ADVANCES IN POLYOLEFINS

The World's Most Widely Used Polymers

Edited by

Raymond B. Seymour
University of Southern Mississippi
Hattiesburg, Mississippi

and

Tai Cheng
Advanced Polymer Systems
Redwood City, California

PLENUM PRESS • NEW YORK AND LONDON

POLYMERIZATION OF OLEFINS WITH MAGNESIUM CHLORIDE-SUPPORTED CATALYSTS

S. Sivaram and P. R. Srinivasan

Research Centre
Indian Petrochemicals Corporation Limited
Baroda INDIA 391 346

INTRODUCTION

Activated magnesium chloride has been established as an ideal support for titanium-based high efficiency olefin polymerization. One of the earliest disclosed methods was to comill anhydrous magnesium chloride and titanium tetrachloride for prolonged periods either alone[1] or in presence of an electron donor, such as ethyl benzoate (EB).[2,3] A later variant involves comilling anhydrous $MgCl_2$ with an electron donor (typically EB) followed by treatment with $TiCl_4$ in the liquid phase.[4] In some cases prior to reaction with $TiCl_4$, the milled $MgCl_2$.EB complex is also treated with a second electron donor and an organoaluminum compound.[5,6]

Unlike these processes which involve physical milling of $MgCl_2$ (physical activation), more recent literature has alluded to the possibility of support activation using only chemical reactions with $MgCl_2$ (chemical activation).[7] The ability to activate $MgCl_2$ without use of mechanical forces is believed to be responsible for the development of supported titanium catalysts capable of yielding polyolefins with spherical shape and controlled particle size distribution.[8]

In spite of the rapid advances in practical catalysis, a detailed understanding of the nature of morphological changes occurring in the support during the process of activation and its effect on catalyst performance has only recently started to emerge. The primary effect of milling $MgCl_2$ with $TiCl^4$ is to break the layered structure of $MgCl_2$ crystal and to create rotational disorders of Cl-Mg-Cl triple layers.[9-11] With prolonged milling, crystallite sizes progressively decrease, whereas surface area initially increases, up to a certain time, beyond which it either remains constant or decreases.[9,12] This has been attributed to crystal aggregation. $MgCl_2$ and $TiCl_4$ are believed to result in the formation of solid solutions similar to that formed by $TiCl_3$ with $AlCl_3$.[13]

Milling $MgCl_2$ with EB also results in the formation of a new crystalline phase. Conflicting reports have appeared on the nature of changes occurring in the support, as a result of this process. Whereas some authors observed a modest increase in surface area,[14,15] Sergeev et al. reported a decrease in the surface area.[16] Crystallite sizes were reported to decrease progressively with increased milling time.

The observation that the reduction in crystallite size was not accompanied by an increase in surface area led Chien to suggest that the small crystallites are held together as an aggregate by complexation with EB. Treatment of $MgCl_2$.EB complex with $TiCl_4$ resulted in the part by the removal of EB as $TiCl_4$.EB complex, penetration of $TiCl_4$ into the $MgCl_2$ lattice and a large increase in surface area.

It has been suggested that the resultant cleavage surfaces of $MgCl_2$ viz., the (110) and (101) plane contain magnesium atoms which are coordinatively unsaturated which can form strongly bonded surface complexes with $TiCl_4$.[13] This concentrates titanium on the lateral faces and crystal edges of $MgCl_2$, similar to that found in $TiCl_4$.[17] Ethyl benzoate thus assists in breaking down the $MgCl_2$ crystallites and stabilizing the surface complex between electropositive magnesium atoms bound to titanium through double halogen bridges.[18] Although ethyl benzoate has been most widely used, it appears that its role is not specific and many other Lewis bases are capable of similar effects.

In contrast, no report has appeared thus far on the nature of chemical, physical and structural changes occurring in $MgCl_2$ during the process of chemical activation. The present paper attempts to delineate these changes occurring at the various steps involved in catalyst preparation.

EXPERIMENTAL

Material

$MgCl_2.6H_2O$ (s. Merck, India), ethyl benzoate (S. Merck, India), $SiCl_4$ (Aldrich) and diethylaluminum chloride (Ethyl Corp.) were used as received. $TiCl_4$ (S. Merck, India) was distilled under N_2 prior to use. All solvents were dried by distilling over triethylaluminum and were stored under N_2 over sodium wire. All other reagents used in the study were purified by standard methods. All operations involving preparation of catalysts were carried out inside a dry box under a stream of high purity nitrogen.

