

Chemical Structure of Active Site Formation in Ziegler-Natta Polymerization

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Abstract- Recent new understanding concerning the chemical structures of active sites formation in the Ziegler-Natta polymerization is being presented. The chemical structures and compositions of the titanium- and aluminum- species existing in the catalyst system have been investigated by X-ray photoelectron spectroscopy (XPS) method. It is identified that the chemical structure of active site is dominantly affected by the complex formation, transformation, their distribution throughout the catalyst, cocatalyst and donor reactions. Higher isospecificity of active sites is seen to be related to the higher fulfilled coordination states of titanium and aluminum species.

Keywords- Ziegler-Natta Catalyst, Active Sites, Electron Donor, XPS

I. INTRODUCTION

Since the discovery in the early 1950s, several generations of ZNC with very high isospecificity and high activity have been successfully developed in the industrial circle by the introduction of different catalytic components such as, support materials, cocatalysts and electron donors making the whole catalyst system chemically complexed [1-7]. As a result, despite the obvious industrial importance, many academic aspects regarding the mechanism of polymerization, the real origin of active sites, the exact structure of active sites and the role of various catalytic components on the stereospecific nature of active sites, the differences between the activities of the transition metal in various oxidation states of classical ZNC still largely remain far from the clear understanding [8-10]. However, the characterization of ZNC has been attempted by means of several experimental approaches. Proceeded with the series of studies [11-12], the investigation on the isospecificity of active sites of the donor-free Ziegler-Natta catalyst provided the first evidence for the origin of active sites isospecificity from the catalyst substrate and the cocatalyst. These basic and profound understandings with respect to the stereospecific roles of cocatalyst and catalyst substrate gave rise to a good basis for further effort to elucidate the isospecific nature and structure of active sites on the catalyst surface as it replicates the polymerization mechanism and polymer microstructure. Busico et al. [13-14], in a series of papers, proposed the existence of two types of active sites depending on the support face acidity, Ti_2Cl_6 being the stereospecific one responsible for the isotactic chain propagation, while $TiCl_3$ the nonstereospecific one responsible for the random propagation. A little more information concerning the types of active sites model in the Ziegler-Natta catalyst has been reported [15] through surface characterization by modern scientific techniques as well as correlation between catalyst surface structure and PP tacticity, which is still insufficient for a clear understanding of the real physico-chemical structure of active sites. Despite considerable efforts with different surface analysis methods, it has not been possible to determine the exact structures of the both isospecific and nonisospecific active sites [16-19].

Clear evidence on the exact structure of isospecific active sites is expected to be relating not only to the microstructure analysis of the PP but also to the catalyst surface structure. The key concept of this study is to elucidate the (i) variation of coordination states in the surface titanium species (ii) chemical structure of the titanium active center (iii) which titanium species is isospecific (iv) which titanium species is non-isospecific (iv) various coordinative states of surface aluminum species on the solid catalyst. From the academic and scientific point of view, these are the main novelty of the present work. To begin with this challenge, a number of previous studies [20-21] have been performed for obtaining a basic understanding concerning the isospecific nature of active sites on $TiCl_3$ -based catalysis.

II. EXPERIMENTAL

A. Raw materials-

Research grade propylene (Chisso Corp.) was used without further purification. Anhydrous titanium trichloride, $TiCl_3$ was supplied by Toho Titanium Co. Ltd. Molecular sieves 13X (Wako Pure Chemical Industries, Ltd.) were

used as moisture scavengers for solvent purification. Heptane and toluene (Wako Pure Chemical Industries Ltd.) solvents were purified by passing through molecular sieves 13X column. Triethylaluminum (TEA) and diethylaluminumchloride (DEAC) (Tosoh Akzo Corp.) and nitrogen (Uno Sanso Corp.) were used without purification. TEA and DEAC were used after dissolving in toluene solvent.

B. Catalyst preparation-

Wet ground (WG) processing of TiCl_3 catalyst was performed by milling 36 grams of supplied catalyst in a ball mill with 200 ml heptane and dry ground (DG) processing was performed in the same way without heptane. The grinding of catalyst was carried out in a 1.2 L stainless steel pot containing 55 balls each of 25 mm diameter for 30 h at room temperature. The processed catalysts were obtained as heptane slurry. The entire process was performed under nitrogen atmosphere. Titanium content in the catalyst slurry was determined by the redox titration method. The catalyst slurry was then kept in a three-necked round-bottomed flask equipped with a magnetic chip under nitrogen atmosphere.

