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Studies of MoO_3-Al_2O_3 Catalyst in Ethylene Polymerization. III. The Nature of Mo(V) and Its Relation with Activity

Keizi HASHIMOTO, Shozi WATANABE, and Kimio TARAMA*
The Osaka Municipal Technical Research Institute, Ogimati, Kita-ku, Osaka 530
**Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606*

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In order to determine the active center of ethylene polymerization over MoO_3–Al_2O_3, the *g*-tensor and the amount of molybdenum(V) in each chemical state were determined by means of ESR measurement. The anisotropy of the *g*-tensor revealed the strength of the crystal field in the state; the decreasing order of the strengths was as follows: state(S)>state(M)>state(W)>MoO_3–$SiO_2$$\fallingdotseq$free MoO_3. In the state(S) molybdenum oxide is insoluble in aq.10M–NH_3, in the state(M) it is soluble in aq. NH_3 but insoluble in water, and in the state(W) it is soluble in water. The amount of molybdenum(V) in the state(W) was studied in connection with the activity, because only the state(W) was suitable for polymerization. The behavior of the activity was in fair agreement with that of the molybdenum(V) content in the state(W) and this content depedned on the amount of supported MoO_3 and on the extent of reduction. The amount of molybdenum(V) in the state (W) corresponded to the amount of chemisorbed hydrogen, which was a polymerization initiator. The chemisorption of oxygen on the catalyst caused a complete disappearance of both the activity and the molybdenum(V) content in the state(W). Therefore, it was concluded that the active center of the polymerization was molybdenum(V) in the state(W).

The polymerization over MoO_3–Al_2O_3 has been studied. In the first paper,[1)] we reported about the activity of the catalyst and the kinetics of the polymerization. In the second paper,[2)] we reported the relation between the activity and the chemical states of molybdenum oxide on Al_2O_3 and concluded that the oxide on Al_2O_3 might be classified into three chemical states: the state(W) in which molybdenum oxide is soluble in water, the state(M), insoluble in water but soluble in aq.NH_3, and the state(S), insoluble in aq.10M-NH_3.

In general it is known that the activity may be attributed to the low valence of molybdenum on the basis of the fact that an olefin is polymerized in a reducing atmosphere.[3)] Emelyanov *et al.*[4)] and Voevodskii[5)] attempted to relate the polymerization activity to molybdenum(V). However, they did not obtain a clear relation between the activity and the molybdenum(V) content. The explanation for the unfavorable results is that they regarded the molybdenum oxide on Al_2O_3 as a single state without considering the properties of the three chemical states.

The present paper deals with a part of an investigation of the active center, in view of the states. The anisotropy of the *g*-tensor of molybdenum(V) in each chemical states is measured by ESR. The strength of crystal field and the field suitable for polymerization will be discussed on the basis of the ESR data and the activity. In order to show the valence of molybdenum ion as an active center, the molybdenum(V) content in the state(W) is determined by the ESR measurement. The activity is compared with this content, which is due to the amount of supported MoO_3 and the extent of reduction. The amount of polymerization initiator, chemisorbed hydrogen, is determined and compared with the molybdenum(V) content in the state(W). The poisoning effects of oxygen chemisorbed on the catalyst are studied. One interesting conclusion to be drawn from these results in the fact that the polymerization activity in MoO_3–Al_2O_3 is related to the strength of the crystal field and the amount of the molybdenum(V) in the state(W).

Experimental

Preparation of Catalyst. MoO_3–Al_2O_3 and MoO_3–SiO_2 were prepared according to the procedure described previously.[1)]

Reactants. Hydrogen and oxygen (more than 99.9%) were used without further purification. Ethylene (99.5%, Seitetu Chemical Co.) was used without further purification. Most of the impurities were methane or ethane.

Treatment of Catalyst. The catalyst were reduced under a hydrogen pressure of 170 Torr at 400 °C before the ESR measurement and the ethylene polymerization. The extent of reduction was determined on the basis of the amount of oxygen completely reoxydating the catalyst. The extent shows the conversion ratio of MoO_3 to MoO_2.

