

Amoco CD commercial polypropylene catalyst tailor-made for the Amoco-Chisso gas phase process

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ABSTRACT

The commercial profile of the Amoco CD MgCl_2 supported polypropylene catalyst is presented. The development, the unique method of preparation/production, with emphasis on particle morphology, and the parameters affecting particle size (PS), particle size distribution (PSD), and particle shape are discussed in detail. The outstanding performance of the catalyst, tailored-made for the Amoco-Chisso gas phase process, is attributable to synergistic effects, originating from catalyst and process design factors. Catalyst median particle size (d50) may be controlled in the 7-100 microns range. Parameters affecting PS and PSD during catalyst support preparation include: agitation speed, temperature, organic reagent to Mg ratios, morphology controlling agents, and deliberate spiking of the aromatic solvent used with appropriate contaminants. Particle shape variation between the cubic and spheroidal is 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 takes place in several steps by thermal treatment of the support with TiCl_4 /toluene solutions. Cost-effective TiCl_4 /toluene reuse system from the activation streams has been put in place to reduce waste material considerably. There is an optimum temperature of activation close to 120°C. The progress of activation as well as catalyst quality may be monitored by IR spectroscopy, expressed in easily identifiable IR fingerprint patterns, which correlate well with the catalyst performance. More recently a new concept of supported catalysts based on the CD technology has been developed. It features organometallic complexes instead of just TiCl_4 as the polymerization active centers. The new catalysts show improved performance and advantageous polymer product properties. We suggest that the newly invented organometallic complexes may open a new era in polyolefin catalysis, including polyethylene copolymers. The success of the CD and Amoco-Chisso process is illustrated by the two dozen commercial plants worldwide that use the technology, and the recent licensing advances by Ineos, the successor of Amoco, for this polypropylene technology.

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INTRODUCTION

Supported catalysts for the polymerization of propylene to isotactic polymer are currently dominating the commercial production of polypropylene (PP), which is now approaching fifty million metric tons annually, worldwide. The majority of commercial supported isotactic PP catalysts consist of TiCl_4 supported on MgCl_2 with di-n-butyl or diisobutyl phthalate (DBP) as internal modifier, and are used along with a trialkyl aluminum (usually AlEt_3) as cocatalyst and a dialkyl

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or dicycloalkyl dimethoxysilane as external modifier [1, 2]. In the past several years there has been a flurry of research activity to replace DBP with other modifiers [3], due to an alleged safety problem of the former. Among the most important supported catalyst attributes are their superior activity, reaching up to 100 kg PP per gram of catalyst in certain cases, and stereospecificity, hovering around 99%. The type of internal (and sometimes external) modifier may also affect several other attributes of the catalyst such as hydrogen response, MFR, MW, molecular weight distribution, polydispersity, etc.

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

The majority of the commercial catalyst manufacturing processes are based on rendering anhydrous MgCl_2 soluble in various alcohols, through the formation of a $\text{MgCl}_2 \cdot n\text{ROH}$ [4], and forming particles by extracting the alcohol (de-alcoholation), following the prescribed recipes. To the contrary, the Amoco CD catalyst support preparation is based on a unique step, involving precipitation of a solid by reaction of Mg alkyl carbonate with TiCl_4 , followed by dissolution of this solid by a cyclic ether, and the subsequent automatic, slow precipitation (crystallization) of a controlled particle morphology support [5]. This approach delivers the maximum control over particle morphology, PS and PSD, crystal density, and particle shape, so important for the Amoco-Chisso gas phase process. For example, by manipulating certain precipitation parameters, we can obtain spheroidal, cubical, hexagonal and other shapes of particles. No other manufacturing process is capable in delivering such diversity in catalyst morphology.

The advantageous morphology characteristics of CD gives rise to polymer powders with excellent

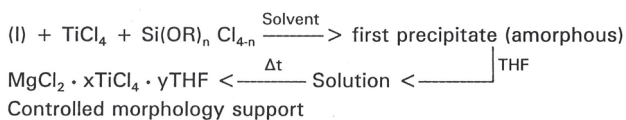
flowability and high bulk density. The catalyst was optimized and tailored for the Amoco-Chisso gas phase (co) polymerization process. The importance of synergism of advanced catalyst, process and product technologies established a leadership position in manufacturing of PP.

