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Studies of MoO_3–Al_2O_3 Catalysts in Ethylene Polymerization. IV. Kinetics and Stoichiometry of the Reduction

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In order to reveal the formation mechanism of the active species in ethylene polymerization, the reduction of three kinds of molybdenum oxides, I, II, and III, which are insoluble in aq 10 M-NH_3, soluble in aq NH_3 but insoluble in water, and soluble in water respectively, was studied under a hydrogen pressure of 170 Torr over the temperature range 350—450 °C. The reduction rate of oxides I and II followed Elovich kinetics with a variable activation energy which increased with the progress of reduction, while that of III followed Elovich kinetics in the multiple kinetic stages and the minimum in apparent activation energy for the reduction lies at the reduction extent of $MoO_{2.7-2.6}$. The final states of reduction of I, II, and III were $MoO_{2.8-2.6}$, $MoO_{2.0}$ and $MoO_{2.2-2.1}$, respectively. The amount of Mo(V) in each oxide was determined by ESR measurements. The results indicate that Mo(V) in the II is related to the decrease of the apparent activation energy on reduction of III through their mutual interaction. A formation mechanism of the active species, Mo(V) in III, was proposed.

The polymerization over MoO_3–Al_2O_3 catalysts has been studied. The activity of the catalysts and the kinetics of the polymerization were reported.[1)] The relation between the activity and chemical states in the supported molybdenum oxides, I, II and III, which are insoluble in aq 10 M-NH_3, soluble in aq NH_3 but insoluble in water, and soluble in water respectively, was reported.[2)] The activity was found to be attributable to molybdenum(V) in III, $[Mo^{5+}]_w$.[3)]

We have investigated the reduction mechanism of each oxide and the formation mechanism of the active species in order to clarify why the amount of $[Mo^{5+}]_w$ on alumina is greater than that on other carriers.

It is well known that in a hydro-cracking reaction[4,5)] and an equilibrium reaction of H_2–D_2[6)] carried out over MoO_3–Al_2O_3 catalysts, the activity is related to the chemical states of the molybdena besides polymerization. Our results might be useful for understanding the formation mechanism of the active species in the reactions.

Sontag *et al.*[7)] were the first to note the extreme difficulty of reducing molybdena supported on alumina in hydrogen as compared with bulk MoO_3. They attributed this to an inhibition effect by water adsorbed on the alumina surface, which seems to raise from a localized surface equilibrium unfavorable to reduction. Kabe *et al.*[8)] and Massoth[9)] reported on the kinetics of reduction of MoO_3–Al_2O_3 catalysts and showed that the reduction followed the Elovich-type equation with a variable activation energy which increased with the progress of reduction. However, thier results differ as regards the final state and activation energy of the reduction. It may be pointed out that their catalysts were reduced under different conditions and that the proportion of molybdenum oxide in the three chemical states differed owing to the different conditions for the preparation of the catalysts.

Catalysts reduced under a hydrogen pressure of 170 Torr over the temperature range 350—450 °C are very active for polymerization. The kinetics of reduction of the oxide in each chemical state was studied under the same conditions. The molybdenum(V) contents were determined by ESR measurements.

The results elucidate some relations between the formation of molybdenum(V) in II and that in III. A formation mechanism of the active species, $[Mo^{5+}]_w$, is proposed.

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Materials. Commercial hydrogen and oxygen (> 99.9%) were used without further purification. MoO_3–Al_2O_3 catalysts were prepared according to the procedure described previously.[1)] Samples contained MoO_3 between 0 and 16.7 wt%. Data for the catalysts were given previously.[2)] The support used was gamma alumina. X-Ray analysis gave no lines attributable to MoO_3 except for 16.7 wt% MoO_3–Al_2O_3.

