Amoco CD Commercial Polypropylene Catalyst Tailor-Made for the Amoco-Chisso Gas Phase Process.OrganotitaniumComplexCoordinated on $MgCl_2$.

ABSTRACT

This paper presents the commercial profile of the Amoco CD MgCl□-supported polypropylene catalyst. It discusses the development and unique preparation method of the catalyst, emphasizing particle morphology and the parameters affecting particle size (PS), particle size distribution (PSD), and particle shape.The catalyst's outstanding performance, specifically tailored for the Amoco-Chisso gas phase process, is due to synergistic effects originating from both catalyst and process design factors. The median particle size (d50) of the catalyst can be controlled within the range of 7-100 microns. Factors influencing PS and PSD during catalyst support preparation include agitation speed, temperature, organic reagent to Mg ratios,morphology-controlling agents, and the deliberate spiking of the aromatic solvent with appropriate contaminants.Variations in particle shape, ranging from cubic to spheroidal, are affected by the types of reagents used, the ratios of these reagents to Mg, the time/temperature profile of the procedure, and the sequence of reagent addition during catalyst support preparation. Catalyst activation occurs in several steps through thermal treatment of the support with TiCl□/toluene solutions. A cost-effective TiCl□/toluene reuse system from the activation streams has been implemented to significantly reduce waste material. The optimum activation temperature is approximately 120°C.The progress of activation and catalyst quality can be monitored by IR spectroscopy, with identifiable IR fingerprint patterns correlating well with catalyst performance. Recently, a new concept of supported catalysts based on CD technology has been developed, featuring organometallic complexes instead of just TiCl□ as the polymerization active centers. These new catalysts demonstrate improved performance and advantageous polymer product properties.We propose that several organometallic complexes may herald a new era in polyolefin catalysis, including single-site catalysts activated by TEA and production of advanced polyethylene copolymers. The success of the CD and Amoco-Chisso process is illustrated by the two dozen commercial plants worldwide using the technology and the recent licensing advances by INEOS, the successor of Amoco, for this polypropylene technology.

Keywords: Amoco CD polypropylene catalyst; gas phase; Amoco-Chisso process, organotitanium

Introduction

Supported catalysts for the polymerization of propylene to isotactic polymer dominate the commercial production of polypropylene (PP), which is now approaching eighty million metric tons annually worldwide. Most commercial supported isotactic PP catalysts consist of TiCl4 supported on MgCl2 with di-n-butyl or diisobutyl phthalate(DBP) as an internal modifier. These are used along with a trialkyl aluminum (usually $AlEt_3$) as a cocatalyst and a dialkyl or dicycloalkyldimethoxysilane as an external modifier[1,2]. In recent years, there has been significant research activity aimed at replacing DBP[3] due to its alleged safety problems .

Among the most important attributes of these supported catalysts are their superior activity, reaching up to 100 kg of PP per gram of catalyst in certain cases, and their stereospecificity, which hovers around 99%. The type of internal (and sometimes external) modifier may also affect several other attributes of the catalyst, such as hydrogen response, melt flow rate (MFR), molecular weight (MW), molecular weight distribution, and polydispersity.

Several well-known international chemical companies manufacture these catalysts for sale, for their own use, or as part of a licensing package for their PP technology. Since the late 1970s, Amoco Chemicals (later BP, and now part of INEOS), the second largest producer of PP in the USA at the time, had an active research program to develop its own $MgCl_2$-supported catalyst, nicknamed "CD". CD was designed for Amoco's low-cost gas-phase process, developed in collaboration with Chisso, called the "Amoco-Chisso Process". This process has strict requirements for catalyst particle morphology, narrow particle size distribution (PSD), density, and resistance to attrition. Additionally, it was desirable for the catalyst to be used "as is," without prepolymerization.

Most commercial catalyst manufacturing processes are based on rendering anhydrous $MgCl_2$ soluble in various alcohols through the formation of $MgCl_2 \bullet nROH$[4] and forming particles by extracting the alcohol (de-alcoholation) following prescribed recipes . In contrast, the Amoco CD catalyst support preparation involves a unique step of precipitating a solid by reacting Mg alkyl carbonate with $TiCl_4$, followed by dissolving this solid with a cyclic ether, and then slowly precipitating (crystallizing) a support with controlled particle morphology[5]. This approach provides maximum control over particle morphology, particle size (PS) and PSD, crystal density, and particle shape, which are critical for the Amoco-Chisso gas-phase process. By manipulating certain precipitation parameters, spheroidal, cubical, hexagonal, and other shapes of particles can be obtained. No other manufacturing process can deliver such diversity in catalyst morphology.

The advantageous morphology characteristics of CD result in polymer powders with excellent flowability and high bulk density. The catalyst was optimized and tailored for the Amoco-Chisso gas-phase (co)polymerization process. The synergism of advanced catalyst, process, and product technologies established a leadership position in PP manufacturing. Three specific features differentiate this technology: the unique horizontal stirred bed reactor design, characterized by a powder residence time distribution approaching the plug-flow ideal; the high-quality CD catalyst, which is "prepolymerized" in situ between catalyst feeding and the particles reaching the polymerizing polymer bed inside the reactor; and the impact copolymer product, which exhibits a superior impact-to-stiffness balance over a wide temperature range[6].

It should be noted that the gas phase process is preferred over the bulk process by several PP manufacturers for many reasons, including simplicity, flexibility, cost, safety, and environmental friendliness (green chemistry). This preference has been gradually recognized by the industry. Today, there are three dozen plants around the globe utilizing this technology, and for several yearsINEOS was the leading company in PP technology licensing[7].

The present paper discusses the CD preparation procedure and several methods to control its particle morphology and catalyst activation.

