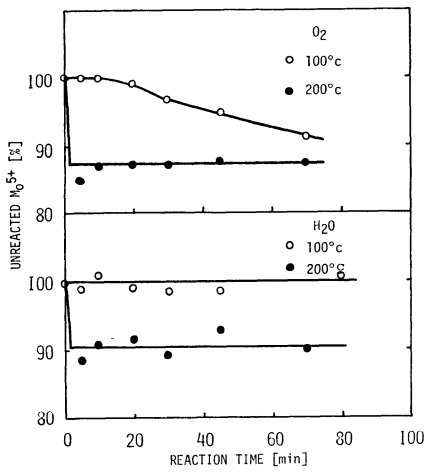


Fig. 1. Reaction of Mo^{5+} with oxygen or water. Effect of reaction time.
catalyst: MoO_3–TiO_2 (MoO_3 25.0 mol%)

The effect of reaction temperature is shown in Fig. 2. Decrease in the amount of Mo^{5+} was observed on reaction with water above 200 °C but not below 175 °C. However, the amount above 250 °C was found to exceed the initial amount presumably due to the formation of new Mo^{5+} in the bulk with a loss of lattice oxygen above 250 °C.

Based on the oxidation temperature, the reaction step can be broadly divided into (a) 57—150 °C, (b) 150—300 °C, and (c) 300—450 °C, attributable to the different reactivities of Mo^{5+} formed on the surface and in the bulk. At 57—150 °C, Mo^{5+} (B) on the surface seems to be oxidized slowly in contrast with the oxidation at 150—300 °C. However, when the temperature exceeds 300 °C, oxygen is assumed to penetrate into the bulk and oxidize Mo^{5+} (B) formed in the lattice. It is notable that the amount of Mo^{5+} decreased on reaction with water at 200—250 °C is approximately equal to that with oxygen. This suggests that water also reacts with surface Mo^{5+} (B) at 200—250 °C. Stable Mo^{5+} was observed in the catalyst not oxidized even at 450 °C. This is in accordance with Mo^{5+} (A) in MoO_3–Al_2O_3 catalyst.

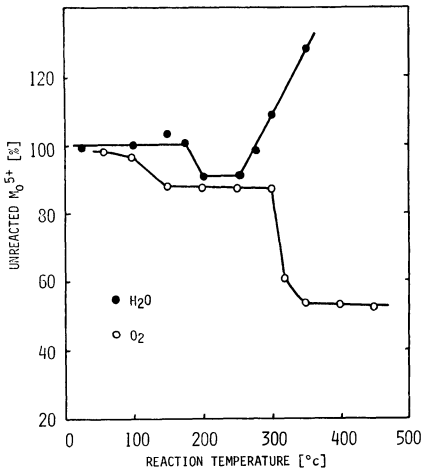


Fig. 2. Reaction of Mo^{5+} with oxygen or water. Effect of reaction temperature.
catalyst: MoO_3–TiO_2 (MoO_3 25.0 mol%)
reaction time: 30 min

The effect of evacuation temperature on the formation of Mo^{5+} in MoO_3–TiO_2 (1 : 3) catalyst is shown in Fig. 3. The catalyst was evacuated for 30 min at 10^{-4}—10^{-5} mmHg and Mo^{5+} was oxidized at 350 °C. The Mo^{5+} disappearing on oxidation is accordingly Mo^{5+} (B) and the rest is Mo^{5+} (A). Mo^{5+} (B) is possibly formed at the sites where lattice oxygen is lost by evacuation. The amount of Mo^{5+} (A) was found to be independent of evacuation temperature, thus suggesting that Mo^{5+} (A) is formed during the preparation of the catalyst. It is possible that water penetrates into the bulk and dissociates to form a bond M–OH (M: Mo^{6+} or Ti^{4+}) during the preparation and that these hydroxyl groups are dehydrated to give water with formation of a bond $-Ti^{4+}$–O–Mo– on heating in water-free atmosphere at higher temperatures. This molybdenum ion is expected to be Mo^{5+} (A). This gives an evidence for the amount of Mo^{5+} (A) exceeding the total amount formed on evacuation below 200 °C.