Methods

Powder x-ray diffraction was obtained with a Phillips instrument operating at 40 K.V and 20 ma using a Ni filtered Cu-K_α radiation. The sample was covered with a thin Mylar film and loaded into the diffractometer. The diffraction pattern was recorded in the range $5° < 2\theta > 60°$. The crystallite sizes were measured in the (101), (001) and (110) direction using the Laue-Scherer equation. The BET surface area was determined using a Carlo Erba Sorptomat Model 1810. The porosity was calculated from surface area values. The estimation of Mg and Cl was carried out using EDTA and argentimetric titrations. Titanium estimation was carried out volumetrically by redox titration.[21]

Anhydrous Magnesium Chloride

$MgCl_2.6H_2O$, 150g was placed in a three necked round bottom flask, fitted with a mechanical stirrer, a nitrogen inlet and outlet. The flask was heated to 135°C with stirring, under a steady stream of nitrogen, for 48 hr. The resulting white powder was preserved under nitrogen. Analysis, Exptl: Mg=25.42%, Cl=73.9%; Calc; Mg=25.49%, Cl=74.5%.

Preparation of $MgCl_2$.6EtOH Adduct

To 5g (52 m moles) of anhydrous $MgCl_2$, 50 mL of absolute ethanol was added and the mixture was refluxed under N_2 for 6 hr. The solution was concentrated and allowed to cool to 0°C. The separated solid was filtered and dried in vacuo. Yield: 19.5g; Analysis, Exptl: Mg=6.50%, Cl=19.08%; Calc. Mg=6.54%; Cl=19.12%.

Preparation of $MgCl_2.2EHA$ Adduct

To 5g (52 m moles) of anhydrous $MgCl_2$, 50 ml of absolute ethanol was added and the mixture was refluxed under N_2 for 6 hr. The solution was concentrated under vacuum, cooled to 0°C and the separated solid filtered and dried in vacuo. Yield: 21g; Analysis, Exptl: Mg=6.81%, Cl=19.3%; Calc. Mg=6.84%, Cl=19.9%.

Reaction of $MgCl_2.6EtOH$ with EB

To 5g (13 m moles) of $MgCl_2$, 6EtOH in 50 ml heptane was added 0.5 ml (3 m moles) of EB. The mixture was heated to 70°C. The solid was then filtered, washed and dried in vacuo. Yield: 5.4g; Analysis for $MgCl_2.(EtOH)_{6.0}(EB)_{0.15}$, Exptl: Mg=6.08%, Cl=18.01%; Calc. Mg=6.17%, Cl 18.03%.

Reaction of $MgCl_2.6EtOH$ with STC and EB

To 5g (13 m moles) of $MgCl_2.6EtOH$ was added 20 ml of STC and the mixture was heated at 60°C for 10 hr. The HCl liberated during the reaction was quantitatively estimated. The excess STC was distilled off 50ml, Heptane and 0.5 ml EB was added and the reaction continued for another 4 hr. The solid was separated, washed with heptane and dried in vacuo. Yield: 7.1 g; Analysis for $MgCl_2.(EtOH)_{4.8}[Si(OEt)_4]_{1.1}$ $(EB)_{0.2}$, Exptl: Mg=4.0%, Cl=12.1%; Calc: Mg=4.2%, Cl=12.3%.

Reaction of $MgCl_2.6EtOH$ with DEAC and EB

To 5g (13 m moles) of $MgCl_2.6EtOH$ was added 20 ml of a 15% by wt. solution of DEAC in heptane and the mixture was heated to 90° for 6 hr. 0.8 ml, EB was added and the reaction continued for another 4 hr. The solid was filtered, washed and dried in vacuo. Yield: 6.8g; Analysis for $MgCl_2$ $(EtOH)_{3.5}$ $(AlEt(OEt)_2)_{2:3}$ $(EB)_{6.15}$ Exptl: Mg=7.6%, Al=15.0%, Cl=12.8%; Calc: Mg=4.0%, Al=10.1%, Cl=11.55%.