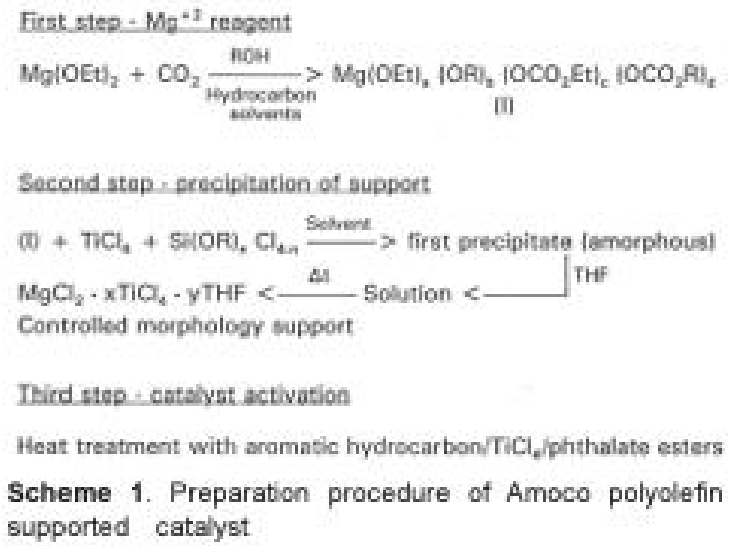
Experimental

All chemicals used for the laboratory preparation or commercial production of CD must be thoroughly dried by conventional methods. Commercial grade TiCl4 was applied as received. Special care must be given to drying the solvent, toluene, as the usual source of unsuccessful runs is "wet" toluene. The original Amoco CD preparation methods have been previously described in detail[5, 8]. A general outline is presented in Scheme 1. The procedure consists of three steps:

1. **Mg alkyl carbonate solution preparation:** This is done by reacting to a suspension of $Mg(OEt)_2$ in toluene-alcohol with CO_2 (MAC solution).
2. **Support preparation in two steps:**
    - **A. Precipitation of an initial solid:** This is achieved by reacting MAC with TiCl4 and a morphology-controlling agent, such as $Si(OEt)_4$, in toluene.
    - **B. Dissolution and re-precipitation:** The initial solid is dissolved by adding tetrahydrofuran (THF) to the suspension, followed by automatic slow re-precipitation (crystallization).
3. **Support activation:** This involves two sequential treatments with $TiCl_4$ and $TiCl_4$-DBP, respectively, in the presence of toluene. This is followed by post-activation treatments of the catalyst solid with toluene and with $TiCl_4$. It is not necessary to use fresh $TiCl_4$ or toluene for each activation step. An elaborate system has been developed for recycling and/or reuse. For example, TiCl4/toluene from the post-activation treatments may be used without purification in the first activation step.

The CD catalyst composition may vary slightly from preparation to preparation; typical values are Ti 3%, Mg 18%, Cl 61%, DBP 14%, solvent 4%. There is a linear relationship between Mg and Ti content, or Mg and DBP content for any given supported catalyst[1]. The linear Mg-DBP correlation supports the conclusion that DBP coordinates with the Mg ion. In commercial gas phase operations, the catalyst yield is between 50 kg and 70 kg per g of CD, with a stereospecificity of 99%.

Several variations were introduced in the above CD preparation procedure to probe the effects on particle morphology. The original morphology-controlling agent $Si(OEt)_4$ was replaced by other suitable compounds, such as Me_3SiOEt[9], di-n-butyl phthalate[10], and $Si(O\text{-}n\text{-}Bu)_4$[11]. The use of $B(O\text{-}n\text{-}Bu)_3$ was also reported during the preparation of supports of the Amoco CD type[12]. Ethanol[9], methanol, and/or n-butanol[10] were included in the reaction mixture prior to the precipitation of the initial reaction product with the MAC solution. The toluene used during



Scheme 1. Preparation procedure of Amoco polyolefin supported catalyst

support precipitation was contaminated on purpose with various levels of xylenes, ethylbenzene, and/or naphthalene[8]. Compounds of the $SiRnCl_4$-n type were used as second chlorinating agents during support preparation. A method for further improvement of the attrition resistance of CD was also developed. Following the activation of the solid with $TiCl_4$ and DBP, a new step involving a long cooling period was inserted, followed by the post-activation treatments[10]. Finally, temperature and agitation speed variations during support preparation have been used to tailor catalyst particle size. Details are given in the next section.

Results and Discussion

The CD preparation procedure provides excellent control over catalyst morphology, which was the primary consideration in the development of the catalyst. The support product that crystallizes after the THF addition has the approximate general formula: $MgCl_2$•0.031TiClx(OEt)y•1.48 THF. It appears that the support crystals are related to the well-known adduct $MgCl_2$•1.5THF[13], with anticipated crystal structure similarities. Determining the various parameters affecting PS, PSD, and shape was integral to improving CD morphology. Table 1 shows the most important of these parameters. The easiest and fastest way to control the median PS (d50) is through the agitation speed (Figure 1). There is a linear relationship between RPM and d50. The reactor configuration may also play an important role in this relationship. For example, the existence of a baffle and the use of a marine impeller appear to contribute to reproducible results. The effect of temperature prior to the THF addition is also significant.

PSD data for CD catalysts were obtained using a Shimadzu SALD-1100 laser diffraction particle size analyzer. Polymer powder PSDs were determined by sieve analysis. Catalyst and polymer photomicrographs were recorded via scanning electron microscopy.