ESR Measurement. The catalysts were placed into a reaction vessel equipped with a pyrex-tube for ESR measurement. The measurement was carried out at room temperature. ESR spectra were obtained with a JES-ME-IX spectrometer (Japan Electron Optics Laboratory Co.) using manganese (II) as an internal standard. The amount of molybdenum (V) in the catalyst was determined by Seshadri's method[6)] using copper(II) as an internal standard.

Polymerization. The ethylene was polymerized at 0 °C using the procedure described previously.[1)]

Results and Discussion

Crystal Field of Molybdenum Oxide. After reduction in each chemical state, the presence of molybdenum(V) was recognized from ESR studies. The molybdenum(V) in each chemical state showed an anisotropy of the *g*-tensor. The values of the anisotropy are shown in Table 1. The value in MoO_3–SiO_2 is also added in

TABLE 1. *g*-VALUE OF MOLYBDENUM (V)

Sample	$g_\perp$	$g_{//}$
MoO_3–SiO_2	1.952±0.001	1.867±0.001
(W)–Al_2O_3	1.953±0.001	1.896±0.001
(M)–Al_2O_3	1.955±0.001	1.909±0.001
(S)–Al_2O_3	1.955±0.001	1.914±0.001

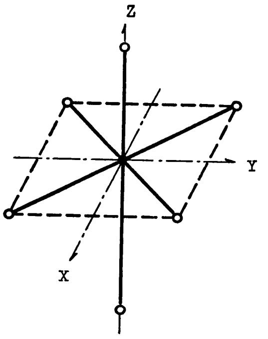

Fig. 1. Model of molybdenum oxide on Al_2O_3. ●: Mo^{6+} ion, ○: O^{2-} ion.

Table 1. As Table 1 shows, the $g_{\perp}$-value was almost constant in the different states. The $g_{/\!/}$-value varied with the kinds of states and of carriers. The decreasing order of $g_{/\!/}$-values was in agreement with the increase of the interaction between the state and the carrier.[2] The strength of the crystal field in the state was determined on the basis of the anisotropy. According to Andersson's report,[7] the crystal structure of free MoO_3 is a distorted octahedron. Therefore, the structure of molybdenum oxide on Al_2O_3 was supposed to be a distorted octahedron, as shown in Fig. 1. The five-fold degenerate levels of d^1-ion are split into 4-levels in the model and the energy levels decrease in the following order: $a_1(d_{z^2})$, $b_1(d_{x^2-y^2})$, $e(d_{zx}, d_{yz})$, and $b_2(d_{xy})$. Several authors have derived equations for the $g_{/\!/}$ and $g_{\perp}$ expected in a d^1-model of a distorted octahedron, using a set of molecular orbitals as the basis functions for the calculation. Ballhausen *et al.*[8] placed the unpaired electron in a non-bonding b_2-orbital(d_{xy}), defined the antibonding orbital as $\Phi^* = C_1^*\Phi(\text{metal}) + C_2^*\Phi(\text{ligand})$, and derived

$$g_{/\!/} = 2\left[1-\frac{4(C_1^*)^2\xi_M}{\Delta E(^2B_2-{}^2B_1)}\right] \tag{1}$$

$$g_{\perp} = 2\left[1-\frac{(C_1^*)^2\xi_M}{\Delta E(^2B_2-{}^2E)}\right] \tag{2}$$

