

Characterization of phthalate internal donor in MgCl_2 supported Ziegler-Natta catalyst by solid state ^{13}C NMR

Masayoshi Saito^{*1}, Toshiya Uozumi¹, Masahide Murata¹, Takuo Kataoka¹, Riichiro Chujo²

¹Research and Development Division, Toho Titanium Co., LTD., 3-3-5, Chigasaki Chigasaki-City, Kanagawa, 253-8510, Japan

²Professor Emeritus at Tokyo Institute of Technology, 2-12-1, Ookayama Meguro-ku, Tokyo, 152-8550, Japan

Received: 24 December 2021, Accepted: 12 March 2022

ABSTRACT

Ziegler-Natta catalyst for propylene polymerization, which TiCl_4 and di-alkyl phthalate were supported on MgCl_2 , was analyzed by solid state ^{13}C NMR. It was confirmed that the spin-lattice relaxation time (“relaxation time” hereafter) of carbonyl group in phthalate was shortened with increasing measurement temperature as a general manner because of the enhancing of molecular mobility at high temperature. The degree of the relaxation period reduction with temperature was influenced by the alkyl group size in phthalate molecule; the larger alkyl group showed a greater shorting of the relaxation period. A short relaxation time should suggest a weak interaction between the phthalate molecule and the MgCl_2 support surface. The change in catalytic performance was discussed by the active site formation mechanism involving the phthalate removal step. **Polyolefins J (2022) 9: 117-127**

Keywords: Ziegler-Natta catalyst; propene polymerization; solid-state ^{13}C NMR; spin-lattice relaxation time; carbonyl(C=O) motion in phthalate molecule.

INTRODUCTION

The Ziegler-Natta catalyst, invented in 1950, opened the polyolefin field [1,2,3] and the progress of catalyst technology has greatly contributed to the market growth and the expansion of the plastic industries.

The propylene polymerization catalyst, which is currently used world-wide, is composed of Ti species and “internal” electron donor compound such as di-alkyl

phthalate supported on the MgCl_2 solid surface. As the catalytic performances are strongly influenced by the kind of internal donor compound, many studies have been performed in order not only to know the interaction between internal donor compound and MgCl_2 surface, but to understand the role of internal donor in the polymerization reaction mechanism [4-30]. Terano et.al.

*Corresponding Authors - E-mail: m-saito@toho-titanium.co.jp

investigated the ethyl benzoate (EB) donor supporting (coordination) mode on the MgCl_2 surface by IR and TG-DTA analyses. They concluded that TiCl_4 and EB are supported on MgCl_2 separately [24,25].

NMR of below 10 tesla of magnetic field, which shall be so-called general purpose level instrument, has been applied to study the structural fashion of internal donor compound in Ziegler-Natta catalyst solid.

For instance, Abis et. al. analyzed the nature of supported ethyl benzoate (EB) molecule, in which the sample was prepared by co-grinding of EB and MgCl_2 , by a solid-state ^{13}C NMR. They confirmed that EB was connected on MgCl_2 via strong chemical bond [31].

Terano et. al. also studied on EB supported on MgCl_2 by the solid-state ^{13}C NMR. They prepared the catalyst samples from MgCl_2 and TiCl_4 -EB complex by changing the mechanical co-grinding time. They confirmed that there was interaction between EB and MgCl_2 [32]. This indicates that TiCl_4 -EB complex is decomposed and EB molecule moved to the MgCl_2 surface during the mechanical grinding.

As briefly reviewed above, the solid-state ^{13}C NMR has been applied to characterize MgCl_2 supported Ziegler-Natta catalysts. Many prior studies have pointed out the presence of chemical interaction between internal donor compound and the MgCl_2 support surface. Looking at the actual polymerization catalyst system, however, the alkyl aluminum and external donor such as alkoxy silane are required to initiate the polymerization reaction.

And it is known that the replacing of internal donor by external donor takes place under the presence of alkyl aluminum [33]. This suggests that the strength of coordination of internal donor to the MgCl_2 surface shall potentially be a control factor how easy to proceed the active site formation, resulting in the changing of catalytic performance.

Regarding the interaction between the internal donor and the MgCl_2 surface, Sormunen et.al. conducted the solid-state ^{13}C NMR analyses with the catalysts containing di-alkyl phthalate internal donor, which is currently one of the major industrial catalyst systems [34]. They conducted the chemical shift assignment of C=O (carbonyl group) in di-isobutyl phthalate (DiBP) which was complexed with the TiCl_4 or MgCl_2

surface. They also obtained fundamental data of the dipole-dipole interaction (T1 ρ) of C=O. The C=O relaxation times (T1 ρ) in TiCl_4 / DiBP complex and $\text{MgCl}_2/\text{TiCl}_4/\text{DiBP}$ were 75ms and 39ms, respectively. The different relaxation times suggested DiBP should be interacted with MgCl_2 in the three components material of $\text{MgCl}_2/\text{TiCl}_4/\text{DiBP}$.

And the long relaxation time in DiBP supported on MgCl_2 indicated that DiBP molecule should electrochemically be constrained by the MgCl_2 surface. Although this work demonstrated the effectiveness of solid-state ^{13}C NMR analyses, T1 ρ might not be the sufficient parameter to quantitatively detect of relatively long relaxation time case such as C=O.

We applied T1 measurement instead of T1 ρ in order to improve the reliability of the relaxation time. It was found that the phthalate having long alkyl group showed short relaxation time, suggesting weak chemical coordination on the MgCl_2 surface. It was also found that such a phthalate molecule has a high catalyst performance. This behavior might potentially suggest that the high performance active sites tend to easily be formed from the weakly coordinated phthalate on the surface.

In our previous work, however, the solid-state ^{13}C NMR measurement was carried out at room temperature [32,35]. On the other hand, the practical condition of propylene polymerization is higher temperature, for instance, typically at 70°C. In order to understand the relationship between the electrochemical nature of phthalate internal donor and the catalytic performance, the effect of temperature on the phthalate molecule mobility on the catalyst surface needs to be investigated.

In the present work, the detail investigation of the temperature dependence of C=O relaxation time (T1) of phthalate internal donors was conducted. In addition, the results were discussed from the view point of the active site formation mechanism by taking into account of the order of the catalyst performances.

EXPERIMENTAL

Preparation of catalysts

All preparation process was conducted under nitrogen

inert atmosphere.

