Chapter 1
Recent Developments in Supported Polyolefin Catalysts: A Review

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1.1 Overview

Over the last 60 years the ability to reduce olefinic refinery gases or liquids into a metastable solid in a controlled manner has created the colossal business of polyolefin materials. Their continued success is thanks to a deep understanding of how to meet and predict a customer's needs in terms of a price/performance package and translate that back through the chain of knowledge (Fig. 1.1). This demand has led to constant evolutions within all areas of the business, punctuated by more than its fair share of revolutionary breakthroughs in the areas of catalyst, polymerization process, and polymer processing technology.

One only has to consider the range of applications where a polyolefin solution finds itself as the preferred option. It is employed in such areas as infrastructure (piping and energy transmission) allowing for the safe consistent supply of water and energy (electricity and gas, etc.) and removal of sewage; advanced packaging, light and reliable packaging that reduces transport emissions (reduced petroleum consumption) and increased shelf life of perishable goods, reducing waste and further reducing transport emissions; automotive application replacing metal with light material allows for lighter automobiles and again further contributes to reduced transport emissions. Examples of the extremely diverse applications of the material can even be found within very niche areas. For example, UHMWPE fibers can be used in securing supertankers, stopping bullets, and surgical sutures.

Polymer synthesis role in this success has come by the ability to control how the macromolecules are put together by sequentially linking α-olefins: the chain length and distribution, skew, and branching present handles by which properties can be

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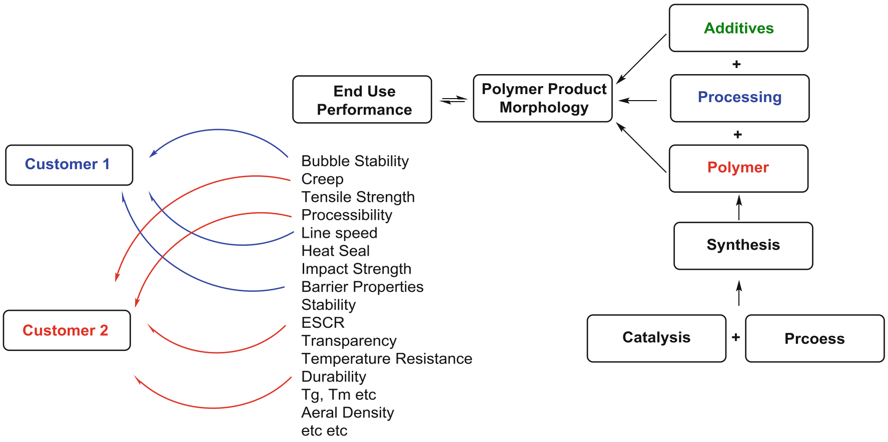


Fig. 1.1 Success through chain of knowledge

tuned. When the monomer is substituted (i.e., an α-olefin), additional opportunities including tacticity (control over stereo- and regio-error type linkages) and comonomer composition distribution become available. In addition, process developments have allowed for the production of advanced materials such as heterophasic alloys. Control over chain length (molecular weight), the population distribution of the chain lengths (molecular weight distribution), and chemical composition distribution (CCD) in and between the chains results in the ability of the chains to form crystallizable, ordered segments. The size and distribution of the crystallites and the ratio of soft amorphous space interspersed between the hard crystallizable segments affect material properties such as melting point, modulus (stiffness), and toughness (resistance to fracture when stressed).

The ability to control the above factors through the use of catalyzed coordination polymerization can be seen throughout the previous and subsequent chapters.

1.1.1 Scope of the Chapter

It is impossible to cover all areas and recent developments within supported polyolefin catalysis utilized in particle-forming process in a single chapter. As a result choices have been made to focus on industrially relevant systems that are at least demonstrated at pilot scale or relevant for the production of multimodal products. As a result there is little academic research discussed in this chapter and will be referred to indirectly via the numerous reviews in this field [1–15]. In most cases the topic will be discussed in terms of illustrative examples of the subject matter.

Finally, the author has focused on patent literature where there is an English-translated version; as a result the author openly acknowledges and apologizes for his ignorance and for not fully covering the tremendous contributions that researchers from companies in Japan, China, Korea, etc. have made to the development in this area.

1.2 Ziegler Catalysts

1.2.1 Ziegler/Natta Polypropylene Catalysis

The history of industrial Ziegler–Natta polypropylene catalysts is generally described in terms of evolutionary generations, corresponding to the chronological order of their development [16–18]. They range from titanium trichloride catalysts, which had their heyday in the late 1950s and the 1960s, to the high-activity magnesium chloride-based catalysts, which have helped fuel the growth and development of these versatile polymers. Advances in process technology have gone hand in hand with the development of polypropylene catalysts, developing from slurry-based processes to the current state-of-the-art, cascade processes which combine bulk or gas-phase technology, allowing for the production of complex copolymers with multiphase structures which have expanded the application range for PP.

$TiCl_3$ Catalysts (First and Second Generation)

The $TiCl_3$ catalysts used in early industrial PP processes were typically prepared by the reduction of $TiCl_4$ with an aluminum alkyl, generating a solid $TiCl_3$ precipitate. $TiCl_3$ exists in four crystalline modifications, α, β, δ, and γ forms. The β-modification has a linear chain-like structure, while α, δ, and γ forms possess layer structures [19, 20]. Typically, the reaction of $TiCl_4$ and $AlEt_3$ (at low Al/Ti ratios) at low temperatures in hydrocarbon solution resulted in the controlled precipitation of catalysts having spheroidal particle morphology, yielding the β-$TiCl_3$ form with cocrystallized $AlCl_3$. This precursor can be converted to the more stereoselective γ-form by heating to 160–200 °C [21]. The catalysts were typically activated by $AlEt_2Cl$ to afford poorly productive systems (*ca.* 1 kg PP/g Cat) which in many cases yielded polypropylene resins that required extractive removal of atactic polymer and removal of catalyst residues (deashing).

An improved (second generation) $TiCl_3$ catalyst developed by Solvay appeared in the 1970s [22]. The catalyst preparation procedure involved the chemical treatment of a $TiCl_3/AlCl_3/AlEtCl_2$ precatalyst, previously produced by the reaction of $TiCl_4$ with $AlEt_2Cl$. The catalytic activity could be greatly improved by extraction of the co-crystallized aluminum chloride with diisoamyl ether, giving a “pure” β-$TiCl_3$. Subsequent treatment with $TiCl_4$ catalyzed the phase transformation from the β- to the δ-form of $TiCl_3$ at a relatively mild temperature (<100 °C) [23]. Lowering the temperature also prevented the growth of the catalyst crystallites. In addition, the extraction of $AlCl_3$ with ether resulted in porous particles with a weakly bonded matrix. The innovation increased the activity and stereoselectivity and resulted in polymerization productivities in the range 5–20 kg/g catalyst in bulk propylene and produced polymers where the removal of the atactic fraction is spared [24]. Although phased out in many locations these catalysts still survive to this day [25, 26].

Third Generation: "Activated" $MgCl_2$

The prehistory of the third generation began in 1960, when Shell patented a catalyst for propylene polymerization that employed $TiCl_4$ supported on $MgCl_2$. The decisive step was achieved however in the late 1960s, when Montecatini and Mitsui independently development "activated" $MgCl_2$ as a support for $TiCl_4$, followed by the incorporation into the catalyst system of electron donors giving higher catalyst stereospecificity [27–29]. Initially, activated $MgCl_2$ was prepared by ball milling a mixture of magnesium chloride and ethyl benzoate, which leads to the formation of very small ($\leq$3 nm thick) primary crystallites of $MgCl_2$ [30].

Third-generation catalysts commonly comprise $MgCl_2$, $TiCl_4$, and an "internal" electron donor and are combined with an aluminum alkyl cocatalyst such as $AlEt_3$ and an "external" electron donor added to the polymerization. The internal donor in third-generation catalysts is typically ethyl benzoate, which is used in combination with a second aromatic ester, such as methyl *p*-toluate or ethyl *p*-ethoxybenzoate (PEEB), as an external donor. An external donor is required due to the fact that, a large proportion of the internal donor is lost as a result of reactions involving the cocatalyst, such as alkylation and/or complexation reactions. The external donor replaces, to a large extent, the internal donor in the solid catalyst, maintaining high catalyst stereospecificity. It has been demonstrated that the most active and stereospecific catalyst systems are those which allow for the highest incorporation of external donors [31], with the effectiveness of a catalyst system depending more on the combination of donors than on an individual internal or external donor. A classic example was disclosed by Scata et al. [32].

Fourth Generation: Phthalate ID/Alkoxysilane ED

The fourth generation of PP catalysts was based on the discovery and development of phthalate/alkoxysilane-based catalyst systems (Fig. 1.2). As was the case for the third-generation catalysts, the function of the external donor is to replace the internal donor lost by alkylation and complexation reactions with the Al alkyl cocatalyst [33, 34]. An additional feature was the development of spherical $MgCl_2$-based catalysts with controlled particle size and porosity, afforded via chemical rather than mechanical activation of magnesium chloride. As a result, catalyst systems with increase stereoselectivity and regioselectivity could be produce, resulting in higher crystallinity polymers, with a considerable increase in catalyst mileage. Phthalate-based catalysts are now regarded as a family of general-purpose systems with which it is possible to cover the majority of product properties and applications. All these

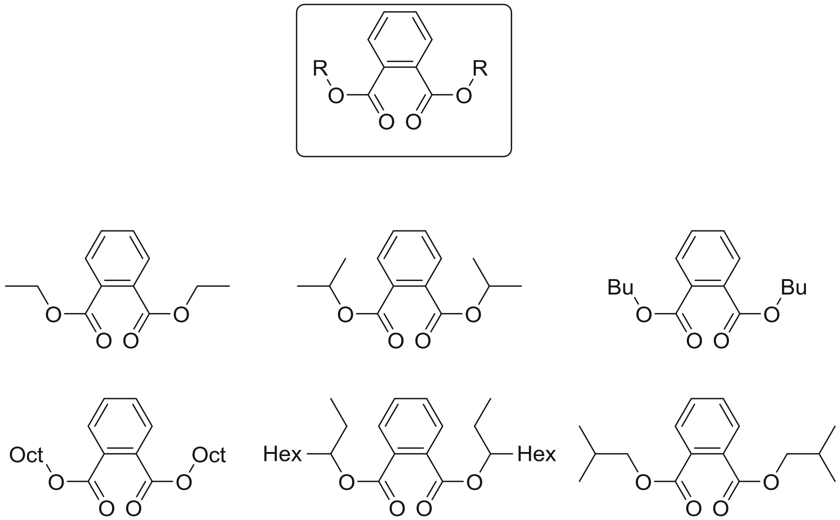
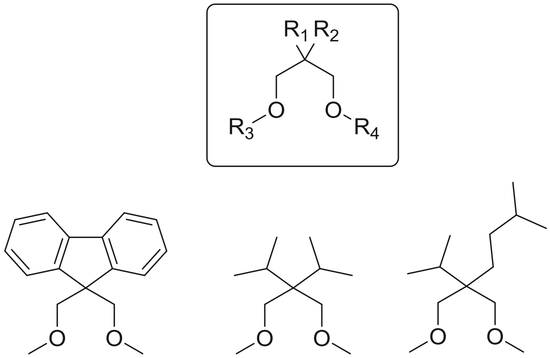


Fig. 1.2 Illustrative example of reported phthalate donors

Fig. 1.3 Illustrative examples of diether internal donors



features have contributed to the colossal commercial success of this type of catalyst, and at present they are the most widely used catalyst system in polypropylene production. However, the coming years will see this dominance slowly erode.

Fifth-Generation Catalysts: Diethers, Succinates, and Polyol Esters

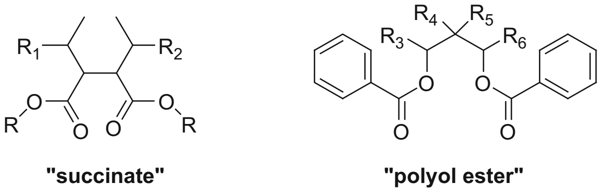
The search for further catalyst improvements led to the development of internal donors which were not readily removed from the support on contact with the alkylaluminum cocatalyst. It was found that certain diether compounds, in particular 2,2-disubstituted-1,3-dimethoxypropanes with an oxygen–oxygen distance in the range 2.8–3.2 Å (Fig. 1.3), similar to those of the alkoxysilane external donors are not extracted when the catalyst is brought into contact with the $AlEt_3$ cocatalyst. As a result, high stereospecificity can be obtained even in the absence of external donor [35–39]. Fifth-generation diether catalyst systems show particularly high polymerization activity and good stability, typically giving yields exceeding 100 kg PP/g catalyst. They also give relatively narrow molecular weight distribution and show high sensitivity to hydrogen. Cui et al. recently reported their investigation into the influence of diether donor ratio on the performance of the final catalyst. Experimental data indicates that higher diether loadings cause a decrease in the titanium content of the catalyst, further indicating that the diether is associated with magnesium not titanium. In addition, an optimum ratio was required for activity and stereoselectivity [40].

A seminal work by Chadwick and coworkers has shown that the high hydrogen response of fifth generation, diether-based catalysts arises from chain transfer after the occasional secondary (2,1-) rather than the usual primary (1,2-) monomer insertion [41]. The group rationalized that even the most highly stereospecific active sites are not totally regiospecific. In addition, the broader molecular weight distributions obtained with catalysts containing ester internal donors were attributed to the presence of (some) isospecific active sites having very high regiospecificity and therefore lower hydrogen sensitivity [42].

There is significant evidence from modeling studies that diether donors preferentially adopt a bidentate coordination mode to the (110) lateral cut of $MgCl_2$ [43, 44]. Strong evidence points to the fact that donor molecules reside in the vicinity of stereospecific active species. Therefore, the above reports indicate that the likely location of active titanium is also on the (110) lateral cut. In addition, it has also been shown [45, 46] that the use of a diether as external donor in combination with a phthalate-based catalyst gives active species which are very similar to those present when the diether is used as internal donor, implying that the active species in phthalate-based catalysts are similarly located on the (110) cut.

