

Solid-State NMR Characterization of a Superactive Supported Ziegler–Natta Catalyst*

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SYNOPSIS

The formation of CH-type catalysts has been investigated by high-resolution and solid-state NMR. These catalysts are prepared from a soluble MgCl_2 and 2-ethyl-1-hexanol adduct ($\text{MgCl}_2 \cdot 3\text{EH}$) by reaction with phthalic anhydride (PA) to form dioctylphthalate (DOP) and then with TiCl_4 in the presence of di-*i*-butylphthalate (BP). In the model systems $\text{MgCl}_2 \cdot 3\text{EH}/\text{PA}$, MgCl_2/BP , and $\text{MgCl}_2/\text{TiCl}_4/\text{BP}$, the ester is complexed with MgCl_2 and/or TiCl_4 in two or more states. Only single-ester $\text{C}=\text{O}$ and OCH_2 resonances are seen in TiCl_4/BP , probably due to exchange of ester coordinations. CH-catalysts prepared by three different procedures exhibit a single mode of bonding for the ester. The chemical shift values are consistent for ester complexed with MgCl_2 . The most active and stereoselective catalyst has the most shielded chemical shift values for the $\text{C}=\text{O}$ and $-\text{OCH}_2-$ carbons, shortest T_1^H and $T_{1\rho}^H$, and longest T_{CH} relaxation times. These parameters change monotonically with the decrease of activity and stereoselectivity of the catalyst preparation. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The invention of MgCl_2 -supported Ziegler–Natta (ZN) catalysts has revolutionized the polyolefin industry. Old plants were retrofitted and new plants were built to take advantage of the new catalysts. The superhigh activity and stereospecificity possessed by the MgCl_2 -supported catalysts results from maximizing the total number of catalytic sites and minimizing the number of nonstereoselective sites.

The preparation of the MgCl_2 -supported ZN catalysts involved elaborate conditioning of the MgCl_2 support employing one or more organic modifiers. The chemical and physical transformations that occurred during each step of catalyst preparation are obscure and complicated. They had been elucidated

for a “third-generation” CW-type catalyst¹ made from ball-milled MgCl_2 /ethylbenzoate (EB)/*p*-cresol (PC)/ AlEt_3 (TEA)/ TiCl_4 , by a combination of elemental analysis,¹ hydrolysis GC–MS,² redox titrations,^{2,3} EPR,⁴ FTIR,⁵ BET,⁶ mercury porosimetry,⁶ X-ray diffraction,⁶ and radioassay.⁷ Subsequently, we conducted comprehensive studies of a “fourth-generation” CH-type catalyst that is soluble $\text{MgCl}_2 \cdot 3$ 2-ethyl-1-hexanol (EH)/phthalic anhydride (PA)/di-*i*-butylphthalate (BP)/ TiCl_4 .^{8–10} This catalyst has a very high activity of 16 kg polypropylene/(g Ti atm h) and > 99% isotactic yield as compared to 4 kg polypropylene/(g Ti atm h) and ~ 92% isotactic yield for the CW catalysts.

Magic angle spinning cross-polarization solid-state NMR spectra and relaxation measurements can reveal the rigidity and orderliness that an adsorbate or reactant is affixed on a support. Investigation of the CW catalyst intermediates by this technique¹² showed the following: Ball milling of MgCl_2 with EB resulted in the rigid complexation of EB on several different kinds of MgCl_2 surface sites. Reaction with PC also caused the formation of a rigid PC with MgCl_2 ; this process rendered the EB complex less rigid. The carbon atoms of

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$\text{Et}_n\text{Al}(\text{OC}_6\text{H}_4\text{Me})_{3-n}$, formed by treatment with TEA, could not be observed by cross-polarization or a single $\pi/2$ carbon polarization, indicating that these groups possess appreciable freedom of motion. The above results demonstrated the utility of solid NMR in the characterization of heterogeneous catalysts. This paper presents the results of solid NMR studies on the CH catalyst materials that shed light on their preparations and structures.

EXPERIMENTAL

CH catalyst samples were prepared as previously described.⁸ All materials were handled under argon by Schlenk techniques.

