# Preparation of highly active Cr-catalysts for ethylene polymerization

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A $Cr(CH_3COO)_3 \cdot (CH_3CO)_2O/MgCl_2/AlEt_2Cl/2$-EHA catalyst was prepared by modifying the Battelle catalyst with $MgCl_2$ in 2-ethyl-1-hexanol(2-EHA), and the polymerization of ethylene was carried out in toluene at 20–60°C. The rate of polymerization increased to reach an individual stationary value during the course of polymerization, and the stationary rate markedly increased with an increase in the molar ratio of Mg/Cr. The polyethylene obtained without $MgCl_2$ had a rather low molecular weight with a very broad polydispersity, whereas those obtained in the presence of $MgCl_2$ had extremely high molecular weights with narrow polydispersities.

Polymerization of ethylene was subsequently performed under similar conditions using various types of metal chlorides in place of $MgCl_2$. A clear relation was found between the polymerization activity and the electronegativity $X(M^{x+})$ of metal ion in MClx:metal chlorides having the electronegativities below $X(Cr^{2+})$ accelerated the activity, whereas those above $X(Cr^{2+})$ retarded it. A plausible mechanism for the enhancement of the activity by metal chlorides was proposed on the basis of these results.

(Keywords: Polymerization; modification of Battelle catalyst; ethylene; metal chlorides; polyethylene)

## INTRODUCTION

In the patent literatures, Battelle[1] has claimed a series of new catalytic systems for ethylene polymerization. We have recently reported[2] the preliminary results on the polymerization of ethylene and/or propylene by using the $Cr(CH_3COO)_3 \cdot H_2O/AlEt_2Cl$ catalyst which seems to show the highest activity. The catalyst actually showed a high activity for ethylene polymerization. However, the activity of Ziegler–Natta catalysts for olefin polymerization has been substantially increased by supporting the titanium compound on a solid carrier[3]. We have recently investigated[4,5] the effect of carriers on the rate of propylene polymerization by using the soluble $Ti(OBu)_4/AlEt_2Cl$ catalyst combined with a variety of metal chlorides (MClx). A clear relation was found between the activity and the electronegativity $X(M^{x+})$ of metal ion in MClx:metal chlorides having the electronegativities below $X(Ti^{3+})$ accelerated the activity, whereas those above $X(Ti^{3+})$ retarded it. From these results together with the X.p.s. spectra of Cl(2p) in MClx and of Ti(2p) in $TiCl_4$/MClx, it has been concluded that the metal chlorides involving in the active species influence the electronic structure of the active $Ti^{3+}$ by inductive effects.

From such a viewpoint, we have prepared Cr-based catalysts by modifying the Battelle catalyst with various metal chlorides in 2-ethyl-1-hexanol, and carried out ethylene polymerization by using them as catalysts in the presence of alkylaluminums. This paper reports the detailed results of the polymerization together with the preparative methods of the catalysts.

## EXPERIMENTAL

### Materials

Research grade ethylene, 2-ethyl-1-hexanol, and toluene (from Takachiho Chemical Co.) were further purified according to the usual procedures. The $Cr(CH_3COO)_3 \cdot H_2O$ was extra pure reagent purchased from Yoneyama Chemical Ltd. Nitrogen of ultra high purity (from Nippon Sanso Co.) was purified by passing through the molecular sieve 3A column cooled at $-196°C$. The other chemicals (research grade) were commercially obtained and used without further purification.

### Preparation of catalysts

The $Cr(CH_3COO)_3 \cdot H_2O$ was treated in the mixture of acetic anhydride and acetic acid at 120°C for 4 h, and then the excess acetic anhydride and acetic acid were removed under reduced pressure to give a bright green fine powdery product, $Cr(CH_3COO)_3 \cdot (CH_3CO)_2O.$[2] 0.84 mmol of the product was dissolved in 167 mmol of 2-ethyl-1-hexanol(2-EHA) by refluxing the solvent. MClx (10 mmol) was also dissolved in 90 mmol of 2-EHA in a similar way.