Reduction of Catalysts. The apparatus was simply a closed system consisting of a furnace containing a reactor for the catalyst and a manometer made of 6-mm ID capillary tubing for measuring pressure. The system had about 160 ml capacity. Catalyst charges of 300—1000 mg were used. The catalyst was evacuated for an hour under a pressure of 10^{-3} Torr at 200 °C and then at 400 °C. The catalyst was reduced under a hydrogen pressure of 170 Torr over the temperature range 350—450 °C. The reduction was carried out in a batch system. One cycle consisted of a hydrogen reduction for a given period of 3—5, 1—2, and 1—2 min at 350, 400, and 450 °C, respectively and of an evacuation for 5 min.

The extent of reduction was determined from the amount of oxygen completely reoxidizing the catalyst. The extent shows the conversion ratio of MoO_3 to MoO_2.

ESR Measurement. The measurement was carried out as described previously.[3)]

Results and Discussion

Activation Energy. The reduction of the molybdenum oxides, I, II and III, was studied in order to determine the activation energy. Since II and III can not be isolated, the following catalysts were used. (A), 16.7wt% MoO_3–Al_2O_3 consisting of I, II, and III; (B), prepared by the removal of III from (A) with water; (C), prepared by the removal of both II and III with aq 10 M-NH_3.

The reduction extent of the catalyst, θ, is given by

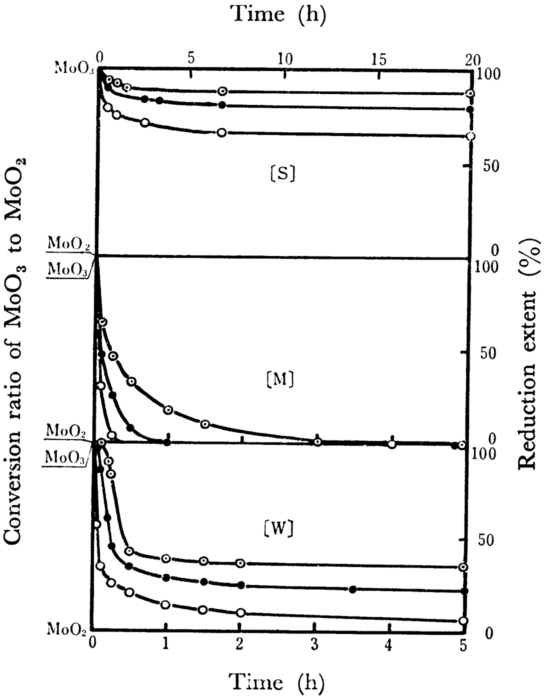

Fig. 1. Variation of the reduction extent of the oxide I, the oxide II and the oxide III with time.
⊙: 350 °C, ●: 400 °C, ○: 450 °C.

$$\theta = \frac{\theta_s[S]+\theta_M[M]+\theta_w[W]}{[S]+[M]+[W]} \tag{1}$$

where θ_s, θ_M, and θ_w denote the reduction extent of I, II, and III for given time, respectively, and [S], [M], and [W] the concentration, respectively. The reduction extent of each oxide can be determined by Eq. 1 on the basis of the reduction extents of catalysts (A), (B), and (C).

The reduction extents of the catalysts were measured at 350, 400, and 450 °C, and were evaluated as shown in Fig. 1. Catalyst(A) is the most active for the polymerization over the molybdena-content range 0—16.7 wt%. At 450 °C, I is reduced to $MoO_{2.6}$ in *ca.* 20 h and II to $MoO_{2.0}$ in *ca.* half an hour and III to $MoO_{2.1}$ in *ca.* 5 h. These final states in each oxide varied little with further reduction. Thus the increasing order of reduction rates is: I, III, and II.

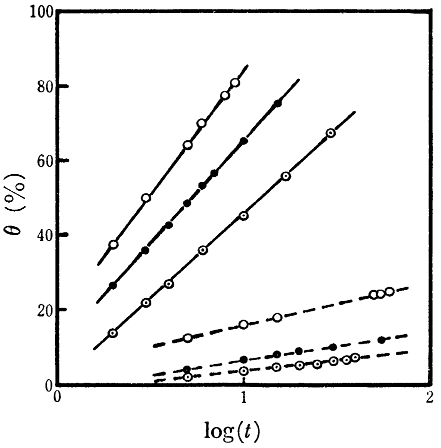

Fig. 2. Elovich plots for reduction of the oxide I and the oxide II at various temperature and 170-Torr H_2.
----: The oxide I, ——: the oxide II, ⊙: 350 °C, ●: 400 °C, ○: 450 °C.