Heptane and *n*-decane were distilled from sodium and stored under argon over molecular sieves. Diisobutylphthalate (Aldrich) and 2-ethylhexanol (Pfaltz-Bauer) were dried over 3 Å molecular sieves and stored under argon. Phthalic anhydride and TiCl_4 (Aldrich) were used as received.

A MgCl_2 alcohol adduct was synthesized by reacting anhydrous MgCl_2 with 2-ethylhexanol (EH/ $\text{MgCl}_2 = 3.0$) in decane for 2 h at 110°C. Phthalic anhydride ($\text{MgCl}_2/\text{PA} = 6.5$) was then added and the clear adduct solution was heated at that temperature for another hour. The adduct solution was added dropwise into neat TiCl_4 ($\text{TiCl}_4/\text{MgCl}_2 = 4.0$) at -20°C over a 1 h period. The temperature was then increased steadily to 110°C over a 4 h period. At that time, diisobutylphthalate was added ($\text{MgCl}_2/\text{BP} = 5.0$). The mixture was stirred for 2 h at the same temperature. The catalyst was hot-filtered and resuspended in TiCl_4 (the same amount used previously). It was then stirred for 2 h at 120°C, subsequently hot filtered, and washed with decane. Typical Ti content was about 2.0% by weight.

For this study, the synthesis was interrupted at several steps. Specimens taken were washed with 4 × 100 mL of heptane and vacuum-dried prior to NMR measurements.

Solution NMR spectra of the adducts in CDCl_3 were obtained on a Varian XL-300 spectrometer. Samples for solid NMR were loaded into 6 mm i.d. sapphire NMR cells equipped with double viton "O"-ring-fitted ceramic end caps (Doty Scientific) in a dry box under argon. High-purity nitrogen was used as the spinning gas to avoid any reaction with air. The samples were exposed only to the atmosphere for a brief time period during the transfer from Schlenk tube to the NMR probe. ^{13}C -NMR spectra were measured at 50.13 MHz with 5 μs 90° pulses for both carbons and protons on an IBM 200 AF

instrument equipped with an IBM solids accessory. Samples were spun at 4 kHz. The number of scans for the model systems was 400; it was 3000–4000 for the support and the catalyst.¹¹

Cross-polarization spectra were obtained with a proton $\pi/2$ -pulse followed by 2 ms simultaneous ^1H and ^{13}C spin-lock and 50 ms acquisition with high-power proton decoupling. The phase of the pulse was alternated between the *x* and $-x$ axes to eliminate base-line irregularities. The cross-polarization rate constant (T_{CH}^{-1}) was estimated from the initial exponential rise of magnetization as a function of spin-lock time. The spin lattice relaxation rate of the protons in the rotating frame (T_{ρ}^{-1}) was estimated from the decay of the ^{13}C intensity with spin-lock time. The spin lattice relaxation rate of the protons in the laboratory frame (T_1^{-1}) was measured by a ^1H π -pulse followed by a variable delay, a ^1H $\pi/2$ -pulse, and then by the above spin-lock and acquisition sequence.

Three additional systems were studied to aid in the spectral assignments and characterization. One system was formed by the ball milling of MgCl_2 with BP (6.25:1) for 72 h. The second was obtained by the reaction of TiCl_4 with an equimolar amount of BP at room temperature in heptane. The third was synthesized by ball milling the $\text{TiCl}_4 \cdot \text{BP}$ complex with MgCl_2 for 72 h in a ratio of 1:10. These ratios were calculated to produce complexes of similar composition as those of the final CH catalysts. In all cases, the solid products were washed with 4 × 100 mL heptane and vacuum-dried.

RESULTS

The synthesis of the CW catalyst began with a crystalline MgCl_2 . This and all subsequent intermediates are solid substances and were suitable for solid NMR characterization. The preparation of the present CH catalyst started with a soluble $\text{MgCl}_2 \cdot 3\text{EH}$ complex; the solid CH catalyst was formed only after treatment with TiCl_4 . Consequently, it is necessary to study model systems and sometimes to use high-resolution NMR.