Figure 3 also shows that the total amount of Mo^{5+} formed on evacuation at 200 °C is nearly equal to that of Mo^{5+} (A), formation of Mo^{5+} (B) being negligible, thus suggesting that dehydration occurs above 200 °C in accordance with the formation of Mo^{5+} (B). From these results, it can be concluded that the Mo^{5+} disappearing on reaction with oxygen or water at 200—250 °C is surface Mo^{5+}.

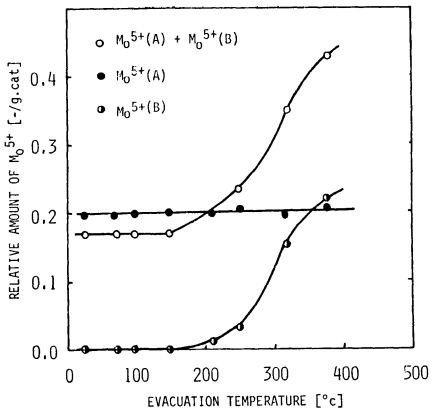


Fig. 3. Correlation between the amount of Mo^{5+} formed and evacuation temperature.
catalyst: MoO_3–TiO_2 (MoO_3 25.0 mol %)
evacuation time: 30 min
oxidation: 350 °C, 30 min, O_2 20 mmHg

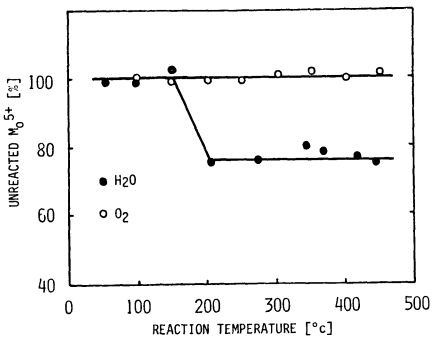


Fig. 4. Reaction of Mo^{5+} with oxygen or water.
catalyst: MoO_3–Al_2O_3 (MoO_3 18.2 mol %)
reaction time: 30 min

Figure 4 shows the result of reaction of oxygen or water with Mo^{5+} formed in MoO_3–Al_2O_3 (2: 9) catalyst, in which the intensity of ESR signal attributable to Mo^{5+} (A) does not decrease on reaction with oxygen even at 450 °C but does so with water above 200 °C. The reactivity of Mo^{5+} (A) with water was thus found to be similar to that of Mo^{5+} (B) on MoO_3–TiO_2 catalyst. The Mo^{5+} (A) disappearing on reaction with water is surface Mo^{5+} (A) since hydroxyl groups are dehydrated easily at higher temperatures and water cannot penetrate into the bulk.

Structure of Mo^{5+}. The amount of Mo^{5+} formed on MoO_3–TiO_2 catalyst was measured by the above method (Table 1). It is of interest to note that the amount of surface Mo^{5+} determined by means of oxidation is approximately equal to that obtained by reaction with water. Decrease in the amount of Mo^{5+} was not observed on reaction with water at 200 °C when Mo^{5+} was previously oxidized at 225 °C. These results suggest that most of Mo^{5+} on the surface is Mo^{5+} (B). The amount of Mo^{5+} (A) increases with a rise in molybdena content to reach a maximum amount at MoO_3 30 mol%, *i.e.*, at a maximum solubility of molybdena in anatase titania, which provides an evidence for the conclusion that most of Mo^{5+} (A) is present in the bulk as predicted by the mechanism for its formation.

