The Role of Two Different Internal Donors (Phthalate and 1,3-Diether) on the Formation of Surface Structure in MgCl$_2$-Supported Ziegler–Natta Catalysts and Their Catalytic Performance of Propylene Polymerization

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ABSTRACT: The role of two different internal donors [a phthalate (diisobutylphthalate) and a 1,3-diether (2,2-diisobutyl-1,3-dimethoxypropane)] on the formation of surface structure in MgCl$_2$-supported Ziegler–Natta catalysts and their catalytic performance of propylene polymerization was investigated by comparing and correlating the catalyst structures and the polymerization characteristics. In the catalyst formation, the 1,3-diether had better affinity for the MgCl$_2$ surface than the phthalate and the 1,3-diether generated the (110) surface more than the (104) surface while the phthalate generated both the (110) and (104) surfaces of MgCl$_2$. With both donors introduced, the (110) and (104) surfaces were generated simultaneously, although the (110) surface was dominant due to the higher affinity via the 1,3-diether. In addition, it seemed probable that the active sites formed on the (110) plane showed isospecific characteristics in the presence of a donor while those formed on the (104) plane could be isospecific regardless of a donor. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40536.

INTRODUCTION

Polypropylene, together with polyethylene, is one of the most widely used plastics because of its good properties at low cost. Currently, MgCl$_2$-supported Ziegler–Natta catalysts are commonly used in the commercial production of polypropylene. Although metallocene catalysts are used a little recently, its usage is limited due to some drawbacks, e.g., high cost and low heat resistance of the resultant polypropylene. For this reason, it is expected that the importance of MgCl$_2$-supported Ziegler–Natta catalysts will continue in the future in the commercial production. Since the discovery of TiCl$_3$ catalyst by Natta, many studies for Ziegler–Natta catalysts have been made. Among them, there were two important breakthroughs in the catalyst development. First, with MgCl$_2$ as a support, the activity of the catalyst was increased dramatically, and second, an internal donor led to a significant increase in the isotacticity of polypropylene. Consequently, a modern MgCl$_2$-supported catalyst usually consists of TiCl$_4$ as an active species and an internal donor as an isotacticity improver, and MgCl$_2$ as a support.

Internal donors are very crucial to catalyst performance, and affect the catalyst reactivity and the polypropylene properties (e.g., isotacticity, molecular weight, and its distribution). Many studies were also attempted to elucidate the role of internal donors. It is well established that internal donors stabilize small MgCl$_2$ crystallites, affect the amount and distribution of TiCl$_4$, and transform poorly isospecific sites to highly isospecific ones. Since the discovery of aromatic monoesters (e.g., benzoates) as the first internal donors, there have been many efforts to develop new internal donors such as phthalates,[1] 1,3-diethers,[2–4] succinates,[5–7] malonates,[8–10] maleates,[11] glutarates,[12] and ketoesters.[13] Among them, the most successful are phthalates, discovered in the early 1980s and the catalysts containing a phthalate have been widely used for the commercial production. Catalysts containing a 1,3-diether also have drawn attention due to unique characteristics such as higher activity and hydrogen response in polymerization, and narrower molecular weight distribution and higher isotacticity in the resultant polypropylene, compared with phthalate-contained catalysts.[14–22]
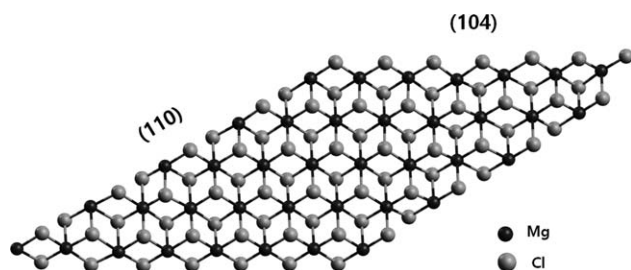
Figure 1. Schematic representation of MgCl₂ monolayer having the (110) and (104) planes.