$\text{MgCl}_2 \cdot 3\text{EH}$

High-resolution C-NMR spectra of $\text{MgCl}_2 \cdot 3\text{EH}$ in CDCl_3 were obtained and compared with the spectrum of EH alone dissolved in CDCl_3 . The $-\text{O}-\text{CH}_2-$ resonance in the former has a chemical shift of 66.8 ppm as compared to 65.2 ppm

Table I ^{13}C -NMR Parameters for Model Systems

System	C=O		—OCH ₂ —		C _{ar}	
	σ (ppm)	T_1^H (s)	σ (ppm)	T_1^H (s)	σ (ppm)	T_1^H (s)
EH ^{a,b}	—		65.2			
MgCl ₂ •3EH ^b			66.8			
DOP ^{b,c}	167.6		68.1		128.9 130.9 132.8	
MgCl ₂ •3EH/PA	170.6 176.5		67.5 70.1		128.3 129.8 132.2	
BP ^b	167.4		71.6		128.8 130.9 132.6	
MgCl ₂ /BP	163.5 166.5 175.0	0.6	70.2 75.0	0.6	126.1 133.7 138.5	0.6
TiCl ₄ /BP ^d	173.4	1.5	77.4	1.3	129.2 131.3 135.0	1.3
MgCl ₂ /TiCl ₄ /BP	163.5 175.0	0.5	70.2 77.4	^e	126.1 138.5	0.4

^a EH = 2-ethyl-1-hexanol.

^b In CDCl₃.

^c DOP = dioctylphthalate.

^d BP = di-*i*-butylphthalate.

^e Not resolved.

in the latter (Table I). This difference in chemical shifts is consistent with the coordination of EB with MgCl₂.¹¹

MgCl₂•EH/PA

Phthalic anhydride was added to MgCl₂•3EH in a ratio of MgCl₂:EH:PA = 1:3:0.15. The C-NMR spectrum displayed two carbonyl carbon peaks of the same intensities at 170.6 and 176.5 ppm and two —OCH₂— carbon resonances of the same intensities at 70.1 and 67.5 ppm. The three aromatic carbons were found at 128.3, 129.8, and 132.2 ppm (Table I). Since EH is present in large excess over PA, the latter should be converted mostly to dioctylphthalate (DOP = di-2-ethylhexylphthalate). A CDCl₃ solution of DOP has C=O and —O—CH₂— resonances at 167.6 and 68.1 ppm, respectively. The aromatic carbons were found at the same chemical shifts as those in the MgCl₂•3EH/

PA spectra (*vide supra*). This comparison indicates that the C=O of DOP has two different bonding modes to MgCl₂ and that there are also two types of complexation between —O—CH₂ of DOP and MgCl₂.

TiCl₄/BP

The C-NMR spectra of butylphthalate (BP) in the carbonyl and aromatic regions are virtually identical to those for DOP. However, the —O—CH₂— resonance in the former is shifted downfield to 71.6 ppm; it has a shift value of 68.1 ppm in DOP.

The 1:1 complex of TiCl₄/BP exhibits well-resolved and simple C-NMR spectrum [Fig. 1(a)]. There were only singlets for the C—O and —O—CH₂— resonances, both deshielded by about 6 ppm from the corresponding peaks in plain BP alone. TiCl₄ caused smaller downfield shifts for the aromatic carbon nuclei.