TiCl₄-di-alkyl-phthalate Complexes

Three complexes were prepared by changing of phthalate compounds of di-ethylphthalate (DEP), di-n-butyl-phthalate (DBP), and di-n-octyl-phthalate (DOP). The structures of phthalates are illustrated in Figure 1.

1000 mL of three-necked flask was used for the reaction by connecting mechanical agitation and a dropping funnel. 200mL of n-heptane and 0.5mol of di-alkyl-phthalate were charged to the flask and the solution was heated up at 40°C. To the solution, 0.5mol of TiCl₄ was slowly fed dropwise.

After the completion of TiCl₄ feeding, the reaction continued at 40°C for 2 h. The precipitated solid was washed with n-heptane. A yellowish powder was obtained by vacuum drying.

The powder compositions was determined based on Ti content measurement as follows; TiCl₄:DEP=1:1.02, TiCl₄:DBP=1:1.09, and TiCl₄:DOP=1:1.05, respectively.

MgCl₂/TiCl₄-phthalate complex catalysts

315 mmol of MgCl₂ (surface area determined by BET method was 11 m²/g), and 45mmol of TiCl₄-di alkyl phthalate complex prepared above were introduced to the stainless vibration mill pot in which 50 bolls of 25mmφ was charged. 20 h co-grinding was performed at room temperature. 20 g of the co-grinding solid was transferred to a 300 mL volume glass flask with mechanical agitation. The solid was washed with n-heptane at 40°C until the free TiCl₄ actually disappeared. The solid catalyst was obtained after drying under vacuum.

Preparation of a reference sample

A reference sample was prepared by mechanical grinding of MgCl₂ with DBP. 315 mmol of MgCl₂ (surface area determined by BET method was 11 m²/g) and 30 mmol of DBP were introduced to

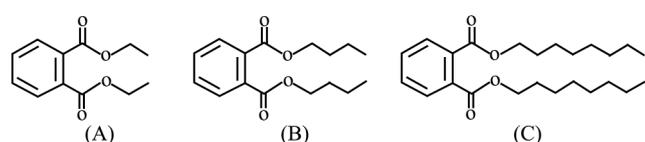


Figure 1. Chemical structures of (A) Diethylphthalate (DEP), (B) Di-n-butylphthalate (DBP) and (C) Di-n-octyl phthalate (DOP).

the stainless vibration mill pot in which 50 bolls of 25mmφ was charged. 20 h co-grinding was performed at room temperature. 20 g of the co-grinding solid was transferred to a 300 mL volume glass flask with mechanical agitation. The solid was washed 10 times with 200 mL of n-heptane at 40°C. The solid reference sample was obtained after drying under vacuum.

Characterization of catalysts

Ti content of the solid material was determined by an ordinarily colorimetric analysis. From the absorbance at 410 nm of Ti-H₂O₂ complex in acidic aqueous solution, Ti content was determined by the calibration. To determine DEP, DBP and DOP content, the catalyst solid was decomposed by hydrochloric acid and sulfuric acid. Organic components were extracted by toluene. DEP, DBP and DOP content was determined by measuring of gas-chromatography of the toluene solution. The compositions of three catalysts prepared are listed in Table 1.

Bulk polymerization of propylene

To 2000 mL volume stainless steel auto clave, 20 mL of n-heptane, 1.32mmol of triethyl aluminum, and 0.132 mmol of cyclo-hexyl methyl di-methoxy silane (CMDMS) as the external donor, and the prescribed amount of catalyst solid (as 0.00264 mmol of Ti) were charged. Liquid propylene (1.0 L) and H₂ (1.5 NL) were fed to the reactor. After 5min of pre-polymerization at 20°C, the temperature rose quickly to the polymerization temperature. Three different polymerization temperatures of 20°C, 50°C, and 70°C were chosen. Polymerization reaction was performed for 1 h. The polymerization was terminated by cooling the temperature to room temperature and purging of propylene gas. The produced polypropylene powder

Table 1. Results of catalyst composition.

Sample	Ti content ^(b) wt%	ID ^(c) content ^(d) wt%
Reference sample (MgCl ₂ /DBP) ^(a)	-	14
MgCl ₂ /TiCl ₄ -DEP complex catalys ^(a)	2.4	10
MgCl ₂ /TiCl ₄ -DBP complex catalys ^(a)	1.9	14
MgCl ₂ /TiCl ₄ -DOP complex catalys ^(a)	2.1	14

(a) co-grinding time for 20h.

(b) Determined by UV.

(c) Internal donor.

(d) Determined by GC.

was collected from the reactor.

Evaluation of isotacticity of polypropylene

4 g PP and 200 mL of p-xylene were charged into a 200 mL volume round bottom flask. The polymer was dissolved under boiling temperature of p-xylene for 2 hours. After cooling of the solution for 1 h at 23°C, the precipitated PP was filtrated. p-Xylene solvent of the filtrate was evaporated and the fraction of p-xylene solution was determined from the amount of polymer remaining. In this report, the isotacticity index (X.I.: p-xylene insoluble weight fraction) was defined by Equation (1).

$$X.I. (wt\%) = 100 - \text{weight fraction of p-xylene soluble} \quad (1)$$

Determination of the spin-lattice relaxation time [36] of C=O in phthalate

Solid-state ^{13}C NMR measurement was conducted with an ECA 400 (JEOL Ltd.) attached MAS instrument. Tocha method [37] was applied for the measuring mode of the spin-lattice relaxation time. The detail operation conditions were as follows; CP contact time was 2.0 to 5.0 ms, the repeat time was 15 s, τ value was in the range of 0.10 to 100 s, the size of NMR sample tube was 4mm ϕ , the rate of MAS was 15kHz to 18kHz, the data point was 8k, the accumulation number was 256 to 5000 times, and the measuring temperature range was 20°C to 70°C.

RESULTS AND DISCUSSION

Figure 2 shows the solid-state ^{13}C -NMRs of the different kinds of $TiCl_4$ -phthalate complexes, which were measured at 20°C. The charts (a), (b) and (c) are the cases with DEP, DBP, and DOP, respectively. As shown, it could be confirmed that the clear signal assignment was made.