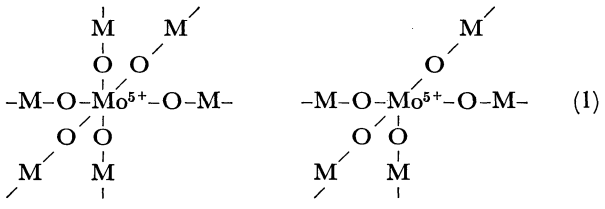
Table 1. Distribution of the amount of Mo^{5+} in MoO_3–TiO_2 catalyst

MoO_3 content (mol %)	Surface area (m^2/g)	Surface amount of Mo^{5+} (%) by H_2O	by O_2	Total Mo^{5+} a)	Mo^{5+} (A) b)
0.0	60	—	—	0.000	0.000
5.0	85	33.3	44.4	0.122	0.050
10.0	126	28.7	37.1	0.247	0.105
13.0	129	25.5	33.6	0.274	0.148
18.0	119	22.0	20.0	0.473	0.190
25.0	63	19.2	18.5	0.576	0.260
30.0	37	18.7	14.0	0.598	0.317
40.0	23	14.4	16.4	0.419	0.264
50.0	23	20.1	14.8	0.436	0.215

a) Evacuated at 365 °C for 30 min.
b) Oxidized with oxygen at 350 °C for 30 min.

Asmolov and Krylov[4,5] investigated the structure of molybdena supported on magnesia or alumina by means of ESR and optical diffuse reflactance spectroscopy, and revealed that Mo^{6+} and Mo^{5+} on the surface are present in octahedric or tetrahedric and square-pyramid coordination, respectively. Mo^{4+} and Mo^{3+} were also found to occupy the lattice points in these carriers in octahedric coordination. It is possible that Mo^{5+} (A) in the bulk has a similar structure to that of Mo^{4+} and Mo^{3+}. Thus, the structure of surface or bulk Mo^{5+} is assumed to be that shown in (1). The structure of Mo^{5+} (B) in the bulk seems to be similar to that of Mo^{5+} (A) in the bulk, but at least one of the oxygen surrounding molybdenum ions is lost with formation of anion vacancy and M is not always metal ion of carrier. In the case of surface Mo^{5+}, M is expected to be metal ion of carrier (Mo^{5+} (A)) or molybdenum ion and metal ion of carrier (Mo^{5+} (B)). Thus, most of Mo^{5+} (A) in the bulk is presumably formed by dispersion and dissolution of molybdena into these carriers followed by the occupation of molybdenum ion at the lattice points of Al^{3+} or Ti^{4+}. Excess electrons appear around the molybdenum ion and are trapped by Mo^{6+} rather than by Al^{3+} or Ti^{4+} forming Mo^{5+} (A). This mechanism is similar to that of acid and base formation in aluminosilicate.[6] Mo^{5+} (A) in the bulk does not seem to be oxidized even at higher temperatures, which agrees with our result. On the contrary, Mo^{5+} (B) is presumably formed with a loss of lattice oxygen at the sites where molybdena is not so dispersed as in the case of Mo^{5+} (A) formation in MoO_3–TiO_2 catalyst. Decrease in the amount of Mo^{5+} on MoO_3–Al_2O_3 and MoO_3–TiO_2 catalyst was observed on reaction with water in contrast with the oxidation. This suggests that the reactions of water with Mo^{5+} (A) and Mo^{5+} (B) follow the same mechanism.

4) G. N. Asmolov and O. V. Krylov., *Kinet. Katal.*, **11**, 1028 (1970).
5) G. N. Asmolov and O. V. Krylov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 10, 2414 (1970).
6) C. L. Thomas, *Ind. Eng. Chem.*, **41**, 2564 (1949); R. C. Hansfold, "Advances in Catalysis," Vol. 3, Academic Press Inc., New York (1952), pp. 1, 7; M. Mcd. Baker, and G. I. Jenkins, *ibid.*, Vol. 7, (1955), p. 39.