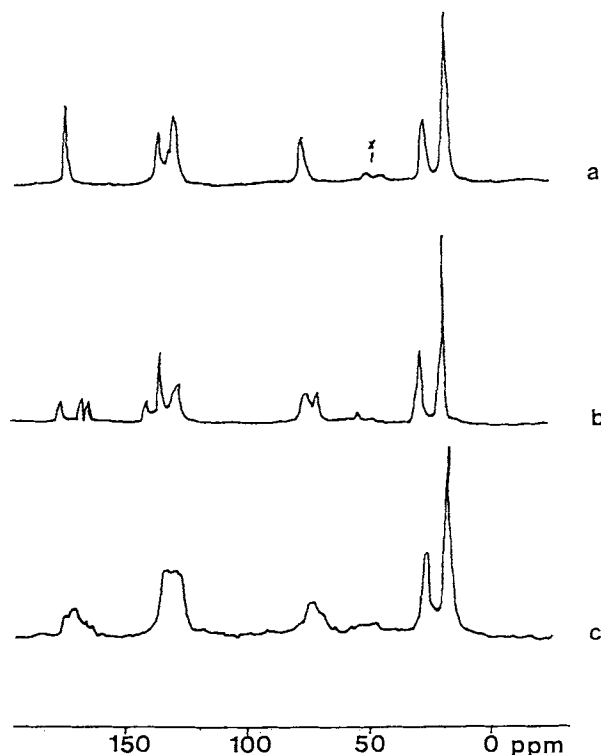


Figure 1 CP-MAS ^{13}C -NMR of (a) $\text{TiCl}_4\cdot\text{BP}$, (b) $\text{MgCl}_2\cdot\text{BP}$, and (c) $\text{MgCl}_2\cdot\text{TiCl}_4\cdot\text{BP}$. Side band is denoted by **x**.

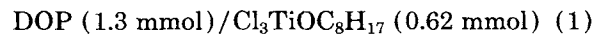
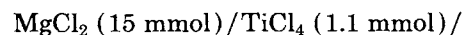
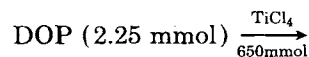
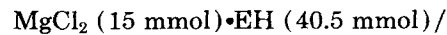
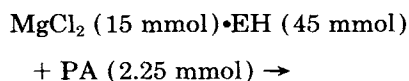
$\text{MgCl}_2/\text{TiCl}_4/\text{BP}$

$\text{TiCl}_4\cdot\text{BP}$ complex was mixed with MgCl_2 in a ratio of 1:10 and ball-milled for 72 h. The washed and dried mixture give the spectrum of Figure 1(c). All the peaks were broad. In fact, the spectrum is very close to the sum of spectra 1(a) and 1(b).

The activity and stereospecificity of the CH-type catalyst are strongly dependent on the structure of the ester and the way in which it is administered. For instance, terephthalates are much inferior to phthalates,¹² and monoesters such as ethylbenzoate are unsuited for the preparation of this CH family of catalysts. Previously, we had reported⁸ four different procedures for the synthesis of CH catalysts using phthalate ester. Three of these were investigated with solid C-NMR in this study.

CH-5 Catalyst ($\text{MgCl}_2\cdot\text{EH}/\text{PA}/\text{TiCl}_4$)

The catalyst, designated as CH-5, was prepared as follows⁸:



The final composition of this catalyst had been determined by elemental analysis and by hydrolysis GC-MS.⁹ The low-field resonances in the C-NMR spectra [Fig. 2(a)] resemble closely the corresponding regions in Figure 1(c) for the $\text{MgCl}_2/\text{TiCl}_4/\text{BP}$ system. However, the aliphatic region in the latter has two peaks for the $-\text{CH}_2\text{CH}_2-$ and $-\text{CH}_3$ carbons of BP; there are four different aliphatic carbons in the ethylpentyl group from EH and DOP. Table II contains the relaxation times for the carbonyl aromatic and oxymethylene carbon resonances.

CH-7 Catalyst ($\text{MgCl}_2\cdot\text{EH}/\text{PA}/\text{TiCl}_4/\text{BP}$)

This catalyst was prepared by the addition of 3 mmol of BP to CH-5 and reacted at 110°C for 2 h followed by filtration and washing. The approximate composition⁹ is $\text{MgCl}_2 (15 \text{ mmol})/\text{TiCl}_4 (0.88 \text{ mmol})/\text{BP} (0.99 \text{ mmol})/\text{DOP} (0.68 \text{ mmol})$. The C-NMR [Fig. 2(b)] exhibits new peaks at 26.7 and 17.6 ppm, indicating the presence of BP, which was absent in Figure 2(a). The $-\text{O}-\text{CH}_2-$ and ar-