Figure 3 is the expansion of C=O signal range of Figure 2. The chemical shift of carbon in C=O in the complex with $TiCl_4$ was changed by the kind of phthalate. This suggests that the coordination strength of C=O to Ti is influenced by the size of alkyl group in phthalate molecule. In the case of DOP, a double signal was observed. Although the course of this

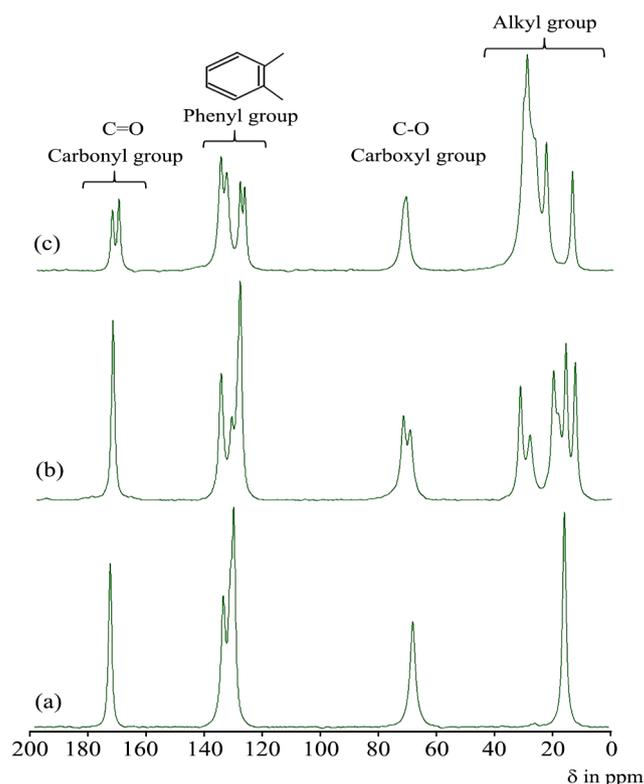


Figure 2. Solid-state ^{13}C NMR spectra of (a) $TiCl_4$ -DEP complex, (b) $TiCl_4$ -DBP complex, and (c) $TiCl_4$ -DOP complex: Measurement temperature = 20°C.

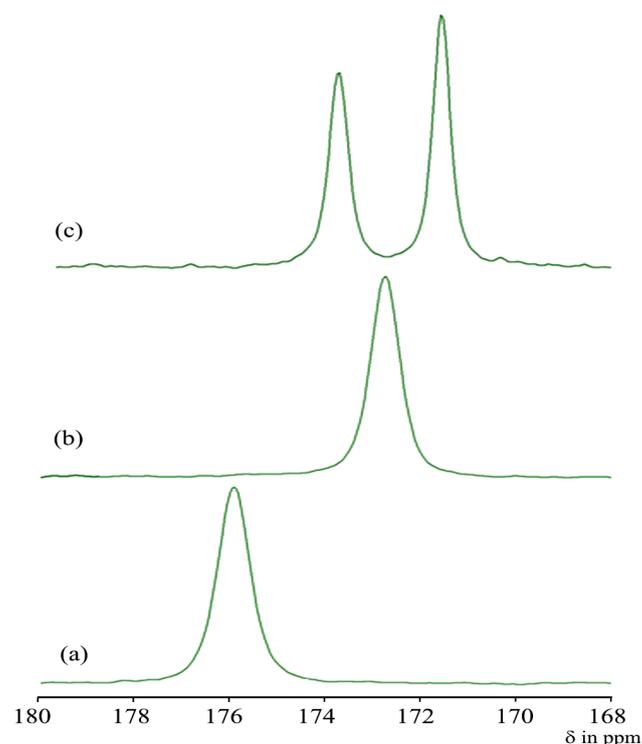


Figure 3. C=O behavior in $TiCl_4$ phthalic acid ester complex by solid-state ^{13}C NMR spectra. (a) $TiCl_4$ -DEP complex, (b) $TiCl_4$ -DBP complex, (c) $TiCl_4$ -DOP complex. Measurement temperature = 20°C.

behavior was not clear, unfortunately, two different coordination structures may be formed, due to some sort of steric hindrance of the large alkyl group of DOP.

Figure 4 is an example to show the effect of NMR measuring temperature on the chemical shift change of carbon atom of C=O group in phthalate. The high field shift was observed at high temperature. This indicated that the electron density of carbon atom was increased at high temperature. The behavior shall be attributable to the weak interaction between Ti and C=O in the complex under heat.

The full width half maximum (FWHM) values of the signal were 45 Hz and 32 Hz at 20°C and 70°C, respectively. The sharper signal at higher temperature supports the weaker coordination of C=O to Ti.

As described so far, the carbon atom signal of C=O in TiCl₄-phthalate complex could be detected by the solid-state ¹³C-NMR. In addition, it could be confirmed that the chemical shift value was changed not only by the kind of phthalate but by the measuring temperature. These should be understandable from the view point of the coordination strength of phthalate to Ti.

The solid-state ¹³C-NMR analyses were also applied

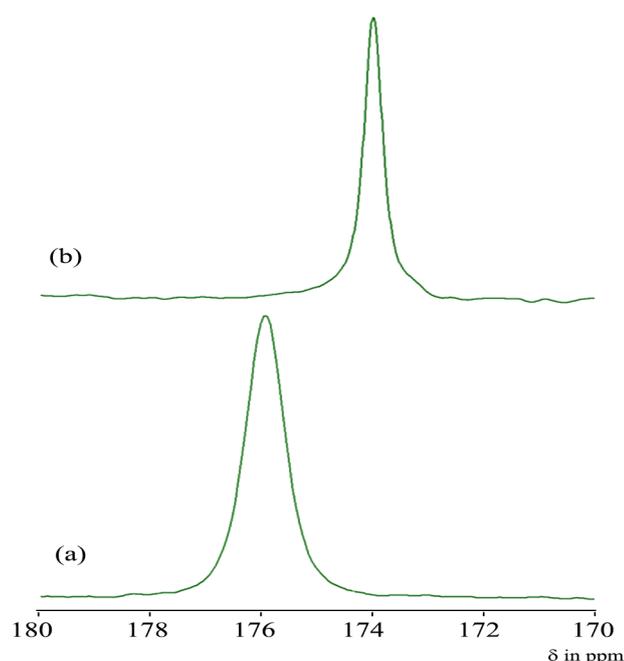


Figure 4. Chemical shift change of C=O in TiCl₄/DEP complex by the measuring temperature of solid-state ¹³C NMR. (a) 20°C spectra, (b) 70°C spectra.

to the catalyst solids prepared by the co-grinding of MgCl₂ with TiCl₄-phthalate complexes.