Lately, new types of internal donor compounds based on aliphatic dicarboxylic esters, such as malonates and glutarates and in particular succinates and polyol esters (Fig. 1.4) have been employed. Researchers at LyondellBasell developed $MgCl_2$-supported catalysts in which the internal donor is a succinate ester [47, 48]. As is the case with phthalate-based catalysts, an alkoxysilane is used as external donor. The essential difference between these catalysts is that the succinate-based systems produce polypropylene having much broader molecular weight distribution. In addition, they also generate ethylene–propylene copolymers having considerably lower glass transition temperature, coupled with better intermolecular and intramolecular comonomer distribution with respect to their conventional counterparts. This

Fig. 1.4 Illustrative examples of succinate and polyol ester internal donors



has allowed for the production of heterophasic copolymers having an improved balance of stiffness and impact strength, taking into account that the incorporation of a rubbery (ethylene–propylene) copolymer phase into a PP homopolymer matrix increases impact strength but leads at the same time to decreased stiffness. Similarly, researchers at BRICI/Sinopec have developed the polyol ester family of internal donors. The catalytic systems resulting from this family of donors have a similar polymerization performance to succinate-based systems. However, unlike the succinates, the polyol ester systems yield high stereoselectivity even in the absence of alkoxysilane external donors [49, 50].

Sixth-Generation Ziegler: Phthalate Replacement

Recent concerns and regulatory restriction (e.g., REACH Regulation (EC) 1907/2006) on the use of phthalates in general has been a source of concern and debate in terms of whether a catalyst is a substance or transported isolated intermediate. From what the author presently understands, dibutyl phthalate (DBP), diisobutyl phthalate (DIBP), and bis(2-ethylhexyl)phthalate (DEHP) are listed on REACH Annex XIV with a sunset date of 21st Feb, 2015. The concentration limit for those three substances requiring an authorization will be 0.3 wt% (3000 mg/kg) and given that PP produced with these catalyst will have at most 1 mg/kg then phthalate/procatalyst-based PP will not be subject to any ban or restriction. All that said, however, offering a customer a totally phthalate-free solution is becoming an attractive offering in terms of responsible care and competitive advantage. As a result, those who treated the debate as an opportunity rather than a threat have reinvigorated research into internal donors, leading to new and interesting donors that not only challenge phthalates. This has led some to define this period as the sixth generation of PP catalysts. Figure 1.5 illustrates some of the numerous disclosures of new donors in recent time [51–70]. In addition to this there has been an increase in mixed donor disclosures, for example blending succinate + diether [71] or succinate + dimethoxytoluene [72].

Undoubtedly it is Dow (now with W.R. Grace) that has been at the vanguard of these developments, with one family appearing to stand out which may well be part of their new non-phthalate offering (Consista Donors). The 1,2-phenylene dibenzoate donors (Fig. 1.6), judging from the recently disclosed large-scale production of PP and a push to protect the donor synthesis routes themselves [73–76], are clearly important as phthalate replacements. It is also clear that these donors may be more complicated in that multiple $TiCl_4$ contact steps and buffering via addition of ethylbenzoate or 2-methoxy ethylbenzonate to the procatalyst and $TiCl_4$, before adding the phenylene dibenzoate, may be required to improve the final morphology and performance of the catalyst [77].

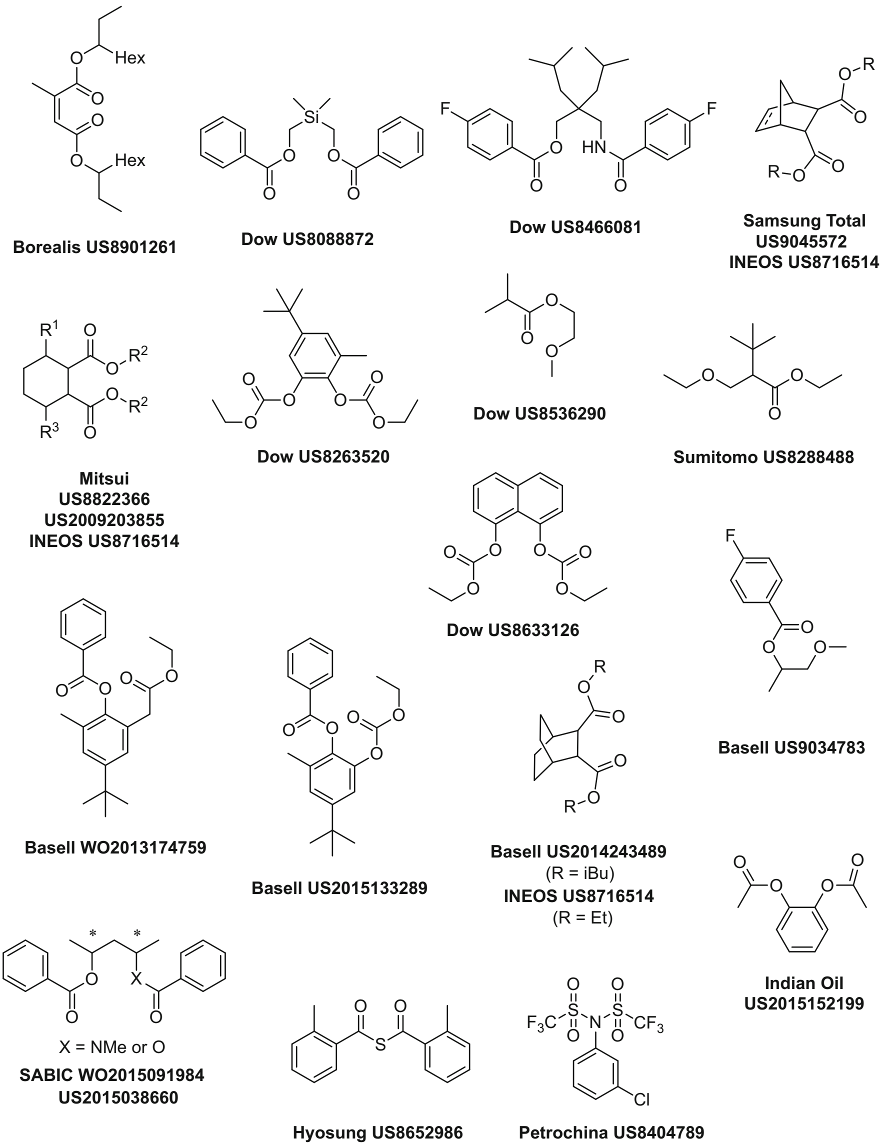


Fig. 1.5 Selection of new donors disclosed in recent time

Catalyst Morphology Control

Several different approaches have been followed for the preparation of catalysts having controlled particle size and morphology. Three main types of reaction have been employed for the controlled preparation of a support material or final catalyst:

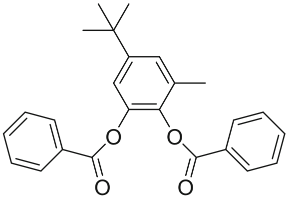


Fig. 1.6 1,2-Phenylene dibenzoate

1. Complexation of $MgCl_2$ with an alcohol, forming a viscous melt at elevated temperature, which is then processed to form a spherical $MgCl_2 \cdot EtOH_n$ support with controllable EtOH content either via spray drying or emulsification/solidification. The support material is treated with the external donor and titanated to form the final catalyst product.
2. Complexation of $MgCl_2$ with an alcohol in a hydrocarbon, followed by controlled precipitation of the reaction products following addition of a chlorinating agent or $TiCl_4$.
3. Controlled precipitation of the reaction products of a magnesium alkyl or alkoxide-containing complex with a chlorinating agent or $TiCl_4$.

Finally followed by the impregnation of a silica carrier with the catalyst reagents.

The latter is the least frequently employed method for the production of Ziegler–Natta PP catalysts, however it is a common technique in Ziegler PE catalysts. Typically, a silica support is treated with a magnesium alkyl complex, followed by chlorination (HCl), addition of $MgCl_2$ and ethanol to form a support material that is converted into the final catalyst via titanation and external donor addition. Representative examples can be found in the work of Novolen/BASF [78–81].

Processes for the preparation of spherical $MgCl_2 \cdot n$EtOH supports are based on spray drying or controlled solidification techniques. The latter is exemplified by the work of LyondellBasell and its previous incarnations. In this preparation molten emulsions of a $MgCl_2 \cdot n$EtOH ($n \approx 2$–3) adduct complex, created in Vaseline and silicone oil, are rapidly cooled in cold hydrocarbon to produce spherical particles with a relatively narrow particle size distribution [82]. As both $MgCl_2$ and ethanol are hydroscopic, care is required in controlling the water content of the final support [83]. This base material has provided the backbone for LyondellBasell developments of Ziegler PP catalyst as well as Zeigler PE catalyst for gas phase polymerization. Recent chemical variation on this base procedure has seen the additions of organoclay such as Cloesite 15A [84] and more recently $Mg(CH_3COO)_2 \cdot 4H_2O$ [85] introduced during the formation of the $MgCl_2 \cdot n$EtOH adduct complex to provide a final catalyst particle with presumably greater strength, as it results in a reduction of the number of “broken” polymer particles. The Cloesite 15A appears to impact the bulk density by possibly increasing the amount of void catalytic space. Similar carrier material is employed in the Sinopec/BRICI DQ-catalyst [86].

$MgCl_2 \cdot n$EtOH (n 2–3) complexes are generally crystalline and consist of a large number of covalent $[MgCl_2]n$ polymeric chains which basically yield the “activated” δ-form of $MgCl_2$ following extraction of ethanol to form the final catalyst.

Relatively recently, Sozzani et al. characterized a number of adducts asserting that $n = 2.8$ or 1.5 represent defined and stable $MgCl_2 \cdot n$EtOH adducts [87]. Auriemma and De Rosa have shown that the high degree of nanoporosity of the derived catalysts may be due to intermediate formation of three-dimensional structures of "amorphous" or highly disordered crystalline $MgCl_2$ polynuclear chain-like species in equilibrium with the "activated" δ-form of $MgCl_2$. The authors postulate that the high degree of "nanoporosity" leads to an increase in the contour length of the lateral faces of $MgCl_2$, which is available for epitactic coordination of titanium and donor species. Further observations point to the fact that control over the $MgCl_2$–EtOH stoichiometry may play a key role in their formation [88]. Experimental observations have indicated that $MgCl_2 \cdot n$EtOH support material in which $n = 3$ is desirable for preparing highly productive and stereoselective catalysts for the homopolymerization of propylene. Reduced alcohol content in the support material either via initial stoichiometry or controlled dealcoholation yields systems with reduced activities and stereoselectivities in homopolymerization but yield catalysts suitable for ethylene–propylene copolymerization [89]. Catalysts derived from support material in which the ethanol contents are lower than 1.5 form the basis of LyondellBasell so called "reactor granule" technology, which when utilized in their proprietary process technology (Catalloy) leads to the formation of heterophasic polyolefin alloys with particularly high rubber contents [48, 90, 91].

LyondellBasell "State-of-the-art" technology allows for high control of catalyst particle dimension, distribution, and surface smoothness (regularity), as illustrated in the scanning electron micrographs of the catalyst particle surface at different levels of magnification in Fig. 1.7a–c.

Spray-dried supports are formed by contacting $MgCl_2$ with ethanol. The adduct is subsequently melted and spray injected into a cooled solvent or gas, which crystallize as spherical particles of $MgCl_2 \cdot n$EtOH ($n \approx 3$) which are screened to extract the required particle size and distribution, the remainder being redissolved and recycled [92–95].

Spherical $MgCl_2 \cdot n$EtOH support materials formed via emulsion or spray drying techniques are converted into the final catalyst via titanation steps. The reaction with excess $TiCl_4$ is undertaken in the presence of the dialkyl phthalate internal donor [17]. Temperatures of at least 80 °C and at least two $TiCl_4$ treatment steps are normally used, in order to obtain high-performance catalysts in which the titanium is mainly present as $TiCl_4$ rather than the $TiCl_3OEt$ generated in the initial reaction with the support. Enhancements in the extraction of superfluous $TiCl_3OR$ from the final catalyst have been reported by Garorff and coworkers at Borealis [96]. The group utilized the addition of dioctyl phthalate as an internal donor "precursor" which undergoes a transesterification reaction to form the final internal donor with the by-product aiding in the extraction of the $TiCl_3OR$.

Catalysts obtained via these routes generally have a BET surface area of around 300 m^2/g and pore volumes in the range 0.3–0.6 cm^3/g [17]. The same supports are now being utilized by Novolen [97] and Süd-Chemie [98], as the basis for some of their PP catalyst offerings.