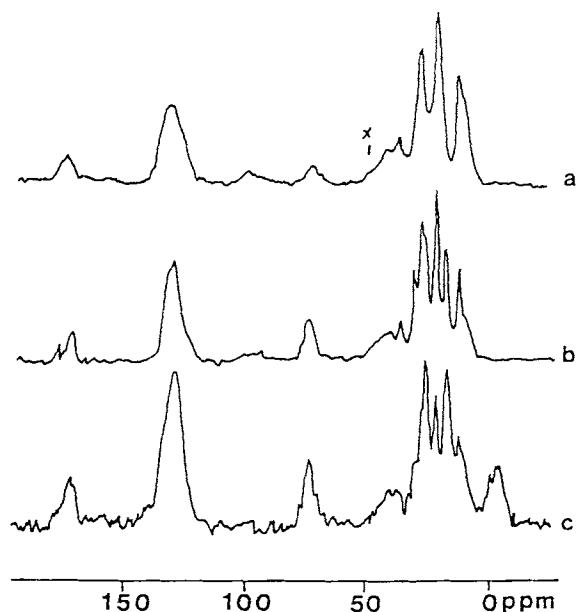


Figure 2 CP-MAS ^{13}C -NMR of (a) CH-5 catalyst, (b) CH-7 catalyst, and (c) CH-8 catalyst.

Table II ^{13}C -NMR Parameters for CH-5 Catalyst

	C=O	—OCH ₂ —	C _{ar}
Chemical shift (ppm)	173.8	74.3	131.3
T_1^H (s)	0.48	— ^a	0.48
$T_{1\rho}^H$ (ms)	41	—	7.9
T_{CH} (μs)	455	—	17

^a Insufficient resolved for relaxation measurement.

omatic resonances have line widths of about 290 and 400 Hz, respectively, as compared to the corresponding widths of 360 and 550 Hz in the case of the CH-5 catalyst. The carbonyl resonances for the CH-7 catalyst have two resolved peaks. The C-NMR parameters are summarized in Table III.

CH-8 Catalyst (MgCl₂·EH/PA/TiCl₄/BP/TiCl₄)

This catalyst has the highest activity and stereospecificity among all the CH-type catalyst that we have prepared. It was obtained by resuspending the CH-7 catalyst in a large excess of TiCl₄ (220 mL, 1.8 mol) and reacted at 120°C for 2 h. This process probably served to remove loosely bound Cl₃TiOC₃H₁₇, TiCl₄, DOP, and BP as shown by the composition⁹ that is found to be MgCl₂ (15 mmol)/TiCl₄ (0.68 mmol)/BP (0.55 mmol)/DOP (0.28 mmol). The decrease in the DOP content is evident by the stronger intensities of the BP peaks in the alkyl region. There is essentially no shifts in the peak positions, but the T_1^H and $T_{1\rho}^H$ values are about 50% shorter than those of the CH-5 and -7 catalysts (Table IV).

DISCUSSION

Model Systems

The MgCl₂-supported stereospecific olefin polymerization catalysts are remarkable technological

Table III ^{13}C -NMR Parameters for CH-7 Catalyst

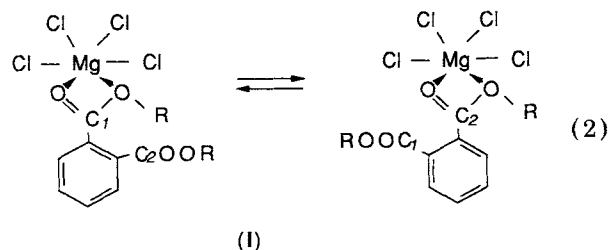
	C=O	—OCH ₂ —	C _{ar}
Chemical shift (ppm)	171.7	74.4	130.7
T_1^H (s)	0.39	0.46	0.45
$T_{1\rho}^H$ (ms)	13.1	13.5	10.7
T_{CH} (μs)	534	10.7	15.7