Figure 5 shows the NMRs of the catalyst solids. The charts (a), (b) and (c) are the cases with DEP, DBP and DOP, respectively. Similar to the TiCl₄-phthalate complex shown in Figure 1, the signal assignment of phthalate could be made even in the catalyst solid supported on MgCl₂.

Regarding the effect of the kind of phthalate and the temperature on the chemical shift of carbon in C=O group, the solid-state ¹³C-NMR measurements of the catalysts were repeated. The chemical shifts and the FWHM values are summarized in Table 2. Details will be discussed later.

In Table 2, the spin-lattice relaxation times of carbon in C=O group are also listed.

Figure 6 shows the attenuation of the signal intensity

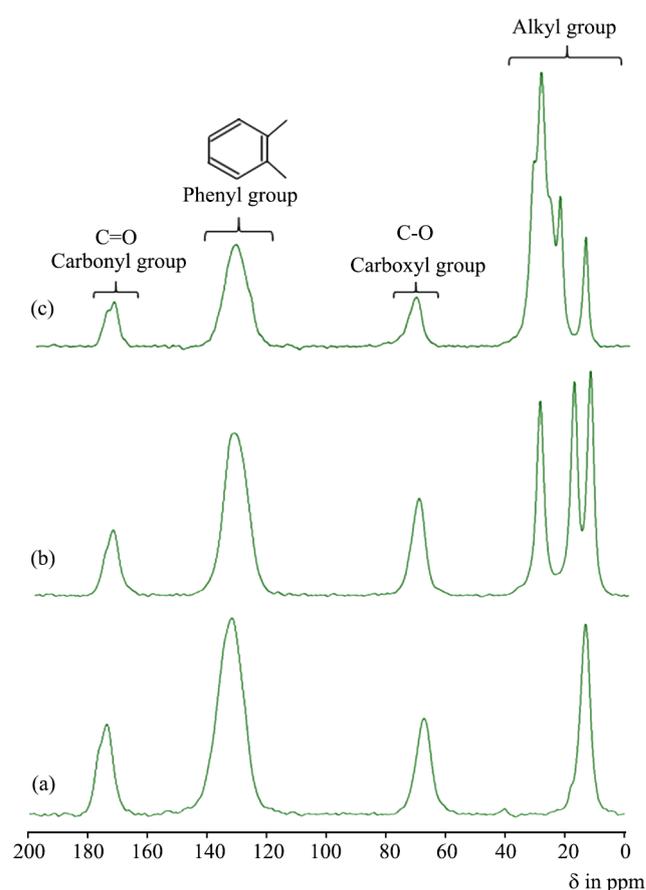


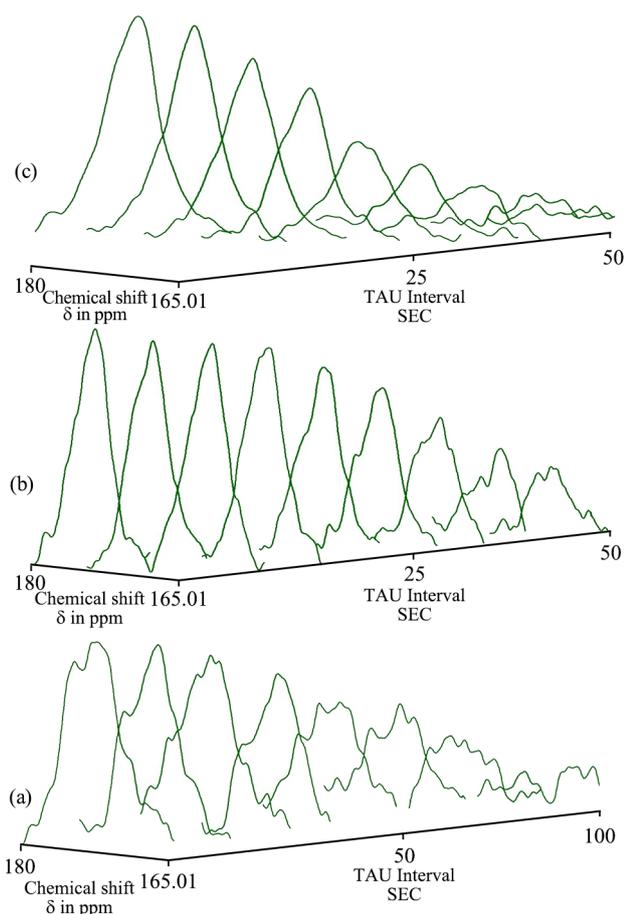
Figure 5. Solid-state ¹³C NMR spectra of (a) catalyst prepared by co-grinding of MgCl₂ with TiCl₄-DEP complex for 20 h, (b) catalyst prepared by co-grinding of MgCl₂ with TiCl₄-DBP complex for 20h, (c) catalyst prepared by co-grinding of MgCl₂ with TiCl₄-DOP complex for 20 h. Measurement temperature = 20°C.

Table 2. Effect of relaxation time and catalyst performance on solid-state ¹³C NMR measurement temperature changes.

Sample	¹³ C Solid-NMR and polymerization temperature °C	Chemical shift of C=O group δ in ppm	Relaxation time of C=O group sec	Full width half maximum of C=O group Hz	Yield g-PP/g-catalyst	X.I. ^(b) %
TiCl ₄ -DEP complex	20	176	129	66	-	-
	70	174	2	41	-	-
MgCl ₂ /TiCl ₄ -DEP complex coground catalyst ^(a)	20	172	57	388	100	59.8
	50	172	58	301	600	75.6
	70	171	4.0	265	4.300	95.1
TiCl ₄ -DBP complex	20	173	75	45	-	-
	70	172	1.0	32	-	-
MgCl ₂ /TiCl ₄ -DBP complex coground catalyst ^(a)	20	171	29	255	210	62.2
	50	171	11	238	720	78.7
	70	170	2.0	207	7.400	94.6
TiCl ₄ -DOP complex	20	171(174)	45	22(33)	-	-
	70	171(173)	0.1	26(57)	-	-
MgCl ₂ /TiCl ₄ -DOP complex coground catalyst ^(a)	20	171	21	244	600	66.2
	50	170	0.5	229	5.500	81.1
	70	169	0.1	177	26.800	95.8

(a) co-grinding time for 20h.

