Precise Arguments on the Distribution of Stereospecific Active Sites on $MgCl_2$-Supported Ziegler-Natta Catalysts

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Summary: The stereospecific nature of active sites on various $MgCl_2$-supported Ziegler-Natta catalysts was investigated by stopped-flow technique combined with temperature rising elution fractionation (TREF) method. A modified three-sites model with precise description of the stereospecific nature of various types of active sites stemmed from surface titanium species, Al-alkyl compounds, Mg-compounds and electron donors has been proposed. It was demonstrated that the isospecificity of active sites strongly depends on the bulkiness of the ligands situated at the two most important ligand positions for construction of asymmetry and chirality of the active sites with steric hindrance. In general, there may exist both monometallic and bimetallic sites in heterogeneous Ziegler-Natta catalyst system. The kinds of active titanium species with different chemical structures on this catalyst system should be limited, whereas, the non-discrete distribution of isospecificity of active sites could be considered to generate from the numerous types of steric and electronic effects from the surroundings of active titanium species as well as large number of reversible and dynamic transformation reactions simultaneously occurred on the heterogeneous catalyst surface.

Keywords: $MgCl_2$-supported catalyst; polypropylene (PP); stereospecific active sites; stopped-flow method; Ziegler-Natta polymerization

Introduction

Ziegler-Natta catalyst is one of the most important discoveries in the chemistry field in the 20th century with respect to its contribution for synthesis of polyolefins at low pressure and temperature through coordination polymerization.[1] Finding the remarkable effect of $MgCl_2$ as support for Ziegler-Natta catalyst in 1960`s is the milestone for achieving super-high catalytic efficiency of this catalyst system as well as subsequent spectacular successes of large-scale commercial production of numerous polyolefin materials. In developing $MgCl_2$-supported Ziegler-Natta catalyst for propylene polymerization, electron donor compound is

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crucial and indispensable for producing highly isotactic polypropylene (PP) with the highest commercial importance. Within the past two decades, PP product with ultra-high isotacticity has been developed based on successful innovation of electron donors in the industrial field.[2] In spite of the great industrial success and several decades of research efforts since 1953, many aspects concerning the active sites and polymerization mechanism in Ziegler-Natta catalysis still remained ambiguous and controversial. For example, the real origin of isospecificity of active sites and specific stereochemical role of electron donor are still open for discussion. The difficulties come from the complexity of this catalyst system due to the very short lifetime of growing polymer chains, low percentage of active titanium species, co-existence of multiple interactions between multi-components as well as many side reactions in the polymerization process.[3] As it has been reported in the literature, the stereospecific nature of active sites on heterogeneous Ziegler-Natta catalyst could be significantly affected not only by electron donors [4] but also by the types of titanium compounds, Al-alkyl cocatalysts and Mg-compounds,[5~10] whereas, the specific stereospecific role of each component has not been clarified yet.

The stopped-flow technique [3] has been proven to be one of the most powerful methods for studying the kinetic and stereospecific natures of active sites on heterogeneous Ziegler-Natta catalysts for propylene polymerization. By this technique, direct information corresponding to the relationship between the stereoregularity of each polymer chain and the stereospecificity of each active site can be obtained.[11] Within recent several years, we have demonstrated the combination of stopped-flow technique with TREF method can be powerful for substantial research on the variation of stereospecific nature of active sites on the $MgCl_2$-supported Ziegler-Natta catalysts.[12] From the results, modified three-sites and island model with precise description of the stereospecific nature of various types of active sites had been proposed. [12] In this paper, a brief review of this series of studies will be demonstrated in pursuing more precise understanding on the origin of isospecificity of active sites from various aspects.

Experimental

Materials and Catalysts: The specifications of various raw materials including propylene,

$MgCl_2$, $Mg(OEt)_2$, $TiCl_4$, nitrogen, triethylaluminum (TEA), heptane, ethylbenzoate (EB) and dibutylphthalate (DBP) as well as preparation procedures for three different catalysts, i.e. donor-free $TiCl_4/MgCl_2$ catalyst, monoester-type $TiCl_4/EB/MgCl_2$ catalyst and diester-type $TiCl_4/DBP/Mg(OEt)_2$ catalyst were previously reported.[12] Ti contents of the three catalysts were 0.50 mmol-Ti/g-cat., 0.40 mmol-Ti/g-cat and 0.54 mmol-Ti/g-cat, respectively.