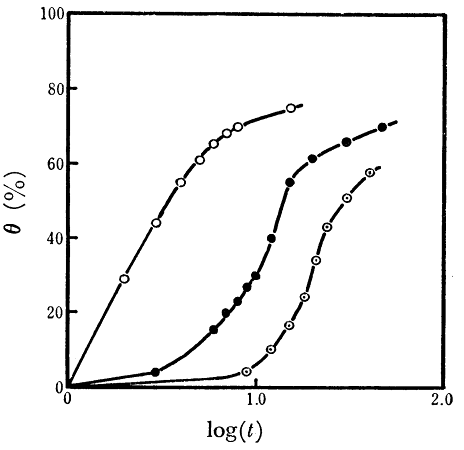

Fig. 3. Plot of reduction extent, θ, *vs.* log *t* for the reduction of the oxide III at various temperature and 170-Torr H_2.
⊙: 350 °C, ●: 400 °C, ○:450 °C.

With catalysts(A), (B), and (C) reduced under the same conditions, no signal was observed except for one of molybdenum(V) by ESR measurements. In X-ray analysis, diffraction of MoO_2 was observed but not of $MoO_{1.5}$. These indicate that I, II and III are reduced to molybdenum(IV).

The reduction extents of I and II are plotted against logarithmic time in Fig. 2 on the basis of the results in Fig. 1. θ shows a linear relation with logarithmic time. Thus, the reduction follows an Elovich-type equation.[10,11]

$$\frac{d\theta}{dt} = a\cdot\exp(-b\theta) \tag{2}$$

where *a* and *b* are constants of the extent of reduction.

Figure 3 was obtained in a similar manner for the θ of III. The values of the θ show a curve with logarithmic time. The curve indicates that the reduction follows an Elovich-type equation in multiple kinetic stages.[11,12]

When the reduction follows an Elovich-type equation, the activation energy, $E(\theta)$, is expressed by an extension of Eq. 2 as follows:[8,9]

$$\frac{d\theta}{dt} = a\cdot\exp(-b\theta) = A\cdot\exp[-E(\theta)/RT] \tag{3}$$

where *A* is constant. Transforming Eq. 3 into logarithmic form, we obtain

$$\ln\left(\frac{d\theta}{dt}\right) = \ln(A) - E(\theta)/RT \tag{4}$$

The rates of reduction at a discrete value of θ are obtained from the slopes of θ-time recorder tracing in Fig. 1. Therefore, the activation energies at a discrete value of θ in both I and II are calculated on the basis of the plot of the rates against θ by Eq. 4. The results are shown in Fig. 4. The energy only at the θ value 10% was calculated for I owing to the difficulty of reducing I in hydrogen in the temperature range 350—450 °C. The result: $E(\theta=10\%)=42.5$ kcal/mol. This

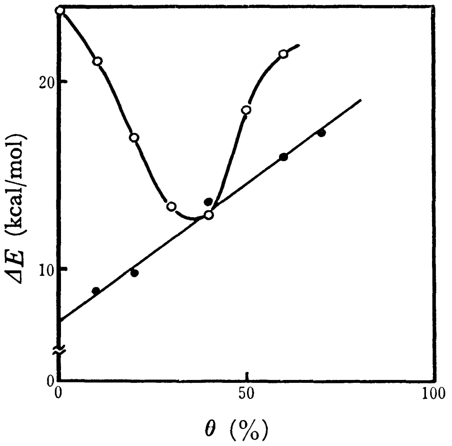

Fig. 4. Effect of reduction extent on activation energy. ●: The oxide II, ○: the oxide III.