(b) X.I.:wt% of xylene insoluble fraction.

**Figure 6.** C=O behavior in MgCl₂/TiCl₄ phthalic acid ester complex 20 h co-grinding catalysts by solid-state ¹³C NMR relaxation time spectra. (a) catalyst prepared by co-grinding of MgCl₂ with TiCl₄-DEP complex for 20 h, (b) catalyst prepared by co-grinding of MgCl₂ with TiCl₄-DBP complex for 20 h, (c) catalyst prepared by co-grinding of MgCl₂ with TiCl₄-DOP complex for 20 h. Measurement temperature = 20°C.

(Int.) detected by the changing of TAU interval (t). The correlation between Int. and t can generally be expressed by the following equation [37].

$$\text{Int.} \propto \exp(-t/T1)$$

Where, T1 indicates the spin-lattice relaxation times.

Based on the above relationship, T1 could be determined from the slope value of logarithm plot of t vs. Int.

Relaxation time was shortened at high temperature in all samples.

This indicated a weak interaction between phthalate with TiCl₄ or MgCl₂ at high temperatures, which should support the discussion on the chemical shift change made in Figure 4. Besides the FWHM of signal was also narrower at higher temperatures as a general manner among the all samples. Based on these results, it could be confirmed that the phthalate molecule tightly coordinated to TiCl₄ or MgCl₂ at low temperatures, which should be quite reasonable from the thermodynamics viewpoint.

Figure 7 shows the ¹³C-NMR charts of C=O of the samples prepared with DBP.

The liquid NMR chart of pure DBP was also shown as a reference (Figure 7(a)). The chemical shift of C atom of C=O group was observed as 167 ppm.

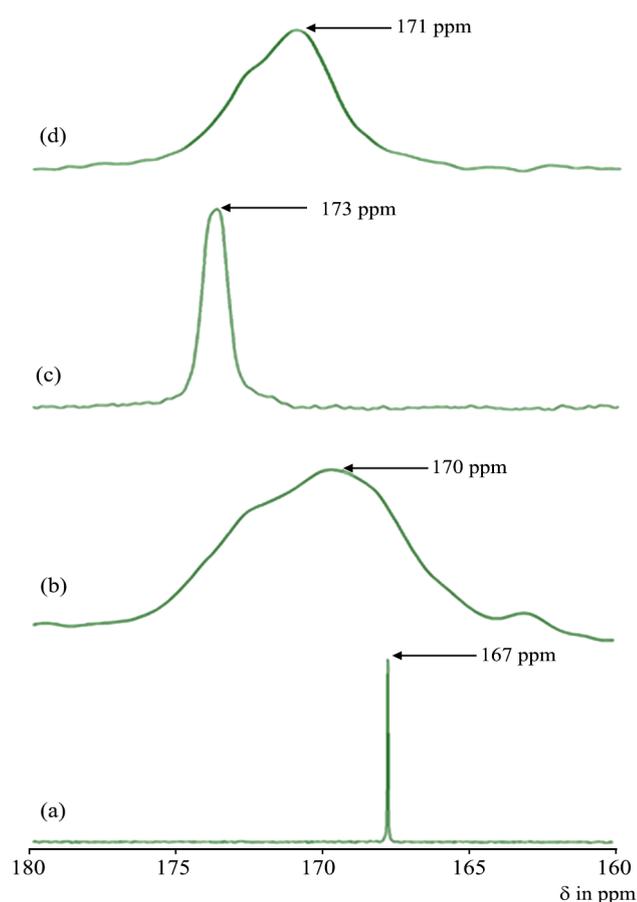


Figure 7. C=O behavior by ^{13}C NMR spectra. (a) DBP (liquid), (b) MgCl_2/DBP 20 h co-grinding for 20 h, (c) TiCl_4 -DBP complex, (d) catalyst prepared by co-grinding of MgCl_2 with TiCl_4 -DBP complex for 20 h. Measurement temperature = 20°C .

Figure 7(b) indicates the solid-state ^{13}C -NMR of the reference sample prepared by the co-grinding of MgCl_2 with DBP, in which the peak top was at 170 ppm. Since this reference material was prepared only with two components of MgCl_2 and DBP, the 170 ppm signal was undoubtedly assigned as C=O of DBP coordinated to the MgCl_2 surface. The low field shift from 167 ppm to 170 ppm suggested that the electron density of C in C=O coordinated on MgCl_2 is lower than that of pure DBP molecule.

Figure 7(c) is the solid-state ^{13}C -NMR of TiCl_4 -DBP complex.

By comparing with pure DBP molecule (Figure 7(a)), the low field shift of the chemical shift was observed from 167 ppm to 173 ppm. This phenomenon seems to be consistent to tight coordination behavior of THF to TiCl_4 [38].

Judging from that chemical shift value gap between

Figure 7(b) and (c), the electron density of carbon in C=O supported on MgCl_2 was higher than that in TiCl_4 -DBP complex. This suggests that C=O supported on MgCl_2 should be less polarized than in TiCl_4 -DBP complex.

Figure 7(d) shows the solid-state ^{13}C -NMR of the $\text{TiCl}_4/\text{DBP}/\text{MgCl}_2$ catalyst. As described in Experimental section, the catalyst solid was prepared by the co-grinding of MgCl_2 and TiCl_4 -DBP complex. The peak top of chemical shift of C=O was at 171 ppm, which was very close to the position shown in Figure 7(b). Accordingly, it could plausibly be interpreted that TiCl_4 -phthalate complex was at least partially decomposed and phthalate molecule moved to the MgCl_2 surface and finally formed MgCl_2 -phthalate complex. The similar behavior and explanation have been reported in ethyl benzoate internal donor catalyst case [8,24,25,29].

Although the clear mechanism was not known, the very unique property of the defect of MgCl_2 surface might contribute to the migration of phthalate molecule. In addition, as the relaxation time was shortened at high temperature, heating up induced by mechanical friction in grinding may potentially enhance the migration.

Arrhenius plots of the relaxation times listed in Table 2 are shown in Figure 8.

The plots can be regarded as the linear correlations, since the order of relaxation time detected was long enough in compare with Larmor frequency (In this work it can be estimated as $1/400\text{ MHz}=2.5\text{ ns}$) [39,40].