C. Surface characterization by XPS

The ultra high vacuum (UHV) chamber used in this study was equipped with a sputter ion gun for surface cleaning, an X-ray source and a double pass cylindrical mirror analyzer (CMA) with a coaxial electron gun for X-ray photoelectron spectroscopy (XPS). The XPS data of the catalyst was taken by Physical Electronics Perkin-Elmer (Model Phi-5600 ESCA) spectrometer with monochromated Al K_{α} radiation (1486.6 eV) operated at 300W. It was carried out in a glove bag under nitrogen atmosphere. The sample holder was then put into a vacuum transfer vessel (Phi Model 04-110, Perkin-Elmer Co., Ltd.), which is connected to the sample introduction chamber of the XPS instrument. The sample was degassed up to 10^{-7} Torr. The main chamber vacuum was kept above 5×10^{-9} Torr during XPS data acquisitions. A neutralizer was used to reduce the charging effect in order to obtain a better signal to noise ratio. All binding energies (BE) were referenced to the Au $4f_{7/2}$ peak at 84 eV to correct for the charging effect during data acquisition. Multiplet fittings of the Ti 2p XPS curves were carried out by the Gaussian-Lorentzian method to determine the mixed states of valences in all the samples. The binding energy (BE) and the full width at half maximum (FWHM) values from the Ti 2p XPS spectra was measured and used as criteria for identification of the oxidation state, distribution state and existing state of surface Ti species on catalyst surface. The XPS spectra of Ti 2p have been deconvoluted into a series of synthetic peaks (67% Gaussian and 33% Lorentzian; FWHM=2.3 eV) that represent the photoelectron emission from different oxidation states. The fitting for each curve was repeated to ensure a reproducible result.

III. EXPERIMENTS AND RESULT

To investigate the states of the titanium species in detail, high resolution XPS narrow scans of the Ti 2p region were performed for each catalyst system. The constituent atoms of the TiCl_3 catalyst (Cl, Ti, C, Al) were observed on the XPS measurable surface, approximately 2 nm in sampling depth, which is shown in the Figure 1.

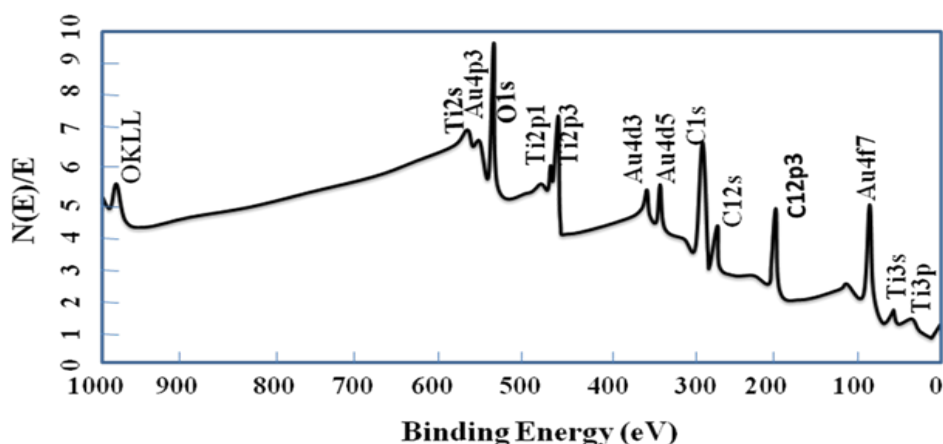


Figure 1. Constituent atoms of the TiCl_3 catalyst observed on the XPS measurable surface.

A typical XPS result as shown in Figure 2 has described the XPS spectra of the Ti2p region of (a)original TiCl₃, (b)Dry ground TiCl₃ and (c)Wet ground TiCl₃ catalysts to rationalize the grinding effect on the nature of the active sites. The doublet at two different binding energies (split between two peaks with an intensity ratio of 2:1) is reported to be due to spin-orbit coupling effects in the final state of the emitted electron. The doublet at 458.5 and 464.6 eV are reported to be due to the Ti 2p_{3/2} and Ti 2p_{1/2} photoelectrons from titanium atoms in its molecular states [22]. Thus, the doublet shown in the XPS spectra is ascribed to the 2p_{3/2} and 2p_{1/2} photoelectrons from titanium atoms existing in the catalyst. It is seen that all catalyst systems indicate two computer-simulated peaks in the region of Ti2p_{3/2} spectra, which can be ascribed by the two kinds of Ti-species on the catalyst surface depending on the different levels of the coordination states of the surface titanium species. One of the Ti-species at a higher binding energy is assigned to the lower coordinated titanium species Ti³⁺(a) with higher coordination vacancies whereas another at a lower binding energy is considered to be the higher coordinated titanium species Ti³⁺(b) with lower coordination vacancies.