Stopped-Flow Polymerization and Characterization of PP: Propylene polymerization procedures using a modified stopped-flow apparatus with each type of catalyst as well as characterization of PPs by GPC and TREF had been previously reported in detail.[12]

Results and Discussions

Donor-Free $TiCl_4/MgCl_2$ Catalyst

Stopped-flow polymerizations were conducted using $TiCl_4/MgCl_2$ catalyst pretreated by TEA cocatalyst for 0 ~ 60s. The active site concentration ([C*]), chain propagation rate constant (k_p) and weight percentage of four fractions of PPs are shown in Table 1. According to the typical distribution states of isospecificity of active sites judged from the TREF curves shown in Figure 1, each PP sample is fractionated in four different temperature ranges namely ~20°C, 20~100°C, 100~110°C and 110~140°C, which are thought to be corresponding to four kinds of active sites with different stereospecificity, here defined as aspecific sites (**AS**), poorly-isospecific sites (**IS_1**), the second highest isospecific sites (**IS_2**) and the highest

Table 1. The dependence of [C*], k_p and weight percentage of fractions of PPs on pretreatment time obtained in stopped-flow polymerization with the donor-free $TiCl_4/MgCl_2$ catalyst.[a)]

Pretreatment time (s)	[C*] mol%	k_p L/mol·s	Fraction[b)] (%) F1	F2	F3	F4
0	5.2	2200	61	24	15	0
0.2	4.0	2730	48	27	23	2
2	3.0	2940	33	36	27	4
10	1.1	3340	44	19	28	9
60	0.54	2700	49	17	23	11

a) The polymerization was carried out with TEA ([Al]=14mmol, Al/Ti=30) in heptane at 30 °C for ca. 0.15s after the pretreatment.
b) Fractionated by TREF, weight fractions: F1 (~20°C), F2 (20~100°C), F3 (100~110°C), F4 (110~140°C).

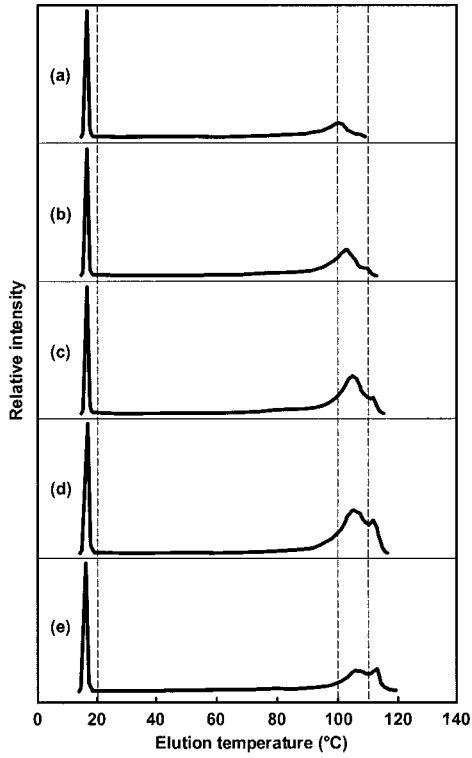


Figure 1. Dependence of TREF profiles on pretreatment time for PPs obtained in stopped-flow polymerization with TEA-pretreated $TiCl_4/MgCl_2$ catalysts, pretreatment time: (a) 0 s (i.e. without pretreatment), (b) 0.2 s, (c) 2 s, (d) 10 s, (e) 60 s.

isospecific sites (**IS$_3$**), respectively. There only exist three kinds of active sites namely **AS**, **IS$_1$** and **IS$_2$** on the donor-free catalyst without pretreatment (Figure 1 and Table 1). Apparently, the absence of electron donor accounts for the existence of large amount of **AS** as well as the non-existence of **IS$_3$** on the catalyst without pretreatment. The most interesting point is to find the emerging of **IS$_3$** on the donor-free catalyst after the pretreatment, which is clearly illustrated in Table 1 and Figure 1. Moreover, the amount of **IS$_3$** is obviously increasing especially up to ca. 10 s of pretreatment. These evidences clearly show **IS$_3$** can also be formed through the interaction between the catalyst and cocatalyst even in the absence of electron donor. The successive formation of **IS$_3$** during pretreatment can be ascribed to the successive transformation of some active sites with lower isospecificity (e.g. **AS**, **IS$_1$** and **IS$_2$**)

into **IS_3** by some secondary bimetallic complexing reactions between the activated titanium species and TEA (or the reaction product diethylaluminumchloride (DEAC)). The **AS** seems to be most easily deactivated up to 2s of pretreatment. The stability of the active sites increases with increasing isospecificity of the active sites probably due to the fact that the active sites with higher isospecificity are usually more sterically hindered and less acidic, thus more over-reduction-resistant.[13] The deactivation of **IS_1** and **IS_2** becomes dominant from 10s and 60s of pretreatment, respectively.