Where ξ_M is the single electron spin-orbit coupling constant for molybdenum. $\Delta E(^2B_2-{}^2B_1)$ is a function of the equatorial Mo–O distance and $\Delta E(^2B_2-{}^2E)$ is a function of both the equatorial and the Mo–O distance along the C_{4v} axis. Since the $g_{\perp}$-value in Table 1 is almost constant, the quantitative variation of $\Delta E(^2B_2-{}^2E)$ might be small in the different chemical states. The values of $\Delta E(^2B_2-{}^2B_1)$ and $\Delta E(^2B_2-{}^2E)$ were determined as follows. In the previous paper, we reported that state(W) and state(M) occupied most of the alumina surface in 16.7wt%MoO_3–Al_2O_3 and (0—6)wt%MoO_3–Al_2O_3, respectively. The catalysts were prepared in the way that Asmolov *et al.*[9] described. They reported that the adsorption bands in 16.7wt%-MoO_3–Al_2O_3 and (0.2—1.8)wt%MoO_3–Al_2O_3 appeared at 31250 and 33900 cm^{-1}, respectively. In the molybdenyl complexes having a similarly distorted octahedron, the values of $\Delta E(^2B_2-{}^2E)$ and $\Delta E(^2B_2-{}^2B_1)$ were (10000—20000) and (20000—30000) cm^{-1}, respectively.[10,11] Therefore, the values of $\Delta E(^2B_2-{}^2B_1)$ in the state(W) and the state(M) were 31250 and 33900 cm^{-1}. The values of $\Delta E(^2B_2-{}^2E)$ in the state(W) and the state(M) were calculated to be 17300 and 17100 cm^{-1} on the basis of a substitution of these values, the $g_{\perp}$ and $g_{/\!/}$-values, in Eqs. (1) and (2). Thus, the variation of $\Delta E(^2B_2-{}^2E)$ was small, as expected from the $g_{\perp}$-values in Table 1. Consequently, the value of $\Delta E(^2B_2-{}^2E)$ was assumed to be 17200 cm^{-1} in both the state(S) and the MoO_3–SiO_2 and those of $\Delta E(^2B_2-{}^2B_1)$ in the state(S) and the MoO_3–SiO_2 were calculated to be 36000 and 24800 cm^{-1}, respectively (Table 2). As Table 2 shows, the value of $\Delta E(^2B_2-{}^2B_1)$ decreased in the following order of states: state(S), state(M), state(W), and MoO_3–SiO_2. Since the value of $\Delta E(^2B_2-{}^2B_1)$ in MoO_3–SiO_2, 24800 cm^{-1}, was nearly equal to that in the single crystal of MoO_3, 24250 cm^{-1},[12] the molybdenum oxide on the SiO_2 had little interaction between the oxide and the SiO_2. The value of $\Delta E(^2B_2-{}^2B_1)$ in the state(S), 36000 cm^{-1}, supported the idea that the state(S) had a strong crystal field. The quantity of $\Delta E(^2B_2-{}^2B_1)$ is a function of the equatorial Mo–O distance as described above and the shortening of the equatorial distance leads to an increase of $\Delta E(^2B_2-{}^2B_1)$. The equatorial Mo–O distance was shortened in the following order of states: MoO_3–SiO_2, state(W), state(M), and state(S). This shortening order was in agreement with the increasing order of the interaction between the molybdenum oxide and the carrier.[2] From the facts presented above, the strengths of the crystal field in each chemical state were not equal and that in the state(W) led the value of $\Delta E(^2B_2-{}^2B_1)$ of molybdenum(V) to *ca.* 31000 cm^{-1}. This strength was suitable for ethylene polymerization and only the state(W) was suitable for it, as described previously.[2]

TABLE 2. SPECTRAL PARAMETERS OF MOLYBDENUM (V) SIGNALS

Sample	($^2B_2$—$^2B_1$), (cm^{-1})	($^2B_2$—^2E), (cm^{-1})
MoO_3–SiO_2	24800	17200[a]
(W)–Al_2O_3	31250[b]	17300
(M)–Al_2O_3	33900[b]	17100
(S)–Al_2O_3	36000	17200[a]

a) Estimated value. b) Ref. 9.

Relation between Activity and Molybdenum(V) content. In order to reveal the valence states of the active molybdenum which was present in the state(W) suitable for polymerization, the catalytic activity was studied in connection with the molybdenum(V) content in the catalysts. The amount of molybdenum(V) in MoO_3–Al_2O_3 is expressed as a sum of the molybdenum(V) contents in three chemical states, that is:

$$(Mo^{5+})_{\text{total}} = (Mo^{5+})_W + (Mo^{5+})_M + (Mo^{5+})_S, \tag{3}$$

Where (Mo^{5+}) is the amount of molybdenum(V) and W, M, and S subscripts refer to state(W), state(M), and state(S), respectively. The apparent $g_{/\!/}'$-value of molybdenum(V) in MoO_3–Al_2O_3 varied with the composition of molybdenum(V) in the three states. The apparent $g_{/\!/}'$-values in various comopsitions were determined by the simulation on the basis of the ESR spectra of molybdenum(V) in each state. Figure 2 shows an ESR spectrum simulated in the following composition: $(Mo^{5+})_W$, $(Mo^{5+})_M$, and $(Mo^{5+})_S$ are