is nearly equal to the value, $E(\theta)=30+52\theta$, reported by Kabe *et al.*[8] We see from Fig. 1. that the value of $E(\theta)$ in II is determined by

$$E(\theta) = 7.2 + 14.4\theta_{\mathrm{M}} \qquad (0<\theta_{\mathrm{M}}<70\%) \tag{5}$$

The value of $E(\theta)$ in II varies only 10 kcal/mol in the θ range 0—70%. This variation is smaller than that in I. This supports the conclusion[2] that as regards the strength of the interaction with alumina, the distribution in II is narrower than that in I. Extrapolation to $\theta=0$ gives $E_0=7.2$ kcal/mol. The value is smaller than 30 kcal/mol reported by Kabe *et al.*[8] and Sukeno *et al.*[13] and 9.8 kcal/mol by Massoth[9] and 27 kcal/mol for crystal MoO_3 by Kennedy *et al.*[14] The explanation for the difference is that the $E(\theta)$ in II could not be measured due to the rapid reduction of II.

The apparent activation energy of reduction in III is determined from the Arrhenius plots of the reduction rates. The results are given in Fig. 4. We see that the energy in III is minimum, 13 kcal/mol, in the θ range 30—40%, no reduction of bulk MoO_3 being observed under the present experimental conditions. MoO_3–SiO_2 catalysts (650 m^2/g) in which molybdena hardly intracts with silica support, could be reduced under a hydrogen pressure of 170 mmHg in the temperature range 400—450 °C and the apparent activation energy of reduction was determined to be constant, 39 kcal/mol, in the θ range 0—50%. These results indicate that III is reduced much more easily than the bulk MoO_3 and the MoO_3–SiO_2 catalysts.

Formation Mechanism of Active Species. MoO_3–Al_2O_3 catalysts were reduced from Mo(VI) to Mo(IV). The intermediate Mo(V) is supposed to be formed in the reduction process. In order to reveal the reduction mechanism of MoO_3–Al_2O_3 catalysts, the variation of the amount of Mo(V) in each oxide with reduction time was measured by ESR. The relation between the apparent $g'_{//}$-value and the Mo(V) content is expressed as follows.[3]

$$g'_{//} = \frac{1.9140[\mathrm{Mo}^{5+}]_{\mathrm{S}}+1.9086[\mathrm{Mo}^{5+}]_{\mathrm{M}}+1.8960[\mathrm{Mo}^{5+}]_{\mathrm{W}}}{[\mathrm{Mo}^{5+}]_{\mathrm{total}}} \tag{6}$$

where $[\mathrm{Mo}^{5+}]$ is a concentration of Mo(V), and S, M, and W subscripts refer to I, II, and III, respectively. The total amount of Mo(V) in the catalysts, $[\mathrm{Mo}^{5+}]_{\mathrm{total}}$, are expressed as follows.[3]

$$[\mathrm{Mo}^{5+}]_{\mathrm{total}} = [\mathrm{Mo}^{5+}]_{\mathrm{S}} + [\mathrm{Mo}^{5+}]_{\mathrm{M}} + [\mathrm{Mo}^{5+}]_{\mathrm{W}} \tag{7}$$

In order to determine the Mo(V) content in each oxide, $[\mathrm{Mo}^{5+}]_{\mathrm{total}}$ and the apparent $g'_{//}$-values in catalyst(A), (B), and (C) were measured by ESR (Fig. 5). We see that $[\mathrm{Mo}^{5+}]_{\mathrm{total}}$ decreases within a reduction period of 50 min in the order (B)>(A)>(C). The apparent $g'_{//}$-value in (A) shows a minimum value for a reduction period of 7—10 min and that in (B) shows a nearly constant value.

