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Origin of Isospecificity of Active Sites on Various Donor-Free Heterogeneous Ziegler-Natta Catalysts for Propylene Polymerization

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Background

In 1953, Karl Ziegler in Germany discovered the transition metal based catalyst ($\text{TiCl}_4 + \text{Et}_3\text{Al}$) for the production of polyethylene and in the next year, Giulio Natta in Italy modified this catalyst as $\text{TiCl}_3 + \text{Et}_2\text{AlCl}$ for the production of polypropylene. The work on the olefin polymerization had a striking impact on the academic and scientific role of macromolecular chemistry as discipline and marked the great development of polymer chemistry. In 1963, Ziegler and Natta were awarded together the Nobel prize for their innovative discoveries of a new type of catalysis in olefin polymerization chemistry. But in the early stage, these catalyst systems showed very poor technological performance. Hence from the beginning of discovery, a great number of tremendous research efforts from both academic and industrial circles have been provided to the Ziegler-Natta catalysis in order to improve the activity and stereospecificity by the introduction of support material and electron donors. Thus over the years, these catalyst systems have subsequently progressed through several generations from the simple TiCl_3 based materials into the currently used modern systems based on MgCl_2 supported TiCl_4 catalyst with electron donors for the commercially production of isotactic polypropylene.

Aim

The successive development makes the catalyst systems more and more complicated due to the interaction between each other of the catalytic components. As a result, many aspects concerning the real origin of isospecificity of active sites and specific stereochemical role of various catalytic components are still yet to be clearly understood even though tremendous research efforts have been conducted for more than 50 years. However, donor-free TiCl_3 based catalyst due to having the simplest components is thought to be an ideal model for the investigation of these unsolved problems. Therefore, the objective of the present study is to elucidate the isospecific nature of active sites on donor-free TiCl_3 based catalyst by the correlation between surface characterization of catalyst and microstructure analysis of polymer.

Experimentals

As a part of our approaches in using donor-free Ziegler-Natta catalysts, in this work, $\text{TiCl}_3/\text{Al-alkyl}$ and $\text{MgCl}_2/\text{TiCl}_3/\text{Al-alkyl}$ catalysts were investigated in terms of the stereospecific effects from various catalyst preparation and types of cocatalysts through systematic characterizations of both the polymer and the catalyst with modern analytical techniques. Characterizations of catalyst include the investigation of coordination states of surface titanium and aluminum species by XPS and ^{27}Al MAS NMR whereas microstructure analysis of polymer with TREF, ^{13}C NMR and GPC methods. A correlation of the results between the microstructures of polymers and the surface structures of the catalysts has been performed to get much deeper understanding on the real origin of isospecificity of active sites on the TiCl_3 -based catalysts.

Results

Figure 1 and Figure 2 describe the XPS spectra of titanium 2p region curves fitted by computer simulation. It can be seen that both AA- TiCl_3 and AA- $\text{TiCl}_3/\text{MgCl}_2$ catalysts contain two types of Ti^{3+} species depending on the coordination states of surface titanium species. The peaks situated at higher binding energy are assigned to the lower coordinated surface titanium species ($\text{Ti}^{3+}(\text{a})$) whereas lower binding energy peaks correspond to the higher coordinated surface titanium species ($\text{Ti}^{3+}(\text{b})$), which are displayed in the Scheme 1. DEAC as a cocatalyst preferentially shows more intense peak of $\text{Ti}^{3+}(\text{b})$ species of unsupported TiCl_3 catalyst than TEA (Figure 1) whereas for supported catalyst, this effect implies the opposite tendency (Figure 2).

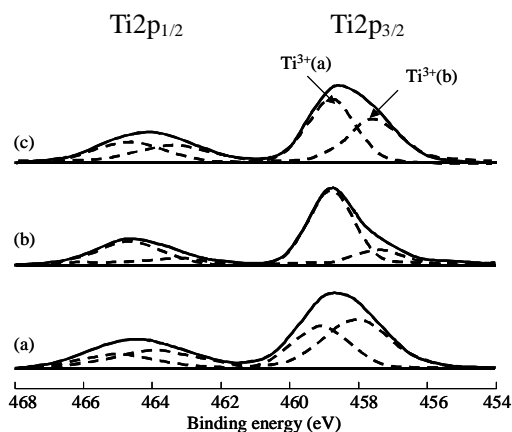


Figure 1. The Ti 2p region of the XPS spectra. (a) WG AA-TiCl₃, (b) WG AA-TiCl₃-TEA, (c) WG AA-TiCl₃-DEAC.