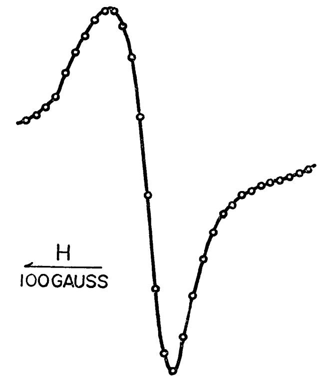

Fig. 2. ESR spectrum of Mo^{5+} in the composition, $(Mo^{5+})_W$, $(Mo^{5+})_M$ and $(Mo^{5+})_S$, respectively, 4.30×10^{18}, 2.14×10^{18} and 3.00×10^{18} spins/g-cat.

○: Points of simulated spectrum, —: measured spectrum.

respectively 4.30×10^{18}, 2.14×10^{18} and 3.00×10^{18} spins/g-cat.. These $g_{//}'$-values of simulated spectra are shown in Table 3. The apparent $g_{//}'$-value was assumed to be approximately expressed as a function of the content, $(Mo^{5+})_W$, $(Mo^{5+})_M$, and $(Mo^{5+})_S$, by the following equation:

$$g_{//}' = \frac{1.8960(Mo^{5+})_W + 1.9086(Mo^{5+})_M + 1.9140(Mo^{5+})_S}{(Mo^{5+})_{total}}, \tag{4}$$

TABLE 3. APPARENT $g_{//}'$-VALUE OF MOLYBDENUM(V)

Composition (mol%)			$g_{//}'$-Value of simulated spectra	Approximated $g_{//}'$-value
$(Mo^{5+})_W$	$(Mo^{5+})_M$	$(Mo^{5+})_S$		
0	80	20	1.9097	1.9097
20	60	20	1.0973	1.9072
40	40	20	1.9047	1.9046
60	20	20	1.9020	1.9021
0	60	40	1.9107	1.9108
40	30	40	1.9070	1.9070
50	10	40	1.9047	1.9045
60	0	40	1.9030	1.9032
0	40	60	1.9116	1.9118
20	20	60	1.9093	1.9093
30	10	60	1.9080	1.9081

The apparent $g_{//}'$-values calculated from Eq. 4 are shown in Table 3. As Table 3 shows, the apparent $g_{//}'$-value calculated is in fair agreement with the apparent $g_{//}'$-value of the simulated spectrum. Therefore, the apparent $g_{//}'$-value might be approximately expressed by Eq. 4. The substitution of $(Mo^{5+})_{total}$, $(Mo^{5+})_S$, and the apparent $g_{//}'$-value in both Eqs. 3 and 4 determined $(Mo^{5+})_W$, which was present in the crystal field of suitable strength for polymerization.

In order to reveal the relation between $(Mo^{5+})_W$ and the supported molybdite-content, the relations of the molybdite-content to $(Mo^{5+})_{total}$, $(Mo^{5+})_S$, and the apparent $g_{//}'$-value were studied and is shown in Fig. 3. Before the ESR measurement, the catalysts were reduced under a hydrogen pressure of 170 Torr at 400 °C for 15 min. The molybdenum oxide in the state(S) was prepared by the removal of molybdenum oxides in both state(W) and state(M) from MoO_3–Al_2O_3 with aq.10 M-NH_3 and reduced under the same conditions before the determination of $(Mo^{5+})_S$. As Fig. 3 shows, $(Mo^{5+})_{total}$ was maximum at a molybdite-content of 10 to 15wt%. The apparent $g_{//}'$-value decreased with an increase of the molybdite-content and $(Mo^{5+})_S$ increased gradually with an increase of the molybdite-content. The behavior of $(Mo^{5+})_{total}$ was in agreement with Voevodskii's result.⁵⁾ $(Mo^{5+})_W$ was calculated by substitution of $(Mo^{5+})_S$, $(Mo^{5+})_{total}$, and the apparent $g_{//}'$-value in Fig. 3 into Eqs. 3 and 4. The relation between $(Mo^{5+})_W$ and molybdite-content is shown in Fig. 4. $(Mo^{5+})_W$ was small in the molybdite-content, less than several percents. $(Mo^{5+})_W$ increased with the further molybdite-content. The behavior of $(Mo^{5+})_W$ differed from that of $(Mo^{5+})_{total}$ in Fig. 3.