### Polymerization and analytical procedures

The polymerization of ethylene was carried out in a 300 ml glass reactor equipped with a magnetic stirrer. In the reactor were placed the measured amounts of the $Cr(CH_3COO)_3 \cdot (CH_3CO)_2O$ solution in 2-EHA, MClx

solution in 2-EHA and toluene under nitrogen. Then the reactor was degassed *in vacuo* followed by introduction of ethylene. After the mixture was agitated for 20 min at a polymerization temperature, a given amount of an alkylaluminum was added. The polymerization was terminated by adding a dilute hydrochloric acid solution in methanol. The precipitated polymer was washed with methanol, followed by drying *in vacuo* at room temperature. The molecular weight distribution of the polymer was measured at 145°C by g.p.c. using 1,2,4-trichlorobenzene as solvent. Different thermal analysis (d.t.a.) measurements (Shimadzu Thermal Analyzer DT-30) were made at a heating rate of 10°C min$^{-1}$.

## RESULTS AND DISCUSSION

The mixture of $Cr(CH_3COO)_3 \cdot (CH_3CO)_2O/2$-EHA and $MgCl_2/2$-EHA in toluene seems to be homogeneous. Upon adding $AlEt_2Cl$ to the mixture, very fine, white precipitates were formed. These precipitates may be considered the reaction products between $AlEt_2Cl$ and 2-EHA. But the precise reaction between these compounds is not clear at present.

*Figure 1* shows typical kinetic curves of ethylene polymerization at 30°C with the $Cr(CH_3COO)_3 \cdot (CH_3CO)_2O/AlEt_2Cl/2$-EHA catalytic system by using different amounts of $MgCl_2$. With an increase in the molar ratio of Mg/Cr, the rate of polymerization drastically increased at first and attained a constant value, followed by a slight decrease as shown in *Figure 2*. The polymerization rates obtained in the presence of $MgCl_2$ did not
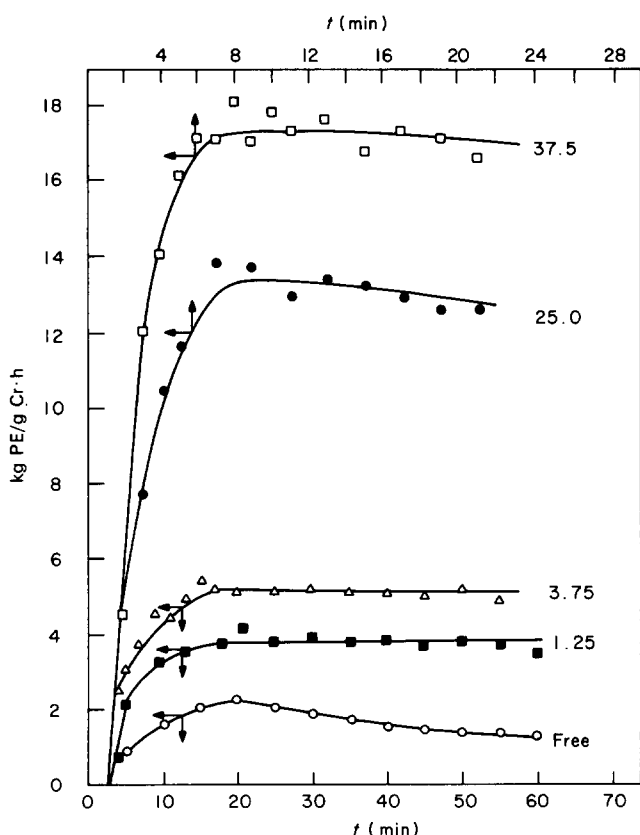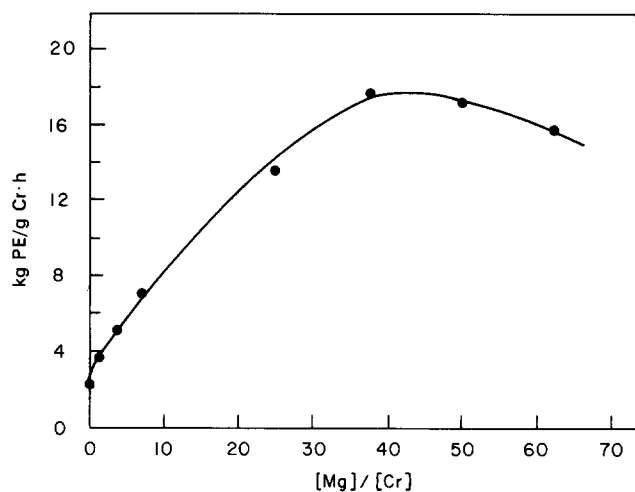