An anhydrous MgCl₂ (α-MgCl₂) has a cubic close-packed stacking (ABCABC) of double chlorine layers with interstitial Mg²⁺ ions in sixfold coordination. In the catalyst preparation, α-MgCl₂ is converted to an activated MgCl₂ by a mechanical or a chemical treatment. The activated MgCl₂ exhibits a disordered structure arising from the translation and rotation of the structural Cl-Mg-Cl layers with respect to one another that destroy the crystal order in the stacking direction. The most stable surface of the activated MgCl₂ is the (001) basal plane obtained by cleaving the MgCl₂ stacking.[23] However, neither internal donors nor TiCl₄ can be adsorbed at the (001) plane because the plane is coordinatively saturated.[24,25] The (110) and (104) lateral planes (Figure 1) have coordinatively unsaturated Mg²⁺ ions, four- and five-fold coordinated Mg²⁺ ions, respectively (i.e., the two planes can accept internal donors or TiCl₄).[26] Recent studies using new techniques, e.g., computational chemistry and detailed characterization, have reported how internal donors and TiCl₄ stabilized MgCl₂ surfaces. A study using density functional theory (DFT) calculations showed that MgCl₂ had the (001) and (104) planes at crystallographic equilibrium, but activated MgCl₂ could also have the (110) plane if internal donors or TiCl₄ were present.[23] Mori et al.[27] observed with high-resolution transmission electron microscopy, that lateral planes of mechanically activated MgCl₂ were predominantly composed of the (110) and (104) planes. Andoni et al.[28] reported preferential growth of MgCl₂ crystal along the (110) direction in the presence of 1,3-diethers, while the growth occurred along both the (110) and (104) directions in the presence of phthalates. Several studies using DFT calculations supported the idea; the (110) termination of MgCl₂ crystal prevails over (104) termination in the presence of ether adsorbates.[29,30] It was also reported that phthalates could be adsorbed at both the (104) and (110) planes of MgCl₂ with bridging or chelating forms; while 1,3-diethers or alkoxysilanes could be adsorbed only at the (110) plane with chelating forms because the distance between their two oxygens was shorter than those of phthalates.[29,31]

TiCl₄ can also be adsorbed at the (110) and (104) MgCl₂ planes, which have coordinatively unsaturated Mg²⁺ ions. It was reported that TiCl₄ coordinated as a mononuclear species at the (110) plane and as a dinuclear species at the (104) plane due to the coordinative saturations[32]; the mononuclear species on the (110) plane could form an aspecific active site while the dinuclear species on the (104) plane could form an isospecific active site because of the structural resemblance of the TiCl₃ catalysts. However, a recent study using DFT calculations reported that TiCl₄ preferentially was adsorbed as mononuclear species on the (110) plane and the coadsorption of donors with it was energetically viable.[33]

In polymerization, the MgCl₂-supported catalyst can be changed in terms of the composition of the catalyst because the catalyst is not used alone but with an alkylaluminum and an external donor.[34] It is well known that alkylaluminums induce Ti-R bonds, which are considered as insertion sites of propylene, by alkylations of TiCl₄ on the catalyst and remove impurities during polymerization. Alkylaluminums can also have a reaction with internal donors, especially with esters, and they extract the internal donors from the catalyst. It is believed that external donors are adsorbed at the sites of internal donors, and play a role to keep the isospecific characteristics of the catalyst.

As described above, the MgCl₂-supported Ziegler–Natta catalysts are very complex systems. Many factors can affect the catalytic active sites in the catalyst formation and polymerization. For this reason, the interpretation for the catalyst characteristics should be approached from an overall perspective. The recent studies using computational chemistry and detailed characterization give useful conclusions on the mechanism in the catalyst formation. However, there are little experimental evidences supporting the conclusions. In the present work, the role of two different internal donors [a phthalate (diisobutylphthalate) and a 1,3-diether (2,2-diisobutyl-1,3-dimethoxypropane)] on the formation of surface structure in MgCl₂-supported Ziegler–Natta catalysts and their catalytic performance of propylene polymerization was investigated based on a practical experimental data. For the purpose, the catalysts with a single donor or two donors were prepared and their compositional and structural differences were compared. Finally, the correlation between the catalytic performance and the compositional and structural differences was provided.