$[\mathrm{Mo}^{5+}]_{\mathrm{M}}$ and $[\mathrm{Mo}^{5+}]_{\mathrm{S}}$ in (B) were calculated by substituting the apparent $g'_{//}$-values and $[\mathrm{Mo}^{5+}]_{\mathrm{total}}$ (Fig. 5) into Eqs. 6 and 7. The results are shown in Fig. 6. The behavior of $[\mathrm{Mo}^{5+}]_{\mathrm{S}}$ is in fair agreement with that of $[\mathrm{Mo}^{5+}]_{\mathrm{S}}$ (Fig. 5). The agreement indicates that I hardly interacts with II. $[\mathrm{Mo}^{5+}]_{\mathrm{M}}$ shows a constant value of 1.5×10^{19} spin/g-cat in the θ range 40—90%. The result supports the view that II exists in fine dispersion on the alumina surface[2] and that I

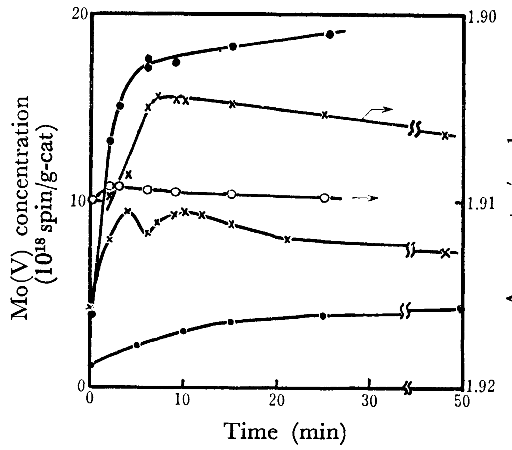

Fig. 5. Variation of Mo(V) concentration and the apparent $g'_{//}$-value in each oxide with reduction time. ×: Catalyst(A), ○: catalyst(B), ●: catalyst(C).

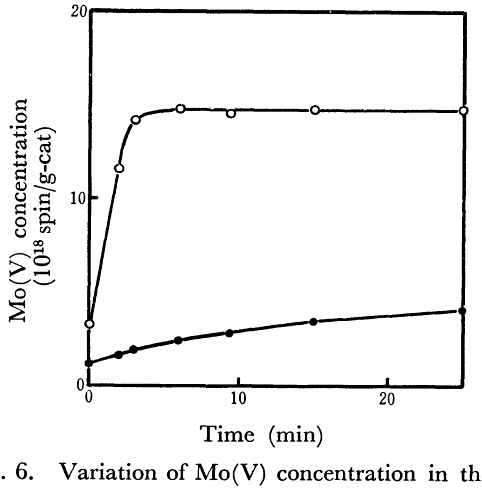

Fig. 6. Variation of Mo(V) concentration in the oxide I and the oxide II of the catalyst(B) with time. ●: The oxide I, ○: the oxide II.

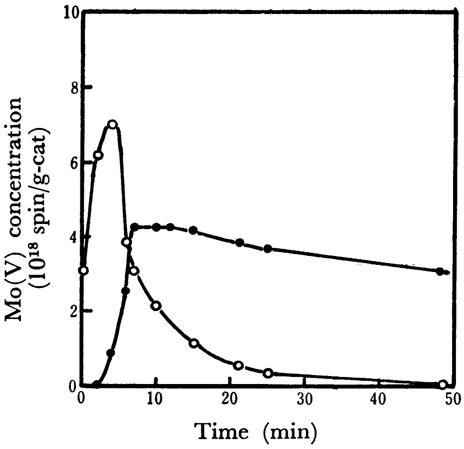

Fig. 7. Variation of Mo(V) concentration in the oxide II and the oxide III of the catalyst(A) with time. ○: The oxide II, ●: the oxide III.

and II exist separately.