Table 1. Support precipitation parameters

Particle size and size distribution control	Particle shape
Agitation speed (RPM) Temperature ROH/Mg THF/Mg $Si(OR)_xCl_{4-x}$ Solvent impurities	THF/Mg $Si(OR)_xCl_{4-x}$

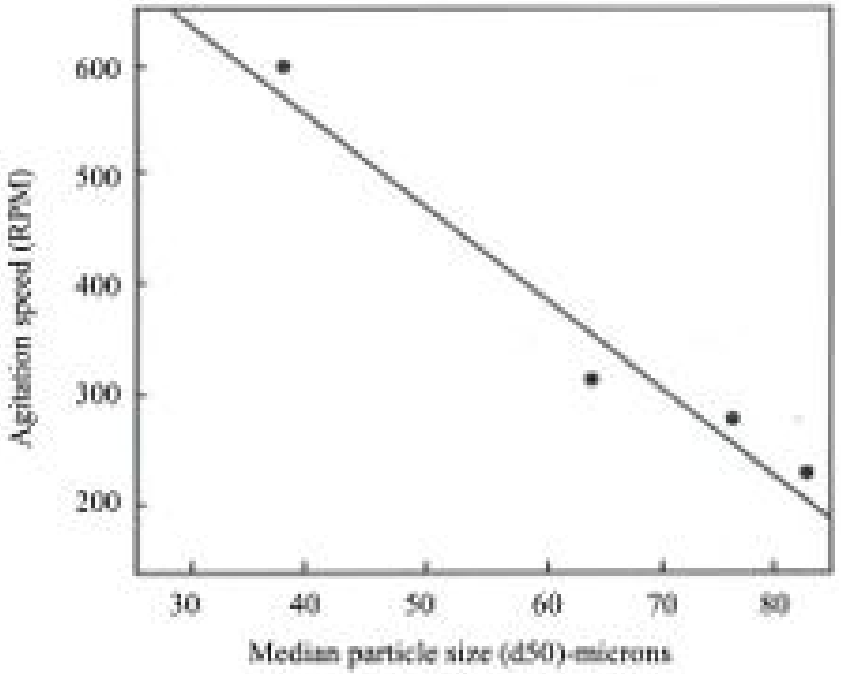


Figure 1. Effect of agitation speed on median particle size of large spheroidal Amoco supported catalyst.

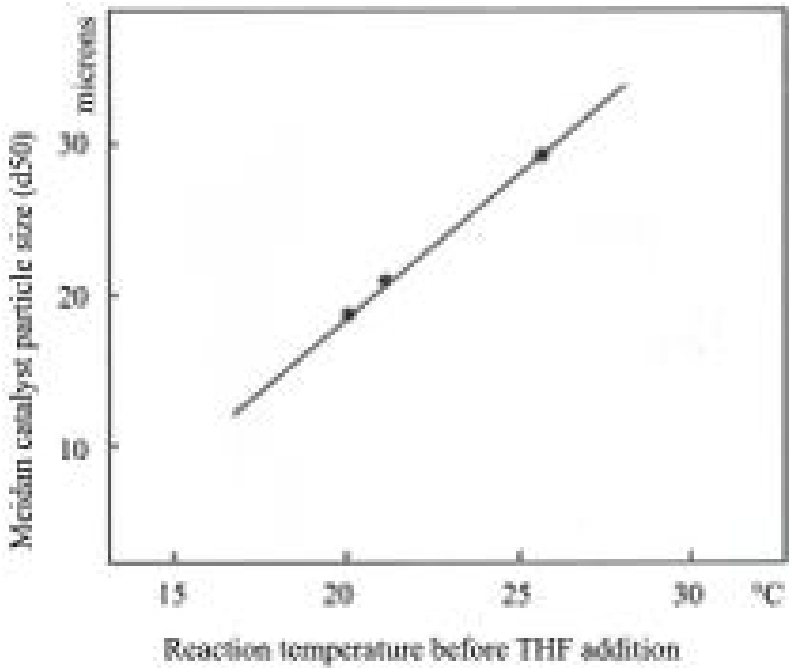


Figure 2. Effect of reaction temperature before THF addition on median particle size of Amoco supported catalyst.

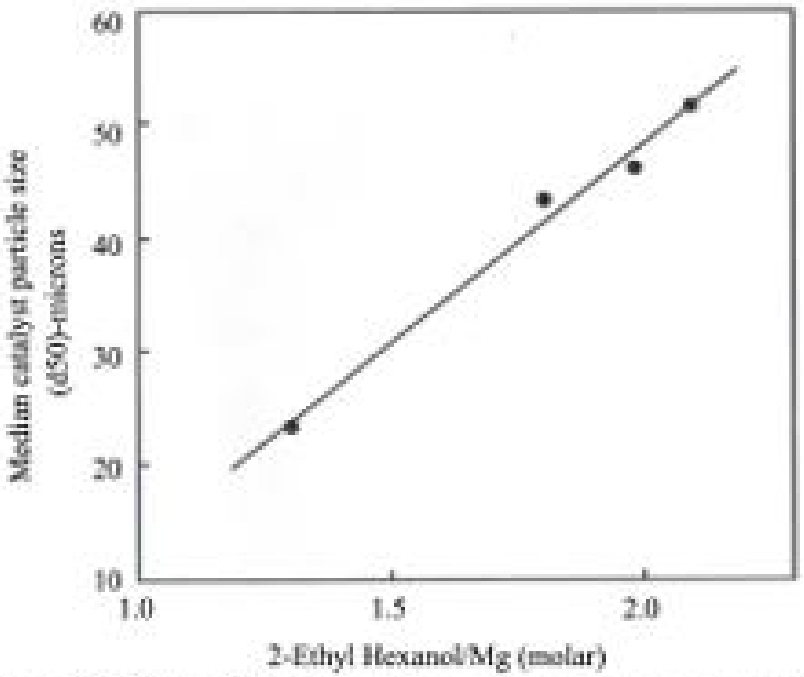


Figure 3. Effect of ROH/Mg molar ratio on Amoco supported catalyst median particle size at constant agitation speed (300 rpm)

The effect of agitation speed on the median particle size (d50) of large spheroidal Amoco-supported catalysts is depicted in Figure 2. Lower temperatures result in faster and multiple crystal "seed" formation, leading to a smaller d50. Agitation speed and temperature can be considered mechanical/thermal parameters.