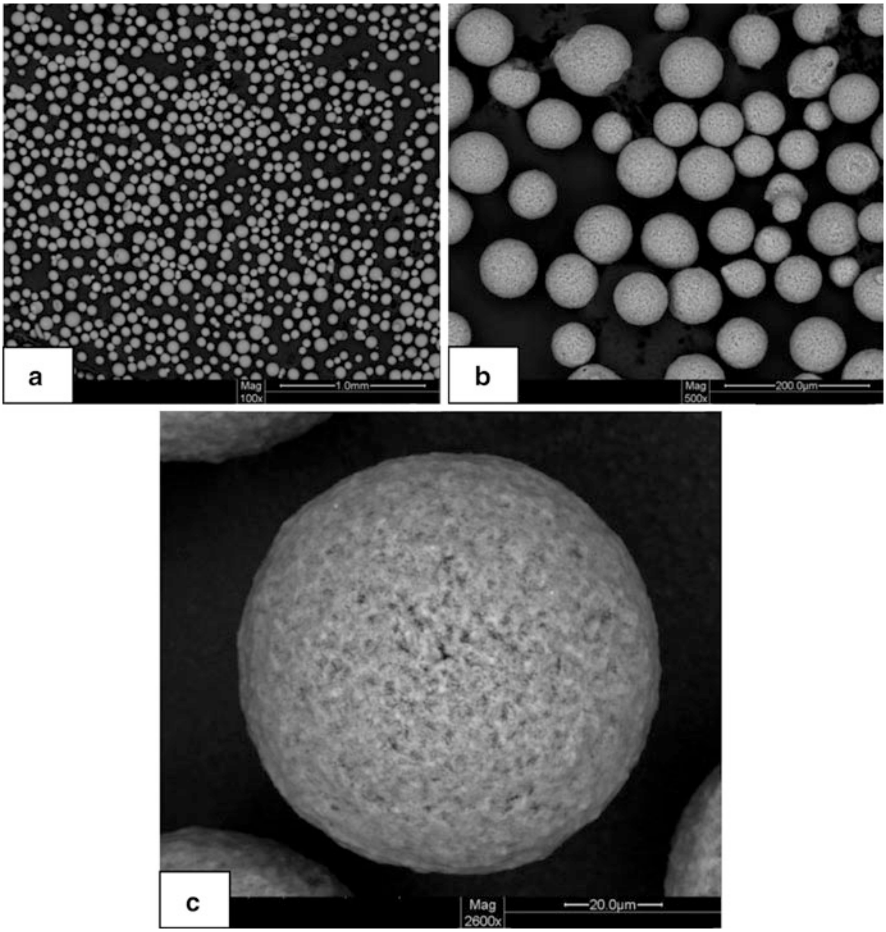


Fig. 1.7 Scanning electron micrographs of catalyst particle surface at different levels of magnification, (**a**), (**b**), and (**c**) (reproduced with permission from LyondellBasell)

Precipitation of a magnesium/titanium precursor with controlled morphology has been a highly successful route and has found significant commercial relevance. The archetypal example of controlled precipitation can be found in the work of Kashiwa and coworkers at Mitsui [99, 100]. In this disclosure $MgCl_2$ is contacted with three equivalents of 2-ethyl hexanol in decane forming a uniform solution. Phthalic anhydride is subsequently added prior to mixing the homogeneous solution with $TiCl_4$. The mixture is allowed to react and precipitate in the presence of an internal donor (diisobutyl phthalate). The titanation step is then repeated on the solid component, prior to washing. These catalysts have been widely applied and have even been claimed to be suitable for challenging film products such as capacitor films where electrical breakdown is directly related to the amount and how finely and homogeneously distributed the catalyst residues are in the product [101].

For the BRICI/Sinopec N-Catalyst and BASF Lynx PP family anhydrous $MgCl_2$ is dissolved in a mixture consisting of an organic epoxide (epichlorohydrin) and tributyl phosphate in toluene to obtain a homogeneous solution. The solution is contacted with phthalic anhydride and treated with an excess of $TiCl_4$. The resultant solid support particles of microspherical form are obtained after heating. The solid catalyst is subsequently treated with the internal donor (diisobutyl phthalate) before isolating the solid, which is further contacted with $TiCl_4$ prior to extensive washing [102, 103]. Factors affecting the particle size of the catalyst produced are discussed in [104, 105].

As stated earlier researchers at Shell were some of the first to note the benefit of coupling titanium to a magnesium surface. This was subsequently followed by the discoveries of Goodall et al. and the development of the Super High Activity Catalyst System (SHAC catalyst) [106–109]. In these basic patents the key breakthrough was the use of $Mg(OEt)_2$ and ethylbenzoate followed by chlorination and titanation. Subsequent iterations of this by Job [110–112] and Kilty and Cuthbert [113], produced morphologically controlled catalyst particles via the creation of a $Mg_3Ti(OEt)_8Cl_2$ precursor from $MgOEt_2$, $Ti(OEt)_4$, $TiCl_4$, ethanol, *o*-cresol, and chlorobenzene. In a subsequent step the catalyst particle is subjected to further titanation in the presence of an internal donor (ethyl benzoate or diisobutyl phthalate) with addition of benzoyl chloride to lower the ethanol content. This produced the so-called BenMag catalyst precursor which had ethyl benzoate in the formulation that could be used as is or easily replaced by another donor, and found commercial relevance in the SHAC 310 (benzoate) and 320 (phthalate) catalyst families. For more recent sixth-generation donor developments the $Mg_3Ti(OEt)_8Cl_2$ precursor has been the starting point without a benzoate-generating step. Similar starting materials have recently been reported by Basell, utilizing $MgCl_2$ and $Mg(OEt)_2$ [114].

$Mg(OEt)_2$ has also been the starting material of choice for the commercially successful Toho Titanium THC family [115–117]. In this case the morphology is set by preparing a spherical $Mg(OEt)_2$ starting point, with chlorination and titanation occurring in the presence of the appropriate donor. Finally $Mg(OEt)_2$ has been converted to a carboxylate via reaction with CO_2 which yields a more soluble Mg starting point, which can either be reacted directly with $TiCl_4$ and $Si(OEt)_4$ to form a solid procatalyst or can be spray-dried with Carbosil TS610 [118]. The former is the basis of the Amoco CD catalyst [119–121]. Catalysts based on mixed Mg(OEt)Cl systems have also been reported by Basell/Akzo Nobel [122, 123] and SABIC [124, 125]. The latter converting a Grignard solution to form controlled morphology Mg(OR)Cl supports. The source of the Grignard appears to be moving from PhMgCl towards an alkyl Grignard such as *n*BuMgCl.

In the past the general belief was that low surface area and compact catalyst particles are connected to low activity due to mass transfer limitations. However, the recent development by Denifl and coworkers at Borealis has shown that a dense low surface area catalyst (ca. 2 m^2/g), prepared via solidification from emulsion, can possess high activity [126].

Borealis emulsion-based catalyst preparation technology is preformed in the absence of an external support. Instead of impregnating a carrier with a solution of

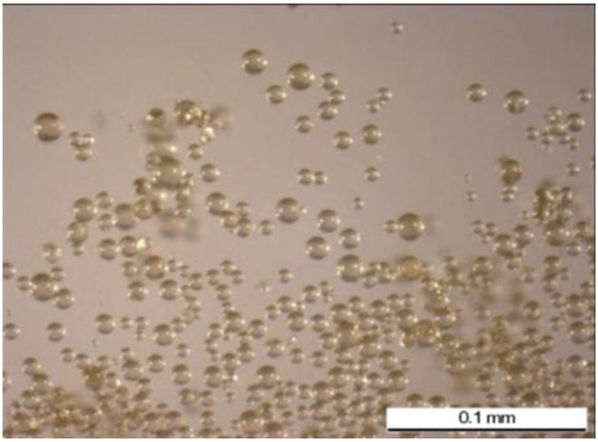


Fig. 1.8 Optical image of "emulsion" derived Ziegler–Natta catalyst (reproduced with permission from Borealis Polymers Oy)

the catalyst components, a two-phase liquid–liquid system is formed in which one phase contains a solution of the catalyst components [81]. The two-phase system itself can be formed either "in situ" by chemical reaction or simply by addition of an inert and immiscible solvent to the catalyst phase. In the second step this liquid–liquid system is then used to make an emulsion, in which the solution of the catalyst components forms the dispersed phase. Finally, the catalyst components of the dispersed phase are solidified and homogeneously distributed in the form of dense transparent spherical particles, of narrow particle size distribution (Fig. 1.8). This technology has the added advantage of reducing the amount of $TiCl_4$ required for titanation. Powder XRD measurements indicated the presence of δ-$MgCl_2$ nanoribbons in the catalyst structure. Scanning electron micrographs have revealed spherical surface species about 40–60 nm in diameter, and chain-like structure within the catalyst particles, with the chains extending from the center of the particle to the surface. Evidently, activation and internal/external donor exchange is not adversely affected by this structure and the monomer does not encounter diffusion problems at the start of the polymerization. Such catalysts undergo rapid and complete fragmentation with controlled particle growth during polymerization, yielding compact polymer particles with high bulk densities (Fig. 1.9) [127]. The fine homogeneous distribution of catalyst residues coupled with the activity of these system leads to potential use in challenging applications such as capacitor films [128]. In addition, the compact nature of the particles does not restrict the ability to produce heterophasic polymers.

The emulsion-based ZN PP catalyst has an inherent ability to insert the ethylene molecules evenly between the propylene molecules, due to the homogeneous nature and distribution of its active sites. The good randomness with these catalyst reduces the problem with sticky ethylene-rich short chains, giving about 5 °C lower melting point (when compared with a standard reference catalyst having the same internal donor producing a random PP with similar ethylene content). Furthermore, good randomness leads to resins with excellent optical properties, such as transparency.

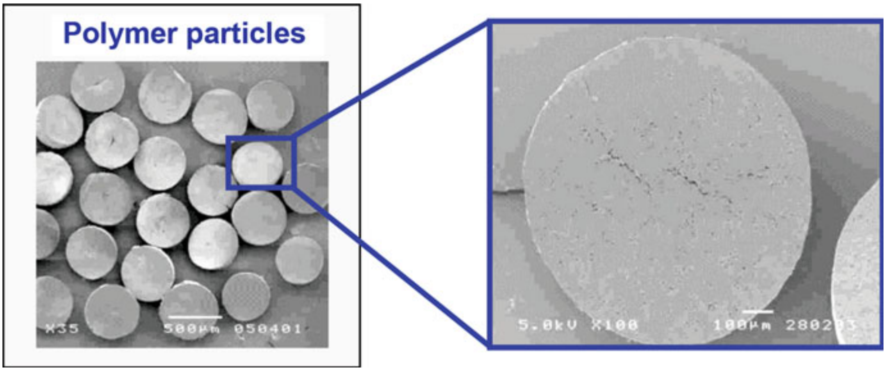


Fig. 1.9 SEM microtomed cross section images of polymer particles resulting from "emulsion"--based Ziegler–Natta catalyst (reproduced with permission from Borealis)

The amount of oligomers, <C15, in the final product is also significantly lower when using this catalyst compared to the abovementioned conventional ZN PP catalysts. This results in additional advantages in the end product with regard to organoleptic properties, migration, blooming, and fuming [129].

External Donors

As stated earlier, an external donor is often required to buffer the extraction of certain internal donors via the AlR_3 cocatalyst. The most effective alkoxysilane external donors for high catalyst stereospecificity are short chain (Me or Et) alkoxysilanes containing relatively bulky groups alpha to the silicon atom (Fig. 1.10) [130–141]. The relationships between the structure of the silane compounds and their polymerization behavior have been discussed in detail by Härkönen and Seppala [133–136]. It has been recognized that silanes containing hydrocarbon substituents with the appropriate size and oxygen atoms with the appropriate electron density are required to produce highly isotactic polypropylenes.

The external donor not only decreases "less-tactics" formation but can also increase the degree of steric control at isospecific sites [139]. Sacchi et al. investigated the effect of silane donors on the highly sensitive first stereoregular insertion of propylene into a Ti-Et bond formed using a phthalate-based catalyst activated with ^{13}C-enriched $AlEt_3$ [140]. The mole fraction of *erythro* (isotactic) placement in the isotactic polymer fraction was 0.67 with no external donor, 0.82 with $MeSi(OEt)_3$ and 0.92 with $PhSi(OEt)_3$. It was therefore concluded that the alkoxysilane external donor was present in the environment of at least part of the isospecific centers.

Typically, an industrial silane donor contains at least one secondary or tertiary carbon linked directly to the silicon atom. This bulky hydrocarbyl group is believed to protect the silane against removal from the catalyst surface via complexation with aluminum alkyl [142]. Examples of such donors can be seen in Fig. 1.17, with

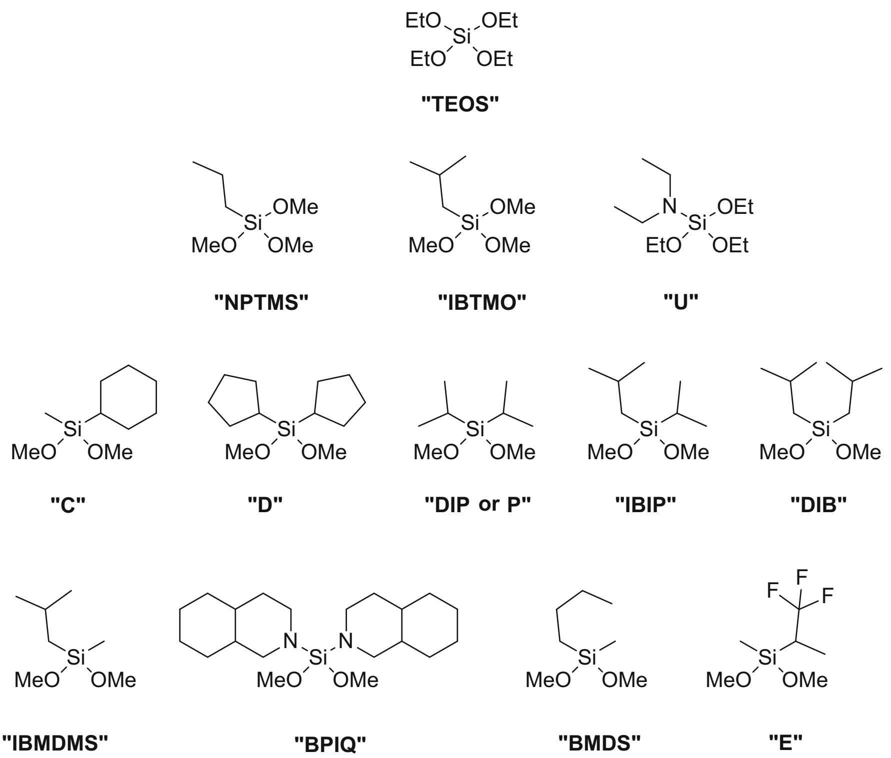


Fig. 1.10 Examples of alkoxysilane external donors

cyclohexyl(methyl)dimethoxysilane (“C” donor) and dicyclopentyldimethoxysilane (“D” donor) being the most commonly employed [142]. When comparing the polymerization performance of cyclohexyl(methyl)dimethoxysilane and dicyclopentyldimethoxysilane, the latter gives particularly high stereospecificity [143] and broader molecular weight distribution [144]. To illustrate the point Streeky et al. compared different silane donors for their impact on activity, microtacticity, melting behavior, and film blowing processability and performance [124].