**Figure 2** Relation between the polymerization rate and the [Mg]/[Cr] molar ratio. Polymerization conditions as in *Figure 1*

decrease during the course of polymerization, indicating that the active species, $Cr^{2+2}$ is stabilized by forming a complex with $MgCl_2$.

Similar phenomena were also observed in the propylene polymerization with the $Ti(OBu)_4/AlEt_2Cl/MgCl_2/2$-EHA catalytic system[4]. However, the optimum ratio of Mg/Cr($\gtrsim$ ca.35) in the present system seems to be much higher than that of Mg/Ti($\gtrsim$ ca.6) in the previous system. Some of the ligands of the original $Cr(CH_3COO)_3 \cdot (CH_3CO)_2O$ might be exchangeable with Cl by the reaction between $Cr(CH_3COO)_3 \cdot (CH_3CO)_2O$ and $MgCl_2$ and/or $AlEt_2Cl$ as suggested in the $Ti(OBu)_4/AlEt_2Cl/MgCl_2/2$-EHA system[4]. Then, a complex of Cr species with $MgCl_2$ might be formed through Cl bridges. A brief discussion will be made later on concerning this point.

In *Table 1* are shown some physical properties of the polyethylenes produced in the presence and absence of $MgCl_2$. From the i.r. and $^{13}$C-n.m.r. measurements these polymers were found to be linear polyethylenes. The polyethylene obtained in the absence of $MgCl_2$ has a rather low molecular weight with a very broad polydispersity, whereas those obtained in the presence of $MgCl_2$ have extremely high molecular weights with very narrow polydispersities. The polymers obtained in the presence of $MgCl_2$ show somewhat higher melting points, which may be attributed to their higher molecular weights.

The polymerization of ethylene was then carried out at various temperatures under the optimum conditions $[Cr(CH_3COO)_3 \cdot (CH_3CO)_2O = 0.016$ mmol, Mg/Cr = 37.5, $AlEt_2Cl = 14$ mmol (confirmed to be optimum from the polymerization by changing the amount of $AlEt_2Cl$), in 160 ml toluene]. The results obtained are shown in *Figure 3*, which indicate that the active species become unstable with an increase in the polymerization temperature. Thus, the highest activity was obtained at around 30°C.

The polymerization of ethylene was also carried out at 30°C by using $AlEt_3$, $Al_2Et_3Cl_3$ or $AlEtCl_2$ in place of $AlEt_2Cl$. The results obtained are illustrated in *Figure 4* together with that obtained by using $AlEt_2Cl$ for a reference.

The activity was markedly dependent upon the cocatalyst used and $AlEt_2Cl$ showed the highest activity among these alkylaluminums. It should be noted here that



**Figure 1** Kinetic curves of ethylene polymerization with the $Cr(CH_3COO)_3 \cdot (CH_3CO)_2O/AlEt_2Cl/2$-EHA catalyst system in the presence of $MgCl_2$. Polymerization conditions; 30°C ethylene pressure = 760 Torr, toluene = 160 cm$^3$, $Cr(CH_3COO)_3 \cdot (CH_3CO)_2O = 0.016$ mmol, and $AlEt_2Cl = 14$ mmol. Numbers in the *Figure* indicate the [Mg]/[Cr] molar ratio