From the slope of each plot in Figure 8, the values of the activation energies were determined as Table 3.

The activation energies of DEP-containing samples were -16.7 kcal/mol in TiCl_4 -DEP complex, and -9.9 kcal/mol in $\text{MgCl}_2/\text{TiCl}_4$ -DEP catalyst, respectively. Considering the significant difference in energy values, these data indicate that DEP molecule supported on the MgCl_2 surface should thermally stable in compare with that in the TiCl_4 complex. As shown in Table 3, the absolute number of energy values of TiCl_4 -phthalate complex was always larger than that of $\text{MgCl}_2/\text{TiCl}_4$ -phthalate catalyst. Therefore, the stabilizing effect by supporting seemed to be a general tendency among the three phthalates investigated.

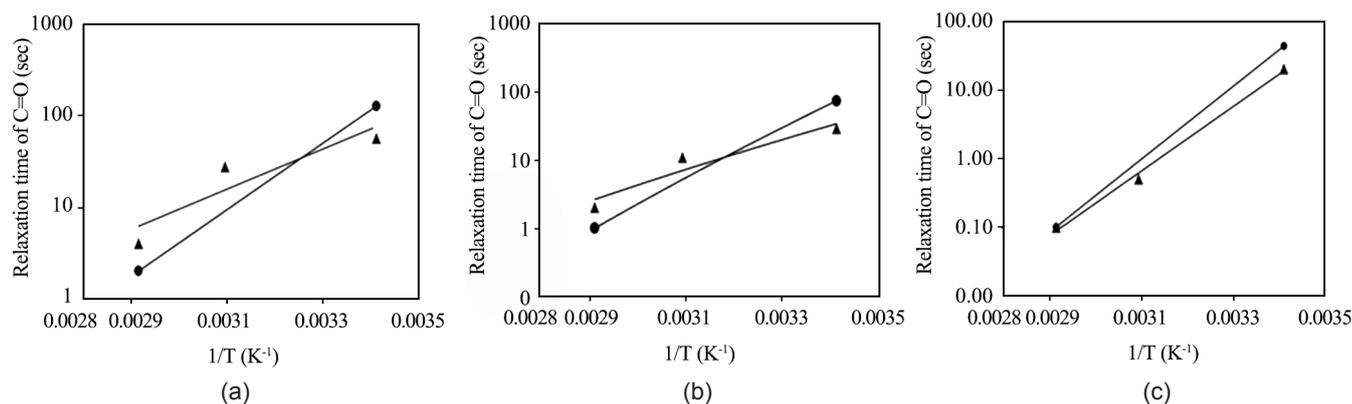


Figure 8. Arrhenius plots of relaxation time of C=O of $TiCl_4$ -Phthalate complexes and their $MgCl_2$ supported catalysts. (a) $TiCl_4$ -DEP Complex (●), $MgCl_2/TiCl_4$ -DEP Complex 20 h co-grinding (▲), (b) $TiCl_4$ -DBP Complex (●), $MgCl_2/TiCl_4$ -DBP Complex 20 h co-grinding (▲), (c) $TiCl_4$ -DOP Complex (●), $MgCl_2/TiCl_4$ -DOP Complex 20h co-grinding (▲).

The activation energies of $MgCl_2/TiCl_4$ -phthalate were estimated ca. -10 kcal/mol for DEP and DBP, and ca. -20 kcal/mol for DOP. The gap suggested DOP should easily be mobilized at high temperature among the three kind of phthalates.

Figure 9 shows Arrhenius plots of polymerization activities of three catalysts. The activation energy was almost constant at around 14 kcal/mol for three kinds of alkyl group in phthalate. It should be noted that the energy parameters shown in Table 3 were related to the reactivity of phthalate molecule with alkyl aluminum to form the polymerization active site. On the other hand, Figure 9 indicates the activation energy for the propagation rate of polymerization reaction.

Accordingly, the nature of the active species for polymerization is basically equivalent to the structure of phthalate molecule. It has been reported that the phthalate donor is exchanged by Si external donor under the polymerization mode [33].

Therefore, once phthalate is replaced by Si donor, the structure of the active sites shall reach to an equivalent and lose the intrinsic chemical property of each kind of phthalate.

Table 3. Activation energies determined from Arrhenius plots of Figure 2.

Material	ΔE Kcal/mol
$TiCl_4$ -DEP complex	-16.7
$MgCl_2/TiCl_4$ -DEP complex catalyst	-9.9
$TiCl_4$ -DBP complex	-17.3
$MgCl_2/TiCl_4$ -DBP complex catalyst	-10.2
$TiCl_4$ -DOP complex	-24.4
$MgCl_2/TiCl_4$ -DOP complex catalyst	-21.6

On the other hand, the absolute activity level of DOP catalyst was the highest among the three catalysts. As mentioned in the relaxation time analyses above, DOP should be weakly coordinated on the catalyst surface. It would be plausible that the easy replacement from DOP to Si donor accelerates the active site formation. Thus, the high activity of DOP catalyst shall be attributable to large numbers of active sites.

In terms of isotacticity of PP, it was significantly enhanced by increasing the polymerization temperature, indicating that the iso-specific active sites were the major contributor to give the impact to the activation energy of polymerization. Besides the slightly high isotacticity in DOP-containing catalyst seems to be from the easier replacement to Si donor than the other phthalates of DEP or DBP.

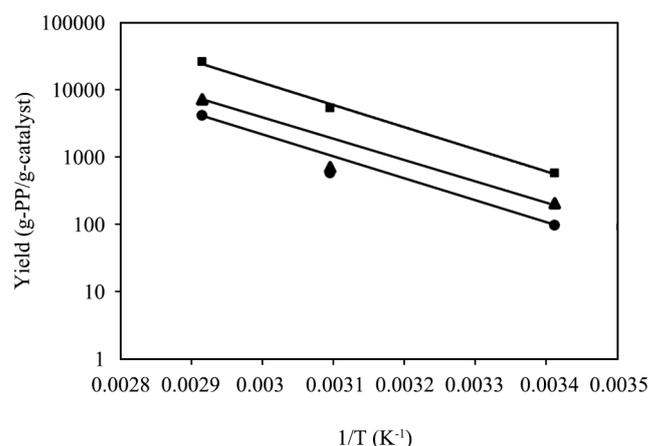


Figure 9. Arrhenius plots of polymerization activity: $MgCl_2/TiCl_4$ -DEP Complex 20 h co-grinding catalyst system (●), $MgCl_2/TiCl_4$ -DBP Complex 20h co-grinding catalyst system (▲), $MgCl_2/TiCl_4$ -DOP Complex 20 h co-grinding catalyst system (■).