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 CD catalyst of consistent high quality, being "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 is preferred over the bulk process by several PP manufacturers for many reasons, including simplicity, flexibility, cost, safety and environmental friendliness (green chemistry). This has been gradually recognized by the industry. Today, there are two dozen plants around the globe utilizing this technology, and in 2013 Ineos was No. one in PP technology licensing [7]. The present paper deals with 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 TiCl_4 was applied as received. Special care must be given into drying the solvent, toluene, since 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 alkylcarbonate solution preparation by reacting a suspension of $\text{Mg}(\text{OEt})_2$ in toluene-alcohol with CO_2 (MAC solution).
2. Support preparation in two steps, i.e.: A. Precipitation of an initial solid by reacting MAC with TiCl_4 and a morphology controlling agent, such as $\text{Si}(\text{OEt})_4$, in toluene. B. Dissolution of the initial solid by addition of tetrahydrofuran (THF) to the suspension, followed by an automatic slow re-precipitation (crystallization)

First step - Mg^{+2} reagentSecond step - precipitation of supportThird step - catalyst activation

Heat treatment with aromatic hydrocarbon/ $TiCl_4$ /phthalate esters

Scheme 1. Preparation procedure of Amoco polyolefin supported catalyst

of a controlled morphology support.

3. Support activation by two sequential treatments with $TiCl_4$ and $TiCl_4$ -DBP, respectively, in the presence of toluene, 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 $TiCl_4$ /toluene from the post-activation treatments may be used without purification in the first activation step. CD catalyst composition may vary slightly from preparation to preparation; typical values are: Ti 3%, Mg 18%, Cl 61%, DBP 14%, solvent 4%. We find that a linear relationship exists between Mg and Ti content, or Mg and DBP content for any given supported catalyst [1]. The linear Mg-DBP correlation lends support to the conclusion that DBP coordinates with the Mg ion.

In commercial gas phase operations, the catalyst yield is between 40 kg and 50 kg per g of CD, and the stereospecificity of 99%.

A number of variations were introduced in the above CD preparation procedure, in order 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], $Si(O-n-Bu)_4$ [11]. Use of $B(O-n-Bu)_3$ was also reported during 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 support precipitation was contaminated on purpose with various levels of xylenes, ethylbenzene and/or naphthalene [8]. Compounds of the SiR_nCl_{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.

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.

RESULTS AND DISCUSSION

The CD preparation procedure gives an excellent handle to manipulate and control catalyst morphology, which had been the primary consideration in the development of the catalyst. The support product that crystallizes after the THF addition has the approximate general formula:

$MgCl_2 \cdot 0.031TiCl_x (OEt)_y \cdot 1.48 THF$. It appears that the support crystals are related to the well known adduct $MgCl_2 \cdot 1.5THF$ [13], with anticipated crystal structure similarities.

Determination of the various parameters affecting PS, PSD and shape was an integral part to improve CD morphology. Table 1 shows the most important of these parameters. The easiest and fastest way to control the median PS (d_{50}) is through the agitation speed, Figure 1. There is a linear relationship between RPM and d_{50} . 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

Table 1. Support precipitation parameters

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

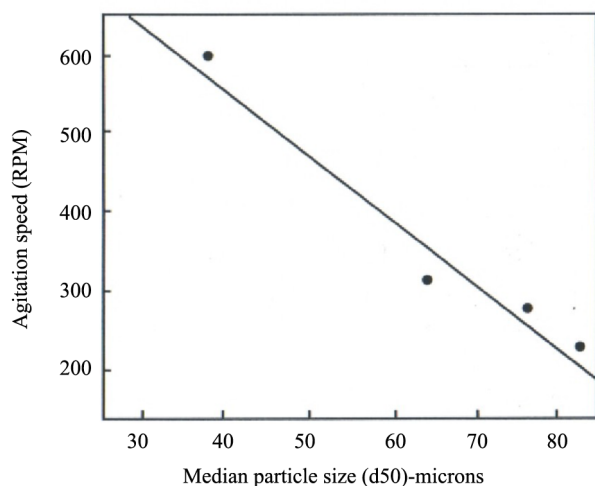


Figure 1. Effect of agitation speed on median particle size of large spheroidal Amoco supported catalyst.