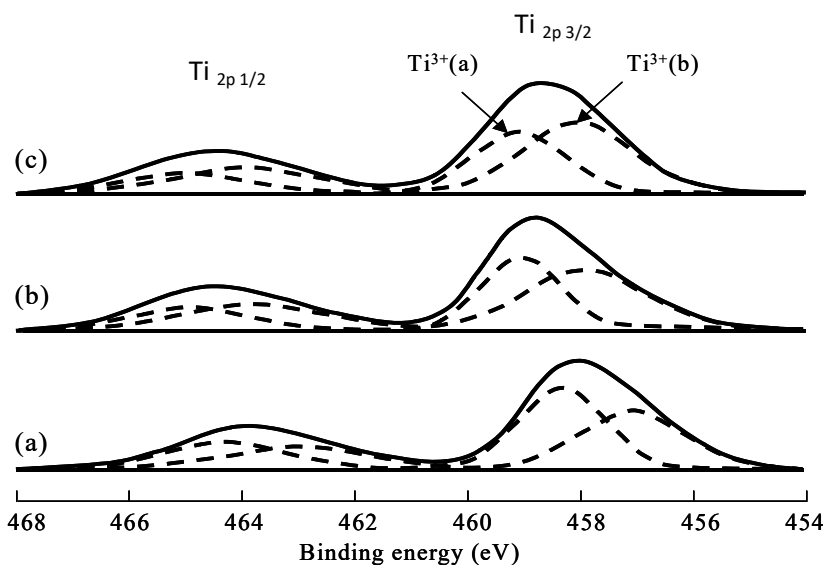
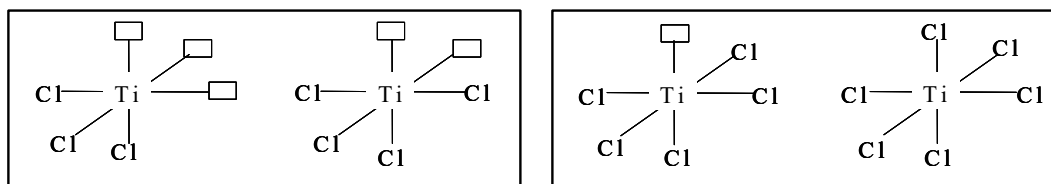


Figure 2. The XPS spectra of the Ti 2p region of (a) Original TiCl₃, (b) Dry-ground TiCl₃, (c) Wet-ground TiCl₃

Depending on this experimental result, the plausible structures of these two kinds of surface titanium species are displayed in the Scheme 1. It is reported that usually, the divalent titanium species exists on the catalyst surface by sharing two chlorine atoms (through chlorine-bridge) with other titanium or aluminum. Thus, the catalyst crystal may be considered as built up of elementary sheets, each consisting of two chlorine layers sandwiching a titanium layer.



Group 1: Low coordinated Ti³⁺(a) Group 2: High coordinated Ti³⁺(b)

Scheme 1. Coordination states of surface titanium species of TiCl₃ catalyst □: Coordination vacancy

According to the literature [23], at the surface of TiCl₃ catalyst, two kinds of surface sites are possible: (i) The first type has one chlorine vacancy and two loosely bound chlorine atoms. (ii) In the second type, there are two chlorine vacancies and one loosely bound chlorine atom. Due to surface heterogeneity of the catalyst, titanium species may

also remain on different surface locations and may exhibit different tendencies in the formation of active sites. Thus, low coordinated Ti^{3+} with two or three vacant sites can be possibly present in solid state, mainly situated at the edges and corners of the crystallite's surface. It has often been supposed that two types of polymerization centers exist in $TiCl_3$, and in addition to these direct observations, John Boor [24] assumed the existence of two different structures for active centers to account for the formation of both isotactic and atactic polymers during Ziegler-Natta polymerization.

Table-1 Multiplet curve fitting data of the XPS Ti 2p spectra of $TiCl_3$ based catalysts.

Catalyst system	Ti 2p _{3/2}		Oxidation state	Atomic percentage
	BE (eV)	FWHM (eV)		
Original	458.53	1.78	Ti^{3+} (a)	52.27
$TiCl_3$	457.17	2.30	Ti^{3+} (b)	47.73
Wet ground	459.32	1.65	Ti^{3+} (a)	41.03
$TiCl_3$	458.08	2.58	Ti^{3+} (b)	58.97
Dry ground	458.99	2.05	Ti^{3+} (a)	41.78
$TiCl_3$	457.82	2.32	Ti^{3+} (b)	58.22
Wet ground	459.02	1.55	Ti^{3+} (a)	80.96
$TiCl_3/TEA$	457.56	1.72	Ti^{3+} (b)	19.04
Wet ground	459.70	1.59	Ti^{3+} (a)	59.16
$TiCl_3/DEAC$	458.05	1.90	Ti^{3+} (b)	40.84

Ti^{3+} (a) stands for Ti^{3+} -species with lower coordination states,
 Ti^{3+} (b) stands for Ti^{3+} -species with higher coordination states

The XPS signals show that the peak has shifted to the higher binding energy due to the decrease of the coordination state of all surface titanium species after grinding. Shifts in BE have a contribution from both the oxidation state and the charge on the nearest neighbor atoms of the excited atom. The chemical shift and the FWHM of the 2p_{3/2} peak in XPS analysis of Ziegler-Natta catalysts indicate the electron density of the titanium species, namely the oxidation state and its distribution, respectively. Therefore, the results of the XPS data analysis in terms of binding energy (BE), full width and half maximum (FWHM), oxidation states, and atomic percentage of surface titanium species are listed in Table 1.