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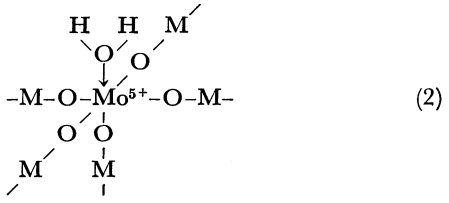

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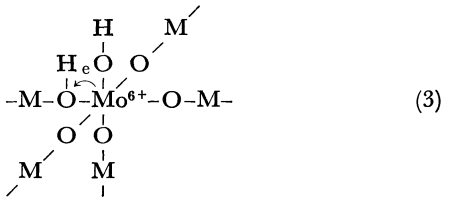

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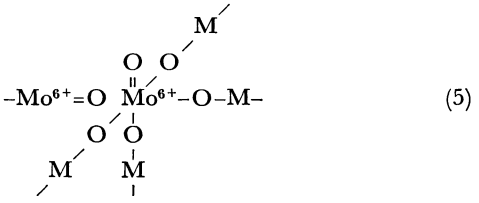

(5)

Mechanism for the Reaction of Mo^{5+} with Water.

Basolo and Pearson[7] showed that $(MoO)^{3+}$ is a hard Lewis acid which interacts more easily with a hard Lewis base than with a soft one. Based on this conception, Mo^{5+} formed on MoO_3–TiO_2 (1 : 3) catalyst by evacuation at 365 °C was reacted with either pyperidine, *n*-butylamine or tetrahydrothiophene as hard Lewis bases or toluene or benzene as soft Lewis bases at 200—250 °C. Pyridine was also used as a hard and soft Lewis base. However, decrease in the signal intensity was not observed in these reactions, thus suggesting that Mo^{5+} does not shift to Mo^{4+} even by the formation of a coordination bond between acidic Mo^{5+} and these Lewis bases. Accordingly, disappearance of the ESR signal on reaction with water can not be attributed to the formation of a complex (2) but to some other mechanism.

It is very possible that coordinated water in (2) dissociates above 200 °C to make a σ-bond with molybdenum ion as shown in (3). In proportion to the evacuation temperature, the amount of Mo^{5+} (A) formed in MoO_3–Al_2O_3 catalyst was found to increase with a decrease in the intensity of a broad absorption band due to OH stretching (3000—3600 cm^{-1}). IR measurement also revealed the presence of molecular water on MoO_3–Al_2O_3 catalyst on admission of water. These results provide a powerful evidence for the mechanism (3). Hence, it is concluded that Mo^{5+} shifts to Mo^{6+} with disappearance of its ESR signal by formation of the σ-bond with OH and extraction of electron by a neighboring oxygen. This mechanism is similar to that of Brønsted acid formation from Lewis acidic site in the presence of water at higher temperatures.[8]

Mechanism for the Reaction of Mo^{5+} with Oxygen.

It is interesting to note that Mo^{5+} on MoO_3–TiO_2 is oxidized with oxygen in contrast with Mo^{5+} on MoO_3–Al_2O_3 catalyst. For the purpose of clarifying this carrier effect, the mechanism for oxidation was studied by observation of adsorbed oxygen species with ESR.

Many papers[9] have appeared on the ESR spectra of oxygen species adsorbed on metal oxides. Shvets and Kazansky[10] investigated the spectra of oxygen species adsorbed on reduced molybdena and identified the triplet signal with g=2.018, 2.010, and 2.004 with O_2^-. Ishii and Matsu-ura[11] also studied the spectra on molybdena and ascribed the triplet signal with g=2.04, 2.01, and 2.00 to O_2^- and a sharp singlet signal with g=2.00 to O^-.