on particles d50 is depicted on Figure 2. The lower temperature results in faster and multiple crystal "seed" formation, at a smaller d50. The above two parameters, agitation speed and temperature, may be regarded as mechanical/thermal. The following are physical/chemical effects. The 2-ethyl hexanol/Mg molar ratio in the MAC solution has a significant influence on particle d50 (Figure 3). A more dilute solution gives rise to larger d50. By choosing now the right combination of all the above factors, we can achieve the desired d50, usually in the range of 7 microns to 100 microns, with sufficient narrow PSD. Yet another parameter, this time affecting both d50 size and particle shape, is the THF/Mg molar ratio. At high ratios (Table 2) smaller particles with cubical shape are formed. At smaller ratios, we obtain larger

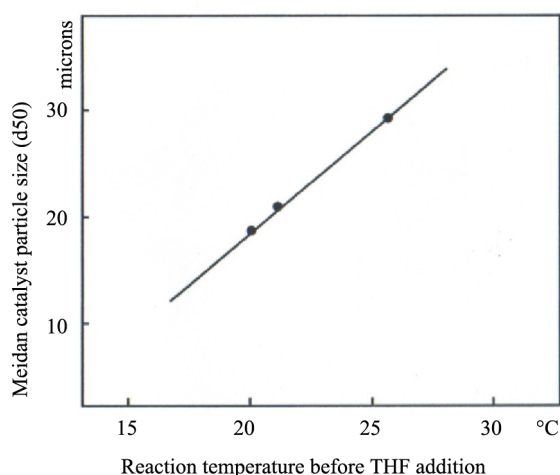


Figure 2. Effect of reaction temperature before THF addition on median particle size of Amoco supported catalyst.

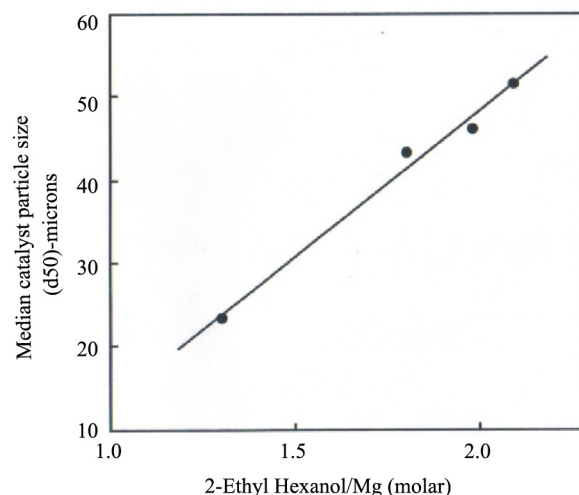


Figure 3. Effect of ROH/Mg molar ratio on Amoco supported catalyst median particle size at constant agitation speed (300 rpm)

spheroidal particles. Substitution of $\text{Si}(\text{OR})_n \text{Cl}_{4-n}$ type compound for $\text{Si}(\text{OEt})_4$ during support preparation leads to the precipitation of spheroidal supports. The point of introduction of $\text{Si}(\text{OR})_n \text{Cl}_{4-n}$, which acts both as a morphology controlling and second chlorinating agent, affects both the PS and the PSD of the spheroidal catalyst produced (Scheme 2). Furthermore, $\text{Si}(\text{OBu})_4$ yields smaller PS than $\text{Si}(\text{OEt})_4$ (Table 3). A different method for the preparation of large spheroidal particles was developed, in the absence of alkoxy silanes [10]. At low agitation speed (300 rpm), DBP and methanol were used as morphology controlling reagents, while the THF was substantially reduced. Finally, toluene solvent contaminants such as xylenes, ethyl benzene and naphthalene were shown to influence PS and PSD [8]. For example, naphthalene contamination within the 2,000 to 12,000 ppm range results in PSD narrowing, and in most cases reduction of the d50 of the catalyst.