EXPERIMENTAL

Materials
As internal donors, diisobutylphthalate (99%) was supplied by Aldrich and 2,2-diisobutyl-1,3-dimethoxypropane was synthesized by the method in the previous study.[35] Anhydrous magnesium chloride (99.3%) was supplied by Okada Chemicals and 2-ethylhexanol (99.6%) was supplied by Aldrich. Titanium tetrachloride (99%) was obtained by Yakuri Pure Chem. n-hexane (95%, Aldrich), n-heptane (99%, Aldrich), n-decane (98%, Samchun), toluene (99.8%, Aldrich), and xylene (98.5%, Aldrich) were used after purification with a purification system (Pure Solv, Innovative Technology). Propylene (99.6%) and hydrogen (99.99%) were supplied by Lotte Chemical and used after passing a purification column filled with molecular sieve 4A. Triethylaluminum (96.0%) was obtained from Gulbransen and cyclohexylmethyldimethoxysilane (99.6%) was obtained from Shin-Etsu.

Preparation of Catalysts
The preparation was carried out using a jacketed glass reactor equipped with stirrer and all procedures were performed under nitrogen atmosphere. In a 300-mL glass reactor, anhydrous magnesium chloride (9.52 g, 100 mmol), n-decane (40 mL),

Table I. The Compositions of the Prepared Catalysts

Catalyst	Used donor[a] (mol mol^{-1}-Mg)		Catalyst composition (mol mol^{-1}-Mg)		
	Phthalate[b]	Diether[c]	Ti	Phthalate[b]	Diether[c]
Pcat	0.15	–	0.055	0.054	–
PEcat-1	0.15	0.05	0.061	0.052	0.033
PEcat-2	0.10	0.10	0.061	0.034	0.054
PEcat-3	0.05	0.15	0.065	0.013	0.074
Ecat	–	0.15	0.066	–	0.100

[a] The quantity of internal donor used during catalyst preparation.
[b] Diisobutylphthalate.
[c] 2,2-Diisobutyl-1,3-dimethoxypropane.

and 2-ethylhexanol (55 mL, 350 mmol) were added successively. The mixture was heated to 135°C under stirring and held at that temperature for 1 h; a clear solution was obtained. The clear solution was cooled down to 70°C and then diisobutyl phthalate or/and 2,2-diisobutyl-1,3-dimethoxypropane (refer Table I for the donors used) was added to the clear solution. The clear solution was held at 70°C for 10 min and was cooled down to room temperature. In another 500-mL glass reactor, n-hexane (70 mL), toluene (70 mL), and titanium tetrachloride (88 mL, 800 mmol) were added successively and cooled down to −20°C. The clear solution containing magnesium chloride was added to the mixture containing titanium tetrachloride during 2 h at −20°C. The mixture was heated to 75°C at a rate of 0.5°C min^{-1} and held at that temperature for 2 h. Solid catalyst was formed during the procedure. The supernatant was removed by siphoning and titanium tetrachloride (44 mL, 400 mmol) and toluene (150 mL) were added. Next, the reactor temperature was ramped up to 110°C and held for 1 h. After that, the supernatant was removed and the solid catalyst was washed and siphoned with n-hexane (200 mL) at 70°C three times. The solid catalyst was dried under nitrogen at room temperature.

Post-Treatment with Alkylaluminum and External Donor
In a 300-mL glass reactor, a catalyst prepared in the previous sections (2.0 g) and n-hexane (100 mL) were added successively at room temperature. Next, triethylaluminum (10 mmol as Al) and cyclohexylmethyldimethoxysilane (4 mmol as Si) were fed to the reactor. The reactor temperature was heated to 50°C and maintained during 10 min. After that, the supernatant was removed and the solid catalyst was washed and siphoned with n-hexane (100 mL) at 50°C three times. The solid catalyst was dried under nitrogen at room temperature.

Characterization of Catalysts
The content of titanium was measured by UV–vis spectrometry (UV-2450, Shimadzu) after the solid catalyst was fully dissolved in acidic water. The content of magnesium was measured by X-ray fluorescence (ZSX Primus-II, Rigaku) and the content of internal electron donor was measured by gas chromatography (HP 6890 Plus, Hewlett Packard) after the solid catalyst was fully dissolved in acidic methanol/toluene. The crystalline

structure of catalysts was obtained by X-ray difftractometer (Empyrean, PANalytical).