Similar procedures were followed for the reaction of $MgCl_2.2$ EHA adduct with STC and DEAC.

Reaction of Activated Supports with $TiCl_4$

To 2g of $MgCl_2.(EtOH)_{4.8}$ $(Si(OEt)_4)_{1.1}$ $(EB)_{0.2}$ complex in 100 ml of heptane was added 8 ml of $TiCl_4$ and the mixture was heated for 3 hr at 80°C. The resulting solid was filtered through a sintered glass crucible, washed with heptane until the filtrate was free of $TiCl_4$ and dried in vacuo. Yield: 3.1 g; Analysis: Ti=2.2%; Mg=8.2%; Cl=22.4%.

RESULTS AND DISCUSSION

Anydrous Magnesium Chloride

Anhydrous magnesium chloride prepared by drying $MgCl_2.6H_2O$ at 135°C showed a hexagonal close packed structure (hcp) similar to δ-$TiCl_3$. (Figure 1a). The XRD showed a strong (101) reflection at d=2.71 Å (32°), (110) reflection at d=1.82 Å (50°) and (001) reflection at d=5.85 Å (15°). The sample had an initial BET surface area of 20-30 m^2/g versus a value

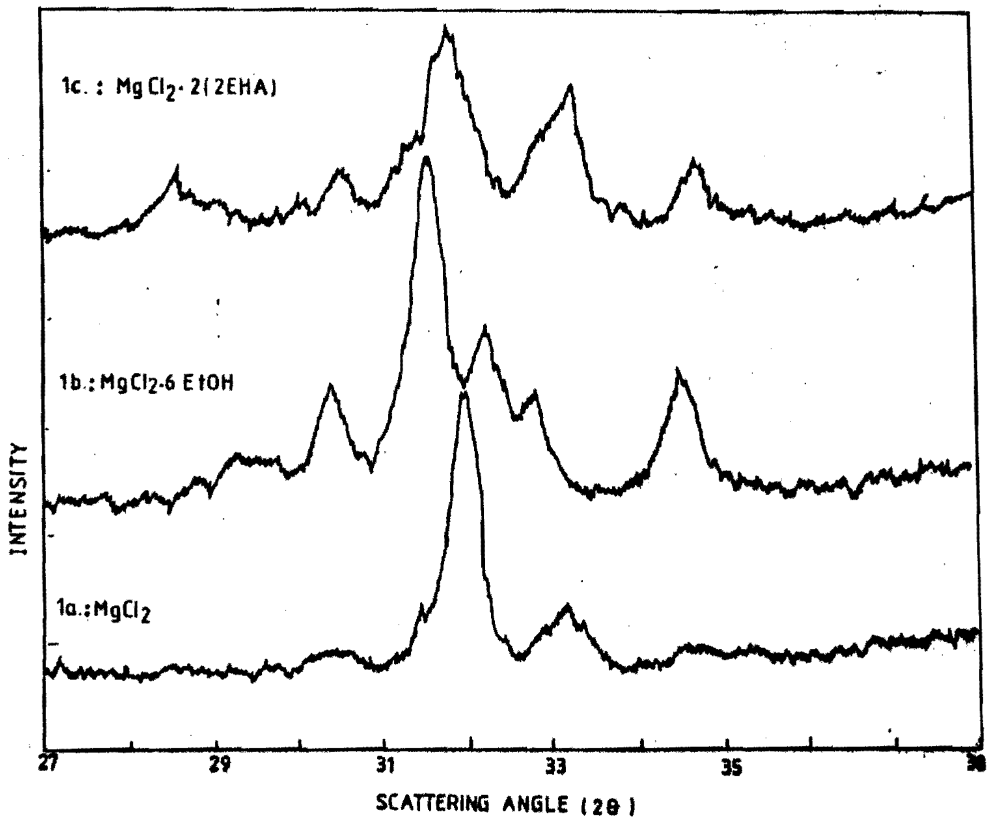

Fig. 1. X-ray Powder Diffraction of $MgCl_2$.Lewis Base Adduct

of 1-2 m^2/g reported for commercial $MgCl_2$.

A hcp structure for $MgCl_2$ has been rarely reported.[19] The most frequently observed structure is the cubic closed packing (ccp), which is thermodynamically more stable and is characterized by a strong (104) reflection at d=2.56 Å (35°) and less intense reflections at (003) plane (d=5.85 Å, 15°) and (110) plane (d=1.82 Å, 50°).