Monoester-Type $TiCl_4$/EB/$MgCl_2$ Catalyst

Stopped-flow polymerizations were conducted using $TiCl_4$/EB/$MgCl_2$ catalyst pretreated by TEA cocatalyst for 0 ~ 180s. The [C*], k_p and weight percentage of four fractions of PPs are shown in Table 2. This catalyst showed lower [C*] and higher k_p, and produced PPs with much lower amount of atactic PP and much higher amount of isotactic PP compared with the donor-free catalyst. There exist four kinds of active sites namely **AS**, **IS_1**, **IS_2** and **IS_3** on this catalyst without pretreatment. Apparently, the presence of internal donor EB accounts for the existence of much larger amount of isospecific sites (including **IS_1**, **IS_2** and **IS_3**) as well as much lower amount of **AS** sites in comparison with the donor-free catalyst. One of the most interesting and important points is the presence of **IS_3** in the EB-containing catalyst even in the absence of pre-treatment, while the results for the donor-free catalyst showed that **IS_3** was

Table 2. The dependence of [C*], k_p and weight percentage of fractions of PPs on pretreatment time obtained in stopped-flow polymerization with the $TiCl_4$/EB/$MgCl_2$ catalyst.[a)]

Pretreatment time (s)	[C*] mol%	k_p L/mol·s	Fraction[b)] (%) F1	F2	F3	F4
0	3.5	3070	4	35	53	8
0.2	2.6	3750	4	21	51	24
2	1.9	4110	4	19	50	27
10	1.1	4580	4	18	47	31
60	0.52	3660	7	22	47	24
180	0.46	3430	-	-	-	-

[a)] The polymerization was carried out with TEA ([Al]=14mmol, Al/Ti=30) in heptane at 30 °C for ca. 0.15s after the pretreatment.
[b)] Fractionated by TREF, weight fractions: F1 (~20°C), F2 (20~100°C), F3 (100~110°C), F4 (110~140°C).

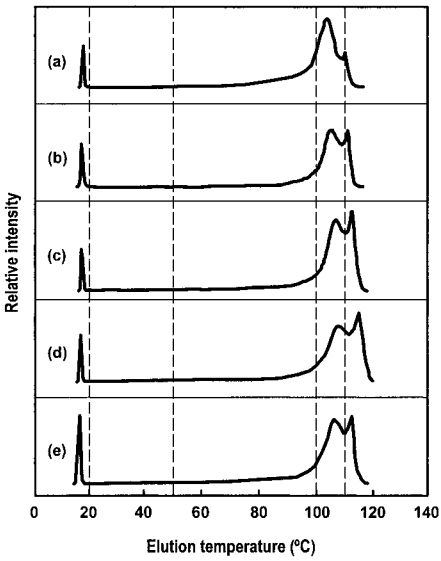


Figure 2.Dependence of TREF profiles on pretreatment time for PPs obtained in stopped-flow polymerization with TEA-pretreated $TiCl_4/EB/MgCl_2$ catalysts, pretreatment time: (a) 0 s, (b) 0.2 s, (c) 2s, (d) 10 s, (e) 60 s.

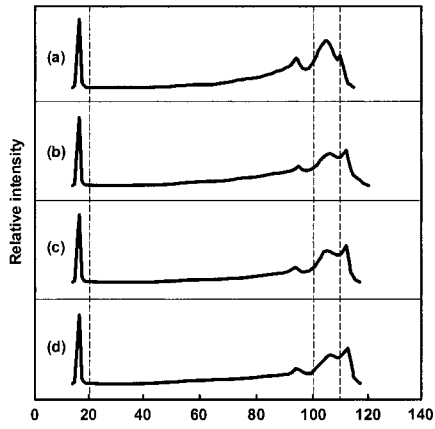


Figure 3. Dependence of TREF profiles on pretreatment time for PPs obtained in stopped-flow polymerization with TEA-pretreated $TiCl_4/DBP/Mg(OEt)_2$ catalysts, pretreatment time: (a) 10 s, (b) 60 s, (c) 180 s, (d) 600 s.