Polymerization
Polymerization was carried out using a reaction system with a 2-L autoclave and all procedures were performed under nitrogen atmosphere. First, 10 mL of n-decane was fed in the reactor at room temperature and then triethylaluminum (2 mmol), cyclohexylmethyldimethoxysilane (0.2 mmol), and catalyst (0.005 g) was introduced successively in the reactor. Nearly 1 L of hydrogen and 500 g of liquid propylene was added in the reactor at room temperature. The reactor temperature was ramped up to 70°C during ~10 min and polymerization was maintained at the temperature during 1 h. After that, the unreacted propylene and hydrogen were vented outside the reactor. The polymerized solid was separated and dried in a vacuum oven at 70°C during 5 h.

Characterization of Polymers
Molecular weight and molecular weight distribution of polymer were measured by gel permeation chromatography (PL-GPC220, Polymer Laboratories) at 160°C with 1,2,4-trichlorobenzene as a solvent. Data were calibrated using polystyrene standards (M_w 10,000–12,000,000, Polymer Laboratories) and polypropylene standards (M_w 10,000–200,000, American Polymer Standards). Isotacticity was measured indirectly by measuring xylene soluble fraction of polymer. The obtained polymer was dissolved fully in xylene at 135°C and cooled down to room temperature. Xylene insoluble part was obtained by drying the precipitated solid; xylene soluble part was obtained by evaporating xylene from the remaining solution.

RESULTS AND DISCUSSION
Composition of the Prepared Catalysts
Five kinds of catalysts were prepared while changing types and amounts of two internal donors, a phthalate (diisobutylphthalate) and a 1,3-diether (2,2-diisobutyl-1,3-dimethoxypropane). Table I shows the results of compositional analysis of the prepared catalysts. First, comparing two catalysts having a single donor (Pcat and Ecat), the Ti contents were slightly different; the Ti content of Ecat (0.066 mol mol^{-1}-Mg) was slightly higher than that of Pcat (0.055 mol mol^{-1}-Mg). There was a significant difference in the donor contents; the 1,3-diether content of Ecat (0.100 mol mol^{-1}-Mg) was much higher, almost 1.9 times on a molar basis, than the phthalate content of Pcat (0.054 mmol mol^{-1}-Mg). In other words, on average, 1 molecule of the phthalate is attached per 18.5 molecules of MgCl$_2$ in Pcat while 1 molecule of the 1,3-diether is attached per 10.0 molecules of MgCl$_2$ in Ecat. This indicates that the 1,3-diether has better affinity for the MgCl$_2$ surface than the phthalate, during the catalyst formation.

In case of the catalysts (PEcat-1, PEcat-2, and PEcat-3) which were prepared with both donors simultaneously, the Ti and Mg contents in the three catalysts were similar to each other, and not significantly different with those of the catalysts having each donor. All the catalysts had significant contents of both donors. It can be inferred from these results that both donors are adsorbed together to the MgCl$_2$ surface, and that one donor is
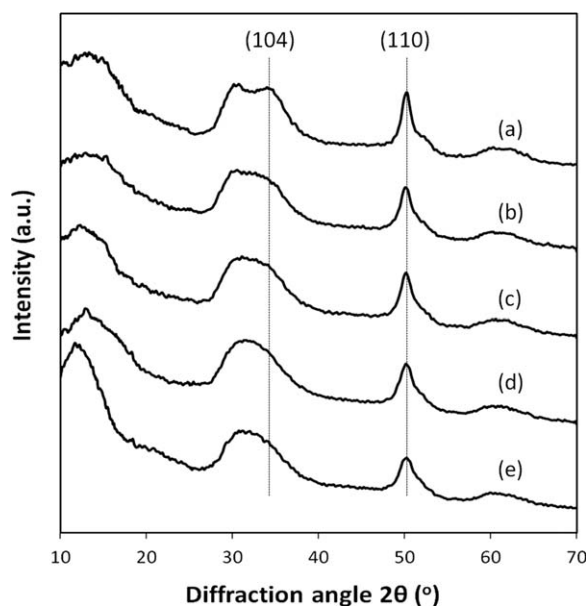
Figure 2. XRD patterns of the prepared catalysts: (a) Pcat, (b) PEcat-1, (c) PEcat-2, (d) PEcat-3, and (e) Ecat.

not adsorbed exclusively to the MgCl$_2$ surface. However, the 1,3-diether content was higher than that of phthalate, if the donors are used with the same amounts during the preparation. These results are consistent with the results of the catalysts having each donor; the 1,3-diether has better affinity for the MgCl$_2$ surface than the phthalate. The total contents of the donors were in the range of 0.085–0.088 mol mol^{-1}-Mg, which were between those of Pcat and Ecat. From the results, it can be expected that the catalysts having both donors show the characteristics between those of the catalysts having each donor.