From the XPS data analysis of these catalyst systems, it can be seen that after interaction with the cocatalyst the binding energy of the Ti^{3+} (b)-species has decreased, which may be due to the association of the electron donating alkyl groups with the surface Ti-species. It can also be speculated that the weakly bonded surface chlorine atoms can be replaced by the electron donating ethyl group of the cocatalyst. The increase in binding energy is due to the formation of a coordination vacancy by the extraction of dangling Cl on the catalyst surface induced by the grinding effect. Thus, the dry-ground catalyst has a binding energy higher than that of the wet-ground catalyst even though the atomic percentage of higher coordinated Ti^{3+} (b)-species has not changed significantly between these two catalyst systems. In the wet-ground catalyst, active species mostly remain on the crystalline layers, which correspond to the titanium species with a higher coordination state (lower Cl vacancy), whereas in the dry-ground catalyst, the active species are mostly located at the edges and defects of the catalyst, which corresponds to the lower coordination state (higher Cl vacancy). The most striking effects of dry grinding is the drastic crystallographic changes induced by shear forces that are strong enough to cause sliding at the metal-free interfaces of the Cl-Ti-Cl double layer; this leads to disorder in the stacking, which essentially becomes random after prolonged intense dry grinding [25,26]. According to the literature [27,28], the electron deficient catalytic species are suggested to be responsible for the binding energy increase. It can be seen that after grinding, the atomic percentage of surface titanium species Ti^{3+} (b) with higher coordination states has significantly increased (about 10%). This is because of the grinding effect of catalyst, catalyst particles are disintegrated into small particles exposing more surface layers as well as Ti-species with higher coordination states.

Although the surface area could be increased due to the break of the large particles into smaller ones, the newly exposed surface Ti-species are mainly situated on the newly-exposed crystalline surface rather than on the newly-exposed edges or corners of the small crystallites. Therefore, the grinding increased the ratio of high coordinate Ti^{3+} -

species. The surface of ground TiCl_3 catalyst may therefore be rather rough, so that the number of active sites (e.g. exposed Ti) can be considered to be the same order of magnitude as the number of surface Ti atoms. However, the wet-ground catalyst shows a slightly higher atomic percentage of Ti^{3+} (b)-species, caused by making more layer-wise fragmentation and a less defective catalytic surface than that of the dry-ground catalyst. According to Mejzlik and co-authors [29], the grinding of TiCl_3 catalyst in hydrocarbon medium not only increases the specific surface but also causes a basic change in the reactivity of the TiCl_3 surface.