Table IV ^{13}C -NMR Parameter for CH-8 Catalyst

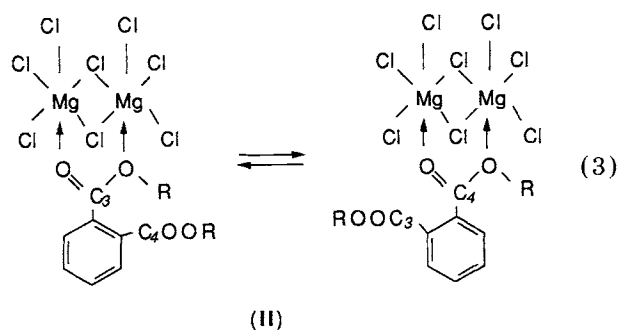
	C=O	—OCH ₂ —	C _{ar}
Chemical shift (ppm)	171.3	74	129.7
T_1^H (s)	0.19	0.2	0.23
$T_{1\rho}^H$ (ms)	12.7	9.2	10.1
T_{CH} (μs)	523	14	21.4

achievements in catalysis and polymer sciences. Their preparations are quite complicated and sophisticated. No single technique is capable of revealing the intricate chemistry and physics involved in the synthesis or the structures of the catalyst intermediates. Those techniques that had been utilized by us for these purposes were listed above.¹⁻¹¹ The interpretation of the results of one technique draws heavily on the results and analysis by the other techniques. C-NMR has already been applied to the CW catalysts.¹¹ The conclusions of that study are helpful to the interpretation of the C-NMR results of this work.

We discuss first the C-NMR results of MgCl₂/BP and compare them with those of MgCl₂/EB, which was the first-stage intermediate of the CW catalyst. Figure 1(b) showed two —OCH₂— peaks and three peaks in the carbonyl and aromatic region. In the case of MgCl₂/EB, those are all broad singlets of 300–600 Hz line width, indicating unresolved chemical shifts of several different kinds of rigidly complexed EB. On the other hand, the T_1^H is only ca. 30 ms, which is unusually short for a rigid organic compounds. We attributed this short T_1^H to electric quadrupole relaxation by the ³⁵Cl and ³⁷Cl nuclei. In the present case of MgCl₂/BP, the T_1^H is 600 ms. A possible explanation for this very long T_1^H is that the quadrupolar process is ineffective. For instance, only one of the two ester groups in BP may be complexed to MgCl₂ and exchange possibly occurs between them. Previously we have shown that EB can complex with four-coordinate or five-coordinate Mg on the (110) and (100) faces of MgCl₂. The suggested exchange of complexation of BP with MgCl₂ may be depicted for the two surfaces as



and



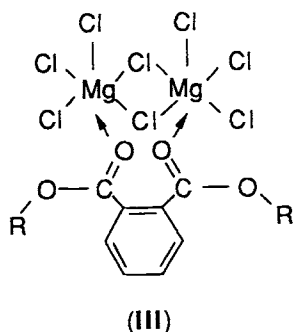
Such exchange could reduce the asymmetric parameter and/or the electric-field gradient with consequent reduction of electric quadruple relaxation. The observation of three carbonyl peaks in Figure 1(b) is consistent with this hypothesis.

The $-\text{OCH}_2$ and $\text{C}=\text{O}$ carbons of EB were downfield shifted by about 5 ppm as a result of complexation with MgCl_2 . Comparison of the C-NMR of MgCl_2/BP and of BP in CDCl_3 showed the presence of downfield shifts in these resonances. There are also unshifted peaks as expected for the ester group not complexed to MgCl_2 .

The T_1^H values for protons on different carbon atoms are the same. This is true for both MgCl_2/EB and MgCl_2/BP . There is rapid intramolecular proton spin-diffusion.

The $\text{MgCl}_2\cdot\text{EH}/\text{PA}$ system is, in fact, DOP complexed to MgCl_2 (*vide supra*). Its C-NMR spectra are consistent with the MgCl_2/BP system discussed above.

The $-\text{O}-\text{CH}_2-$ carbon resonances are sharp singlets with very long T_1 of 1.4 s. The singlet peaks can be due to either one single type of rigidly complexed ester group or two types of ester that are in rapid exchange. The former would also require the complex to have very small electric-field gradients. IR spectra of dicarboxylic ester/ TiCl_4 complexes¹³⁻¹⁵ showed two types of complexation: coordination of carbonyl-ester oxygens with two metal centers as in **I** or coordination of two carbonyls with a metal center as in **III**:



If there are multiple types of complexation of BP with TiCl_4 , then they need to be in rapid exchanges in order to explain the observed spectra.