The following are physical/chemical effects: The 2-ethyl hexanol/Mg molar ratio in the MAC solution significantly influences particle d50 (Figure 3). A more dilute solution results in a larger d50. By selecting the right combination of all these factors, we can achieve the desired d50, typically in the range of 7 to 100 microns, with a sufficiently narrow PSD.

Another parameter affecting both d50 size and particle shape is the THF/Mg molar ratio. At high ratios (Table 2), smaller particles with a cubical shape are formed.

Table 2. THF/Mg molar ratio vs. particle size/shape

THF/Mg molar ratio	Median catalyst particle size (d_{50})	Shape
6.1 - 4.1	Small (7 - 30 microns)	Cubical
3.3 - 2.8	Large (30 - 100 microns)	Spheroidal

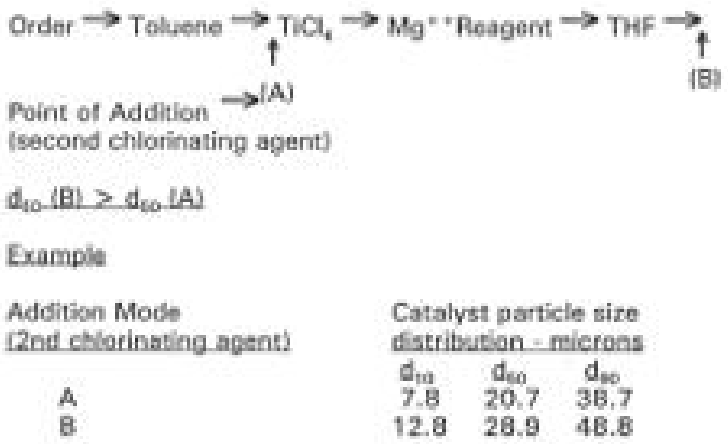
At smaller ratios, larger spheroidal particles are obtained (Figure 2).

The substitution of $Si(OR)nCl_4$-n type compounds for $Si(OEt)_4$ during support preparation leads to the precipitation of spheroidal supports. The introduction point of $Si(OR)nCl_4$-n, acting as both a morphology-controlling and second chlorinating agent, affects both the PS and the PSD of the spheroidal catalyst produced (Scheme 2). Furthermore, $Si(OBu)_4$ yields smaller PS than $Si(OEt)_4$ (Table 3).

Table 3. Effect of silanes catalyst size- (microns)

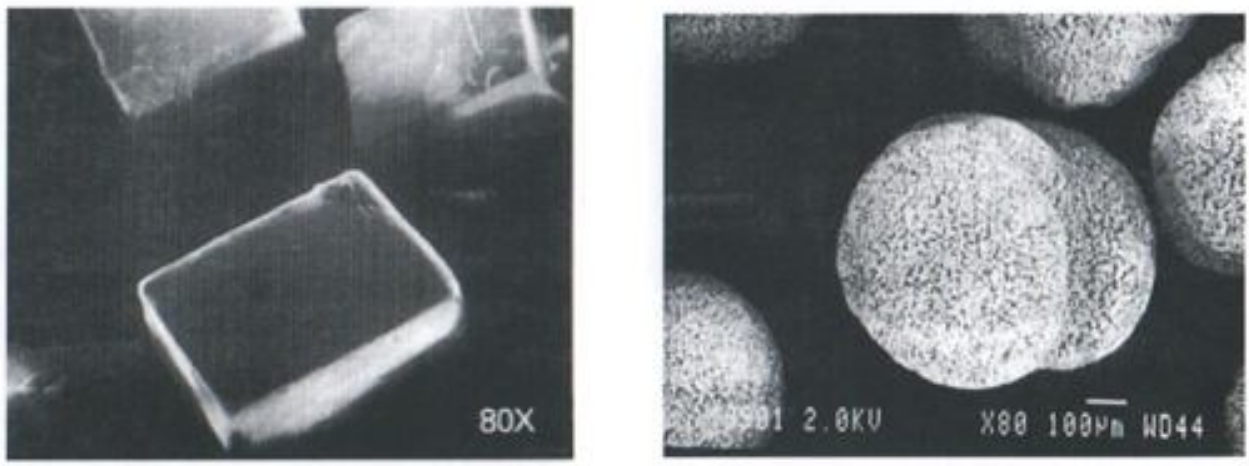
	$Si(OEt)_4$			$Si(OBu)_4$		
	-d-10	-d-50	-d-90	-d-10	-d-50	-d-90
	7.4	16.9	28.5	2.3	7.7	16.5
	8.5	17.8	28.4	5.3	12.6	21.9
				2.2	7.7	17.1
				2.8	9.8	21.5
Avg.	8.0	17.4	28.5	3.2	9.5	19.3

A different method for preparing large spheroidal particles was developed in the absence of alkoxysilanes. At low agitation speed (300 rpm), DBP and methanol were used as morphology-controlling reagents, while THF was substantially reduced. Additionally, toluene solvent contaminants such as xylenes, ethyl benzene, and naphthalene were shown to influence PS and PSD. For example, naphthalene contamination within the 2,000 to 12,000 ppm range results in PSD narrowing and, in most cases, a reduction of the d50 of the catalyst.