The importance of particle shape lies primarily on its effects on polymer powder flowability and bulk density, since, as it is well known, the shape of polymer particles are replicas of those of the catalyst. We have the ability to develop CD supports in a wide variety of shapes, such as cubes, spheres, clusters

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

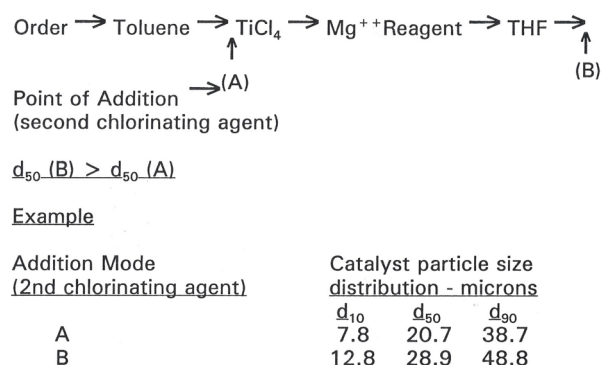
Table 3. Effect of silanes catalyst size- (microns)

	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

thereof, hexagonal prisms, football, and even needle-shaped particles. Two of the most common shapes are depicted in Figure 4.

Support activation

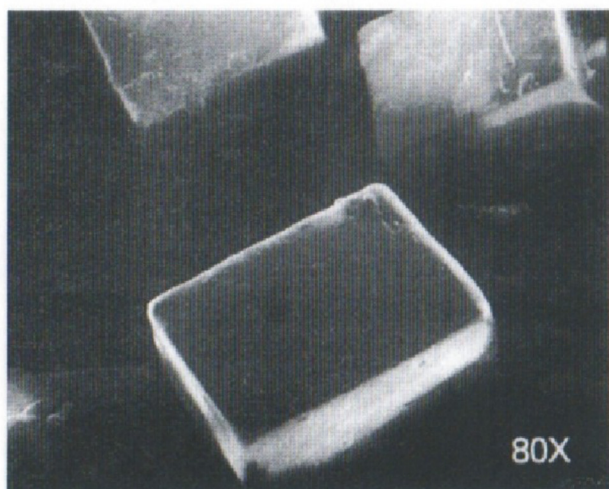
Catalyst activation is a two-step process, followed by toluene and TiCl₄ treatments, and finally, to complete the preparation, several hexane washes and drying in a nitrogen stream. The first activation is carried out in an agitated suspension of the support in a toluene solution of TiCl₄ at an elevated temperature, usually 110-120°C, for one to two hours. During this time, the majority of THF is being removed, leaving behind porous particles, and the MgCl₂ 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 very critical, and there is an optimum close to 120°C. The activation progress may be monitored by

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

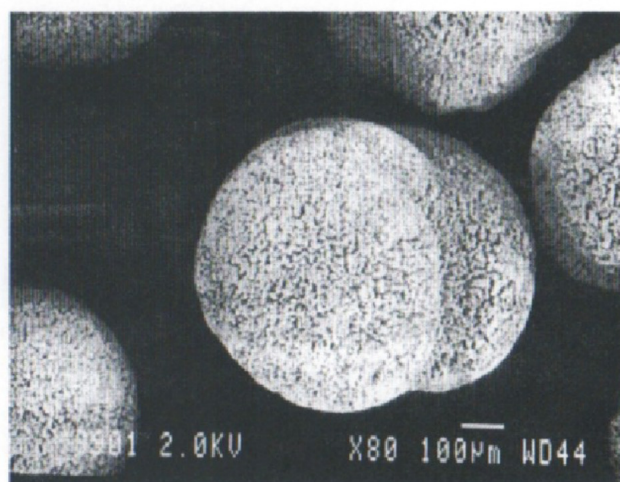
IR spectroscopy [14] under-or over-activated catalysts show typical IR fingerprints, which are also reflected in their polymerization performance and catalyst composition. Over-activated catalysts may contain phthaloyl chloride, from the reaction of DBP with TiCl₄, under the higher temperature. The final toluene and TiCl₄ treatment serve as removal of a number of minor contaminant/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