The desired molecular weight distribution (MWD) of a polypropylene depends on the end-use application of the polymer. A narrow MWD, as well as relatively low molecular weight, is advantageous in fiber spinning applications. In contrast, extrusion of pipes and thick sheets requires high melt strength, and therefore relatively high molecular weight and broad molecular weight distribution. A broad molecular weight distribution, along with high isotactic stereoregularity, is also beneficial for high crystallinity and therefore high rigidity.

High PP stereoregularity and broad molecular weight distribution has also been obtained by employing dimethoxysilanes containing polycyclic amino groups, as exemplified by di(perhydroisoquinolinyl)dimethoxysilanes (*BPIQ* donor Fig. 1.10) [145]. Cyclic amino substituted silane donors first appeared in a Himont patent application [146], however it is the work of scientists in Ube Industries that further developed the potential of these donors [147, 148]. Ikeuchi and coworkers reported that dipiperidinyldimethoxysilane, which possesses a similar geometrical structure to dicyclopentyldimethoxysilane, yields more isospecific polypropylene and rationalized this increase via interaction of the nitrogen atom of the piperidinyl moiety with the active titanium center, increasing the steric influence at the metal center [148].

The increased demand for melt processible TPO, for applications in vehicles and household electrical appliances, has seen the need for a homo-PP matrix that has not only a high stereoregularity but also a high melt flow rate (low Mw). In a multimodal process this places demands on the operation of the homopolymerization phase. Industrially the molecular weight is controlled by hydrogen. In these instances, a larger quantity of hydrogen is required to achieve this goal, but a high hydrogen concentration a bulk phase process may lead to the formation of bubbles (cavitation on loop pumps), which can lead to reactor shutdown. In a gas phase process the amount of hydrogen required may exceed the safety limits of the reactor in terms of pressure. In this case the partial pressure of monomer needs to be reduced to achieve the desired $C_3^{=}/H_2$ ratio, resulting in a decrease in productivity of the catalyst. One way of solving such an issue is to increase the hydrogen response of the catalyst with a suitable external donor. To this end amino trialkoxy silane donors, such as diethylaminotriethoxylsilane (*U* donor Fig. 1.10), have been employed to yield catalytic systems with an increased hydrogen response [145, 149]. Further developments have been made by Toho Titanium with the use of mixed amino-alkoxysilanes [150].

Mixed Donors

An alkoxysilane external donor, as illustrated, can be used to control the stereoregularity and molecular weight distribution of a polymer resin, as well as the H_2 response and ethylene copolymerization capability of the catalyst system. However, it is often the case that an external donor that yields desirable control over one polymer property is ineffective or detrimental with respect to additional properties of the polymer. To combat this shortcoming, combinations of external donors have been employed in order to adjust polymer properties either according to an expected average or through the use of multiple reactors in the hope of achieving beneficial effects over an individual external donor [151–155].

Employing combinations of external donors does have some disadvantages. It is not uncommon for one of the external donors to be dominant, so as to exclude the effect of the other(s). As a result, polymerization in single/multi stage processes often produces resins whose properties are determined essentially by the dominating external donor. Miro and coworkers at Exxon have exploited the dominant behavior of certain external donors [154]. When a combination of dicyclopentyldimethoxysilane (“D” donor) and tetraethoxysilane (TEOS) is used, “D” donor acts as the dominant donor, forming resins similar to those produced by “D” donor alone, that is, high stereoregularity and low melt flow rate. However, the group discovered that they could take advantage of this dominant effect by using a two-stage polymerization process. The first stage utilized TEOS alone, forming polymer with a high melt flow rate, “D” donor being added at the second stage. The combination of mixed donor and a two-stage process achieved a final polymer with high stereoregularity, a relatively high melt flow rate and moderately broad molecular weight distribution. Recently, Chen and Nemzek extensively studied, mixed "D" donor and TEOS systems [155]. The group discovered that at lower total molar ratio of donor to titanium (E.D./Ti = 1–10) it is still possible for the weaker donor TEOS to participate in the reaction, specifically with respect to its effect on the melt flow of the resultant polypropylene resins and hence hydrogen response. The dominating influence of the "D" donor is unsurprisingly related to the total molar ratio of donor to titanium (E.D./Ti) and therefore the total amount of dominant donor. In addition to the increased hydrogen sensitivity, the mixed donor system showed higher incorporation of ethylene in continuous copolymerization experiments with ethylene for a given feed rate [155]. More recently Exxon has shown that a combination of a LyondellBasell succinate-based catalyst and a combination of NPTMS and "D" donor (Fig. 1.10) can produce rheologically interesting homo-PP [156]. The mixed donors addition points can be split across different reactors ("D"-donor first loop; TEOS second loop) as with SINOPEC Split donor technology to also produce high melt strength polymers [157]. An additional example of mixed donors can be seen in the combination of NPTMS and BPIQ [158].

The main advantage of the fourth-generation catalysts over the third-generation systems is their greater stability during polymerization. The ethyl benzoate-based catalysts exhibit very high initial activity but then decay rapidly, losing around 90% of their activity during the course of a polymerization. This limits their productivity to around 30 kg PP/g catalyst under typical polymerization conditions (bulk liquid monomer, approx. 70 °C). In contrast, productivities up to around 70 kg PP/g catalyst are achievable with the fourth-generation, phthalate-based systems. The increased stability also allowed for the further development of cascaded process technologies, which has allowed for further tailoring of technical polymer resins. However, this increase in activity and stability may lead to operability problems, particularly in gas phase processes. For example some of Dow's SHAC™ catalyst systems operating in the Unipol gas-phase process require catalyst kill systems to be installed in order to kill the catalyst in the event of a pressure or fluidization loss [159]. This problem has led to the development of the "self-extinguishing/limiting" catalysts concept. In the initial disclosures a mixture of external donors (alkyl benzoates (PEEB) and alkoxysilanes) are employed. It is claimed that this results in catalyst systems that are very active at the standard operating conditions, but rapidly lose their activity at higher temperatures and therefore prevent the formation of sheets or large polymer chunks in the fluidized bed reactor. Therefore, if a disruption does occur, the catalyst will deactivate quickly, leaving an intact particle bed. Upon recovery, the bed can be refluidized and reactivated with a minimum of downtime and effort [159–161]. Further development has seen the preferred use of aliphatic esters such as isopropyl myristate or di-*n*-butyl sebacate (Fig. 1.11) in combination with NPTMS (Fig. 1.10) [162] and the extension to "self-limiting" polyethylene catalysts systems.

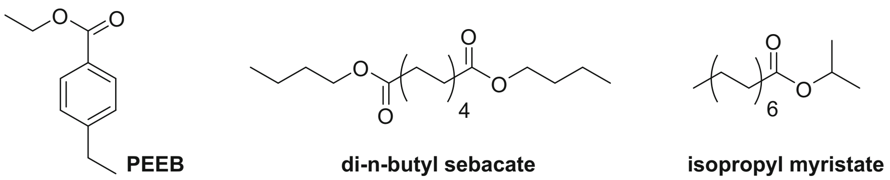


Fig. 1.11 Examples of "self-limiting" donors

1.2.2 Ziegler Catalysts: Polyethylene

It is harder to classify Ziegler PE catalysts in terms of generations, when compared to PP. However, there have been common development areas that are focused on making a catalyst more suited to the process to make an added-value product range. For example, operators of Ziegler catalysts in single phase reactors (GPR and Slurry) sought the need to increase the molecular weight distribution (MWD) of their products to improve polymer processability, and the ability to alter the comonomer composition distribution (CCD) to reduce hexane-solubles, for example. The MWD and CCD of Ziegler were limiting when compared to Cr-based catalyst systems, which still are alive and well in production of MDPE-HDPE grades. This in turn ultimately led to the development of bimodal Ziegler processes, due to restricted availability to license Cr technology in certain areas of the world. The development of bimodal technology has called for improved CCD and slightly narrower MWD for certain applications, but mainly an improvement in hydrogen response. High hydrogen response is required to maintain high catalyst activity (in contrast to propylene polymerization, addition of hydrogen leads to decreased ethylene polymerization activity) and to avoid loss of ethylene due to ethane formation. In addition, control over the particle size and, equally importantly, the particle size distribution of the catalyst, has become extremely important for bimodal operation. Smaller polymer particles allow for better mixing of the interparticle heterogeneity in terms of split (ratio of LMW to HMW) on the polymer particle as a consequence of operating in a multistage continuous process with residence time distributions. This reduces imperfections in the final product such as "white-spots" and gels. However, it is paramount that the generation of fines be kept to an acceptable level for smooth and safe operation, and hence the smaller the polymer particle targeted, the narrower the particle size distribution required [163–168].

In the following section we will concentrate on commercially relevant catalyst developments in these areas.

$MgCl_2$–Titanium Catalysts on Silica

Silica-based catalysts have found wide use, especially in gas-phase processes where a controlled particle size and distribution is needed in order to keep the bed in position. The silica support acts as a carrier material, imparting morphology control to the catalyst. In theory, it is not considered as a part of the active center, but it offers a large pore volume and surface area. A wide variety of catalysts can also be achieved by altering the physical properties of the silica support material (particle size and distribution, pore volume, surface area, etc.). The resulting catalyst carrier may consist of up to 50 wt% of the procatalyst. In addition, the calcination conditions for the support can be altered, thereby altering the proportions of isolated and hydrogen-bonded silanol and siloxane bridge groups and also affecting the friability of the support. The activities of these catalysts depend to some degree on the amount of titanium that is chemically bound and the amount of "free" $TiCl_4$ (the more "free" titanium, the higher the activity).

The silica is either physically impregnated with a solution of $MgCl_2/TiCl_4$ in THF or chemically impregnated with the catalyst components, which can either be added together or in differing orders. Common practice is to pacify the surface with an alkyl-aluminum, magnesium complex or an organosilane [169–188]. Chemical and physical impregnation procedures are exemplified in the work of Mobil [189] and UCC [190, 191], respectively. These catalysts, when combined with $AlMe_3$ as a cocatalyst, were the first to produce so called "super-hexene" grade LLDPE, with improved dart impart strength and hexane extractables [192, 193].

The development of impregnated silica catalysts has more recently been led by the work of NOVA Chemical, resulting in their NOVACAT range. In NOVACAT type catalysts, silica is first pacified by treatment with an aluminum alkyl. Magnesium chloride is then deposited on the treated silica by chlorinating a magnesium alkyl compound. To this is then added an electron donor, a titanium compound and a second aluminum compound (so-called split Al addition); the original goal of the development was to produce polymers with high MFR (broader molecular weight distributions) [194]. Figure 1.12 depicts the general synthetic route, however, Kelly et al. also elegantly showed that by varying the order of addition of the components following the magnesium alkyl addition, one could produce a range of polymers (density, M.I. and hexane extractables) under the same polymerization conditions. The group even succeeded in making "super-hexene" grade LLDPE without the need for $AlMe_3$ as a cocatalyst ($AlEt_3$) [195]. Cocatalyst concentration is also crucial in defining the mechanical performance of the final product in film applications, for example dart impact strength [196]. Deviation from THF as an electron donor has also been claimed to influence the hydrogen response of these systems [197].

With respect to bimodal processes, the silica-based catalysts of Borealis for Borstar and CX processes have excelled [181, 198, 199].

Spray-Dried $MgCl_2$–Titanium Catalysts

Spray-drying techniques are commonly used to prepare $MgCl_2$-based Ziegler PE systems, and is core to the ubiquitous Union Carbide UCAT family of catalysts [191, 200, 201] that were primarily designed to operate in a UNIPOL process, but have been extended to bimodal hexane slurry processes [202]. In spray drying, droplets containing a solution or slurry of the catalyst components are sprayed into

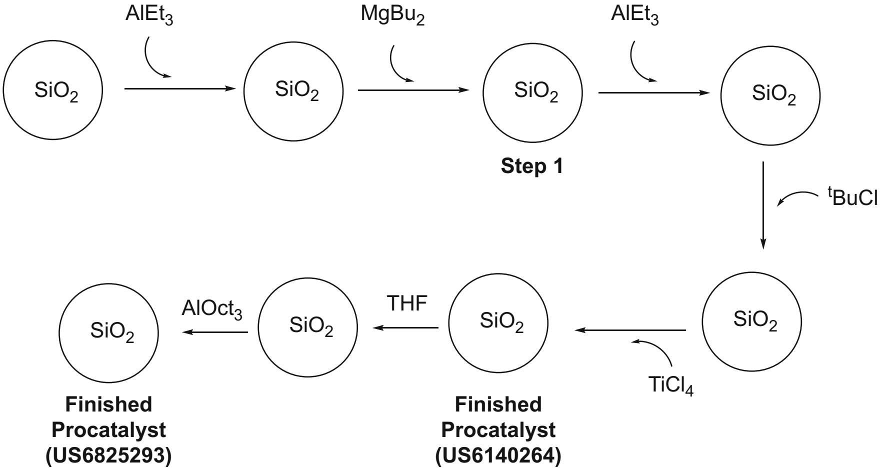


Fig. 1.12 Generic example of a NOVACAT Ziegler procatalyst synthesis

a chamber under drying conditions to remove the solvent or slurry diluent, leaving behind a solid spheroidal catalyst.

The characteristics of the droplets formed can be used to tailor the particle size of the final catalyst. Structural reorganization of the particle can be influenced by volume and size changes. In addition, spray-drying conditions can be used to form substantially spheroidal catalyst particles (large or small) or aggregated particles, with a homogeneous composition or porosity. Typically, spray-drying techniques employ a “filler” component to aid control of the shape and composition of the catalyst. Common fillers are hydrophobic fumed silicas, which impart a relatively high viscosity to the slurry to be spray-dried and also improve the mechanical strength of the final catalyst (Fig. 1.13). Further modifications of this recipe include the addition of EtOH to increase the solubility of $MgCl_2$ and hence the maximum achievable concentration in THF [203], improving the final morphology of the product, and the addition of a combination of one or more group 4 halides ($ZrCl_4$ or $HfCl_4$) [204]. The filler which makes up to 30 wt% of the catalyst may also generate increased porosity in the final catalyst [205–208].