Reaction of Anhydrous Magnesium Chloride with a Lewis Base

The first step in the process of chemical activation, usually involves the reaction of magnesium chloride with a Lewis base. In our study, we chose a series of aliphatic alcohols and phenols, as Lewis bases. It was found that alcohols solubilized anhydrous $MgCl_2$ near their boiling points resulting in the formation of well defined molecular complexes (Table 1). The BET surface area increased two to four fold and the crystallite sizes decreased. Ethylene glycol and phenol were generally less effective than monohydric aliphatic alcohols in destroying the crystalline nature of $MgCl_2$. Alcohols with higher carbon numbers as well as branching caused a more efficient disruption of $MgCl_2$ layer structure (Table 2).

The XRD spectra of $MgCl_2$.6EtOH and $MgCl_2$.2EHA are shown in Figures 1b and 1c.

Reaction of $MgCl_2$.ROH Adducts with a Second Additive

Two adducts viz, $MgCl_2$.6EtOH and $MgCl_2$.2EHA were reacted with one the following additives: ethylbenzoate (EB), silicon tetrachloride (STC) and diethylaluminumchloride (DEAC).

Reaction of $MgCl_2$.6EtOH with EB led to the formation of a new compound, $MgCl_2.(EtOH)_6.(EB)_{0.15}$. Repeated washing with an inert

Table 1. Reaction of Anhyd.$MgCl_2$ With Lewis Bases

R-OH	TEMP., °C	COMPOSITION	S.AREA, m^2-g^{-1}	D_{101}, Å	D_{001}, Å	D_{110}, Å
-	-	$MgCl_2$	30	300	130	68.4
ETHANOL	70	$MgCl_2$.6EtOH	70	186	98	65.3
2-ETHYL HEXANOL(EHA)	120	$MgCl_2$.2EHA	120	158	79	64.6
HEXANOL	150	$MgCl_2$.2 HEXANOL	105	170	100	66.1
p-CRESOL	200	$MgCl_2$.p-CRESOL	85	195	113	66.8
2,6-Di-t-BUTYL-p-CRESOL(BHT)	120	$MgCl_2$.BHT	42	254	123	67.0
ETHYLENE GLYCOL	140	$MgCl_2$.EG	92	175	108	66.8

Table 2. Effect of Branching in Alcohol on $MgCl_2$.Alcohol Properties

R-OH	TEMP. °C	COMPOSITION	S.AREA, m^2g^{-1}	D_{101}, Å	D_{001}, Å	D_{110}, Å
n- BUTANOL	100	$MgCl_2$.2.5(BUTANOL)	95	183	107	66.9
s-BUTANOL	110	$MgCl_2$.2(s-BUTANOL)	90	180	105	66.4
t-BUTANOL	100	$MgCl_2$.2(t-BUTANOL)	110	165	84	64.4

Table 3. Reaction of $MgCl_2$.6EtOH With a Second Additive

ADDITIVE	COMPOSITION	S.AREA, m^2g^{-1}	D_{101}, Å	D_{001}, Å	D_{110}, Å
NIL	$MgCl_2$.6EtOH	70	186	98	65.3
EB	$MgCl_2\cdot(EtOH)_6\cdot(EB)_{0.15}$	148	132	79.3	60.1
STC	$MgCl_2\cdot(EtOH)_{4.8}(Si(OEt)_4)_{1.1}$	172	110	54.8	59.6
STC+EB	$MgCl_2\cdot(EtOH)_{4.8}(Si(OEt)_4)_{1.1}$ $(EB)_{0.2}$	193	92	43.1	58.2
DEAC	$MgCl_2\cdot(EtOH)_{3.5}(EtAl(OEt)_2)_{23}$	154	125	65.7	59.7
DEAC+EB	$MgCl_2\cdot(EtOH)_{3.5}(EtAl(OEt)_2)_{2.3}\cdot(EB)_{0.15}$	165	100	50.3	58.5