formed only after pre-treatment with the cocatalyst. This is clearly illustrated in Table 2 and also in curve (a) of Figure 2. So far, the main effects of the addition of internal donor EB to the $TiCl_4/MgCl_2$ catalyst can be summarized as follows: (1). to significantly restrain the formation of **AS** sites; (2). to drastically promote the formation of $\mathbf{IS_2}$ sites; (3). to construct some new $\mathbf{IS_3}$ sites. The **AS** seems to be not so easily deactivated during pretreatment compared with the $\mathbf{IS_1}$ and $\mathbf{IS_2}$ on this catalyst, as well as the **AS** on the donor-free catalyst. It means that the **AS** becomes much more stable after addition of donor EB. As for the isospecific active sites, the stability is still increasing with increase of isospecificity. Another most interesting and important point here is the successive increasing of $\mathbf{IS_3}$ sites due to transformation of active sites with lower isospecificity (e.g. **AS**, $\mathbf{IS_1}$ and $\mathbf{IS_2}$) into $\mathbf{IS_3}$ sites up to 10 s of pretreatment derived from bimetallic complexing between the catalyst and

cocatalyst. This active site transformation is especially dominant within 0.2 s of pretreatment (Table 2 and Figure 2). The extraction of EB by TEA from the catalyst surface is thought to initiate from 10s of pretreatment judging from Table 2 and Figure 2 corresponding to the dynamic process of interaction between cocatalyst and internal donor approaching to an equilibrium state as suggested by Sacchi et al.[14]

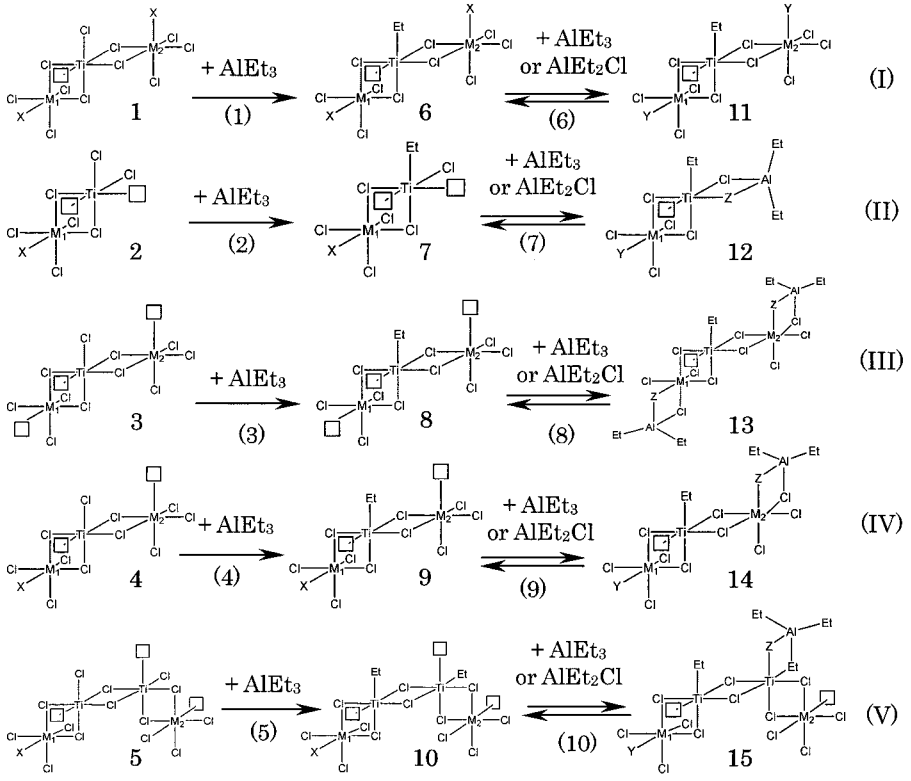
Diester-Type $TiCl_4$/DBP/$Mg(OEt)_2$ Catalyst