**Table 1** Analytical results of polyethylene obtained with various molar ratios of [Mg]/[Cr]*

| [Mg]/[Cr] | Molecular weight | | | $T_m$ |
| | $\bar{M}_n (\times 10^4)$ | $\bar{M}_w (\times 10^4)$ | $Q(\bar{M}_w/\bar{M}_n)$ | (°C) |
|---|---|---|---|---|
| 0 | 1.7 | 61.6 | 35.5 | 140 |
| 6 | 124 | 317 | 2.6 | 145 |
| 25 | 96 | 307 | 3.2 | 145 |
| 37.5 | 153 | 330 | 2.2 | 144 |

* Polymerization conditions as in *Figure 1*
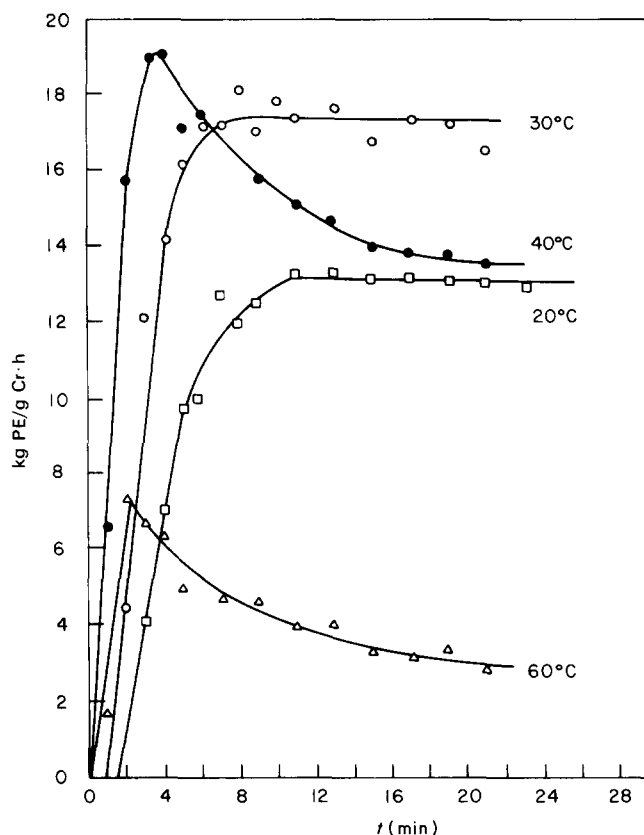