The catalyst systems are then partially activated with two different alkyl aluminum-containing compounds (Fig. 1.14) before full activation in the final reactor with TEA for example. The proportions and nature of the alkyl can affect the MFR and hexane extractables in LLDPE production. For example, if $Al(n\text{Hex})_3$ and DEAC are replaced with $AlMe_3$ and $AlMe_2Cl$, respectively, and $AlMe_3$ is used in the reactor as the final cocatalyst, it is possible to produce so-called “Super-hexene” grades [193].

More recently the application of self-limiting donors, previously discussed for polypropylene, has been extended to these types of catalysts [209, 210].

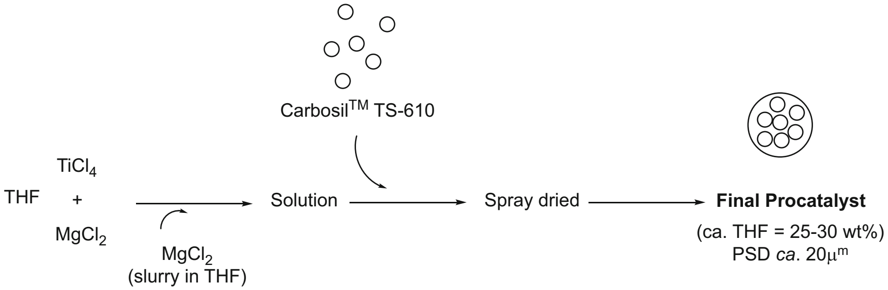


Fig. 1.13 Generic example of a UCAT Ziegler procatalyst synthesis

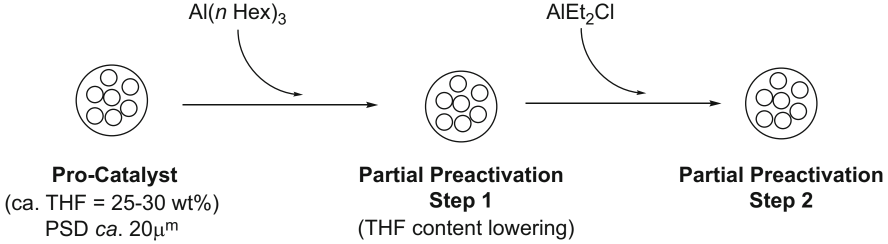


Fig. 1.14 Partial activation of the spray-dried procatalyst

MgCl2–Titanium Catalysts Based on $Mg(OR)_2$

Ziegler catalysts are prepared by first bringing $Mg(OR)_2$ into a dissolved/dispersed state or preparing the alkoxide in situ via reaction of MgR^1R^2 with an alcohol. $MgCl_2$ is then precipitated as an amorphous material, imparting high catalytic activity to the system. Usually, this is done by the addition of a suitable chlorination agent. Titanium can be added either as a soluble complex or used as one of the chlorination agents. By using different "tricks" during precipitation, and by adding suitable donor compounds, particle size and particle size distribution can be directed to a certain extent. Catalysts based on $Mg(OR)_2$ are by far the most utilized systems in bimodal slurry processes.

Researchers at Solvay developed the original system, which was based on making a solution of $Mg(OEt)_2$ and $Ti(OBu)_4$ and then chlorinating via an aluminum chloroalkyl containing species [211–213]. Further evolution of this system can be seen in the work of researchers at INEOS [214, 215] (Figs. 1.15 and 1.16) and SABIC [216, 217]. Figure 1.16 illustrates the example of an ethylbenzoate-modified catalyst; as one can imagine, the final procatalyst may also have a variety of alkylbenzoate donors produced by the reaction of ethylbenzoate and the other components. In the disclosure of Friederichs et al. we can also see that the addition of 1-allyl-3,4-dimethoxybenzene as an electron donor results in a significant reduction of unwanted ethane formation in the LMW phase of a bimodal composition when compared to unmodified and THF- or ethyl benzoate-modified formulations [216].

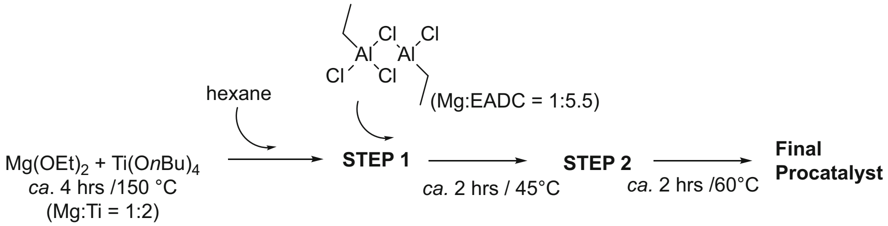


Fig. 1.15 Example of $Mg(OEt)_2$-based procatalyst

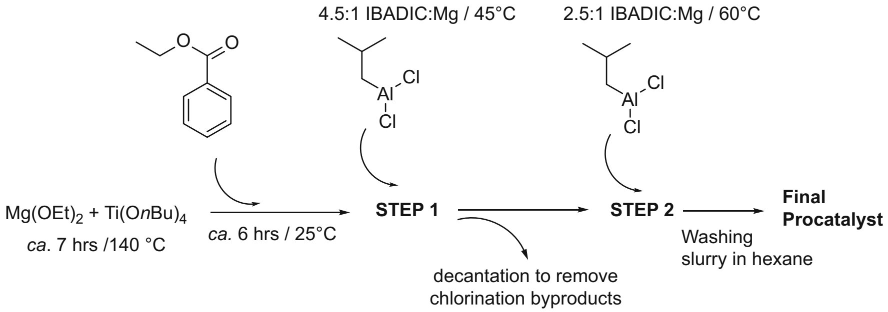


Fig. 1.16 Example of donor modified $Mg(OEt)_2$-based procatalyst

The $Mg(OR)_2$ may not require to be 100% dissolved, depending on its particle size. Lecht, Blöm, Berthoud, and others from Hoechst utilized finely dispersion Mg $(OEt)_2$ (Fig. 1.17) [218] and $Mg(OMe)_2$ (Fig. 1.18) [219, 220] in the preparation of catalyst systems. The two synthetic pathways described below differ in the strength of the reducing agent employed and one could imagine that $Mg(OEt)_2$ is the preferred support. These $Mg(OR)_2$ supported catalysts technology are current the backbone of recent developments in the multimodal Hostalen process to produce multimodal pipe, blown film, and blow molding [221–224]. In the case of blow molding the group has also shown the possibility to form LCB via a Ziegler catalyst [221].

Total and its previous incarnation, on the other hand, have utilized a path that includes creating a soluble $Mg(OR)_2$ via reaction of $MgEtBu/AlEt_3$ (1:0.03) with 2-ethylhexanol [225, 226]. The compound is treated with successively stronger chlorinating titanium reagents $TiCl(OiPr)_3 \rightarrow 2\ TiCl_4/Ti(OnBu)_4 \rightarrow TiCl_4$ to form the final catalyst. Vizzini et al. have also disclosed how the catalyst can be tuned via altering the reaction conditions and reagent ratios [227, 228]. This system produces a catalyst well suited for operation in bimodal slurry processes due its narrow particle size distribution, high activity, good hydrogen response and the relatively narrow Mw/Mn of the resulting polymer [229, 230]. Similar long-chain $Mg(OR)_2$ starting points have very recently been disclosed by DSM Stamicarbon [231], Borealis [232, 233], and SINOPEC [234]. The latter converted soluble $Mg(OR)_2$ to a final procatalyst via mixed chlorination steps (step 1: BCl_3 or $SiCl_4$ etc.; step 2: $TiCl_4$) in the presence of a SBS triblock copolymer (Kraton FG1901X) to form morphologically controlled catalysts [234].

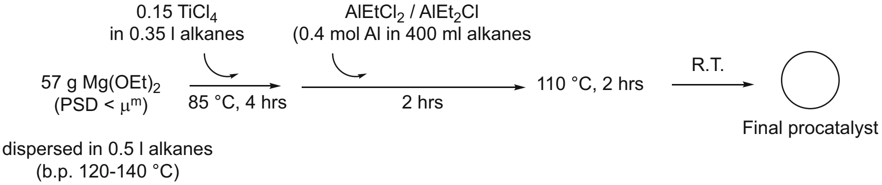


Fig. 1.17 Synthetic route from particulate $Mg(OEt)_2$

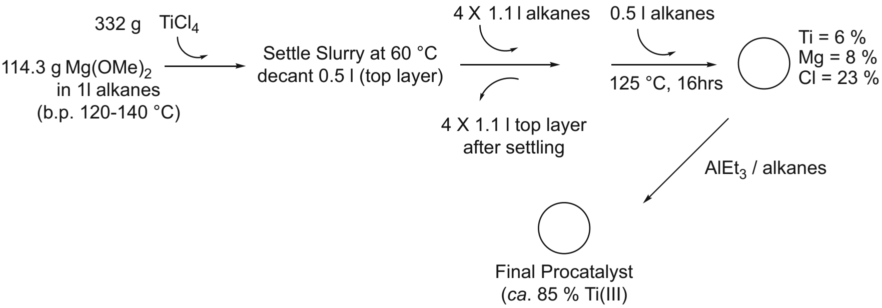


Fig. 1.18 Synthetic route from $Mg(OMe)_2$

$MgCl_2$–Titanium Catalysts Based on $MgCl_2$ alcohol adducts

There are two distinct synthetic routes with respect to $MgCl_2$–Titanium catalysts based on $MgCl_2$ alcohol adducts, as we have seen for PP catalysts. Controlled formation of a solid spherical $MgCl_2$ adduct support that can be titanated in a separate step, or controlled precipitation using a solubilized $MgCl_2$ adduct. For the latter, illustrative routes to catalysts relevant for multimodal operation will be discussed, based on the use of 2-ethylhexanol to form a soluble adduct with $MgCl_2$. The genesis of this is the work of the morphology master of Mitsui, who have taken this technology from PP to PE and to the point of a fine art. For example, the system can be controlled to almost submicron levels with retention of a narrow PSD, which has allowed for the production of fine UHMWPE particle grades known as the Mipelon product line3 [235] (Fig. 1.19). In addition, the support can be combined with AlR_3 and a phenoxyimine complex to form an excellent MAO-free support [236]. Examples of the synthetic routes can be found below in Fig. 1.20 [237, 238]. The use of different combinations of alcohol and donors and their effect has also been disclosed [239].

The second illustrative example of a relevant multimodal catalyst, based on in excess of 100 patent citations as being the preferred embodiment of titanium/magnesium catalyst systems, is that of Invetep [240] and subsequent similar disclosures from BASF [241, 242]. The basic difference between these systems appears in the composition of the mixed aluminum alkoxide–siloxide additive that is added to the $MgCl_2$ adduct. In addition, Chang et al. discovered that the addition of $Si(OEt)_4$

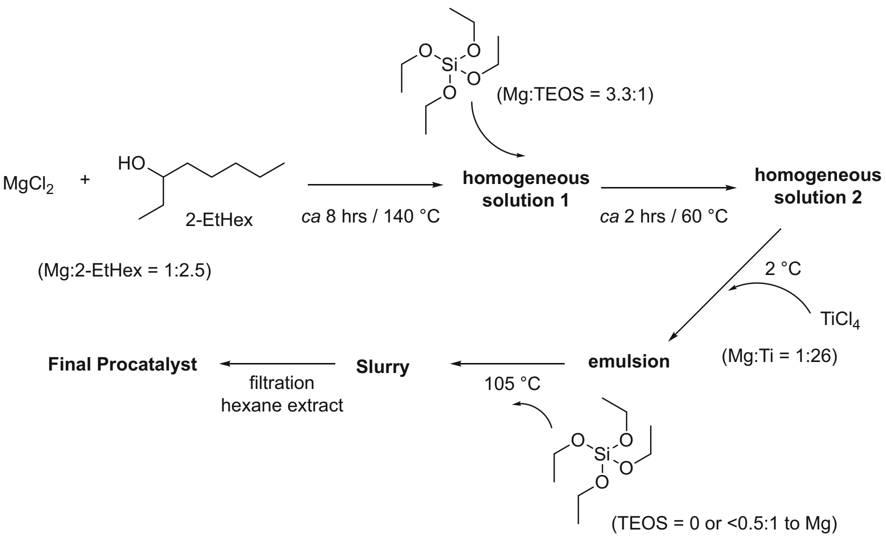


Fig. 1.19 Synthetic route to fine catalyst particles

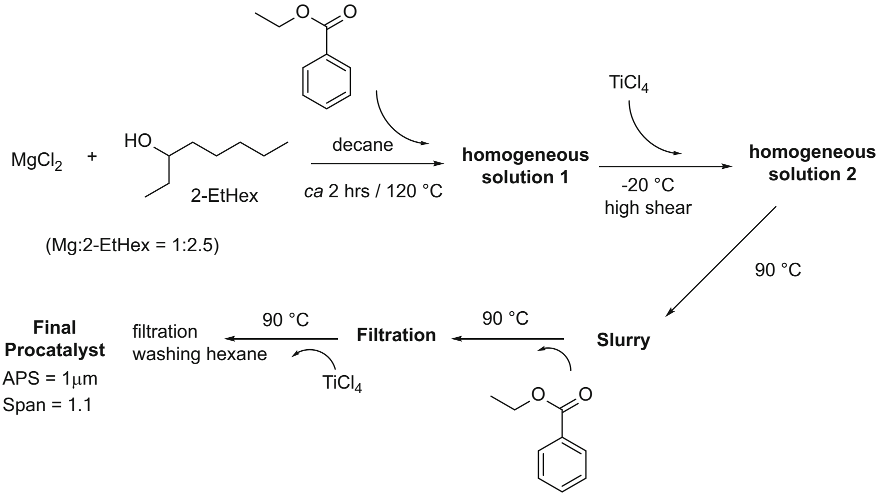


Fig. 1.20 Example of Mitsui $MgCl_2 \cdot n ROH$ adduct-based procatalyst synthesis

and ethylbenzoate yielded a catalyst that had high activity, hydrogen response, and reduced fines [242], while Garoff et al. utilized malonate donors to reduce the molecular weight distribution (Fig. 1.21) [241].