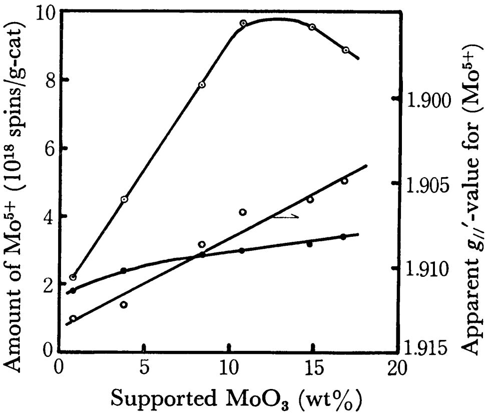

Fig. 3. Relation of the molybdite-content to $(Mo^{5+})_{total}$, $(Mo^{5+})_S$ or the apparent $g_{//}'$-value

○: $(Mo^{5+})_{total}$, ●: $(Mo^{5+})_S$, ○: apparent $g_{//}'$-value for $(Mo^{5+})_{total}$.

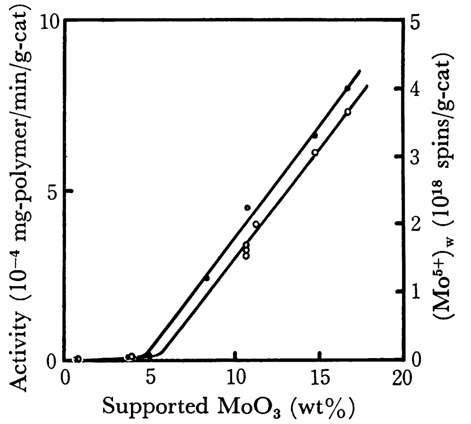

Fig. 4. Relation between the activity and $(Mo^{5+})_W$.

●: $(Mo^{5+})_W$, ○: activity.

Moreover, the relation between the catalytic activity and the molybdite-content is shown in Fig. 4. The catalysts were reduced under a hydrogen pressure of 170 Torr at 400 °C for 15 min before ethylene polymerization. In order to avoid solvent effects and a further reduction of the catalyst with ethylene, ethylene was polymerized under a pressure of 100 to 200 Torr at 0 °C in a gas-solid phase. The activity showed the polymerization rate. As Fig. 4 shows, the behavior

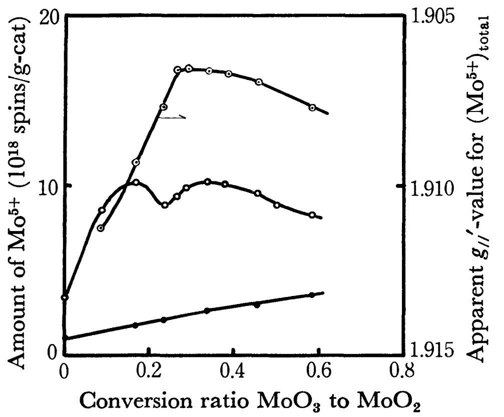

Fig. 5. Relation of the extent of reduction to $(Mo^{5+})_{total}$, $(Mo^{5+})_S$ or the apparent $g_{//}'$-value in 10.7 wt% MoO_3–Al_2O_3.
○: $(Mo^{5+})_{total}$, ●: $(Mo^{5+})_S$, ⊙: apparent $g_{//}'$-value for $(Mo^{5+})_{total}$.

of the activity was in fair agreement with that of $(Mo^{5+})_W$. Therefore, the activity might be attributed to molybdenum(V) in the state(W).