**Figure 3** Temperature dependence of the rate of ethylene polymerization. Polymerization conditions; ethylene pressure = 760 Torr, toluene = 160 cm³, $Cr(CH_3COO)_3 \cdot (CH_3CO)_2O = 0.016$ mmol, $AlEt_2Cl = 14$ mmol, and [Mg]/[Cr] = 37.5
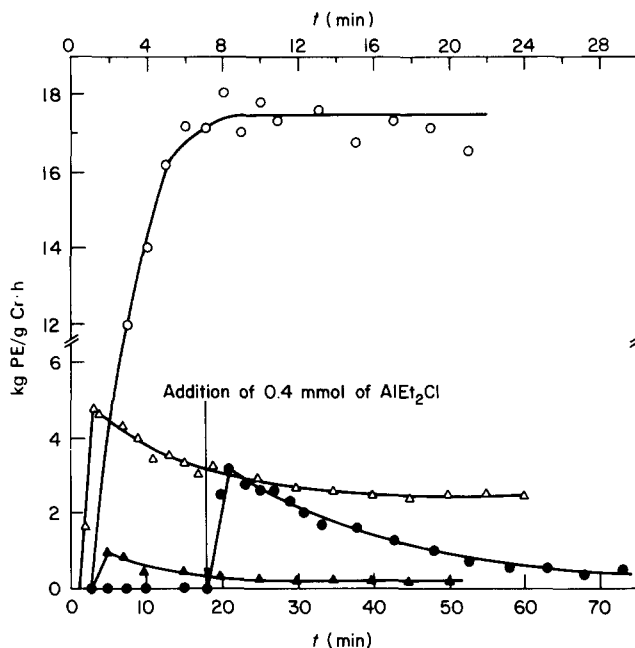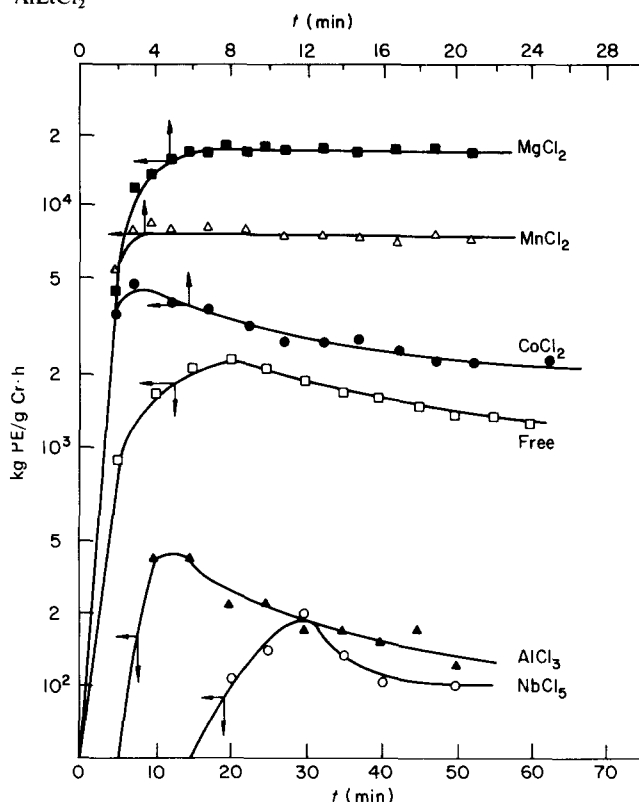
the $Cr(CH_3COO)_3 \cdot (CH_3CO)_2O/AlEt_3/MgCl_2/2$-EHA catalytic system was incapable of polymerization of ethylene. This might be partly attributed to the over-reduction of Cr species from active $Cr^{2+}$ to inactive $Cr^{1+}$ or $Cr^0$ as reported previously in the $Cr(CH_3COO)_3 \cdot (CH_3CO)_2O/AlEt_3$ system[2]. However, some activity appeared upon admitting $AlEt_2Cl$ as shown in *Figure 4*, indicating that the ligands exchange reaction takes place between $Cr(CH_3COO)_3 \cdot (CH_3CO)_2O$ and $AlEt_2Cl$, not between $Cr(CH_3COO)_3 \cdot (CH_3CO)_2O$ and $MgCl_2$.

Accordingly, the difference in the optimum molar ratios of Mg/Cr and Mg/Ti may be considered to reflect the difference in the equilibrium constants of the complex formation of transition metal compounds having Cl ligands and $MgCl_2$ through Cl bridges. The precise structure of the active species is, however, not clear at the present stage.

The polymerization of ethylene was then performed at 30°C by using various types of metal chlorides

([MClx]/[Cr] = 37.5) in place of $MgCl_2$. The results are shown in *Figure 5*.

In *Figure 6* are plotted the stationary polymerization rates against the electronegativities of the metal ions in MClx. The electronegativity of each metal ion ($Xi$) was



**Figure 4** Kinetic curves of ethylene polymerization with the $Cr(CH_3COO)_3 \cdot (CH_3CO)_2O/AlEt_2Cl/MgCl_2/2$-EHA catalyst system in the presence of various kinds of alkylaluminums. Polymerization conditions; 30°C, ethylene pressure = 760 Torr, toluene = 160 cm³, $Cr(CH_3COO)_3 \cdot (CH_3CO)_2O = 0.016$ mmol, alkylaluminum = 14 mmol, and [Mg]/[Cr] = 37.5. (●) $AlEt_3$; (△) $Al_2Et_3Cl_3$; (○) $AlEt_2Cl$; (▲) $AlEtCl_2$