Scheme 2. Effect of the order of addition (second chlorinating agent) on catalyst particle size

The importance of particle shape lies primarily in its effects on polymer powder flowability and bulk density. The shape of polymer particles replicates those of the catalyst. We can develop CD supports in various shapes, such as cubes, spheres, clusters, hexagonal prisms, footballs, and even needle-shaped particles. Two common shapes are depicted in Figure 4.



(a) (b)

Figure 4. SEM photomicrographs of PP particles from Amoco catalysts

Support Activation Catalyst activation is a two-step process involving toluene and $TiCl_4$ treatments, followed by several hexane washes and drying in a nitrogen stream. The first activation occurs in an agitated suspension of the support in a toluene solution of $TiCl_4$ at an elevated temperature (110-120˚C) for one to two hours. During this time, most of the THF is removed, leaving behind porous particles, and the $MgCl_2$ undergoes a crystalline transformation. After settling and decantation of the supernatant, a second activation under similar conditions takes place, this time in the presence of the internal modifier, DBP. The temperature of this step is critical, with an optimum close to 120˚C. The activation progress can be monitored by IR spectroscopy. Under- or over-activated catalysts show typical IR fingerprints, which are also reflected in their polymerization performance and catalyst composition. Over-activated catalysts may contain phthaloyl chloride from the reaction of DBP with TiCl4 at higher temperatures. The final toluene and TiCl4 treatment remove minor contaminants/byproducts that may reduce catalyst performance. These treatments, however, could be avoided without adverse consequences on catalyst quality.

Amoco CD and the Amoco-Chisso Gas Phase Process The CD catalyst was tailor-made for the Amoco-Chisso process, which features a unique horizontal stirred bed reactor characterized by a powder residence time distribution approaching the plug flow ideal. This design ensures nearly equivalent reactor residence times for all powder particles, resulting in faster, sharper product transitions, higher catalyst yields, minimal "bypassing" of the catalyst, ensuring high-impact copolymer product quality, and rapid start-ups and shut-downs. The impact copolymers produced using the Amoco-Chisso process and CD catalyst exhibit a superior balance of stiffness and impact properties over a wide temperature range.

Internal Modifiers and Their Role

Significant research efforts have been devoted to replacing the original butyl phthalate internal modifiers (IM) in $MgCl_2$-supported polypropylene catalysts, primarily due to safety concerns. A

new approach has now been developed where the IM can be partially replaced by a Ti or Zr organometallic complex, imparting enhanced catalytic performance.

Ninety-five percent of the world's production of polypropylene (PP) and ninety percent of polyethylene (PE) is currently carried out using $MgCl_2/TiCl_4$-supported catalysts, activated by triethylaluminium (TEA). For PP, the catalytic system incorporates internal donors (ID), which are electron-donating organic compounds adsorbed on the surface of $MgCl_2$, and external donors (ED), which are added to the catalyst mix and are necessary for stereoregulation. The ID plays a key role by blocking non-stereospecific active sites, competing with $TiCl_4$ molecules for adsorption sites on $MgCl_2$ faces. IDs affect the molecular weight (MW) and molecular weight distribution (MWD), two fundamental parameters controlling polymer properties[18]. The most common IDs are phthalate and succinate diesters, as well as diethers[19].Diethers strongly coordinate on the $MgCl_2$ surfaces and cannot be removed by TEA, unlike phthalates and succinates that may be partially removed by TEA. The ED's role is to replenish the removed ID during the polymerization process and maintain the stereoregularity of the catalytic system, which is why no ED is necessary with diether $MgCl_2$ catalysts. Common EDs include various dimethoxysilanes (DMS), which form stable complexes with TEA, preventing the formation of unwanted byproducts. The most commonly commercially used system is $MgCl_2/TiCl_4$/Dibutylphthalate (DBP)/DMS.

In the late 2000s, safety issues were raised regarding the use of DBP, prompting a surge of industrial research activity to find suitable substitute IDs. Another incentive for this research was for industrial concerns to establish proprietary positions. Most well-performing IDs are bidentate, attaching to the well-established (100) and (110) surfaces of $MgCl_2$ in either bridge or chelate bonding modes. There is also the zip coordination mode, where the two oxygen atoms of the ID are coordinated to two Mg atoms on different adjacent MgCl2 layers, Figure 5.