In order to confirm this conclusion, the relation between the conversion ratio of MoO_3 to MoO_2 and either $(Mo^{5+})_W$ or polymerization activity was studied, because $(Mo^{5+})_W$ must vary with the ratio. The relation of the ratio to $(Mo^{5+})_{total}$, the apparent $g_{//}'$-value, and $(Mo^{5+})_S$ were studied in 10.7wt%MoO_3–Al_2O_3 and are shown in Fig. 5. $(Mo^{5+})_S$ was determined by the ESR measurement of the state(S), which was prepared by the same procedure as described above. Before the measurement, the molybdenum oxide in the state(S) and 10.7wt%MoO_3–Al_2O_3 were reduced under a hydrogen pressure of 170 Torr at 400 °C. As Fig. 5 shows, $(Mo^{5+})_{total}$ had two variation points. The apparent $g_{//}'$-value was minimum in the ratio of 0.25 to 0.50. $(Mo^{5+})_S$ increased gradually with an increase of the ratio.

$(Mo^{5+})_S$ was calculated by substitution of $(Mo^{5+})_{total}$, $(Mo^{5+})_S$, and the apparent $g_{//}'$-value in Fig. 5 into Eqs. 3 and 4. The relation between the ratio and $(Mo^{5+})_W$ is shown in Fig. 6. $(Mo^{5+})_W$ was small in the ratio less than 0.20. However, $(Mo^{5+})_W$ increased remarkably in the ratio of 0.20 to 0.24 and showed constant value of *ca.* 2.5×10^{18} spins/g-cat. in the ratio of 0.25 to 0.45. $(Mo^{5+})_W$ decreased gradually for higher ratios.

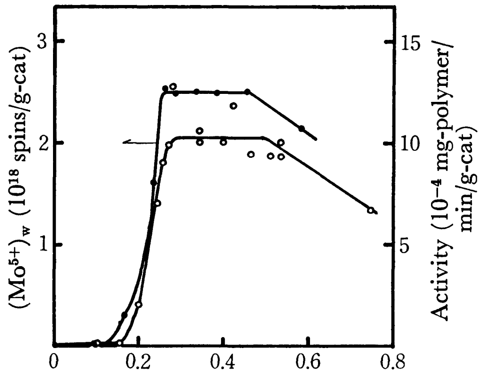

Fig. 6. Relation between the conversion ratio of MoO_3 to MoO_2 and either activity or $(Mo^{5+})_W$.
○: Activity, ●: $(Mo^{5+})_W$.

The relation between the ratio and the catalytic activity is shown in Fig. 6. For the determination of the activity, ethylene was polymerized under the same conditions as described above. As Fig. 6 shows, the behavior of the activity was in fair agreement with that of $(Mo^{5+})_W$.

The polyethylene, which was produced at 50 °C for 5 hr over 10.7wt%MoO_3–Al_2O_3, had an average value of 19000 in polymerization degree. The amount of chemisorbed hydrogen, the polymerization initiator, was calculated on the basis of this polymerization degree and from a consideration of the reaction mechanism.[1] The amount of chemisorbed hydrogen had a value of 1.0×10^{18} site/g-cat. This value corresponded closely to 2.5×10^{18} spin/g-cat. of $(Mo^{5+})_W$.

Exposure to oxygen poisoned completely the active 10.7wt%MoO_3–Al_2O_3 which had been reduced to the ratio of 0.35 and increased the apparent $g_{//}'$-value from 1.907 to 1.910. This increase could be explained by the assumption of the disappearance of $(Mo^{5+})_W$ from the active catalyst in which $(Mo^{5+})_{total}$, $(Mo^{5+})_S$, and $(Mo^{5+})_W$ were 10.2×10^{18}, 2.6×10^{18} and 2.5×10^{18} spin/g-cat, respectively, as Figs. 5 and 6 show. $(Mo^{5+})_W$ was determined to be 5.1×10^{18} spin/g-cat. by the substitution of these values in Eq. 3. The apparent $g_{//}'$-value was determined to be 1.910 by the substitution of $(Mo^{5+})_S$ and $(Mo^{5+})_W$ into Eq. 4. This $g_{//}'$-value was in fair agreement with the experimental one. Exposure to oxygen accompanied the complete disappearance of both catalytic acitivity and $(Mo^{5+})_W$ in 16.7wt%MoO_3–Al_2O_3 as well. Therefore, exposure to oxygen was proved to cause the complete disappearance of both catalytic activity and $(Mo^{5+})_W$.

From the facts described above, it was concluded that the activity should be attributed to molybdenum(V) in the state(W).

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