EB: ETHYL BENZOATE STC: SILICON TETRACHLORIDE DEAC = DIETHYLALUMINUM CHLORIDE

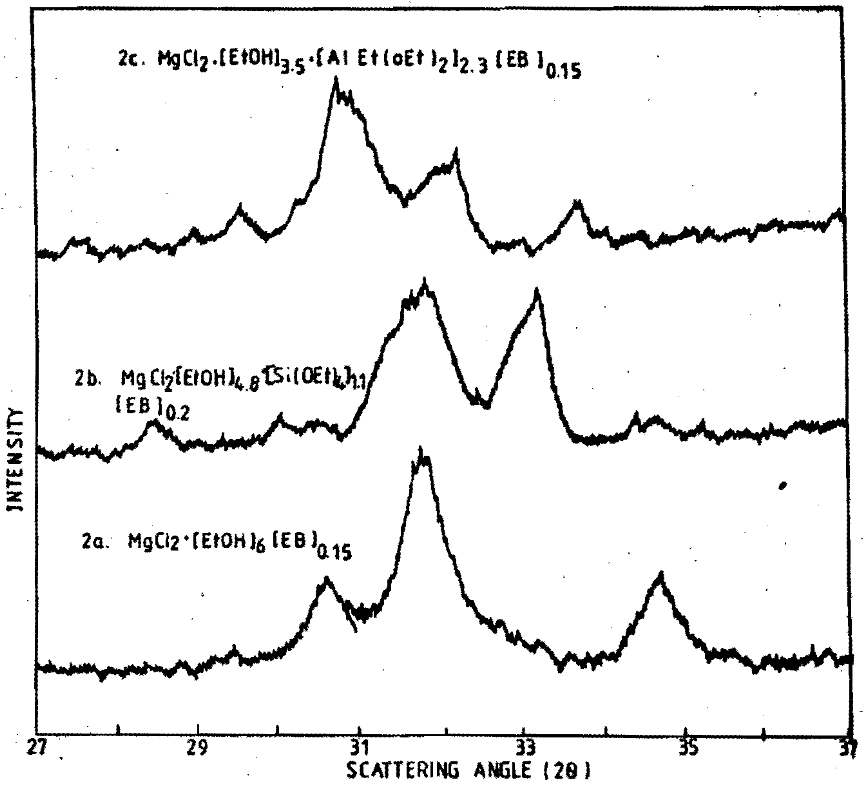

Fig. 2. X-ray Powder Diffraction of the Reaction Product of $MgCl_2$.Lewis Base With Second Additive

Table 4. Comparison of Properties of $MgCl_2$.EB Adduct Obtained by Physical Milling and Chemical Reaction

COMPOSITION	MILLING TIME,HR	D_{110},Å	S.AREA,m^2g^{-1}	REFERENCE
$MgCl_2.(EB)_{0.17}$	NIL	120	70	16
	2	80	6	
$MgCl_2.(EB)_{0.15}$	4	85	6.5	15
$MgCl_2.(EtOH)_6.(EB)_{0.15}$	NIL	60	148	THIS WORK

Table 5. Reaction of $MgCl_2.2EHA$ With a Second Additive

ADDITIVE	COMPOSITION	S.AREA, m^2g^{-1}	D_{101}, Å	D_{001}, Å	D_{110},
NIL	$MgCl_2.2EHA$	120	158	79	64.6
EB	$MgCl_2.(EHA)_2.(EB)_{0.14}$	142	144	69.8	59.2
STC	$MgCl_2.(EHA)_{1.5}.(Si(OR)_4)_{0.5}$	150	134	61.2	58.3
STC+EB	$MgCl_2.(EHA)_{1.5}(Si(OR)_4)_{0.5}.(EB)_{0.15}$	155	130	56.8	58.0
DEAC	$MgCl_2.(EHA)_{1.1}.(EtAl(OR)_2)_{0.9}$	148	149	68.3	59.4
DEAC+EB	$MgCl_2.(EHA)_{1.1}(EtAl(OR)_2)_{0.9}.(EB)_{0.14}$	153	136	58.8	58.3

EHA: 2-ETHYL HEXANOL EB: ETHYL BENZOATE STC: SILICON TETRACHLORIDE DEAC: DIETHYLALUMINUM CHLORIDE - OR : 2-ETHYL HEXANOL

not change the composition indicating complexation. The composition of this adduct, with respect to EB, is similar to that which Chien and coworkers reported obtained after ball milling $MgCl_2$ and EB for 162 hr.[20] The reaction with EB did not displace any of the alcohol already complexed with $MgCl_2$, but caused an increase in surface area and further reduction in crystallite sizes (Table 3, Figure 2a).