Stopped-flow polymerizations were conducted using $TiCl_4$/DBP/$Mg(OEt)_2$ catalyst pretreated by TEA cocatalyst for 0 ~ 600s. The [C*], k_p and weight percentage of four fractions of PPs are shown in Table 3. This catalyst shows an induction period up to 0.2s. The unique feature in terms of slow active sites formation, and slow deactivation may be mainly ascribed to the much stronger electron donating effect from DBP compared with EB. The effect from residual amount of $-OC_2H_5$ ligand should be negligible due to the wash by toluene followed a second $TiCl_4$ treatment during catalyst preparation. There exist four kinds of active sites namely **AS**, $\mathbf{IS_1}$, $\mathbf{IS_2}$ and $\mathbf{IS_3}$ on the catalyst with 2s of TEA pretreatment. The successive formation of $\mathbf{IS_3}$ sites from 10s to 60s of pretreatment can be observed from Table 3 and Figure 3, which can be ascribed to similar active sites conversion through bimetallic complexing. The stability of active sites increases with the increasing isospecificity of the active sites up to 60s of pretreatment. Thereafter, all types of active sites on the catalyst become relatively stable.

Table 3. The dependence of [C*], k_p and weight percentage of fractions of PPs on pretreatment time obtained in stopped-flow polymerization with the $TiCl_4$/DBP/$Mg(OEt)_2$ catalyst.[a)]

Pretreatment time (s)	[C*] mol%	k_p L/mol·s	Fraction[b)] (%) F1	F2	F3	F4
0	-	-	-	-	-	-
0.2	-	-	-	-	-	-
2	0.38	1500	-	-	-	-
10	0.62	2810	24	40	29	7
60	0.41	3730	21	41	23	15
180	0.38	3840	30	32	24	14
600	0.38	3750	34	32	20	14

a) The polymerization was carried out with TEA ([Al]=14mmol, Al/Ti=30) in heptane at 30 °C for ca. 0.15s after the pretreatment.
b) Fractionated by TREF, weight fractions: F1 (~20°C), F2 (20~100°C), F3 (100~110°C), F4 (110~140°C).



Scheme 1. Modified three-sites model in terms of formation and transformation of stereospecific active sites on heterogeneous Ziegler-Natta catalyst, M_1 and M_2: Ti or Mg, and M_1 and M_2 are bound to the catalyst substrate through chlorine bridges; X: Cl, or ED; Y: Cl, Et, or ED; Z: Cl or Et; ⌇: coordination vacancy, for donor-free $TiCl_4/MgCl_2$ catalyst: X=Cl, Y=Cl or Et; for $TiCl_4$/EB/$MgCl_2$ and $TiCl_4$/DBP/$Mg(OEt)_2$ catalyst: X=Cl or ED, Y=Cl or ED or Et.

The extraction of DBP by TEA is thought to occur from 60s of pretreatment judging from Table 3 and Figure 3 and was observed to be much more difficult, slower and in much lower extent than the case with EB. This is consistent with some previous reports that DBP can coordinate much more strongly with catalyst surface compared with EB.[6, 13]

Modified Three-Sites Model

Busico et al. proposed a three-sites model of stereospecific active sites, which provides a reasonable explanation for the formation of stereoblock characteristics of PPs synthesized with Ziegler-Natta catalysts.[15] Whereas, the substantial difference regarding stereospecific roles between catalytic titanium species, alkyl-Al cocatalyst, $MgCl_2$ support and electron donor has not been specified in this model. According to our new understandings, a modified three-sites model of stereospecific active sites (as shown in Scheme 1) for $MgCl_2$-supported Ziegler-Natta catalysts was depicted as follows. The stereospecificity of active sites on the catalyst without TEA pretreatment was thought to originate mainly from the catalyst substrate namely neighboring $MgCl_2$, titanium chloride species and electron donor (ED). The most typical active sites formation reactions are summarized as reactions (1)~(5) in Scheme 1. Before contact with TEA cocatalyst, there exist different kinds of of Ti- precursors (**1~5** in Scheme 1) with different local steric environments. These Ti- precursors (**1~5**) were activated to form active sites (**6~10** in Scheme 1) on the catalyst after the first contact with TEA.[16] The isospecificity of these active sites is thought to be mainly determined by their local steric environments in terms of the number of coordination vacancy, pendant chlorine and ED.[17, 18] Interconversions between these active sites might be induced by ligand migration on the surface of catalyst substrate.[6] **6** with the highest steric hindrance among **6~10** is isospecific active site. For the donor-free catalyst, **6** is mostly composed of multinuclear titanium species (with X=Cl), which was previously speculated to be isospecific active sites by Soga et al.[5, 6] and Busico et al.[7]. The island model of monolayer multinuclear titanium species was further established to describe one typical existing state of titanium species in either donor-free or donor-contained Ziegler-Natta catalysts.[11d] One of the most important points is that **6** with X=Cl is only $\mathbf{IS_2}$, which can not produce PP with the highest isotacticity. This means that the bulkiness of the chlorine atoms on the X positions in **6** is still not enough to construct $\mathbf{IS_3}$. Further contact with alkyl-Al compounds during pretreatment (reaction (6)) gets the isospecific site **11**, which can be a $\mathbf{IS_3}$ when ethyl ligands are introduced into the X positions through ligand exchange between the catalyst and cocatalyst during pretreatment. For donor-contained catalysts, both **6** with X=ED and **11** with Y=ED are $\mathbf{IS_3}$ sites. **7** with the lowest steric hindrance around is **AS** and can not act as isospecific site even when X=ED due to the existence of two coordination vacancies. Further contact with alkyl-Al compounds during