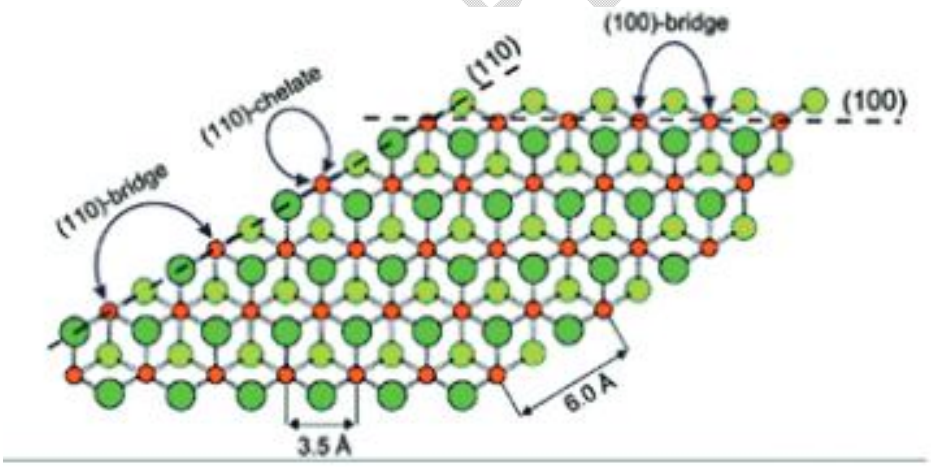


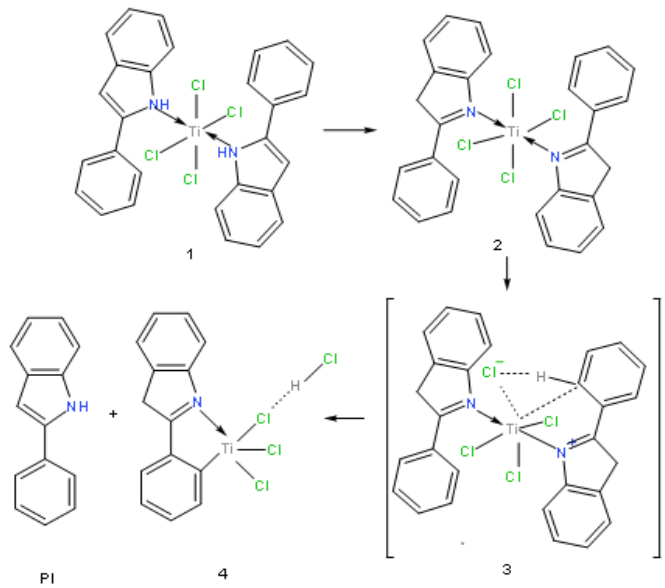
Figure 5. Coordination Modes of IDs on MgCl2 lateral surfaces.

The adsorption modes of various IDs and $TiCl_4$ on the (100) and (110) lateral cuts of $MgCl_2$, along with the implications of their coordination modes on catalyst performance, have been continuously studied, mainly by various academic groups since the 1990s, an activity still ongoing[20]. In the (110) cut, the Mg and Cl atoms are all on the same plane, with the Mg atom

tetracoordinated and having two open coordination sites, which can accept both chelate and bridge ID bonding modes. On the (110) cut, $TiCl_4$ coordinates only as a monomer. The (110) cut is more acidic than the (100). In the (100) cut, only the Cl atoms are on the surface, and the Mg atoms are in a layer below. Here, the Mg is pentacoordinated with one open coordination site, allowing only bridge bonding. On the (100) cut, TiCl4 may coordinate as a monomer, dimer, or even oligomer. The $TiCl_4$ dimer/oligomer after reduction with TEA resembles and mimics the purple unsupported (Solvay) TiCl3 catalyst.

It is noteworthy that all commercially useful internal donors (IDs) are oxygen derivatives. Among nitrogen-containing IDs, tetramethylpiperidine(TP), a hindered amine, was previously considered under extensive investigation but was quickly abandoned. Surprisingly, TP is a very good external donor (ED) but a poor ID. We decided to reexamine the role of other hindered amines as IDs and initially chose 2-phenyl indole (PI), which is readily available and related to a natural product. When tested as an ED, it increased the yield of Amoco CD catalyst in the gas phase by 35%, although the polymer was off-white.

During this investigation, we serendipitously discovered a new and previously unreported ortho-metalation reaction involving PI and $TiCl_4$, as shown in Scheme 5. Mixing PI and TiCl4 in toluene at a 1:2 molar ratio at room temperature under anaerobic conditions initially forms complex 1 in solution, which quickly isomerizes to complex 2. The solution color changes from yellow to light orange. Raising the temperature to 105°C under magnetic agitation turns the color dark burgundy, and complex 4 precipitates out. Complex IV was characterized by analytical and spectroscopic methods. This reaction appears to be general for other ligands capable of undergoing ortho-metalation and is expected to have a significant impact on polyolefin catalysis.



The reaction can be repeated using $ZrCl_4$ instead of $TiCl_4$.

Scheme 5: Mechanism of ortho-metalation, 2-phenyl indole with $TiCl_4$ at the 2:1 ratio.

The H-shift from N to C in complex**1** to **2** was modeled by DFT, and the energy calculated by Dr. Ernest Camot. Complex **2** was found to be lower in energy than complex **1**, suggesting the H-shift should occur spontaneously. The lowest energy conformation has the phenyl group rotated by 3 degrees, bringing the ortho hydrogen within 2.89□ of the Ti, indicating an agostic interaction (transient complex **3**). The Ti-N distance is 2.23□, and Ti is roughly trigonal bipyramidal, with the N in an equatorial position. The agostic bond geometry is 2.0 kcal more stable than the alternative geometry, where the phenyl is perpendicular to the indole.

In complex **2**, the ortho H does not transfer to the Ti and then inserts into a Ti-Cl bond as initially expected. Instead, it transfers to the neighboring axial Cl ligand on Ti through a 4-member transition state in complex **3**. In ortho-metalated complex **4**, the rings are coplanar, with Ti forming a trigonal bipyramid and N in the axial position. The Ti-N bond is 2.20□, and the Ti-C bond is 2.12□.

Coordination of the Organometallic Complex on $MgCl_2$

Next, we discuss how these complexes interact with the $MgCl_2$ lateral cuts and the performance of catalysts incorporating organometallic complex 4 or similar complexes. It is necessary first to explain how an ID like DBP is incorporated into the $MgCl_2$ during catalyst preparation. In commercial $MgCl_2/TiCl_4$ PP catalyst production, such as the Amoco CD, activation is a tedious process, typically taking place in 2-4 stages within an optimum time/temperature profile. The first stage, usually at about 80°C, involves adding DBP to a suspension of $MgCl_2$ in toluene/$TiCl_4$ solution, agitated at about 80-90°C, forming a DBP.$TiCl_4$ complex. The bond of DBP with Mg is stronger than with Ti, and DBP.TiCl4 coordinates on the $MgCl_2$ surface by dissociating into its components, which attach separately on either (100) or (110) cuts (dissociative coordination). This has been clearly established using IR spectroscopy by numerous investigators. The final catalyst's molar ratio of DBP:$TiCl_4$ in the final catalyst is still 1:1.