In our experiments, no ESR signal of adsorbed oxygen species appeared on alumina and silica even at −100 °C, but the signal was observed on supported molybdena catalysts. At room temperature, a triplet signal with g=2.019, 2.009, and 2.003 was observed on MoO_3–TiO_2 (1 : 99) catalyst on admission of oxygen. At 60—100 °C, the signal intensity at g=2.019, and 2.009 decreased and at the same time the signal with g=2.002 became sharp and increased. When N_2O was adsorbed on the MoO_3–TiO_2 catalyst at 100 °C, a sharp singlet signal with g=2.002 was obtained. Thus, the triplet signal with g=2.019, 2.009, and 2.003 can be ascribed to O_2^-, and a sharp singlet signal with g=2.002 to O^-. This signal of O^- is similar to that of Setaka and Kwan[9] and of Ishii and Matsu-

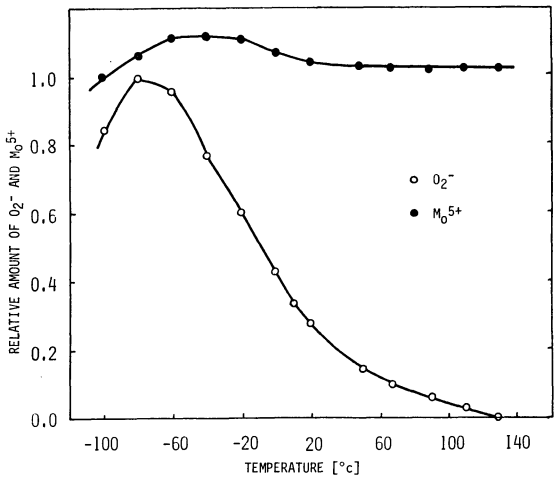

Fig. 5. Effect of temperature on the amount of O_2^- and Mo^{5+} ion.
catalyst: MoO_3–Al_2O_3 (MoO_3 18.2 mol %)

7) F. Basolo and R.G. Pearson, "Mechanism of Inorganic Reactions. A Study of Metal Complexes in Solution," John Wiley & Sons, Inc., New York (1967), p. 25.

8) M. W. Tamele, *Discuss. Faraday Soc.*, **8**, 270 (1950).

9) T. Kwan and Y. Fujita, *Shokubai*, **5**, 206 (1963); R. J. Kokes, *J. Phys. Chem.*, **66**, 99 (1962); K. M. Sancier and T. Freund, *J. Catal.*, **5**, 293 (1965); M. Setaka and T. Kwan, This Bulletin, **38**, 1414 (1965).

10) V. A. Shvets and V. B. Kazansky, *J. Catal.*, **25**, 123 (1972).

11) Y. Ishii and I. Matsu-ura, *Nippon Kagaku Zasshi*, **89**, 553 (1968).

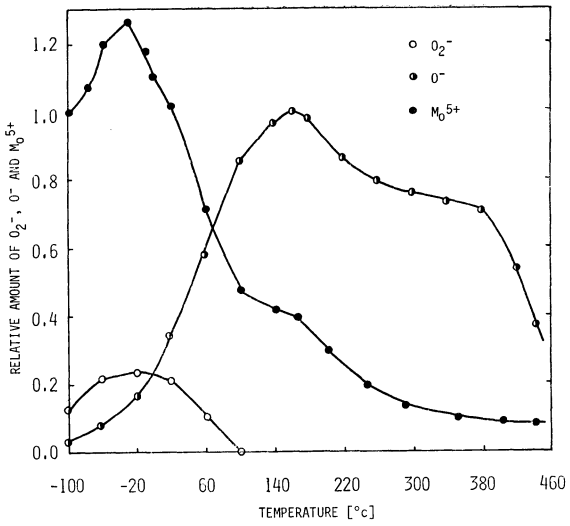

Fig. 6. Effect of temperature on the amount of O_2^-, O^-, and Mo^{5+} ion.
catalyst: MoO_3–TiO_2 (MoO_3 1.0 mol%)