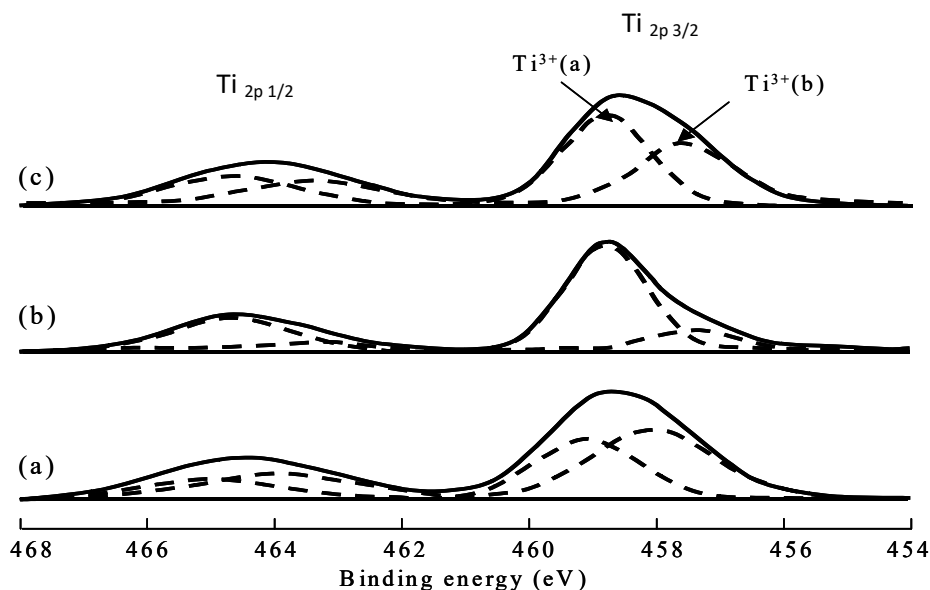
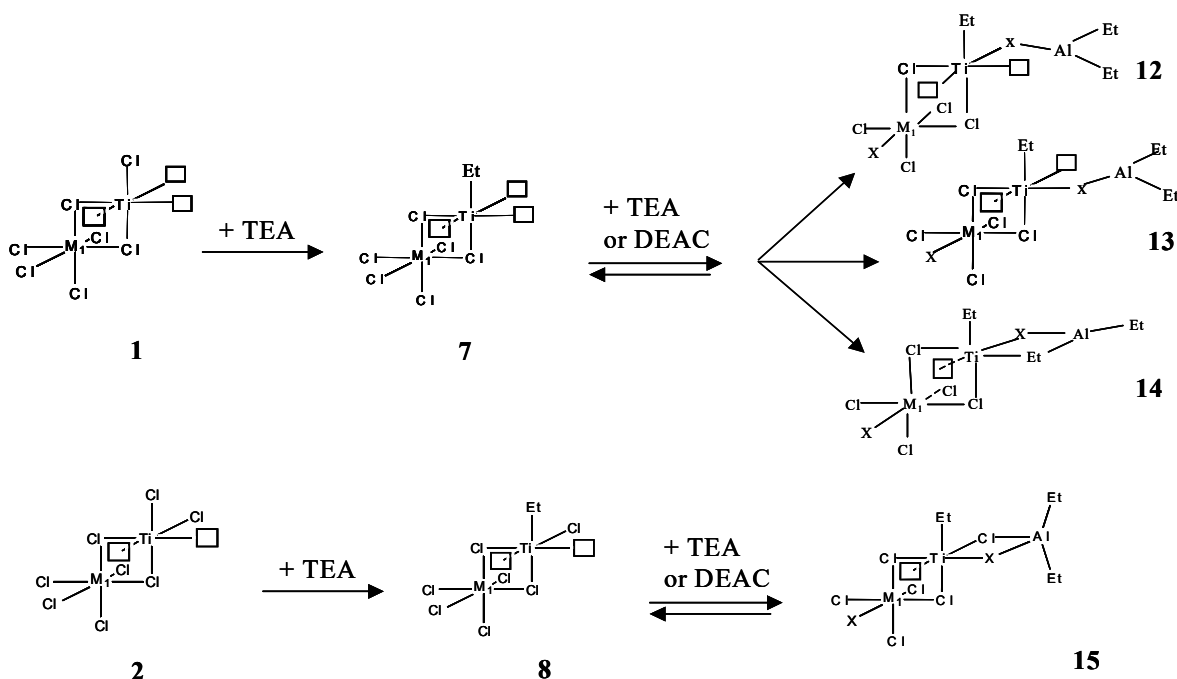


Figure 3. The XPS spectra of the Ti 2p region of (a) WG TiCl_3 , (b) WGTiCl₃/TEA, (c) WG TiCl_3 /DEAC.