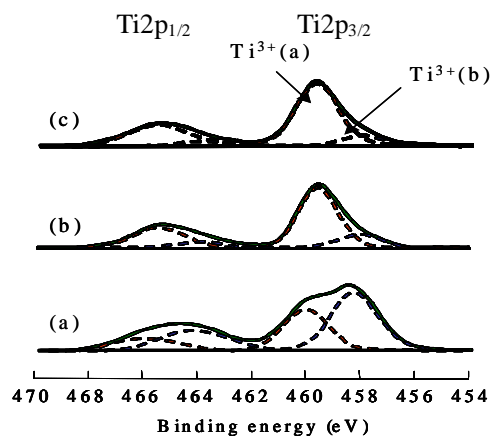
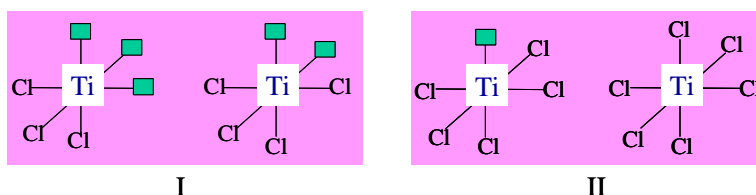


Figure 2. The Ti 2p region of the XPS spectra. (a) WG AA-TiCl₃/MgCl₂, (b) WG AA-TiCl₃/MgCl₂/TEA, (c) WG AA-TiCl₃/MgCl₂/DEAC



Scheme 1. Surface titanium species with different coordination states. I: low coordinated titanium species (Ti³⁺(a)); II: high coordinated titanium species (Ti³⁺(b)).

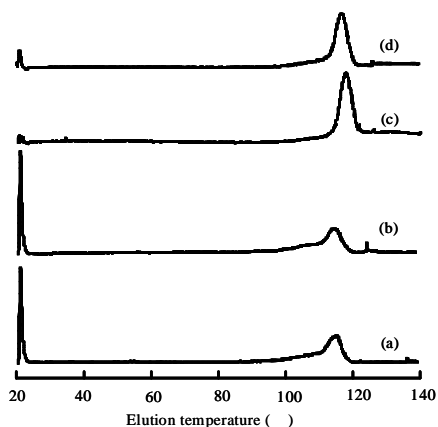


Figure 5. TREF diagrams of PP obtained from AA-TiCl₃ based catalyst with Al/Ti molar ratio=3 at 40 °C for 30 min polymerization. (a) WG/TEA, (b) DG/TEA, (c) WG/DEAC, (d) DG/DEAC.

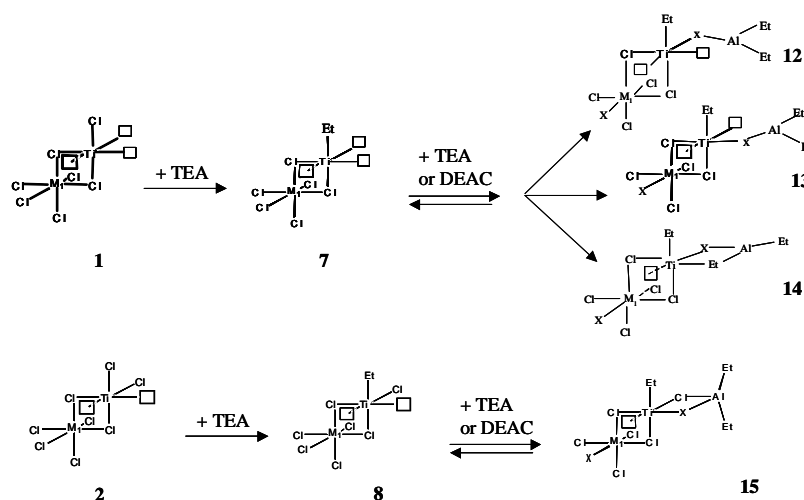
Table 1. Dependence of activity, isotacticity, molecular weight and molecular weight distribution of PP produced with unsupported and MgCl₂ supported TiCl₃ catalyst using TEA or DEAC as a cocatalyst. (Polymerization conditions: Ti = 2 mmol, Al/Ti = 3, temp. = 40 °C, time = 30 min.)