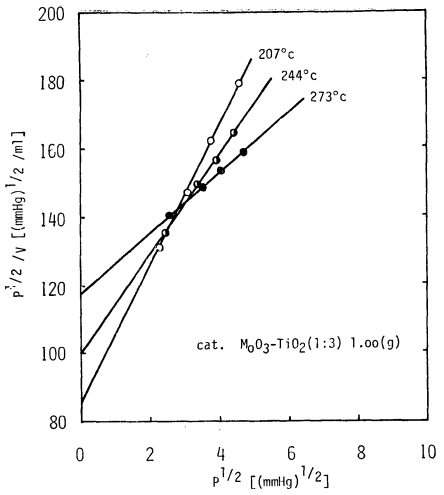

Fig. 7. Langmuir plot of oxygen adsorption on MoO_3–TiO_2 catalyst.
catalyst: pre-evacuated at 540 °C for 1 hr
P: oxygen pressure (mmHg)
V: volume of adsorbed oxygen (NTP ml)

ura[11] but does not agree with the results of Shvets and Kazansky.[10] In the case of anatase titania, there appeared only one adsorbed oxygen species O_2^- which showed the maximum amount at 50 °C and disappeared at 230 °C. On the contrary, the MoO_3–TiO_2 catalyst showed the maximum amount of O_2^- at −20 °C and the ion disappeared at 100 °C with formation of a great amount of O^- which showed a maximum at 150 °C, thus suggesting that these oxygen species are not formed on titanium ions but on molybdenum ions.

The effect of temperature on the amount of adsorbed oxygen species formed on MoO_3–Al_2O_3 (2: 9) and MoO_3–TiO_2 (1: 99) catalyst is shown in Figs. 5 and 6, the amount of Mo^{5+} modified with temperature also being shown. Only O_2^- was observed on the MoO_3–Al_2O_3 catalyst, the ion disappearing at 130 °C without any decrease in the amount of Mo^{5+} (Fig. 5). In the case of the MoO_3–TiO_2 catalyst, the amount of Mo^{5+} and O_2^- decreased at higher temperatures with formation of O^-. Thus, the following reaction can be assumed to proceed on the catalyst surface at higher temperatures.

$$O_2(g) \xrightarrow{e} O_2^- \xrightarrow{e} 2O^- \xrightarrow{2e} 2O^{2-} \qquad (4)$$

O^{2-} combines with molybdenum ion to form Mo^{6+}.

Adsorption of oxygen on Mo^{5+} (B) at higher temperatures follows a dissociative mechanism of Langmuir type (Fig. 7), which supports the above reaction mechanism. In contrast with Mo^{5+} (B), this reaction does not seem to proceed on Mo^{5+} (A) formed on MoO_3–Al_2O_3 catalyst, to which the inactivity of Mo^{5+} (A) for oxygen is attributable.

As shown in Figs. 5 and 6, increase in the amount of Mo^{5+} was observed at −100—+20 °C, which is presumably due to formation of Mo^{4+} on these catalysts on evacuation at 540 °C and of Mo^{5+} and O_2^- on admission of oxygen.

These different reactivities of Mo^{5+} with oxygen are presumably attributed to the different dispersions of molybdena in the carriers, *i.e.*, molybdena seems to be finely dispersed in alumina and magnesia with formation of the molybdates in contrast with anatase titania and silica. Accordingly, it is possible that the bond Mo–O–Al^{3+} in MoO_3–Al_2O_3 is strong and difficult to be cut off in contrast with Mo–O–Mo in MoO_3–TiO_2 catalyst. Hence, Mo^{5+} (B) on the latter catalyst is expected to be oxidized with oxygen through cutting off the weak Mo–O–Mo bond followed by formation of the double bond as shown in (5). By IR analysis, the double bond type lattice oxygen was proved to be reduced easily with hydrogen and recovered by reoxidation,[12] which supports the above mechanism for the oxidation of surface Mo^{5+} (B). The formation of this double bond is presumably impossible in the case of alumina and magnesia carriers.

In conclusion, the nature of the Mo^{5+} formed when molybdena is supported on a carrier is remarkably affected by the property of the carrier through its dispersion and formation of the chemical bond. Mo^{5+} (A) on the surface has extra ability in making a single bond, while Mo^{5+} (B) on the surface can make, in addition, a double bond.

12) M. Akimoto and E. Echigoya, to be published.