MgCl$_2$ Structure of the Prepared Catalysts
According to a study using X-ray diffraction (XRD), the activated MgCl$_2$ usually exhibits an XRD pattern having three broad peaks centered around 15°, 32°, and 50° (corresponding to (003), (101), and (110) reflections, respectively).[36] Another study reported that the broad peak centered at 32° could be fitted to three peaks, at 30.0°, 32.0°, and 34.9°.[37] The peak at 30.0° corresponds to the overlap of the peaks from the (012) and (006) planes of α-MgCl$_2$ and the (002) plane of the β-MgCl$_2$. The peak at 32.0° is from the (011) plane of β-MgCl$_2$ and the peak at 34.9° is from the (104) plane of α-MgCl$_2$.

Figure 2 shows the XRD patterns of the prepared catalysts. All the catalysts had three broad peaks in the ranges of 10°–20°, 27°–37°, and 48°–53°. However, there were clear differences between the patterns of the two catalysts having each donor. Pcat (based on phthalate) had a distinct peak near 34° and a little sharper peak near 50° compared with Ecat (based on 1,3-diether). Referring to the studies above, the peaks near 34° and 50° can be assigned to the (104) and (110) reflections, respectively. In the XRD pattern, both the (104) and (110) reflections of MgCl$_2$ were observed clearly in Pcat while the (104) reflection was not observed clearly in Ecat. During the catalyst formation, one of the most important roles of an internal donor is to stabilize the growing MgCl$_2$ crystallites. Therefore, it

seems reasonable to conclude that the phthalate stabilize both the (104) and (110) surfaces of MgCl$_2$ while the 1,3-diether stabilize the (110) surface more than the (104) surface. These results are also consistent with those of other recent studies reported that MgCl$_2$ crystals grow preferentially along the (110) direction in the presence of 1,3-diethers; while they grow along both the (110) and (104) directions in the presence of phthalates.[28,30] In addition, Ecat had a broader peak around 50° than Pcat and this implies that Ecat has smaller crystallites having the (110) surface. It is in agreement with the results of the donor contents that the 1,3-diether content of Ecat is higher than the phthalate content of Pcat.

In case of the catalysts having both donors, all the catalysts had one broad peak in the range of 27°–37° but did not have a separate peak near 34° clearly unlike Pcat. The broadness of the peak changed with the 1,3-diether content; the higher the content, the narrower the peak. In particular, the XRD pattern of PEcat-3 (which had the highest 1,3-diether content) was very similar to that of Ecat based on the 1,3-diether only. From the results, it is believed that the surface structure of the catalysts prepared with both donors is a combination of the structures of Pcat and Ecat, which has both the (110) and (104) surfaces. However, the results clearly show that the 1,3-diether influence much more on the surface structure of the catalysts because of its higher affinity for the MgCl$_2$.

Influence of Alkylaluminum on Composition and Structure of Catalysts
In propylene polymerization, a catalyst is not used alone but with an alkylaluminum and an external donor. It is well known that phthalates can react easily with alkylaluminums and can be extracted from catalysts; while 1,3-diethers do not react easily with alkylaluminums and remain in the catalysts. The prepared catalysts were treated with an alkylaluminum (triethylaluminum) in the presence of an external donor (cyclohexylmethyldimethoxysilane). Table II shows the results of compositional analysis for those treated catalysts. For Pcat after the treatment, most of the phthalate was extracted from the catalyst (0.054 → 0.002 mol mol^{-1}-Mg). On the other hand, the 1,3-diether content of the treated Ecat was little changed; having been retained in the catalyst (0.100 → 0.099 mol mol^{-1}-Mg). In the results of

Table II. The Compositions of the Catalysts After Treatment with Triethylaluminum and Cyclohexylmethyldimethoxysilane