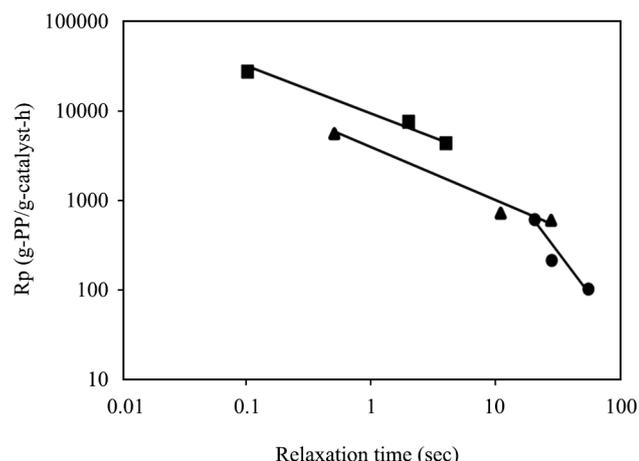


Figure 10. Relationships between the yield and the solid-state ^{13}C NMR measurement relaxation time, (●) Solid-state ^{13}C NMR measurement temperature at 20°C , (▲) Solid-state ^{13}C NMR measurement temperature at 50°C , (■) Solid-state ^{13}C NMR measurement temperature at 70°C .

Figure 10 is the plot between the relaxation time and the catalytic activity. When the temperature is constant, higher polymerization rate (R_p) is obtained at shorter relaxation time case, indicating that easier replacement of phthalate by Si donor contributes to form the larger amount of active sites. In actual situation in the polymerization, however, donor exchange reaction shall not be perfect, and the small amount of the remaining phthalate molecule shall influence to change the isotacticity level as listed in Table 2. The high isotacticity of DOP-containing catalyst can be understood by the weak interaction with MgCl_2 and easy replacement by Si external donor.

CONCLUSION

In order to evaluate the characteristics of phthalate internal donor molecule in MgCl_2 supported Ziegler-Natta catalyst, the relaxation time of $\text{C}=\text{O}$ group in phthalate was investigated by changing the size of alkyl group of phthalate and the NMR measuring temperature.

The short relaxation time was observed in the catalyst prepared with the phthalate having large alkyl group. The short relaxation time was also observed at high temperature of solid-state ^{13}C NMR measurement.

These phenomena were understandable that the interaction strength between phthalate molecule and

the surface is markedly influenced by the phthalate molecule structure and temperature. The high mobility of phthalate, i.e. weak interaction with surface, shall relatively easily be replaced by Si donor under the polymerization mode, resulting in the promoting the formation of high active/istotactic polymerization sites.

ACKNOWLEDGEMENT

We would like to express our appreciation to Dr. Yusuke Nishiyama and Dr.Katsuo Asakura in JEOL RESONANCE Inc. for their support of the relaxation time measurement with the solid-state ^{13}C NMR.

We would like to express our deepest condolences on the loss of Dr. Yuuichi Shimoikeda of JEOL RESONANCE Inc. from whom we had the privilege of receiving invaluable advice on this study while he was alive.

CONFLICTS OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Ziegler K, Holzkamph E, Breil H, Martin H (1955) Das Mulheimer normaldruck polyathylen verfahren. *Angew Chem* 67: 541-636
2. Natta G (1955) Une nouvelle classe de polymers d' α -olefines ayant une regularite de structure exceptionnelle. *J Polym Sci* 16: 143-154
3. Natta G (1956) Stereospezifische katalysen und isotaktische polymere. *Angew chem* 68: 393-424
4. Keszler B, Bodor G, Simon A (1980) Studies on highly active coordination catalysts for polymerization of α -olefins:1. X-ray diffractomeric investigations of the catalyst supports. *Polymer* 21: 1037-1040
5. Pino P, Fochi G, Piccolo O, Gianni U (1982) Experimental evidence for the existence of catalytic sites with different steric structures in