Of the three important planes, namely (110), (101) and (001), the (001) plane represent the plane perpendicular to chlorine layer while (110) and (101) represent the planes along the chlorine layers. In the structure of $MgCl_2$, individual Cl-Mg-Cl layers are held by weak van der Waal's forces, whereas within layers, stronger ionic and even covalent bonds dominate.

As observed during milling, treatment of $MgCl_2$ with EtOH and EB appears to cause a breakdown of crystallites, both in the (001) and in (110) direction. However, the breakdown is more rapid in the energetically favored (001) direction than in the (110) direction. Earlier reports on physical milling of $MgCl_2$ with EB indicate that prolonged milling causes the small $MgCl_2$ crystallites to aggregate, resulting in a smaller surface area than anticipated[15,17] (Table 4). In the case of chemical activation, such crystallite aggregation does not occur and results in small crystallite dimensions having high BET surface area.

It is also observed that the value of particle size along the (110) direction is smaller with the $MgCl_2.(EtOH)_6\ (EB)_{0.15}$ compared to milled samples of $MgCl_2.(EB)_{0.15}$. Similar results were obtained with $MgCl_2.2EHA$ (Table 5). The reaction of $MgCl_2$. alcohol adducts with STC was conducted 60°C. HCl was evolved and part of the ethanol (or 2-ethylhexanol) complexed with $MgCl_2$ was converted to $Si(OR)_4$.

The composition and properties of the new compounds formed are shown in Table 4 and 5. Further reaction of this compound with EB led to almost quantitative 90% adsorption of EB (0.2 moles/mole $MgCl_2$), further increase in surface area and a decrease in crystallite size (Figure 2b).

Use of silicon halides in the preparation of high efficiency olefin polymerization catalysts has been recently reported.[7,21] It was suggested that the role of silicon halide is to react with the alcohol and at least partially remove it from the $MgCl_2$.alcohol adduct.[7] Our results show that only about 20 mole % of the alcohol is lost from the $MgCl_2$.alcohol adduct. Under similar conditions free ethanol reacted quantitatively with STC giving silicon tetraethoxide.

Silicon tetraethoxide by itself caused negligible change in the properties $MgCl_2$. However, STC and EB caused substantial changes in the crystal structure of $MgCl_2$. STC was far less effective in the case of $MgCl_2$. EHA adduct although it displaced approximately 25 mole % of the alcohol. (Table 5).

In the $MgCl_2$. alcohol adducts, the crystallites are probably held together by complexation with alcohols in the form of larger agglomerates. The role of STC is to remove these alcohols by reaction, thus causing the collapse of the agglomerates. The reason why STC is more effective with the ethanol adduct compared to 2-EHA adduct may be due to the relatively smaller size of primary crystallites being held together by 6 moles of complexed ethanol as against 2 moles of 2-ethylhexanol.

The reaction of $MgCl_2$. alcohol adduct with DEAC also resulted in the partial displacement of alcohol (Table 4 and 5). However, reaction with DEAC and subsequently with EB, resulted only in a marginal increase in surface area and a decrease in crystallite sizes (Figure 2c). It is apparent that whereas DEAC is superior to STC in displacing the alcohol from the adduct, STC is far more effective in activating the support. Further treatment of these compounds with EB causes absorption of EB and a further increase in surface area/decrease in crystallite sizes.

Reaction of Activated $MgCl_2$ with $TiCl_4$

The various adducts prepared previously were treated with excess $TiCl_4$ at 80°C in heptane as solvent. The composition and properties of the product after washing free of excess $TiCl_4$ are shown in Table 6. XRD pattern (Figure 3) shows broadening of the peaks around $2\theta=32.3°$, indicating the diffusion of $TiCl_4$ and further cleavage of $MgCl_2$ surfaces.