Catalyst system	Activity (g-PP/g-Ti·h)	Isotacticity ^{a)} (mmmm%)	M _n ^(b) ×10 ³	M _w /M _n ^(b)
AA-TiCl ₃ /MgCl ₂ /DEAC	44.6	43.4	16.7	10.8
AA-TiCl ₃ /MgCl ₂ /TEA	118.0	53.9	9.1	13.4
AA-TiCl ₃ -DEAC	14.4	93.6	51.0	13.5
AA-TiCl ₃ -TEA	86.4	72.1	18.3	14.0

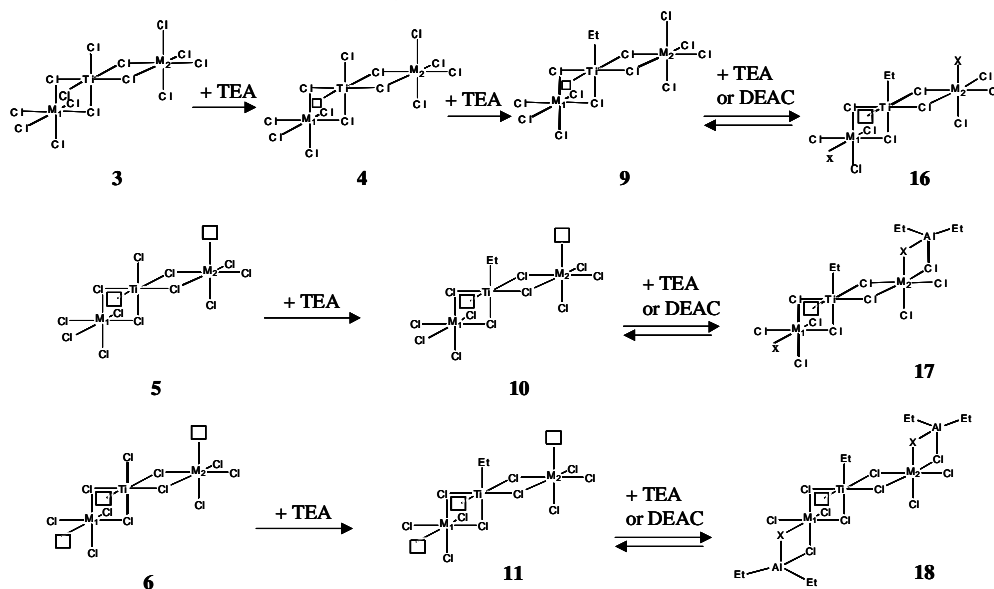
a) measured by ¹³C NMR
b) measured by GPC

Figure 3 shows the isotacticity distribution of polypropylene produced with TiCl₃ catalyst. DEAC represents much intense peak of the highest isotactic fractions with very few fraction of atactic PP. On the other hand, TEA shows very strong peak of completely atactic PP with weaker peak of the highly isotactic PP. Table 1 shows the catalytic activity, isotacticity, molecular weight and molecular weight distribution of polypropylene, which were significantly affected by the types of cocatalyst and MgCl₂ support. TEA shows much more higher activity with both supported and unsupported catalyst than DEAC. DEAC shows higher isotacticity with unsupported TiCl₃ catalyst than MgCl₂ supported TiCl₃ catalyst. TEA shows lower molecular weight with both MgCl₂ supported and unsupported TiCl₃ catalysts.

Depending on the coordination states of surface titanium species (Scheme 1) and three sites models proposed by Busico et al.^[1], the nature of isospecific active sites on TiCl_3 based catalysts, formation and transformation into highly isospecific sites are shown in Schemes 2 and Scheme 3.



Scheme 2. Active sites models originated from the low coordinated surface titanium species.



Scheme 3. Active sites models originated from the high coordinated surface titanium species.

After interaction with TEA cocatalyst, low coordinated surface titanium species (1,2) produce monometallic aspecific active sites (7,8), which after further interaction with cocatalyst makes less isospecific bimetallic active sites (12,13,14,15). On the other hand, highly coordinated surface titanium species (3,4,5,6) form monometallic less isospecific active sites (9,10,11), which also transform into highly isospecific bimetallic active sites (16,17,18) through complexation with cocatalyst^[2]. Low coordinated aluminum of bimetallic active sites (12,13,14) due to having pronounced Lewis acidic property^[3] may coordinate with another aluminum compound or with surface titanium through chlorine/ethyl bridges to increase its coordination states, which also affects the isospecificity of active sites.

References

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