pretreatment (reaction (7)) can transfer **7** (**AS**) into**12** (**IS_3**) through Al-Ti bimetallic complexing reaction. **8** is a syndiospecific site governed by chain-end control mechanism.[15] According to the reports by Doi,[9] Xu et al.[10] and Busico et al.[15], the syndiotactic-sequence-rich stereoblock PP mainly existed in the atactic PP fraction most probably due to the poor stability of **8**. Further contact with alkyl-Al compounds during pretreatment (reaction (8)) can transfer **8** into **13** (**IS_3**) through Al-Ti bimetallic complexing reaction. **9** and **10** (both **IS_1**), which can only produce poorly isotactic PP,[15] can also be converted into **14** (**IS_3**) and **15** (**IS_3**), respectively, by bimetallic complexing reactions (reactions (9) and (10)) during pretreatment. It is worth to mention that **10** is actually a twin-site involving two neighboring **IS_1** centers. The bimetallic complexing during pretreatment might deactivate one center [8, 19] and consequently the other is transferred to **15** (**IS_3**) (reaction (10)). The essential of these reversible bimetallic complexing reactions is to increase local steric hindrance with asymmetry and chirality through bridging with coordination vacancy, pendant chlorine or alkyl ligand around the activated Ti-species. The presence of much bulkier group on the two most important ligand positions on these bimetallic active sites (**12~15**) seems to be crucial for their higher isospecificity compared with those monometallic active sites (**6~10**) derived solely from the catalyst substrate. Extraction of ED by cocatalyst from those ED-contained sites (**6**, **11**, **12**, **13**, **14**, **15** with X=ED or Y=ED) will transfer these isospecific sites into active sites with lower isospecificity.

Conclusion

In this work, we have shown the recent new and precise understanding regarding the stereospecific nature of active sites obtained through the combination of TREF method with stopped-flow technique using heterogeneous Ziegler-Natta catalysts. A modified three-sites model with precise description of the stereospecific nature of various types of active sites stemmed from surface titanium species, Al-alkyl compounds, Mg-compounds and electron donors was proposed. It has been shown that isospecificity of active sites strongly depends on the bulkiness of the ligands situated at the two most important ligand positions for construction of the asymmetry and chirality of the active sites with steric hindrance. The bulkiness of Cl atoms at the positions is not enough for the construction of the highest

isospecific active sites, which is necessary for the introduction of much bulkier ligands e.g. ethyl group or ED through either ligand exchanging or bimetallic complexing reactions. The existence of aspecific sites with two coordination vacancies should be also taken into consideration. These aspecific sites can be possibly transferred into the highest isospecific sites through Al-Ti bimetallic complexing reactions. In general, it can be concluded that there might exist both monometallic active sites and bimetallic active sites in the conventional heterogeneous Ziegler-Natta catalyst systems. The kinds of active titanium species with different chemical structures on the heterogeneous catalysts should be limited, whereas, the non-discrete distribution of isospecificity of active sites could be considered to generate from the numerous types of steric and electronic effects from the surroundings of the active titanium species as well as large number of reversible and dynamic transformation reactions simultaneously occurred on the heterogeneous catalyst surface with multi-components. The modified three-sites model combined with the island model gave rise to much more precise understanding of the real origin of stereospecificity of active sites on $MgCl_2$-supported Ziegler-Natta catalysts.

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