We prepared a catalyst using PI as the ID, following the Amoco CD procedure. To our disappointment, the catalyst had low activity, well below the standard DBP catalyst. However, we confirmed by solid ^{13}C NMR that the solid contained complex **4**. We then prepared catalysts by introducing mixtures of DBP/PI at 50/50, 75/25, 85/15, and 90/10 molar ratios. The best polymerization results were obtained with the 85/15 and 90/10 catalysts, showing a 60% activity increase over the standard DBP catalyst in a semi-continuous gas-phase polymerization system. The polymer color was normal, unlike the off-white color when PI was used as an ED. Additionally, these catalysts did not contain any free PI, but only about 10% DBP compared to about 14.5% in the standard DBP catalyst, as analyzed by gas chromatography after hydrolysis. The latter also produced a black oily film, apparently originating from complex **4**.

Conversely, the 75/25 and 50/50 catalysts contained free PI, 0.5% and 1.8%, respectively. This was unexpected since the activation temperature reaches 110°C, and ortho-metalation is complete at 105°C. Additionally, the activity of the 50/50 and 75/25 catalysts was inferior to the standard DBP catalyst. Based on these results, we formulated a hypothesis for the mode of PI coordination on the lateral cuts of MgCl2, which may constitute novel ideas in MgCl2 supported polyolefin catalysis:

A. In catalysts using ID mixtures of DBP/PI, the optimum molar ratio maximizing activity is about 85/15. We estimate that this ratio exists in the catalyst itself.

B. At the 85/15 or lower PIlevel, the organometallic complex **4** coordinates to a $MgCl_2$ lateral cut.

C. Addition of PI during the first catalyst activation stage at about 80°C initially forms complex II, which is soluble and coordinates on the $MgCl_2$ surface.

D. At the higher temperature of about 110°C in subsequent activation stages, complex **2** coordinated on the $MgCl_2$ surface converts to ortho-metalated complex 4, remaining strongly attached to the $MgCl_2$ support when the level of PI relative to DBP is 15% or less.

E. At higher PI levels, such as 75/25 and 50/50, part of PHIND coordinates on the $MgCl_2$ surface as complex **2** and part as free PI (dissociative coordination).

The latter dual behavior is unprecedented and perhaps the most interesting. To our knowledge, a similar dual action has not been previously reported in chemical literature. To rationalize this phenomenon, we hypothesize that complex **2**, at the PI level of 15% or lower relative to DBP, coordinates exclusively on the acidic 110 cut of $MgCl_2$ in a chelate mode, with the N and one Cl attached to the Mg.

In essence, complex 2 competes with DBP and TiCl4 for coverage (adsorption) on the 110 cut, but this process appears to proceed entirely in favor of II. A similar pattern is observed in the case of 2,6-diacetylpyridine (DAP), a molecule with two carbonyl groups and one N, which coordinates only by the N on the 110 surface[21]. Thus, complex **2** is the only one preferentially covering the entire 110 cut, estimated to constitute only about 10% of all $MgCl_2$ surface, almost the same as the optimum amount of PI in the catalyst. Complex **2** converts to 4 at the higher temperature of 105°C. On the same $MgCl_2$ particle, DBP and $TiCl_4$ coordinate on the 100 cut. Accordingly, we now have two types of active sites on the same $MgCl_2$ particle: TiCl4/DBP on the 100 cut and complex IV on the 110 cut. Realizing this fact may be the basis for new developments in olefin polymerization catalysis.

At high PI levels (20% or more relative to DBP), complex **2** covers cut 110 first and then coordinates on cut 100 in a dissociative fashion, as only the N on PI can attach to the single coordination site on this cut, in a bridge mode. This type of coordination "protects" PI from further reaction with $TiCl_4$ at the higher activation temperature of 110°C, allowing PI to be analytically detected from the catalyst particle. The excess PI on the 100 cut is detrimental to catalyst performance, as evidenced by our experimental results. Conversely, complex **2** coordinated on the 110 cut at 110°C undergoes ortho-metalation and is expected to form a stronger bond with the $MgCl_2$ support.

Advantages of the Organometallic Complex Coordinated on $MgCl_2$

The immediate advantage of the new catalysts is a polymerization activity increase of up to 60% compared with the standard DBP catalyst. Additionally, it has been observed that the charge of

the DMS ED could be reduced by about 30% without any detrimental effect, suggesting that the ED does not affect the complex **4** active site. Using a combination of $MgCl_2$ supported catalysts incorporating organometallic complexes like **4** as IDs with ligands like PI as EDs may synergistically increase the system's activity by up to 100%. One significant advantage of this catalytic system is the activation with simple alkyls like TEA, unlike metallocenes and post-metallocenes that require MAO for activation.

Besides the catalytic activity improvement of catalysts incorporating organometallic complexes like **4**, the xylene solubles of the produced polymer are less than 2%, and the powder bulk density is usually higher by about 10%. There have also been changes in the hydrogen response of such catalysts and other property improvements. A thorough study has not been conducted in this area, and our findings are summarized below:

1. A Ti organometallic polymerization catalyst coordinated (supported) on $MgCl_2$ is a novel finding with several commercial and scientific implications.
2. The technology can be easily applied to existing commercial systems since the activator (TEA) remains the same.
3. Our catalyst preparation utilizes a soluble complex **2**, which at an elevated temperature converts into an insoluble complex **4**. This is very advantageous in catalyst manufacturing.
4. PI is only one example of a ligand capable of undergoing ortho-metalation with $TiCl_4$ and $ZrCl_4$, improving $MgCl_2$ supported catalyst performance. We have successfully worked with many other ligands showing similar or even better performance.
5. The possibility exists to develop a single-site $MgCl_2$ supported polymerization catalyst if we succeed in introducing complex **4** as the only active site[22]. The obvious advantages of such development would be the production of metallocene-like polymers by every commercial plant.