The $\text{MgCl}_2/\text{TiCl}_4/\text{BP}$ substance was prepared by ball-milling 1 part of TiCl_4/BP complex with 10 parts of MgCl_2 . Several kinds of complexes could result: BP complexed to MgCl_2 ; BP complexed to both MgCl_2 and TiCl_4 ; BP complexed to TiCl_4 , which is attached to MgCl_2 , etc. Table I shows that all the carbon resonances for $\text{MgCl}_2/\text{TiCl}_4/\text{BP}$ are also found in MgCl_2/BP and that the two materials have nearly the same T_1^H . Based on these similarities, one can say that the principal species is BP complexed to MgCl_2 .

CH Catalysts

The fourth-generation ZN catalysts are based on MgCl_2 derived from soluble precursors. The CH catalysts used the $\text{MgCl}_2\cdot\text{ROH}$ complex as the starting material. Catalyst supports prepared by reacting $\text{Mg}(\text{OR})_2$, $\text{Mg}(\text{CO}_2\text{R})_2$, MgR_2 , etc., with HCl are known. Our experience is that diesters, such as phthalate, are very effective Lewis base modifiers to produce CH catalysts high in both polymerization activity and selectivity. Monoesters are much inferior in all respects.

The CH-5, -7, and -8 catalysts are prepared by very similar procedures but they differ in many ways as summarized in Table V. The catalyst productivity of CH-8 is two and three times greater than that of CH-7 and CH-5 catalysts, respectively. CH-8 also has better stereoselectivity than that of CH-5 catalysts. CH-7 has larger pore volume and radius than the other two, which are about the same. However, these properties seem not to be correlated to their performances in propylene polymerizations.

One important difference between CH-5 and the other two catalysts is that it contains much EH and DOP. The measurements on CH-5 samples indicate the presence of TiCl_3OR or even EH itself. TiCl_3OR would have either very little catalytic activity to produce stereoirregular polypropylene or none. The diester is essential for both high activity and stereoselectivity. The aliphatic carbon region of the C-NMR spectra (Fig. 2) are consistent with these hydrolysis GC-MS results.

The C-NMR parameters for the $\text{C}=\text{O}$ resonance in Tables II-IV also showed differences between the three CH catalysts. The best CH-8 catalyst has the most shielded chemical-shifted values for the $\text{C}=\text{O}$ resonances. Both T_1^H and T_{ρ}^H decrease in the order $\text{CH-5} > \text{CH-7} > \text{CH-8}$, whereas the T_{CH} shows the opposite trend. T_{CH}^{-1} is the cross-polarization rate

Table V Comparison of CH Catalysts

	CH-5	CH-7	CH-8
Mg (mmol g ⁻¹)	6.56	6.64	7.96
Ti (mmol g ⁻¹)	0.74	0.39	0.36
Cl (mmol g ⁻¹)	16.3	15.8	18
Mg/Ti	8.9	17	22
EH (mmol g ⁻¹)	0.27	0.009	0.006
BP (mmol g ⁻¹)	0	0.44	0.29
DOP (mmol g ⁻¹)	0.57	(0.3) ^a	(0.15) ^a
Surface area (m ² g ⁻¹)	258	246	279
Pore volume (cm ³ g ⁻¹)	0.23	0.37	0.24
Pore radius (Å)	27	45	26
Productivity [kg PP (g Ti atm h) ⁻¹]	5.5	7.1	15.5
IY (% PP insoluble in refluxing heptane)	96.5	98	98

^a Obtained by difference.

constant. Efficient proton-to-carbon transfer is reflected in short T_{CH} values and requires static dipolar interaction between the two nuclei of concern. The results indicate a more rigid environment for the C=O group in CH-5 than in the other two CH catalysts. This is consistent with the large relaxation times in the CH-5 catalyst. This may reflect a more coordinatively unsaturated site that can complex the ester more rigidly to MgCl₂. The phthalate esters are less rigidly complexed, for instance, to TiCl₄ as discussed for TiCl₄/BP. Once the Ti is reduced, EPR showed delocalization of unpaired electrons from Ti(III) to phthalate.

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