We cannot conclude this article without saying a few words about the Amoco-Chisso process. The CD was



(a)



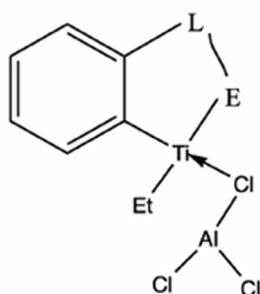
(b)

Figure 4. SEM photomicrographs of PP particles from Amoco catalysts

tailor-made for that process, and there exist an eclectic synergism between the two. A short comparison between the two leading gas phase processes, UNIPOL and Amoco-Chisso has been made elsewhere [2]. The performance of the unique horizontal stirred bed reactor is characterized by a powder residence time distribution approaching the plug flow ideal, such that all powder particles have nearly equivalent reactor residence times. Advantages derived from the unique design are: faster, sharper product transitions; higher catalyst yields [15] than an equivalent conventional stirred tank reactor; minimal "bypassing" of catalyst, ensuring high impact copolymer product quality; and rapid start-ups and shut-downs [6]. The impact copolymers produced using Amoco-Chisso process and CD catalyst exhibit a superior balance of stiffness and impact properties over a wide temperature range [16].

New Trends

The CD technology has recently been the springboard for the development of a new concept in supported catalysts. Whereas all the known catalysts so far, commercial or experimental, claim "naked" TiCl_4 in various forms, e. g., monomeric, dimeric, etc., as their active sites, the new types feature organometallic complexes as the centers of activity [3]. The immediate benefit from this development is an increase in activity up to 60%, improved stereospecificity, higher powder bulk density, changes in hydrogen response, and certain other improvements in product properties. The complexes may be prepared by a single step reaction of various ligands with TiCl_4 , ZrCl_4 or other metal halogenides, followed by reaction with AlEt_3 , and may be represented by the following general formula:



where L = a polycyclic or monocyclic heteroaromatic ligand, containing one or more heteroatoms, E = heteroatom available for coordination/bond formation with the metal. The complexes appear to have some

similarities with Mitsui's FI catalysts for olefin polymerization [17], in terms of performance, and activation with aluminum alkyls. As such they may be used in several other applications, including PE, copolymerizations, etc. By comparison, FI catalysts have two heteroatoms bonded to the metal, whereas the new complexes feature one carbon-metal and a second heteroatom-metal bond. We believe these newly discovered, easily accessible organometallic complexes will open a new and exciting chapter in polyolefin catalysis.

CONCLUSION

Supported PP catalysts are expected to be in commercial use for the foreseeable future. Among the available commercial catalysts, Amoco CD, tailored-made for the Amoco-Chisso gas phase process, distinguishes itself for its unique manufacturing method, the advanced methodology to control morphology, and the synergistic effects between catalyst, process, and product. Apart from the effort to replace DBP as the internal modifier [3] with "greener" substitutes, it appears that globally we reached a plateau of supported PP catalyst performance, which nevertheless satisfies the needs and the growth of PP in the marketplace, at the present time. The fear expressed several years ago, that metallocene catalysts will take over this business from the MgCl_2 supported catalysts did not materialize, due to the efficiency, lower cost, and easy, simplified operation with the latter.

New, important breakthroughs in this technology would be welcome, but not currently seen on the horizon, despite the intense R&D efforts around the globe by numerous research groups. The desire has been expressed [18] for the development of a single site catalyst supported on MgCl_2 . I believe, this would be possible by replacing the TiCl_4 -based active sites on the catalyst with single-site complexes. For a variety of reasons, this may not be so easy to accomplish, as it probably appears to be. Good candidates for the replacement may be an FI catalyst or the organometallic complexes we introduced earlier. The most important reason for the preference of an FI or the organometallic complexes is their activation with aluminum trialkyls.

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