In the case of catalyst containing aluminum, a shift in the peaks around $2\theta=32°$ and the appearance of new peaks around $2\theta=25°$, indicate a process of annealing and cocrystallization of $MgCl_2$ with $TiCl_3$, similar to the observation of Chien.[15] Treatment with $TiCl_4$ also caused an increase in surface area and catalyst porosity. It was found that as much as 50-60% of added titanium is fixed on the support. The efficiency of fixing on a chemically activated support is superior to what has been reported for supports prepared by milling $MgCl_2$ with $TiCl_4$ or EB.[12,16] The ultimate surface area and crystallite size of the catalyst prepared during the present study were similar to those obtained by earlier workers using physical techniques for $MgCl_2$ activation.

CONCLUSIONS

1. Alcohols and phenols solubilize anhydrous magnesium chloride with the formation of well-defined molecular complexes. This is accompanied by increase in BET surface area and decrease in crystallite size, indicating that the layer structure of $MgCl_2$ is disrupted. The smaller crystallites of $MgCl_2$ are held together in the form of layer aggregates by complexation (hydrogen bonding) with alcohols.

2. Alcohols with higher carbon numbers and branching appear more efficient in this process. Phenols are less effective. However, ethanol may be preferred for the formation of stable crystallite agglomerates.

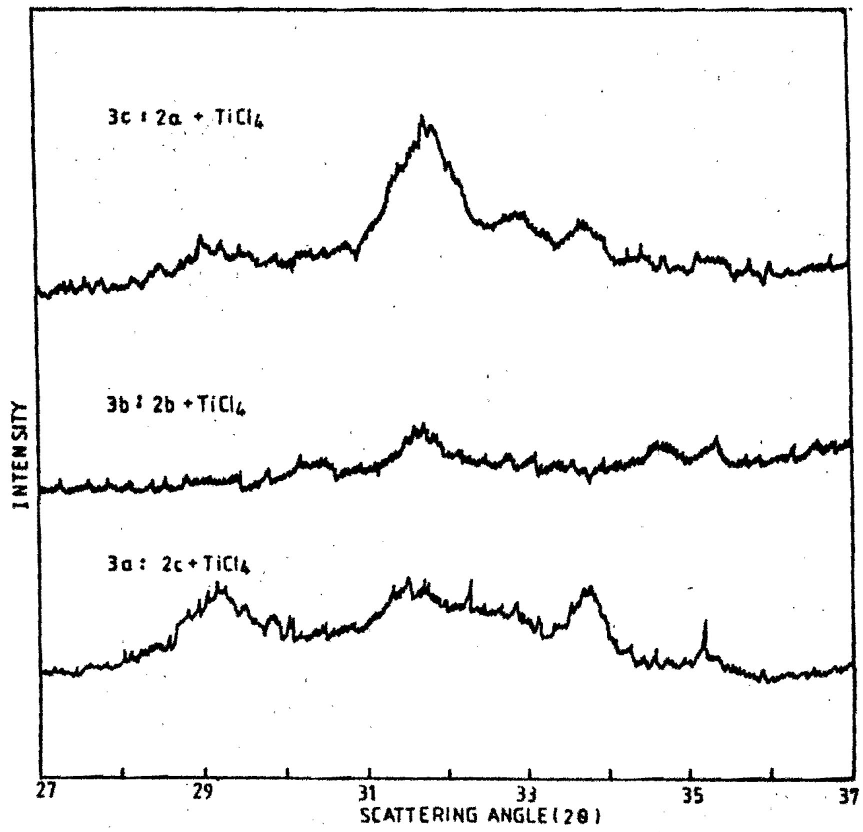

Fig. 3. X-ray Powder Diffraction of $TiCl_4$ Treated Final Product

Table 6. Reaction of Activated Support With Titanium Tetrachloride

PRECURSOR	Ti,%	S.AREA,m^2g^{-1}	POROSITY,Cm^3g^{-1}	D_{101},Å	D_{001},Å	D_{110},Å
$MgCl_2 \cdot (EtOH)_6 \cdot (EB)^a_{0.15}$	2.0	194	1.03	65	38.7	61.5
$MgCl_2 \cdot (EtOH)_{4.8} \cdot (Si(OEt)_4)_{1.1}$ $(EB)^b_{0.2}$	2.2	242	1.38	52	30.5	60.1
$MgCl_2 \cdot (EtOH)_{3.5}(EtAl(OEt)_2)_{2.3}$ $(EB)^c_{0.15}$	1.9	186	0.94	58	40.3	62.1

[a] Mg=12%; Cl = 24.6% [b] Mg = 8.2%; Cl= 22.4% [c] Mg = 9.7%; Cl= 22.6%

3. Treatment of the $MgCl_2$. alcohol complex with ethylbenzoate causes further disruption of the $MgCl_2$ structure. Ethyl benzoate does not displace the complexed alcohol. Unlike physical milling, reduction in crystallite size during chemical activation is not accompanied by reduction in surface area, indicating that crystal reaggregation may not be occurring.