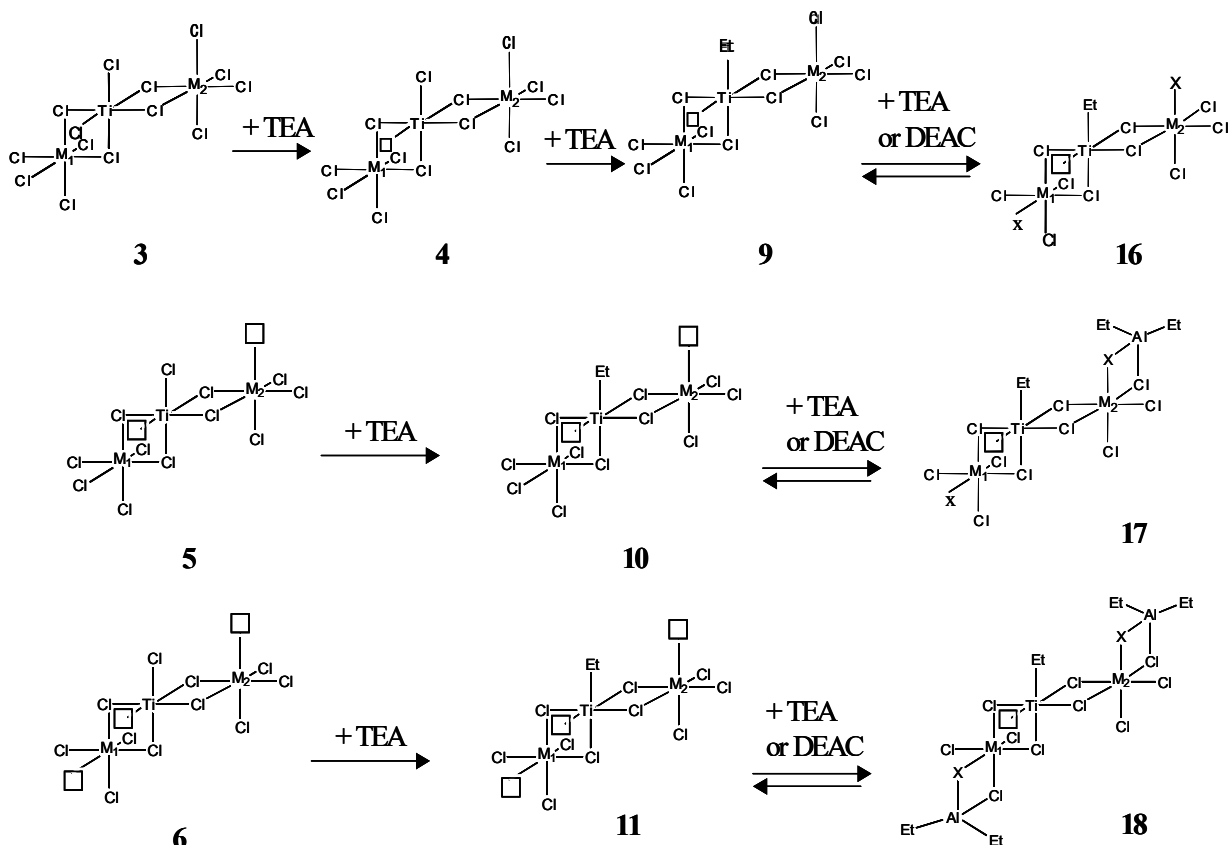
To investigate the effect of Al alkyl cocatalyst on the coordination states of surface titanium species, XPS analysis was also performed for the wet-ground TiCl_3 catalyst before and after reaction with TEA or DEAC. The XPS spectra of these catalyst systems are shown in Figure 3. After interaction with the cocatalyst, the peak intensity of the higher coordinated Ti^{3+} (b)-species has drastically decreased in comparison to that of the titanium species obtained from the wet-ground TiCl_3 catalyst. TEA shows a more drastic decrease of the peak intensity of the Ti^{3+} (b)-species and at the same time increased the peak of Ti^{3+} (a)-species (Figure 3b) but DEAC did not show a big change (Figure 3c). XPS data analysis also shows that the atomic percentage of Ti^{3+} (b)-species has decreased to about 70% after interaction with TEA and to about 32% with DEAC. This explanation is that TEA as a cocatalyst has remarkably transformed the higher coordinated titanium species Ti^{3+} (b) into a lower coordination state titanium species Ti^{3+} (a) due to its stronger reactivity than that of DEAC. Another explanation can be explored for the drastic decrease of surface atomic percentage of Ti^{3+} (b) species, which may be due to the extraction of surface dangling Cl by the effect of a cocatalyst. The extraction of surface dangling Cl is significantly affected by the effect of TEA, which shows a lower percentage of Ti^{3+} (b) species (only 19.04%), while DEAC shows higher percentage of Ti^{3+} (b) species (40.84%). By the way, another point possibly associated with the slight decreasing of the average binding energies of those Ti-species after Al-alkyl cocatalyst treatment might be the possible reduction of a small fraction of Ti^{3+} (b) into Ti^{2+} , which had not been considered in the previous explanations. The over-reduction of Ti (from Ti^{3+} to Ti^{2+}) becomes inactive especially for propylene polymerization. Here, it is worth-while using XPS observation to detect the difference in the titanium species in terms of coordination number produced by the reaction with various alkylaluminums suggesting that the variation in the coordination state of the titanium species is closely related to the reactivity of the alkylaluminum. The binding energy (BE) decreased, indicating the progress of the reduction of the titanium species on the catalyst. It is well known that surface Ti-species of heterogeneous Ziegler-Natta catalysts are first reduced and then alkylated by the effect of the cocatalyst. The FWHM of the $\text{Ti } 2p_{3/2}$ peaks of both Ti-species show different values after grinding and reacting with the cocatalyst, suggesting the different chemical environment of the catalyst surface. In fact, however, the alkylaluminum cocatalyst interacts with the heterogeneous Ziegler-Natta

catalyst through the ligand change of the surface Ti-species [30]. Depending on this experimental result, the physico-chemical structures of stereospecific active sites are shown in the Scheme 2 and Scheme 3.



Scheme 2. Formation and transformation of active sites originated from low coordinated Ti^{3+} -species.