**Figure 5** Kinetic curves of ethylene polymerization with the $Cr(CH_3COO)_3 \cdot (CH_3CO)_2O/AlEt_2Cl/2$-EHA catalyst system in the presence of various kinds of metal chlorides. Polymerization conditions; 30°C, ethylene pressure = 760 Torr, toluene = 160 cm³, $Cr(CH_3COO)_3 \cdot (CH_3CO)_2O = 0.016$ mmol, $AlEt_2Cl = 14$ mmol, and [Metal Chloride]/[Cr] = 37.5
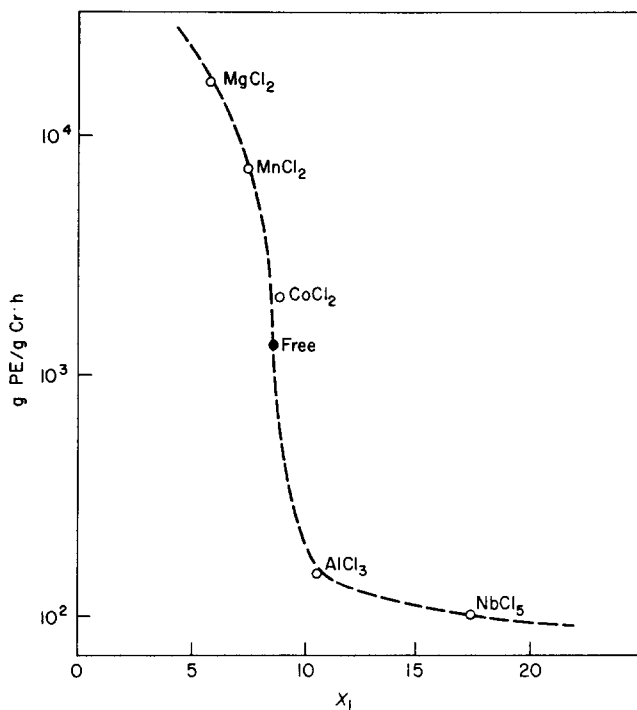
**Figure 6** Relation between stationary rate and electronegativity of metal ion in metal chloride. Polymerization conditions as in *Figure 5*

these catalytic systems, the present results can also be interpreted by the same mechanism as reported previously in the soluble $Ti(OBu)_4/AlEt_2Cl/MgCl_2/2$-EHA catalytic system[4]. The back-donation of electron from the active $Cr^{2+}$ to ethylene seems to be the main factor in determining a $Cr^{2+}$-ethylene interaction, and the electron-donating capability of $MgCl_2$ or $MnCl_2$ may stabilize the coordination of an ethylene molecule with $Cr^{2+}$, resulting in an acceleration of a subsequent insertion of the coordinated ethylene into an active $Cr^{2+}$-polymer chain bond. In contrast, the electron withdrawing capability of metal chlorides may cause an unfavourable effect in the chain propagation.

## CONCLUSION

Highly active catalysts for ethylene polymerization were obtained by modifying $Cr(CH_3COO)_3 \cdot (CH_3CO)_2O$ with suitable metal chlorides in 2-EHA. A clear relation was observed between the polymerization activity and the electronegativity of metal ion in the metal chloride, which suggested a plausible mechanism for the enhancement of the activity by modifying the Cr-catalyst with metal chlorides.

calculated from the following empirical equation derived by Tanaka *et al.*[6], where $i$ is the oxidation number of the metal ion and $Xo$ denotes the Pauling's electronegativity of the metal atom.

$$Xi = (1 + 2i)Xo \qquad (2)$$

In the present study were examined a limited number of metal chlorides. However, judging from the results shown in *Figure 6* it may be said that the chlorides of metal ions with $Xi$ below 8.5 (the electronegativity of $Cr^{2+}$) act as accelerators whereas those with $Xi$ above 8.5 do as inhibitors for the polymerization. Provided that the number of active species does not change so much among

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