4. Treatment of $MgCl_2$. alcohol complex with silicon tetrachloride or organoaluminum compound, results in the partial removal of alcohol, causing further collapse of the $MgCl_2$ crystal aggregates.

5. Reaction of the activated $MgCl_2$ support with $TiCl_4$, leads to efficient fixing of titanium on the support, with further increase in surface area and porosity and a decrease in crystallite dimensions.

6. During the entire process of activation, crystallite size in the (101) plane decreases from 300 Å to 50-60 Å. This cleavage face, containing coordinatively unsaturated magnesium ion bonded to five chlorine atoms, is believed to form a complex with $TiCl_4$.

ACKNOWLEDGEMENT

The authors thank Dr. J. D. Patel, Mr. J. H. Oza and Mr. R. M. Shah for experimental assistance and Dr. K. V. Rao for assistance with x-ray measurements. Thanks are also due to IPCL management for permission to publish this paper.

REFERENCES

1. Ger. 2,153,520 to Montedison S.p.A, CA 77:62505s (1972).
2. Ger. 2,347,577 to Montedison S.p.A, CA 83:59870a (1972).
3. Ger. 2,638,429 to Montedison S.p.A, CA 86:140706x (1975).
4. Belg. 848, 427 to Montedison S.p.A, CA 87:68893v (1977); Japan 79,118,484 to Mitsubishi Industries, CA 92:59450z (1979).
5. Ger. 2,809,318 to Montedison S.p.A, CA 89:216056h (1978).
6. N. Kashiwa and J. Yoshitake, Makromol. Chem., 185, 1133 (1984).
7. U.S. 4,227,589 to Montedison S.p.A, CA 86:172169d (1981); Ger. 3,022,738 to Mitsui Petrochemical Ind., CA 94:122303n (1981); H. L. Hsieh, Catal. Rev. - Sci. Eng., 26, 631 (1984).
8. P. Galli, L. Luciani, and G. Cecchin, Die Angew. Makromol. Chem., 94, 63 (1981).
9. P. Galli, P. C. Barbe, G. Guidetti, R. Zanetti, A. Martorana, A. Marigo, M. Bergozza, and A. Fichera, Eur. Polym. J., 19, 19 (1983).
10. C. Dumas and C. C. Hsu, J. Macromol. Sci. - Rev. Macromol. Chem. Phys., C-24, 355 (1984).
11. U. Giannini, Makromol. Chem. Suppl., 5, 216 (1981).
12. N. Kashiwa, Polymer J., 12, 603 (1980).
13. P. Galli, P. C. Barbe, and L. Noristi, Die Angew. Makromol. Chem., 120, 73 (1984).
14. B. Keszler, G. Bodor and A. Simon, Polymer, 21, 1037 (1980).
15. J. C. W. Chien, J-C. Wu, and C-I. Kuo, J. Polym. Sci. Polym. Chem. Ed., 21, 737 (1983); J. C. W. Chien, Catal. Rev. - Sci. Eng., 26, 613 (1984).
16. S. A. Sergeev, G. D. Butakov, V. A. Zakharov, and E. M. Moroz, Makromol. Chem., 184, 2421 (1983).

17. J. Boor, J. Polym. Sci., Pt A-1, 9, 617 (1971).
18. F-J. Karol, Catal. Rev. - Sci. Eng., 26, 557 (1984).
19. S. Xiao, S. Cai, H. Lui, S. Zhang, and L. Zhou, Tsui Hua Hsuch Pao, Polymer, 1(4), 291 (1980).
20. J. C. W. Chien, J-C. Wu, C-I. Kuo, J. Polym. Sci., Polym. Chem. Ed., 20, 2019 (1982).
21. Japan 80-1510 10 to Mitsui Petrochemical Industries, CA 94:122292h (1980).