Scheme 2 displays the lower coordination number titanium species (**1,2**) with three- or two-coordination vacancies. After interaction with the cocatalyst, the surface Ti^{3+} -species are alkylated through the replacement of one chlorine atom by the ethyl group of the cocatalyst. This alkylated Ti^{3+} species containing higher number of coordination vacancies acts as monometallic active sites (**7,8**) with very low isospecificity. Rodriguez and van Looy [31-33] thought that the monometallic sites with either one- or two-coordination vacancies in $TiCl_3$ based catalysts do not present asymmetry and can only produce atactic polymers. After a reversible complexation with Al-alkyl cocatalyst, the monometallic sites with three coordination vacancies (**7**) could be converted into bimetallic active sites (**12, 13, 14**) with comparatively lower coordination vacancies. The complexation between higher coordination number monometallic active sites and the cocatalyst can occur through either one alkyl group (**12,13**) or one chlorine and one alkyl group (**14,15**). However, bimetallic active sites (**12,13**) due to bearing two coordination vacancies and one bridge are considered as the aspecific, whereas monometallic active site (**14**) containing two bridges could be thought as the less isospecific site. On the other hand, monometallic aspecific site (**8**) could be transformed into bimetallic isospecific site (**15**) by complexing with two bridges. Low coordinated aluminum of active sites (**12,13,14,15**) with strong Lewis acidic properties can coordinate with another aluminum compound in the solvent or with surface titanium through an ethyl/chlorine bridge to increase the coordination number. Scheme 3 displays the higher coordination number titanium species (**3,4,5,6**) with one or without coordination vacancy. For the highest coordinated surface titanium species (**3**), one chlorine atom can be abstracted first by the effect of the cocatalyst to make another titanium species (**4**) with one coordination vacancy. After alkylation of the titanium species (**4,5,6**) through the interaction with the cocatalyst, all of the monometallic active sites (**9,10,11**) are transformed into bimetallic active sites (**16,17,18**) through a complexation reaction with a further interacted cocatalyst.



Scheme 3. Formation and transformation of active sites originated from high coordinated surface Ti^{3+} species.

If the bimetallic active sites of both Schemes 2 and 3 make complexes through a chlorine-bridge (Cl) then they are considered to be more stable than active sites produced through an alkyl-bridge (x). During further interaction of monometallic active sites with cocatalyst, one chlorine atom can be replaced by the ethyl group of a DEAC cocatalyst (15,16,17). Among the enormous number of polymerization mechanisms proposed in the literature, the most important ones are the Cossee-Arman monometallic mechanism [34,35], the bimetallic mechanism proposed by Sinn et al. [36], Natta [37], and the three-sites model established by Corradini, Busico et al. [38-43]. Depending on these mechanisms, the nature and distribution state of active sites can be investigated through direct characterization of the donor-free $TiCl_3$ based catalyst combined with the microstructure analysis of the produced polypropylene. Moreover, we can not overlook the coexistence of another possible route for increasing the isospecificity of active sites, through ligand exchange from chlorine atom to ethyl group by the effect of further alkylation at the ligand position. Thus, ligand exchange can occur in the monometallic active sites (7,8,9,10) by the replacement of one chlorine atom at the ligand position with the ethyl group to form more isospecific active sites (12,13,14,15,16,17) due to the greater steric hindrance induced by the bulkier ligand. One of our previous study [44] has had detailed experimental approach to the real nature of isospecific active sites through surface characterization and microstructure analysis of polymer produced.

IV. CONCLUSION

XPS analyses revealed that two types of active sites exist depending upon the different level of coordination states. The higher coordination numbers are thought to be the precursors of higher isospecific active sites, the lower coordinated species are thought to be the precursors of less isospecific active sites. However, the isospecific nature of Ti-species combined with the coordination state of Al compounds completely replicates the polymer

microisotacticity. Highly coordinated titanium and aluminum species known as isospecific active sites produced isotactic polypropylene whereas low coordinated titanium and aluminum species provided less isotactic as well as atactic polypropylene.