Post-treated catalyst	Catalyst composition (mol mol^{-1}-Mg)			
	Ti	Phthalate[a]	Diether[b]	Silane[c]
Pcat	0.047	0.002	–	0.033
PEcat-1	0.045	0.002	0.029	0.040
PEcat-2	0.045	0.001	0.048	0.039
PEcat-3	0.052	0.001	0.071	0.035
Ecat	0.053	–	0.099	0.030

[a] Diisobutylphthalate.
[b] 2,2-Diisobutyl-1,3-dimethoxypropane.
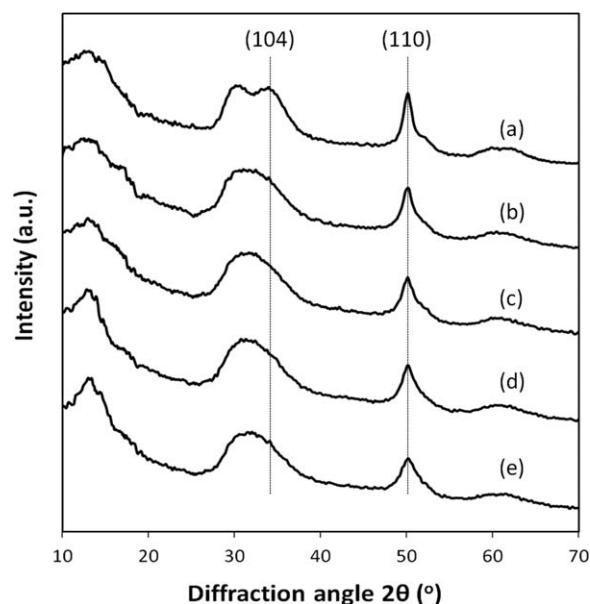[c] Cyclohexylmethyldimethoxysilane.

Figure 3. XRD patterns of the catalysts after treatment with triethylaluminum and cyclohexylmethyldimethoxysilane: (a) Pcat, (b) PEcat-1, (c) PEcat-2, (d) PEcat-3, and (e) Ecat.

the catalysts having both donors, the phthalates were also mostly extracted from the catalysts; while the 1,3-diethers were mostly retained. The results confirm the reactivity difference of both donors toward alkylaluminums. In addition, the external donor (cyclohexylmethyldimethoxysilane) was observed in a considerable amount in all the catalysts. In case of the catalysts containing phthalates, it is expected that the external donor is adsorbed on the extracted site of the phthalate and takes over the role to form a isospecific site. For Ecat, it is inferred that the external is adsorbed adsorbs on another site rather than the site of the 1,3-diether.

The XRD patterns of the treated catalysts are shown in Figure 3. The results showed that the catalyst structure did not change significantly after the treatment; the treated Pcat had still a distinct peak near 34° while the treated Ecat had only a broad

peak. The treated catalysts prepared with both donors had also only a broad peak in the range of 27°–37° but the peak broadness was slightly narrower compared with that of the original catalysts.

Catalytic Performance in Propylene Polymerization

The results of propylene polymerization for the prepared catalysts are given in Table III. The polymer formed using Pcat without an external donor had relatively low molecular weight and low isotacticity (high xylene solubles). This confirms that an external donor is crucial for a phthalate-based catalyst to give high isotactic polypropylene. As shown in Table II, most of the phthalate in Pcat was extracted in the condition of polymerization. Thus, the extracted phthalate cannot continue to play its role as an electron donor which gives an electronic and steric effect on an active site. However, although the polymer had high xylene solubles (28.2 wt %), it showed a certain level of isotacticity. Therefore it is believed that isotactic sites not related with the phthalate exist in the Pcat. It was reported that $TiCl_4$ coordinated as a mononuclear species at the (110) plane showing aspecific characteristics and as a dinuclear species at the (104) plane showing isospecific characteristics.[32] On the other hand, recent studies using DFT calculations reported that $TiCl_4$ was adsorbed as a mononuclear species on the (110) plane, because of the energetic preference.[33,38,39] However, according to another study using DFT calculations, $TiCl_4$ could have a coordination of a dinuclear species on the (104) zip coordination mode, which was energetically preferential, besides the original dinuclear species on the (104) plane of one Cl-Mg-Cl layer.[40] Moreover, Andoni et al.[30] reported that polypropylene was produced on the (104) plane using SEM-EDX mapping. Thus, it is possible that Pcat has isospecific sites induced from the dinuclear species of $TiCl_4$ at the (104) plane, which is not related with the phthalate. In addition, it is presumed that the active site formed on the (110) plane of Pcat gives an aspecific characteristic without an external donor in polymerization. On the contrary, in polymerization with the external donor, Pcat showed higher activity and produced a polypropylene having higher molecular weight and isotacticity (low xylene solubles) compared with the case without the external donor. Especially,