Finally, the ubiquitous $MgCl_2 \cdot n EtOH$ adducts [82, 83], have found extensive application in gas phase PE, in particular the Spherilene S and C processes [243, 244]. In this case the support particles are usually larger than for the PP disclosures and are often employed at lower ethanol contents. As with the PP system,

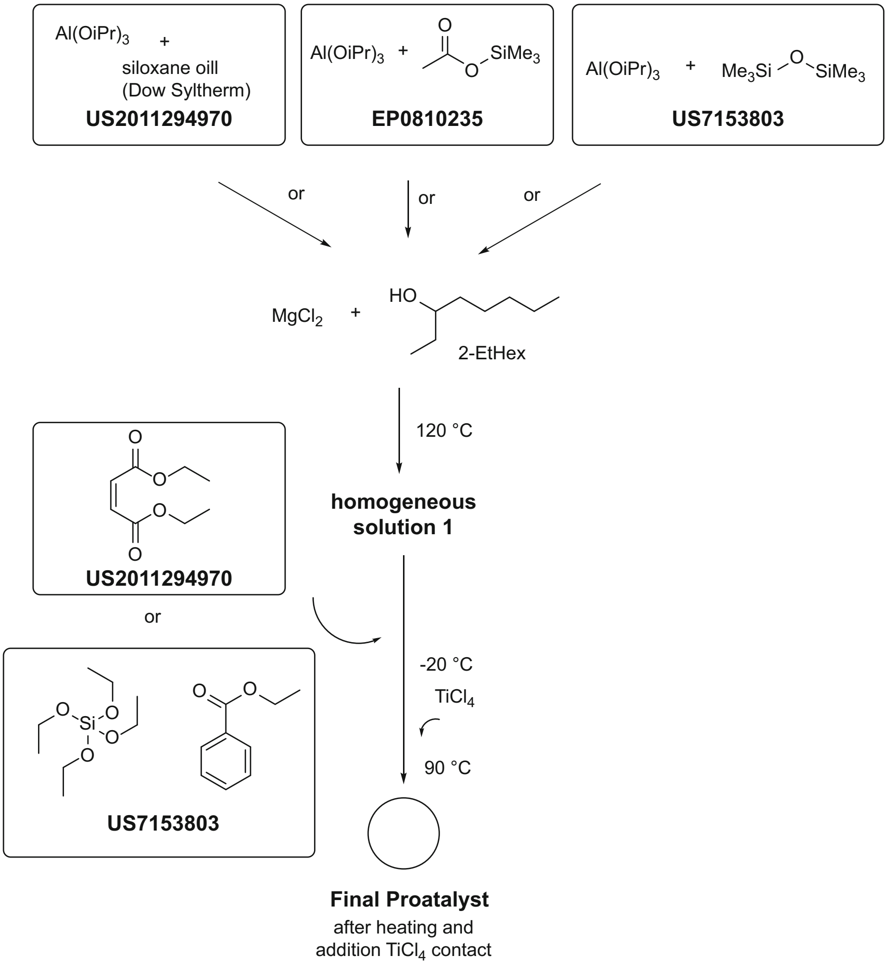


Fig. 1.21 Example of catalyst synthesis with malonate donors

the removal of the residual ethanol is done by $TiCl_4$. A donor, most commonly ethyl acetate, can be added during this phase. The catalyst is prepolymerized with propylene. Recent reported developments in donors are 1,2-dimethoxy-benzene derivatives [245, 246], diethers [247], methyl *tert*-butyl ether [246], silanes [248], and the addition of $GeCl_4$ as a mileage enhancer [249].

MgCl2–Titanium Catalysts Based on MgRCl

Numerous catalysts have been synthesized utilizing a step involving a Grignard reagent, including the formation of $Mg(OEt)_2$. The following section will focus on

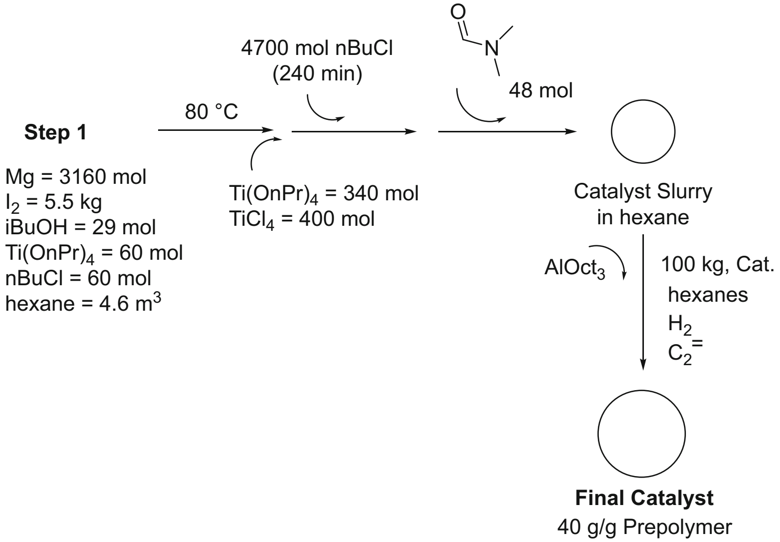


Fig. 1.22 Example of an industrial scale recipe for an Innovene G catalyst

two illustrative systems developed for unimodal gas phase and bimodal slurry processes. For the former, one of the catalysts for the Innovene G gas phase process has been selected, mainly due to the sheer scale of the disclosed preparation and further in-reactor modification [250, 251] (Fig. 1.22).

The choice of cocatalyst in the polymerization, as we have seen above, is crucial in achieving added value LLDPE and plant operability. Berardi et al. clearly illustrated that in the case of this catalyst and process $AlEt_2Cl$ is preferred over Al-Me_2Cl [251]. The catalyst is also utilized in Westlake Energx Technology [252, 253], which is used to make Mxsten grades slate of LLDPE, which are unsurpassed in terms of the performance of Ziegler film grades. The Grignard-based catalyst system in Fig. 1.23 [254, 255] was developed for the Mauzren bimodal slurry process [256–258]. The system has also utilized mixed V/Ti systems [259]. Similar systems have also been disclosed by Sumitomo [260].

1.3 Supported Molecular Catalysts

1.3.1 *Polypropylene Complex Development*

In today’s world, classic heterogeneous Ziegler–Natta catalysts are beyond comparison in performance and cost. Nevertheless, the quest for understanding the polymerization mechanism and the promise of greater control over the synthetic macromolecular process to produce new materials still fuels the development of supported molecular PP catalysts. Stereoregular polypropylene and copolymers

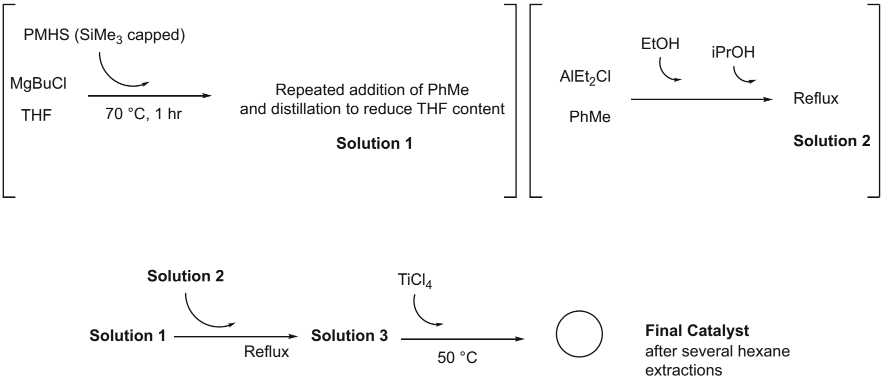


Fig. 1.23 Example of a procatalyst for the Mauzren bimodal slurry process

made with single site catalysts have been extremely slow in penetrating into the market, due in part to the amount of chemistry that can be done on PP in an extruder, for example LCB for high melt strength (HMS)PP and controlled rheology. However, the author's organometallic blood finds it hard to resist the briefest discussion of the structural elegance of homogeneous catalyst complexes for PP and the ingenuity of the researchers to find holes in apparently seamless patents. It is also a reminder of the majesty of catalysis in how seemingly minor changes in substitution patterns affect relative activation energy barriers, often resulting in major impact on resultant polymer properties.

The areas of focus in terms of complex development from the matriarch Spaleck complex (*rac*-$Me_2Si(2\text{-}Me,4\text{-}PhInd)_2ZrCl_2$) [261], have been in the area of ligand substitution to overcome the limitations compared to Ziegler–Natta catalysts and to exploit a definite advantage. Substitution of the standard ligand framework has sought to increase the melting point of the homo-PP through better regio- and stereo-selectivity and to increase the molecular weight of propylene/ethylene copolymers. The area in which metallocenes outperform Ziegler–Natta catalysts, and the source of present interest, is in the area of copolymerization of propylene with longer-chain olefins (1-butene, 1-hexene, 1-octene, etc.), giving access to new crystalline morphologies. Figure 1.24 illustrates recent complexes that have sought to tackle the above limitations and opportunities [262–276].

1.3.2 Polyethylene Complex Development

Supported molecular catalyst use for polyethylene, unlike polypropylene, is still seeing reasonable year-on-year growth and is becoming somewhat commoditized. Reviews of the development of molecular catalysts are numerous [1, 3, 4–7, 14, 15]. The illustrative examples of metallocenes in Fig. 1.25 are currently either the workhorses for current mPE products or are well on the road, predominantly on

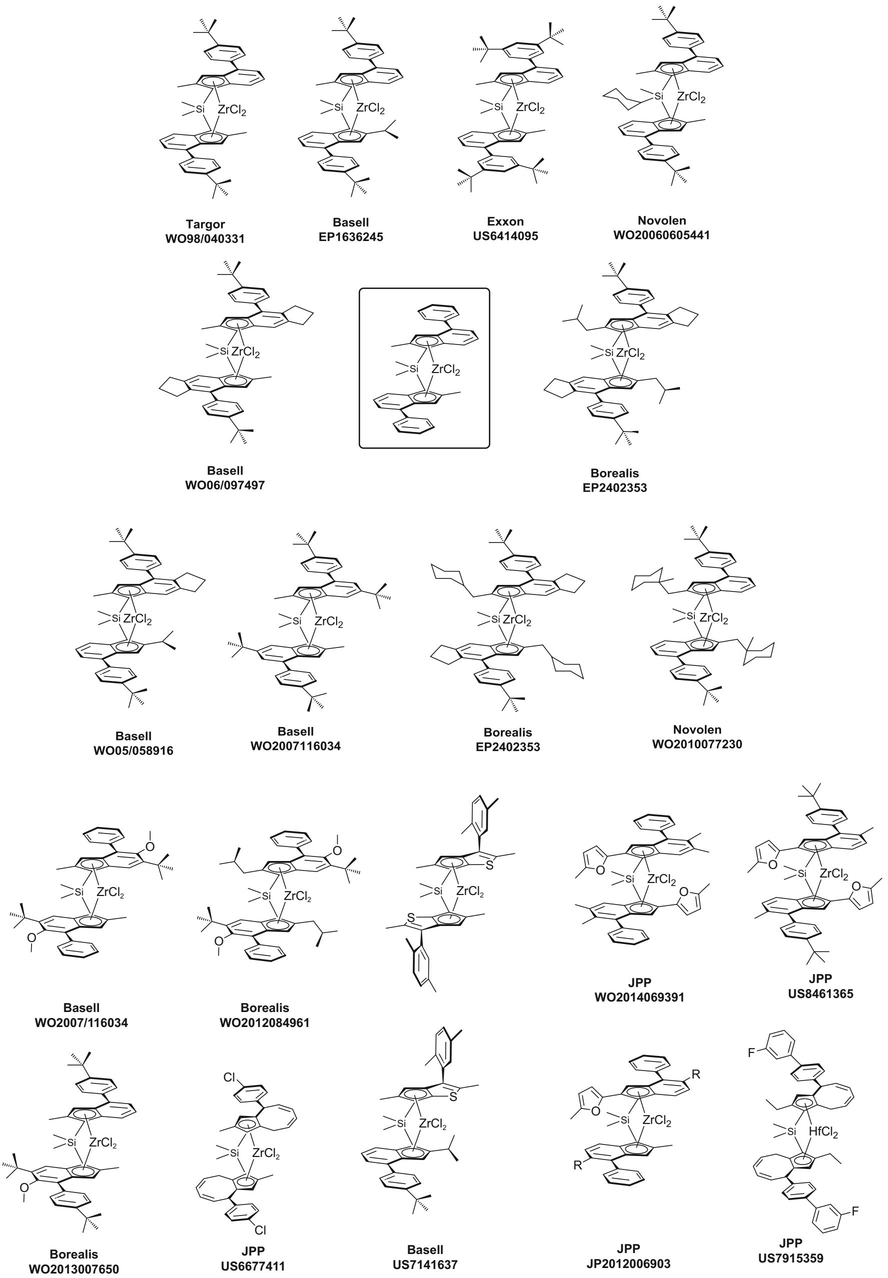


Fig. 1.24 Overview of recent complexes used for copolymerization of propylene with longer-chain olefins (1-butene, 1-hexene, 1-octene etc.)