- supported Ziegler-Natta catalysts. *J Am Chem Soc* 104: 7381-7383
- Soga K, Sano T, Yamamoto K, Shiono T (1982) The role additives on the improvement of the isotacticity of polypropylene-A possible interpretation. *Chem Lett* 12: 425-428
 - Chien JCW, Wu JC, Kuo CI (1983) Magnesium chloride supported high-mileage catalysts for olefin polymerization. IV. FTIR and quantitative analysis of modifiers in the catalysts. *J Polym Sci Polym Chem Ed* 21: 725-736
 - Doi Y, Soga K, Murata M, Suzuki E, Ono Y, Keii T (1983) Additive effect of metal chlorides on propylene polymerization with a soluble titanium-based Ziegler catalyst. *Polym commun* 24: 244-246
 - Keszler B, Bodor G, Simon A (1984) Studies on highly active coordination catalysts for polymerization of α -olefins:1. X-ray diffractometric investigations of the catalyst supports. *Polymer* 21: 1037-1040
 - Busico V, Corradini P, Martino LD, Proto A (1986) Polymerization of propene in the presence of MgCl_2 -supported Ziegler-Natta catalysts, 2a) effects of the co-catalyst composition. *Makromol Chem* 187: 1115-1124
 - Terano M, Kataoka T, Keii T (1989) Stopped flow polymerization of propene with typical MgCl_2 -supported high-yield catalysts. *J Mol catal* 56: 203-210
 - Chujo R, Kogure Y, Vaananen T (1994) Two-site model analysis of ^{13}C NMR of polypropylene polymerized by Ziegler-Natta catalyst with external alkoxy silane donors. *Polymer* 35: 339-342
 - Harkonen M, Seppala JV, Chujo R, Kogure Y (1995) External silane donors in Ziegler-Natta catalysis: a two-site model simulation of the effects of various alkoxy silane compounds. *Polymer* 36: 1499-1505
 - Chujo R, Shimozawa K, Saito M, Kataoka T, Nishiyama I, Ishida M, Sawa N (2000) Internet system for the determination of stochastic parameters in the two-site model in olefin polymerization, Progress and development of catalytic olefin polymerization, Technology and Education Publishers. Tokyo, 264-271
 - Shimozawa K, Saito M, Kataoka T, Chujo R (2002) Effect of internal donors in propylene polymerization analyzed with the two-site model. *Polym Int* 51: 530-533
 - Taniike T, Terano M, (2007) Coadsorption and support-mediated interaction of Ti species with ethyl benzoate in MgCl_2 -supported heterogeneous Ziegler-Natta catalysts studied by density functional calculations. *Makromol Chem Rapid Commun* 28: 1918-1922
 - Correa A, Piemontesi F, Morini G, Cavallo L (2007) Key elements in the structure and function relationship of the $\text{MgCl}_2/\text{TiCl}_4$ /Lewis base Ziegler-Natta catalytic system. *Macromolecules* 20: 9181-9189
 - Taniike T, Funako T, Terano M (2014) Multilateral characterization for industrial Ziegler-Natta catalysts toward elucidation of structure-performance relationship. *J Catal* 311: 33-40
 - Ratanasak M, Rungrotmongkol T, Saengsawang O, Hannongbua A (2014) Towards the design of new electron donors for Ziegler-Natta catalyzed propylene polymerization using QSPR modeling. *Polymer* 56: 340-345
 - Funako T, Chammingkwan P, Taniike T, Terano M (2015) Addition of a second alcohol in magnesium ethoxide synthesis as a way to vary the pore architecture of Ziegler-Natta catalysts. *Polyolefins J* 2: 65-71
 - Hongmanee G, Chammingkwan P, Taniike T, Terano M (2016) Probing into morphology evolution of magnesium ethoxide particles as precursor of Ziegler-Natta catalysts. *Polyolefins J* 3: 47-57
 - Piovano A, D'Amore M, Thushara KS, Groppo E, (2018) Spectroscopic evidences for TiCl_4 /donor complexes on the surface of MgCl_2 -supported Ziegler-Natta catalysts. *J Phys Chem C* 122:5615-5626
 - Taniike T, Goto K, Terano M (2015) Active site nature of magnesium dichloride-supported titanocene catalysts in olefin polymerization. *Polyolefins J* 2: 57-63
 - Terano M, Kataoka T, Keii T (1986) Analysis of MgCl_2 -supported high-yield catalysts by thermal

- analysis and infrared spectroscopy. *Macromol Chem Rapid Commun* 7: 725-731
25. Terano T, Kataoka T, Keii T (1987) A study on the states of ethyl benzoate and TiCl_4 in MgCl_2 -Supported high-yield catalysts. *Makromol Chem* 188: 1477-1487
 26. Ohashi R, Saito M, Fujita T, Nakai T, Utsumi H, Deguchi K, Tansho M, Shimizu T (2012) Observation of $^{47,49}\text{Ti}$ NMR Spectra of $\text{TiCl}_4/\text{MgCl}_2$ catalysts under an ultrahigh magnetic field. *Chem Lett* 41: 1563-1565
 27. Vittoria A, Meppelder A, Friederichs N, Busico A, Clipullo R (2020) Ziegler–Natta catalysts: Regioselectivity and “hydrogen response”. *ACS Catal* 10: 644-651
 28. Piovano A, Wada T, Amodio A, Takasao G, Ikeda T, Zhu D, Terano M, Chammingkwan C, Groppo E, Taniike T (2021) Formation of highly active Ziegler–Natta catalysts clarified by a multifaceted characterization approach. *ACS Catal* 11(22): 13782-13796
 29. Saito M, Murata M, Kataoka T, Sakuda Y, Takahashi H (Received 2021) Characterization of electronic properties of titanium atom in heterogeneous Ziegler-Natta catalyst analyzed by Soft X-ray Emission Spectrometer (SXES). *Bulletin of the Chemical Society of Japan* 95: 367-373
 30. Piovano A, Groppo E, (2022) Flexible ligands in heterogeneous catalysts for olefin polymerization: Insights from spectroscopy. *Coordination Chem Rev* 451: 214258
 31. Abis L, Albizzati E, Giannini U, Giunchi G, Santoro E, Noristi L (1988) Cross polarization/magic angle spinning ^{13}C solid state nuclear magnetic resonance of model compounds related to supported Ziegler-Natta catalysts. *Makromol Chem* 189: 1595-1601
 32. Terano M, Saito M, Kataoka T (1992) Solid-state ^{13}C NMR study on the state of the electron donor in MgCl_2 -supported catalysts. *Makromol Chem Rapid Commun* 13: 103-108
 33. Ishii K, Mori T, Fujita T (1994) An NMR analysis of coordination of alkoxysilane compounds on MgCl_2 -supported Ziegler-Natta catalyst. *Kobunshi Ronbunshu* 51: 685-687
 34. Sormunen P, Hjertberg T, Iiskora E (1990) A solid-state ^{13}C NMR study on heterogeneous Ziegler-Natta catalyst components. *Makromol Chem* 191: 2663-2673
 35. Saito M, Uozumi T, Sugano T, Kataoka T, Chujo R (2018) Correlation between catalyst performance and relaxation time of electron donor in olefin polymerization catalyst by solid ^{13}C NMR. *Kobunshi Ronbunshu* 75: 570-575
 36. Bloembergen N, Purcell EM, Pound RV (1948) Relaxation effects in nuclear magnetic resonance absorption. *Phys Rev* 73: 679-712
 37. Torchia DA (1978) The Measurement of proton-enhanced carbon-13 T1 values by a method which suppresses artifacts. *J Magnetic Resonance* 30: 613-616
 38. Peng Liang, Wei Li, Yuming Chen, Chuanding Dong, Qi Zhou, Yirong Feng, Mei Chen, Jincheng Dai, Congjing Ren, Binbo Jiang, Jingdai Wang, Yongrong Yang (2021) Revealing the dynamic behaviors of tetrahydrofuran for tailoring the active species of Ziegler–Natta catalysts. *ACS Catal* 11: 4411-4421
 39. Apperley DC, Harris RK, Hodgkinson P (2012) *Solid-state NMR basic principles & practice*, Momentum press, New York, Chapter 7: Relaxation exchange & quantitation
 40. Rohr KS, Spiess HW (1994) *Multidimensional Solid-State NMR and Polymers*. Anthropology Culture and Society, 1st ed Academic Press, 127