Table III. The Results of Propylene Polymerization for the Prepared Catalysts

Catalyst	External donor	Activity (kg g^{-1}-cat)	M_w (g mol^{-1})	MWD (M_w/M_n)	Xylene solubles (wt %)
Pcat	–	22	126,400	6.5	28.2
	CHMMS[a]	32	266,800	6.8	3.0
PEcat-1	–	36	160,200	6.0	11.9
	CHMMS[a]	38	235,000	5.9	2.3
PEcat-2	–	36	170,800	5.4	7.5
	CHMMS[a]	42	229,600	5.8	3.9
PEcat-3	–	38	180,000	5.6	5.0
	CHMMS[a]	33	213,900	5.5	2.2
Ecat	–	46	184,800	5.4	4.5
	CHMMS[a]	38	207,700	4.6	2.5

[a] Cyclohexylmethyldimethoxysilane.

the molecular weight and isotacticity were dramatically increased. Thus, it is expected that the active site induced with the external donor shows the characteristics having high reactivity and producing polypropylene having high molecular weight and isotacticity. It was reported that alkoxysilanes could be adsorbed only at the (110) plane of $MgCl_2$ due to the short distance between their two oxygens.[29,31] In short, it can be inferred from these data that the isospecific sites of Pcat, in polymerization with the external donor, consist of the sites formed with external donors on the (110) plane and the sites formed not related with donors on the (104) plane.

By the way, Ecat produced polypropylene with considerably high molecular weight and isotacticity without an external donor. In the presence of the external donor, the catalytic performance was not significantly changed although the activity was slightly lower compared with that without the external donor. This implies that the active sites of Ecat are little changed in the condition of polymerization because the catalyst composition and structure are little changed. In addition, Ecat showed better activity and hydrogen response (lower molecular weight) and produced polymer having a narrower molecular weight distribution than did Pcat. These characteristics are typical for catalysts containing a 1,3-diether and are in agreement with those reported in former studies.[14–16,35] It was found from the results that the isospecific sites of Ecat were the sites formed with the 1,3-diether on the (110) plane.

In case of the catalysts having both donors, the characteristics of the catalysts in polymerization were between those of Pcat and Ecat (e.g., activity, hydrogen response, molecular weight and its distribution, and isotacticity). However, the characteristics were more close to that of Ecat as expected from the results of the catalyst structures. For Example, polypropylene made using PEcat-3, which had the highest 1,3-diether content, showed properties very similar to polypropylene formed using Ecat.

CONCLUSIONS

Five kinds of catalysts having a phthalate (diisobutylphthalate) or/and a 1,3-diether (2,2-diisobutyl-1,3-dimethoxypropane) were compared in terms of the catalyst structures and their catalytic performance. The 1,3-diether had better affinity for the $MgCl_2$ surface than the phthalate and the 1,3-diether generated the (110) surface more than the (104) surface while the phthalate generated both the (110) and (104) surfaces of $MgCl_2$ during the catalyst formation. With both donors introduced, they were adsorbed together at the $MgCl_2$ surface; consequently, the (110) and (104) surfaces were generated simultaneously, although the (110) surface was dominant due to the higher affinity of the 1,3-diether. After the treatment with an alkylaluminum and an external donor, most of the phthalate was extracted from the catalysts while the 1,3-diether was retained in the catalysts. For that reason, the external donor had a significant effect on isotacticity in polymerization in case of the catalysts having phthalate internal donor. In view of the XRD patterns and catalytic performance, it was likely that the isospecific sites of the catalysts having the phthalate as an internal donor consisted of the sites formed with external donors on the

(110) plane and the sites formed not related with internal or external donors on the (104) plane. On the other hand, it was expected that the isospecific sites of the catalysts having the 1,3-diether were the sites on the (110) plane.

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