Conclusion

Supported PP catalysts are expected to remain in commercial use for the foreseeable future. Among available commercial catalysts, Amoco CD, tailor-made for the Amoco-Chisso gas phase process, stands out for its unique manufacturing method, advanced methodology to control morphology, and the synergistic effects between catalyst, process, and product. Although there is an ongoing effort to replace DBP with greener substitutes, it appears that we have reached a plateau in supported PP catalyst performance, which currently meets market needs and growth. The fear that metallocene catalysts would take over from $MgCl_2$ supported catalysts did not materialize due to the latter's efficiency, lower cost, and simplified operation. While new breakthroughs in this technology would be welcome, they are not currently seen on the horizon despite intense R&D efforts worldwide. The development of a single-site catalyst supported on $MgCl_2$ may be possible[23] by replacing $TiCl_4$-based active sites with single-site complexes, although this may not be easy to accomplish. Good candidates for replacement may include FI catalysts or the newly introduced organometallic complexes, which offer activation with aluminum trialkyls.

References

1. **Arzoumanidis G, Karayannis N, Khelghatian M, Lee S (1992)**. "Commercial polypropylene catalysts." *Catal. Today* 13:59-71.
2. **Arzoumanidis G, Karayannis N (1993)**. "Fine-tuning polypropylene." *Chem Tech* 23:43-48.
3. **Arzoumanidis G (2014)**. "Novel Ti-Aryl complexes as internal or external modifiers, improving performance of MgCl□ supported polypropylene catalysts." In: SPE polyolefins conference, Houston, TX.
4. **Hadian N, Hakim S, Nokoomanesh-Haghighi M, Bahri-Laleh N (2014)**. "Storage time effect on dynamic structure of MgCl□·nEtOH adducts in heterogeneous Ziegler-Natta catalysts." *Polyolefins J.* 1:33-41.
5. **Arzoumanidis G, Karayannis N, Khelghatian H, Lee S (1989 Dec 9)**. "Olefin polymerization catalyst," US Patent 4,866,022; (1991 Jan 29) US Patent 4,988,656; (1991 May 7) US Patent 5,013,702.
6. **Corbin G, Lee K (1993)**. "Paper O-Amoco impact copolymer." In: DeWitt petrochemical review. Houston, TX.
7. **Ineos Technologies**. Website.
8. **Cohen S, Arzoumanidis G, Karayannis N, Khelghatian H, Lee S (1990 Aug 7)**. "Morphology-controlled olefin polymerization catalyst," US Patent 4,946,816.
9. **Arzoumanidis G, Dredzdon M, Lee S (1992 Jun 23)**. "Olefin polymerization and copolymerization catalyst," US Patent 5,124,297.
10. **Lee S, Karayannis M (1993 Jun 29)**. "Olefin polymerization and copolymerization catalyst," US Patent 5,223,466.
11. **Arzoumanidis G, Peaches C (1993 Jan 26)**. "Olefin polymerization and copolymerization catalyst," US Patent 5,182,245.
12. **Tachibana M, Uwai T, Matsukawa T, Hayashida T (1992 Jan 28)**. "Catalysts for Polymerization of Olefins," US Patent 5,084,429.
13. **Gnomakumar S (2013)**. "Synthesis and molecular properties of new MgCl□-based molecular adducts towards catalytic polyolefin production." PhD Thesis, CSIR-National Chemical Laboratory, Pune, India.
14. **Arzoumanidis G, Karayannis N (1990)**. "Infrared characterization of supported polypropylene polymerization catalysts-a link to catalyst performance." Study in Surface Science and Catalysis 56: 142-154
15. **Caracotsios M (1992)**. "Theoretical modeling of Amoco's gas phase horizontal stirred bed reactor for the manufacturing of polypropylene resins." *ChemEngSci* 47: 2591-2596.
16. **Novac M (1992)**. "New polypropylene products." In: Polypropylene world congress. Zurich, Switzerland.
17. **Haruyuki M, Hirashi T, Akihiko I, Terumori F (2011)**. "FI catalysts for olefin polymerization-A comprehensive treatment." *Chem Rev* 111: 2363-2449.
18. **Groppo E, Seenvasan K, Barzan C (2013)**. "The potential of Spectroscopic Methods Applied to Heterogeneous Catalysts for Olefin Polymerization." *Catal. Sci. Technol.* 3: 858.

19. **Albizzati E, Giannini U, et al. (1995)**. "Advances in Propylene Polymerization with MgCl Supported Catalysts." In: Fink G., Malhaupt R., Brinnzinger H. (Eds), Ziegler Catalysts: Springer, p. 413.
20. **Bukatov GD, Sergeev SA, Matsko MA (2019)**. "Effect of Internal Donor on the Performance of Ti-Mg Catalysts in Propylene Polymerization: Donor Introduction During or After MgCl Formation." *Applied Catalysis A, General* 577: 69-75.
21. **Stukalov DV, Zakharov VA, Potpov AG, Butakov GB**. (2009). Supported Ziegler-Natta Catalysts for Propylene Polymerization. Study of Surface Species Formed at Interaction of Electron Donors and TiCl4 with Activated MgCl2. Journal of Catalysis, 266(1):39-49
22. **Arzoumanidis GG (2015)**. "Novel Single Site Z-N Catalyst Development." Presented at "Advances in Polyolefins 2015" PolyACS, Sonoma Valley, California, DOI: 10.13140/RG.2.2.32676.37769.
23. **Kashiva N (2003).** The discovery and progress of MgCl2-supported TiCl4. Catal.J. Poly Sci. Part A. Polym. Chem 42: 1-8