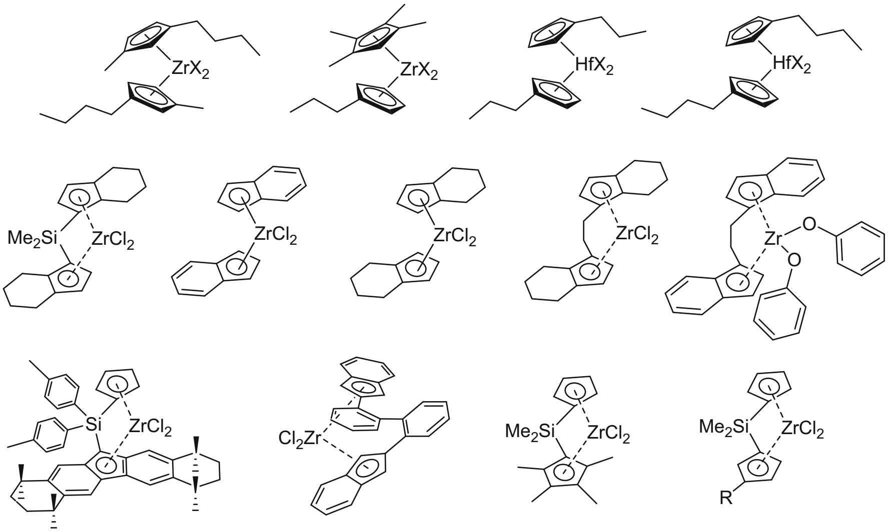
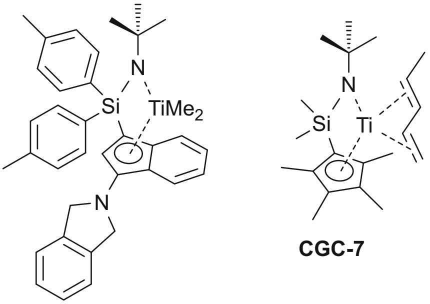


Fig. 1.25 Metallocene complexes used for mPE production

silica/MAO carriers. For example, the current Univation catalyst family [277–282] has been commercially successful for a number of years, particularly in single phase reactors. Simple unbridged metallocenes have also been employed in the Mitsui Evolue bimodal gas phase process [283, 284] and the Borealis Borstar loop/gas phase process [285–287].

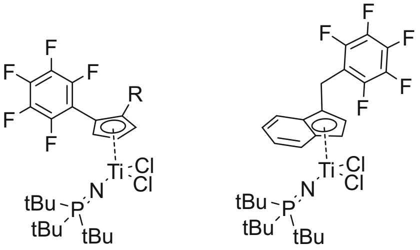
Bridged complexes such as *rac*-bis(tetrahydroindenyl)zirconium dichloride have been utilized by Total in their bimodal double-loop processes and have been shown to be capable of making a wide range of advanced grades, including high pressure PE100+ pipe material based on 1-hexene comonomer [288–291]. The challenge of producing the next generation pipe and blown molding material has also seen Mitsui develop the Evolue H grades based on a bridged Cp-Fluorenyl catalyst system [292, 293].

In terms of post-metallocenes, in single component systems the constrained geometry catalysts (CGC, Fig. 1.26) based on borate-supported activators developed by researchers at Dow [294–296], have now been commercialized in supported systems by Asahi who cite reference [294] (HDPE slurry) and by INEOS [297] (LLDPE gas phase), Dow's former collaboration partners for the utilization of CGC in particle-forming processes until Dow's merger with UCC. At Asahi the system has formed the basis of their Creolex product range, from reasonably low molecular weight HDPE to their Sunfine UHMWPE powder. The latter is interesting in that the process needs to run with hydrogen to avoid fouling but then needs Tebbe reagent to be constantly added to the reaction to help the catalyst achieve UHMWPE ranges. The response to hydrogen in terms of activity with the CGC-7 complex is also an added advantage when compared to some complexes and the system as a result has also found use by Dow in a bimodal process to once again produce outstanding PE100+ material [298].



CGC-7

Fig. 1.26 Examples of supported constrained geometry catalysts (CGC)



R = Et, Pr, But, Hex

Fig. 1.27 Illustrative examples of supported phosphinimide catalysts

Nova Chemicals appears to be quite far down the road with a supported version of its phosphinimide family of catalysts (Fig. 1.27), previously developed for its bimodal solution process [299–303]. Adaption to the original bonding pattern via addition of the pentafluorophenyl moiety has brought in a better hydrogen response. This, coupled to the indenyl ligand which had previously been shown to be relatively fluxional, has led to the development of the Ind–CH_2–C_6F_5 ligand. These developments have led to systems that can be tuned via the addition of an antistatic agent to produce materials that are heterogeneous in terms of comonomer distribution (reverse) [303]. In the case of Ind–CH_2–C_6F_5 the system has a broader Mw/Mn due to the indenyl moiety; the incorporation of the antistatic agent significantly increase the heterogeneity in terms of comonomer distribution and a significant increase in Mz.

The combination of CGC catalyst and phoshinimides has also been employed as a hybrid catalyst for bimodal polyethylene in a single gas phase reactor, a concept that will be dealt with in more detail in the subsequent section [303].

The newest kids on the block are the bis(hydroxylarylaryloxy) “O_4” based systems (Fig. 1.28). This catalyst system, with the extensively varied structure modification points, has been a veritable gold mine for innovation, and as a result these complexes have been employed in numerous processes and product families [304–309]. The complexes have also been supported on silica/MAO or the tethered borate system by Symyx/Ticona [310, 311] and Dow, respectively [312]. The former demonstrated the prodigious molecular weight capabilities that these catalysts possess and also the effect that scavenger selection can have on the activity and molecular weight capability.

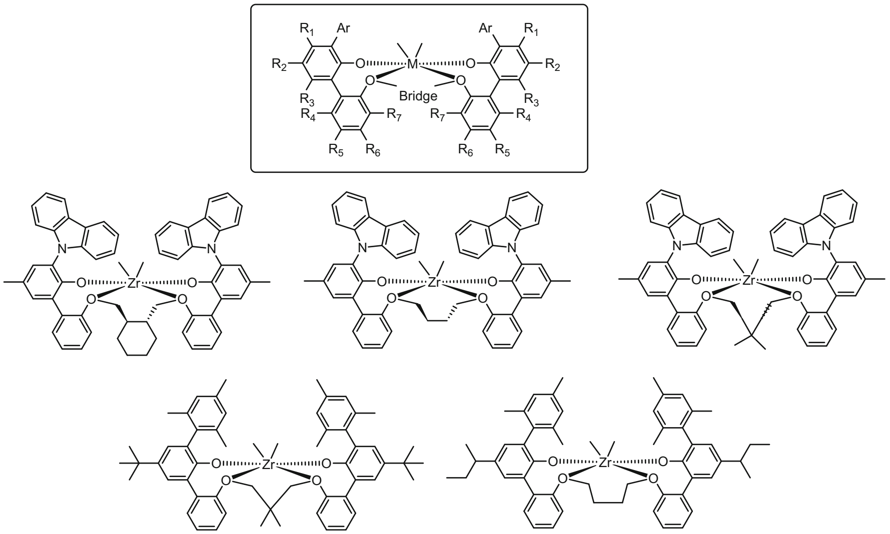


Fig. 1.28 Illustrative examples of supported bis(hydroxylarylaryloxy)-based catalysts

1.3.3 Supported Activator Development

There have been numerous disclosures on how to support a molecular catalyst and on what sort of support. The extent of these efforts can be seen in the reviews of Hlatky [313], Severn et al. [314], and Severn and Chadwick [315]. The following section concentrates on the latest commercial developments in this area.

Silica-Supported Methylaluminoxane or Boron-Based Cocatalysts

Predominantly, combinations of silica and MAO have been used to support a molecular catalyst, with extensive variation being disclosed and optimized to match a molecular catalyst with a certain process. An overview of what has been disclosed can be seen in the review of Severn [315]. Within this area current developments appear to be on doping either the MAO or the silica to improve the performance.

Researchers at Albemarle have shown a near doubling in activity for a SiO_2/MAO system via addition of $AlMe_2F$ after the MAO has been contacted with the silica. The group links this boost in activity to an increase in the production of $[AlMe_2]^+$ cations that form part of the activation step [316].

The addition of SO_4^{2-}, NO_3^{2-}, F^-, and SiF_6^{2-} containing salts to the silica prior to calcination has also been shown to provide significant improvements in the performance of the final catalyst. Nova Chemicals for example have introduced NaF [317], $[(NH_4)_2SiF_6]$ [318], and more recently $Zr(SO_4)_2$ [299, 319]. While

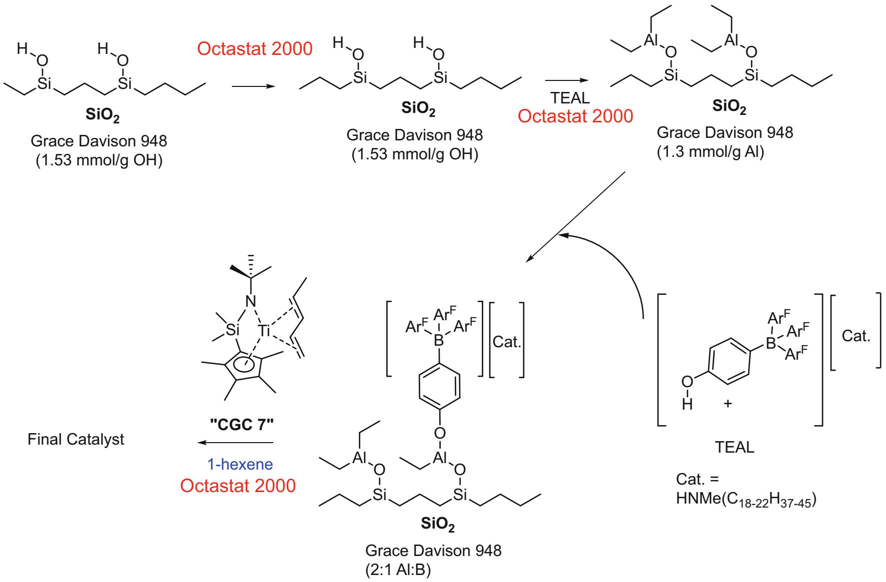


Fig. 1.29 Synthetic route to INEOS HP-LL catalyst

Exxon have focused more on the addition of [$(NH_4)_2SiF_6$] to silica prior to contact with either MAO/molecular catalyst [320] solution or MAO [321].

As mentioned earlier, the supported borate activators developed by researchers at Dow [294–296] have now been commercialized in supported systems by Asahi (HDPE slurry) and INEOS [297] (LLDPE gas phase) and are appearing in recent disclosures of Dow. Key to this development was the synthesis of a soluble borate starting material and numerous treatments with antistatic agents to reduce the static loading of the fresh catalyst that is injected into the reactor (Fig. 1.29). The advantages of addition of an antistatic agent to the catalyst have also been seen for the metallocene catalysts discussed earlier.

Supported Methylaluminoxane System Free of a Support

Solidifying MAO with controlled morphology has several attractions, one of which is the reduction in the "dead weight" that the carrier brings to the catalyst. Two companies have developed systems to form solidified MAO support where the morphology of the final catalyst can be controlled. The first system is the Borealis Sirius catalyst system developed by Deniﬂ et al., in which the catalyst is activated in a homogeneous phase before the activated solution is mixed with a perfluorocarbon containing a perfluorocarbon-containing surfactant [322–325]. An emulsion is formed at low temperature with a perfluorocarbon and the solidification is induced via dropping this solution in a reactor containing excess perfluorocarbon at elevated

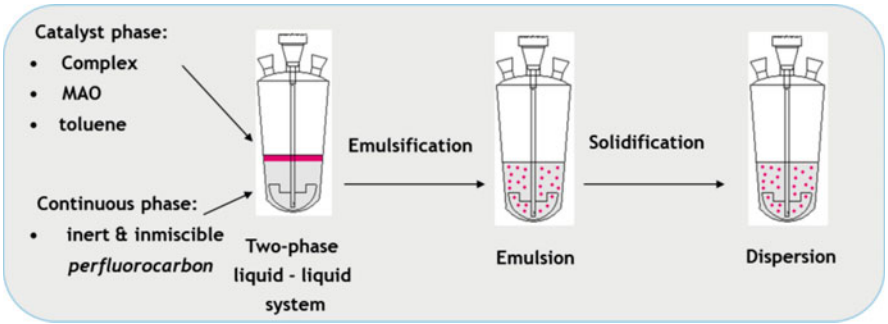


Fig. 1.30 Schematic representation of the Sirius molecular catalyst platform

temperature. Solidification occurs by virtue of the toluene in the MAO/Complex phase being extracted into the perfluorocarbon phase (Fig. 1.30). The catalyst is filtered hot, and the catalyst requires prepolymerization before use [326]. Continuous production of this catalyst system has also been disclosed.

Modifications to this method have been the introduction of an additional boron-containing cocatalyst [327, 328] or the utilization of clathrated MAO, previously described by Albemarle [329, 330].

The preferred clathrating agent until recently appeared to be octamethyldisiloxane which forms a two-phase system with a MAO-lean top phase that contains free TMA and a viscous bottom layer that increases in viscosity on washing with PhMe [331]. A way was then found to solidify clathrated MAO via non-perfluorocarbon routes that produced spherical compact catalyst particles with high activity [332–334]. An example of polyethylene particles formed by these systems can be seen in Fig. 1.31, in which the image on the right hand side is a microtomed cross section of an individual polymer particle illustrating the dense polymer particles formed with these catalysts.

More recently, Tosoh Fine Chemicals have produced a solid MAO system that can be precontacted with a metallocene to form a support-free catalyst system [335, 336].