$[Mo^{5+}]_M$ and $[Mo^{5+}]_W$ in (A) were calculated by substituting $[Mo^{5+}]_{total}$, the apparent $g_{//}$-value and $[Mo^{5+}]_S$ (Fig. 5), into Eqs. 6 and 7. The results are shown in Fig. 7. $[Mo^{5+}]_M$ in (A) increases remarkably within a reduction period of 4 min and decreases rapidly during further reduction time. The behavior of $[Mo^{5+}]_M$ differs from that in (B). $[Mo^{5+}]_W$ begins to form after a remarkable increase in $[Mo^{5+}]_M$, the behavior being in contrast to that of $[Mo^{5+}]_M$ (Fig. 7). This indicates that II interacts with III. The increase and decrease of $[Mo^{5+}]_M$ in Fig. 7 correspond to the decrease and increase, respectively, of activation energy for reducing III. Recently, it has been reported that the bulk MoO_3 is easily reduced in hydrogen at a lower temperature in the presence of 0.1—0.01 mol% of Pd or Ni.[15–19] The Pd- and Ni-catalyzed reduction was explained in terms of the transfer of hydrogen chemisorbed on Pd and Ni. This supports the view that $[Mo^{5+}]_M$ catalyzes the reduction of III. This is also supported by the following : As compared with III, it is difficult to reduce the bulk MoO_3 and the MoO_3–SiO_2 catalysts, in which $[Mo^{5+}]_M$ is absent. No relation between the amount of adsorbed hydrogen and the total amount of Mo(V) was observed. We reported that the amount of chemisorbed hydrogen agrees with the concentration of $[Mo^{5+}]_W$.[3] Hydrogen is chemisorbed on Mo(V) in MoO_3–Al_2O_3 catalysts[20] and the reduction of bulk MoO_3 is auto-catalytic in hydrogen.[19] In view of these facts, the formation mechanism of active species Mo(V) in III is proposed as follows: First, II is reduced in the MoO_3–Al_2O_3 catalysts and the $[Mo^{5+}]_M$ is formed and then the hydrogen to be chemisorbed on the $[Mo^{5+}]_M$ promotes the reduction of III from Mo(VI) to Mo(V); second, the hydrogen is chemisorbed on the formed $[Mo^{5+}]_W$ which also promotes the reduction of III from Mo(VI) to Mo(V). Therefore, more $[Mo^{5+}]_W$ is formed in the MoO_3–Al_2O_3 catalysts than in the MoO_3–SiO_2 catalysts and in the bulk MoO_3.

Structure of Molybdena on Alumina. The properties of molybdena supported on alumina in the content range of 0—16.7wt% and calcined over the temperature range 400—550 °C were explained in terms of a distorted octahedral structure.[3] Concerning the structure of I, we see that I interacts strongly with alumina but hardly interacts at all with II to exist on the alumina surface[2] and the crystal field is the strongest of the three oxides;[3] I is reduced only to $MoO_{2.8-2.6}$ in the temperature range 350—450 °C, the activation energy of reduction being greater than 42.5 kcal/mol. Thus, it is concluded that Mo atom of I has 6 Mo–O bondings which are nearly equal in strength and probably located inside the alumina lattice (Fig. 8).

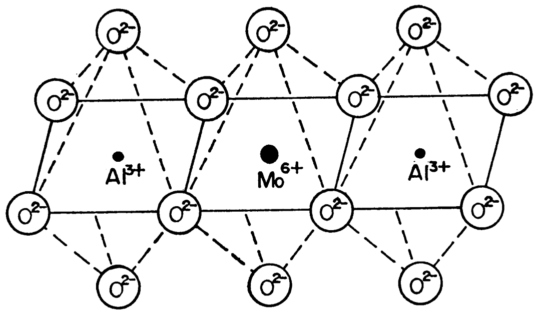

Fig. 8. Model of the oxide I.

Concerning the structures of II and III, we see that: II interacts with alumina, the interaction being weaker than that of I; the diffraction of a crystal MoO_3 is observed in the molybdena content 16.7wt%;[2] II is reduced easily to MoO_2, interacts with III and promotes the reduction of III. These facts support the view that Mo atom of II has 6 Mo–O bondings, two bondings of which are weaker than the other four bondings, and that a part of III forms a crystal MoO_3 with an increase of III.

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