REFERENCES

- [1] G. Natta, Nobel Lectures in Chemistry, 1963-1970; Elsevier: Amsterdam, p 27, 1972.
- [2] K. Ziegler, Nobel Lectures in Chemistry, 1963-1970; Elsevier: Amsterdam, p 6, 1972.
- [3] Y. V. Kissin, Isospecific Polymerization of Olefins; Springer-Verlag: New York, 1985.
- [4] P. C. Barbé, G. Cecchin and L. Noristi, *Adv. Polym. Sci.* 81:1, 1987.
- [5] E. P. Moore Jr. "The Rebirth of Polypropylene: Supported Catalysts" Hanser Publishers, Munich, 1998.
- [6] F. Daniele, G. Antonella, M. Stefano, A. R. Gian, T. Eugenio and B. Silvano, *J. Mol. Catal. A: Chem.* 178:115, 2002.
- [7] G. Monaco, M. Toto, G. Guerra, P. Corradini and L. Cavallo, *Macromolecules*; 33:8953, 2000.
- [8] M. C. Sacchi, F. Forlini, I. Tritto and P. Locatelli, *Macromol. Chem. Phys.* 196: 2881, 1995.
- [9] S. Kojoh, M. Kioka and N. Kashiwa, *Eur. Polym. J.* 35: 751, 1999.
- [10] G. D. Bukatov and V. A. Zakharov, *Macromol. Chem. Phys.* 202: 2003, 2001.
- [11] H. Mori, H. Iguchi, K. Hasebe and M. Terano, *Macromol. Chem. Phys.* 198: 1249, 1997.
- [12] H. Kono, H. Mori, M. Terano, H. Nakatani and I. Nishiyama, *J. Appl. Polym. Sci.* 83: 2976, 2002.
- [13] P. Corradini, V. Busico and R. Cipullo, *Stud. Surf. Sci. Catal.* 89:21, 1994.
- [14] H. Mori and M. Terano. In: T. Sano, T. Uozumi, H. Nakatani and M. Terano, *Progress Catalytic* p 65, 2000.
- [15] S. H. Kim, G. A. Somorjai, *Surf. Interface, Anal.* 31: 701, 2001.
- [16] V. Ville, L. Pasi, P. Päivi and S. Franciska, *Polymer* 45: 3091, 2004.
- [17] M. Toto, G. Morini, G. Guerra, P. Corradini and L. Cavallo, *Macromolecules* 33:1134, 2000.
- [18] L. Cavallo, G. Guerra and P. Corradini, *J. Am. Chem. Soc.* 120: 2428, 1998.
- [19] M. Kakugo, T. Miyatake, Y. Naito and K. Mizunuma, In transition metal catalyzed polymerization, Ziegler-Natta and metathesis polymerizations; Quirk R P, Ed. Cambridge University Press: Cambridge p 624, 1988.
- [20] A. T. M. K. Hasan, B. Liu and M. Terano, *Polymer Bulletin* 54: 225, 2005.
- [21] A. T. M. K. Hasan, Q. Wang, B. Liu and M. Terano ISBN 978-4-88361-616-9 C3058; Sankeisha 44-51, 2008.
- [22] C. M. Desbuquoit, J. Riga and J. J. Verbist, *J. Chem. Phys.* 79: 26, 1983.
- [23] J. Boor Jr. *J. Macromol. Rev.* 2: 115, 1967.
- [24] J. Boor Jr. *Macromol. Review. Interscience* 2: 115, 1967.
- [25] Z. W. Wilchinsky, R. W. Looney and E. G. M. Tornqvist, *J. Catal.* 28: 351, 1973.
- [26] E. G. M. Tornqvist and N. Y. Ann, *Acad. Sci.* 155: 447, 1969.
- [27] D. Fregonese, A. Glisenti, S. Mortara, G. A. Rizzi, E. Tondello and S. Bresadola, *J. Mol. Catal. A: Chem.* 178:115, 2002.
- [28] B. Liu, K. Fukuda, H. Nakatani, I. Nishiyama, M. Yamahiro and M. Terano, *J. Mol. Catal. A: Chem.* 219: 363, 2004.
- [29] K. Veselý, J. Ambrož, J. Mejzlík and E. Spousta, *J. Polym. Sci. Part C: 16: 417, 1967.*
- [30] K. Soga, H. Y. Yanagihara, and D. H. Lee, *Makromol. Chem.* 190: 995, 1989.
- [31] A. G. Potapov, V. V. Kriventsov, G. D. Bukatov and V. A. Zakharov, *J. Mol. Catal. A: Chem.* 122: 61, 1997.
- [32] Z. Černý, J. Macháček, J. Fusek, S. Heřmánek, O. Kříž and B. Čásenký, *J. Organomet. Chem.* 402: 141, 1991.
- [33] J. J. A. Dusseault and C. C. Hsu, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* C33 103, 1993.
- [34] J. Boor Jr., *Ziegler-Natta Catalysts and Polymerizations*, Academic Press, N. Y., 403 and reference therein, 1979.
- [35] E. J. Arlamm and P. Cossee, *J. Catal.* 3: 99, 1964.
- [36] P. Patat and H. Sinn, *Angew. Chem.* 70: 496, 1958.
- [37] G. Natta and G. Mazzanti, *Tetrahedron* 8: 86, 1960.
- [38] P. Corradini, V. Busico and R. Cipullo, *Stud. Surf. Sci. Catal.* 89: 21, 1994.
- [39] J. C. Bailly and R. Hagege, *Polymer* 32: 181, 1991.
- [40] P. Cossee, *Tetrahedron Lett.* 17:12, 1960.
- [41] T. Keii, *Stud. Surf. Sci. Catal.* 56: 1, 1990.
- [42] Y. V. Kissin, *J. Polym. Sci Part A: Polym Chem* 39:1641, 2001.
- [43] V. Busico, R. Cipullo, G. Monaco and M. Vacatello, *Macromolecules* 30:6251, 1997.
- [44] A. T. M. K. Hasan, B. Liu and M. Terano, *Polymer* 51 3627-3635, 2010.

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