Supported System Free of Methylaluminoxane

Several groups have made good use of MAO-free solutions to produce commercially relevant supported molecular catalysts. CPChem has gained a tremendous knowledge on doping SiO_2, SiO_2/Al_2O_3, and Al_2O_3 supports with salts as part of their chromium-based catalyst developments. They have found that doped supported systems can activate molecular catalysts even in the absence of methylaluminoxane. The development of these systems has been reviewed by McDaniels, one of the lead developers of this technology [337]. Looking at the tremendous amount of patent literature on this topic, it appears that two technologies have been developed,

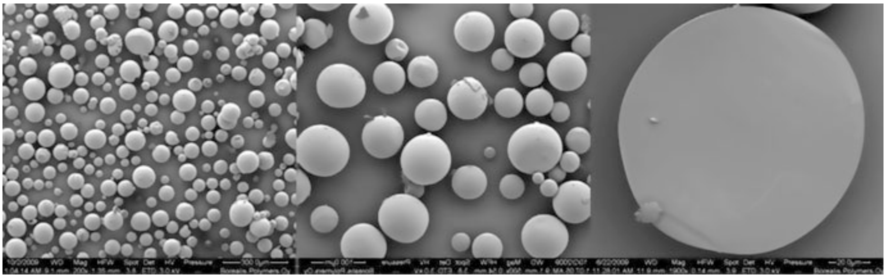


Fig. 1.31 Polymer particle produced with the Sirius molecular catalyst platform

depending on the ease of activation of the metallocene complex used. For example, relatively easy to activate metallocenes such as $^{n}Cp_2ZrCl_2$ and Ind_2ZrCl_2 are employed in combination with SiO_2/Al_2O_3 (ca. 13 wt% Al_2O_3) supports that have been precontacted with $[NH_4][HF_2]$ prior to an optimized calcination step. This in turn is treated with a "precontact solution" consisting of the metallocene, $AlEt_3$ and hexene to form the final active species. The precontact step leads to significant activity improvements via formation of a cyclic dialkylaluminum complex and has been disclosed with an example at full commercial scale [338]. The second technology for more challenging to activate complexes is the use of Al_2O_3 (Bohemite) with $[(NH_4)_2(SO_4)]$; as with the above, the ratio of reagents and the thermal history of the calcination step are crucial in gaining the most from these systems [339].

Fluorophenols have been used to form an active heterogeneous molecular catalyst system. Albemarle utilized C_6F_5OH in the scene below to produce a Brönsted acidic activator (Fig. 1.32) [340, 341]. Ineos have also recently been looking into these systems [342].

Researchers at Targor [343] and Basell [344, 345] have also produced MAO-free activators based on simple alkylaluminum and $B(C_6F_5)_2OH$ (Fig. 1.33) and $B(C_6F_5)(OH)_2$, (Fig. 1.34) respectively.

Additional use of organofluoro modifiers can be seen in the work of researchers at Exxon and Sumitomo. Holtcamp and coworkers at Exxon were able to produce heterogeneous cocatalyst packages via contacting 4,5,6,7-tetrafluoroindole with $AlEt_3$ or Al_2OEt_4 silica [346–348]. Sumitomo on the other hand have demonstrated the formation of a zinc-based supported cocatalyst system with a trifluoro-phenol complex (Fig. 1.35) [349].

Last but certainly not least is the work of Japan Polypropylene and the supported cocatalyst for their Wintec and Welnex product lines [274, 349–352]. In this concept the clay particles are treated with H_2SO_4 to form a larger controlled morphology particle, with trioctylaluminum (TOAL) added to finish the product (Fig. 1.36).

Another notable clay-based development can be seen in W.R. Grace IOLA-A [353] and IOLA-B [354] supports produced by spray-drying hydrogels with clay and MgO.

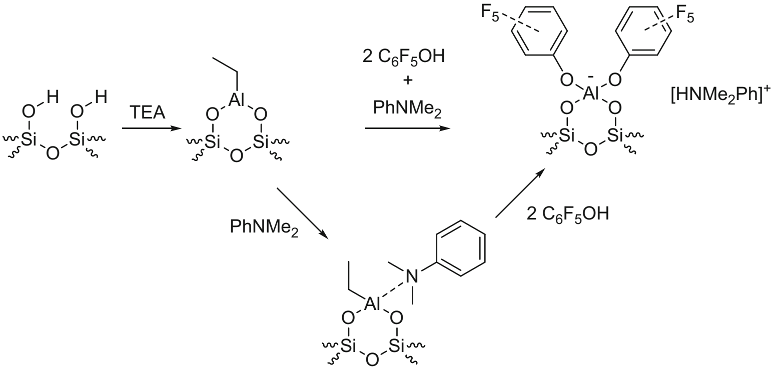


Fig. 1.32 Example of Albemarle MAO-free supported activator

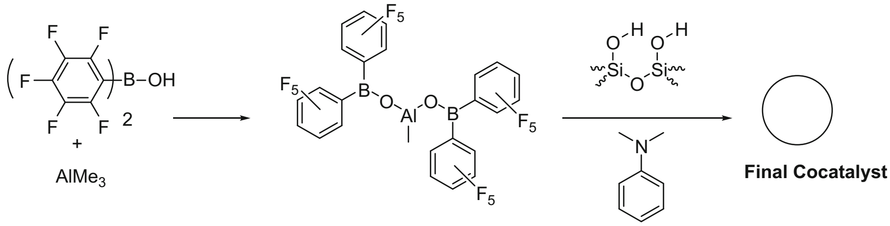


Fig. 1.33 MAO-free supported activator

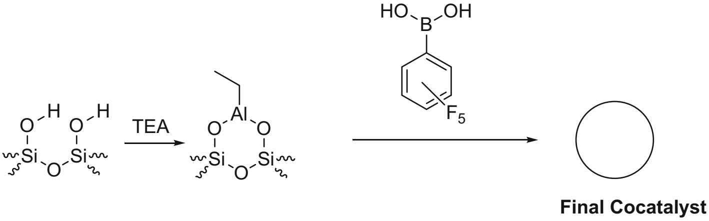


Fig. 1.34 MAO-free supported activator

1.3.4 Supported Hybrid Catalyst for Multimodal Polyethylene

The success of single gas-phase processes (UNIPOL, Innovene-G, and Spherilene-S) and slurry loop processes (Phillips Process and Innovene-S) has seen a significant amount of capacity installed in licensors' and licensees' manufacturing sites. For economic reasons and in view of the wider availability of such reactors, efforts have been made for some time to prepare polymers having broader (multimodal) and

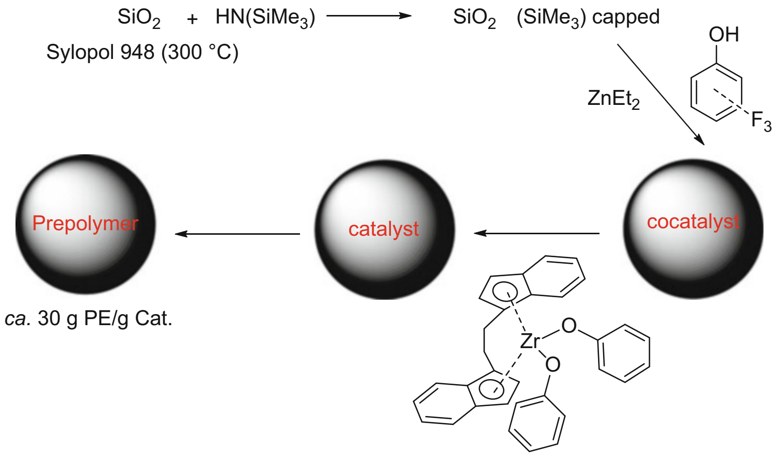


Fig. 1.35 Example of Sumitomo zinc-based supported activator

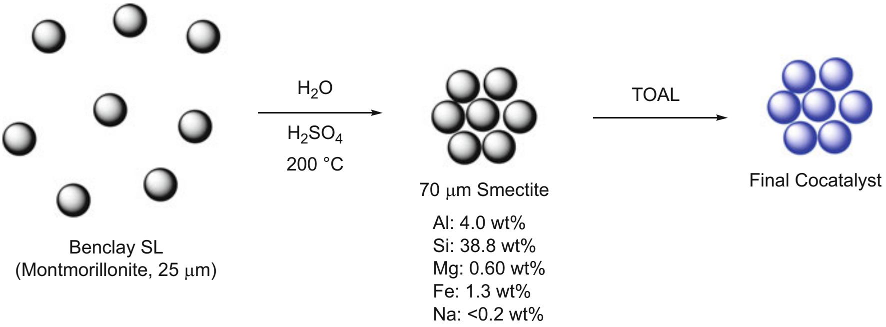


Fig. 1.36 Example of Japan Polypropylene clay-based activators

tailored comonomer compositions in continuous single reactor processes. To achieve this objective, catalyst mixtures or catalysts having different active centers on the same carrier particle (Hybrid Catalysts) have frequently been described and have been discussed by Friederichs et al. [355].

Hybrid catalysts can comprise the same or different classes of catalyst.

- Ziegler or chromium catalyst + molecular catalyst
- molecular catalyst 1 + molecular catalyst 2, etc.

In the following section we will only focus on the combination of molecular catalysts for polyethylene and refer the reader to the illustrative examples of Mink et al. [356, 357] and the excellent overview of Friederichs et al. for discussions on the former and polypropylene systems.

Challenges of Single Supported Systems

Before discussing hybrid systems it is worthwhile recapping on some of the challenges that impact even a single component system. It has already been shown above and in the literature that a molecular catalysts is very sensitive to its supporting protocol, carrier material and activator [315]. This combination impacts the final catalyst in terms of kinetics, plant operability and powder properties. Unfortunately there is no one size fits all procedure. It has also been shown, and this is the core of the hybrid concept, that there is a wide range of response to hydrogen and comonomer, for example [358]. So different catalyst complexes can make different products under the same polymerization conditions. Unfortunately however, this asymmetric response to process variables does not stop at just hydrogen, ethylene, and comonomer. For example, asymmetric responses can occur with respect to process poisons, scavenger, continuity/antistatic agents, and operation in condensed mode.

A little discussed fact outside of industry is the asymmetric ability for a molecular catalyst to generate hydrogen, especially during copolymerization (Figs. 1.37 and 1.38).

This impacts the upper molecular weight capability of the system. The ability to generate hydrogen also does not translate to response to hydrogen [359, 360]. Solutions to increase the upper molecular weight capability have involved the use of Tebbe reagent as a hydrogen scavenger [361].

Challenges of Hybrid Supported Systems

In the continuous polymerization of olefins in a single reactor with hybrid catalysts, there is the problem that the properties of the polymers obtained depend not only on the polymerization conditions but also significantly on the ratio of the individual active sites present. Fluctuations in the compositions of different hybrid catalyst batches used can thus lead to different proportions of the polymer components formed by the individual catalyst components. The shift in active site ratio can also be impacted for example by ageing, that is, if one of the components is more sensitive than the other to storage or shipment, this can also result in different products even when the same batch is used [362]. Finally, fluctuations of the polymerization conditions can also influence the activity of the individual sites in a disproportionate way. Therefore a significant amount of the academic work published on such systems in a batch process is somewhat irrelevant from an

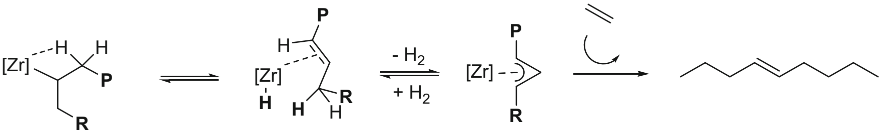


Fig. 1.37 Schematic representation of the proposed mechanism for hydrogen formation

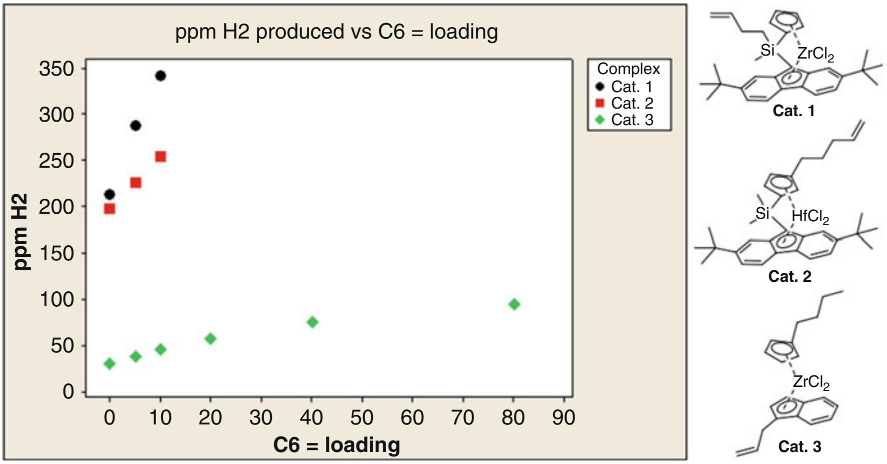


Fig. 1.38 Hydrogen generation as a function of 1-hexene concentration for different complexes

industrial perspective. For the abovementioned issues of composition control in continuous single reactor trains, there is a great need for finding ways of controlling this with hybrid catalysts. That said however, one cannot help being impressed by the scientific competence and sheer ingenuity of the industrial scientists who have risen to this challenge.

Hybrid Systems

A combination of metallocene complexes in the same process is not a new concept with, Ewen and Welborn being the first to combine different metallocenes in a solution process [363, 364]. The following section, however, is focused on particle-forming processes.

Possibly the best known hybrid systems are the Prodigy BMC catalyst series developed by Univation [358, 365]. An illustrative example is the BMC-200 system in which unbridged metallocene (Cp)(^{Me4}Cp)ZrCl$_2$ is used to make low molecular weight comonomer-lean material, while the dibenzyl McConville complexes produce the high molecular weight comonomer-rich fraction (Fig. 1.39) [366]. The catalyst is made via spray-drying the two complexes together with MAO and Carbosil TS-610, in a ratio of *ca.* 3:1 McConville to metallocene. As mentioned earlier there is no one size fits all and within this technology of supportation difference can be seen in the preparation method. For example, the spray drying temperature can impact the activity and active site ratio of the final catalyst [367].

As we saw earlier there needs to be a control mechanism in the process to compensate for variation in split and so on. To this end Univation developed its

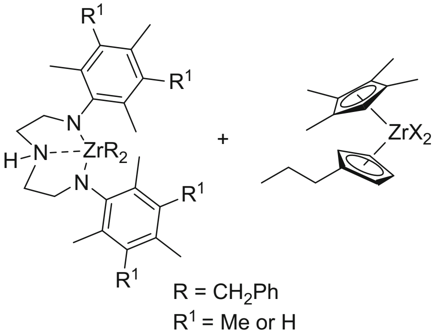


Fig. 1.39 Example of combination of different metallocene complexes

own means to solve the problem. The spray-dried catalyst (complexes, MAO, Carbosil TS-610) system is injected into the reactor in a mineral oil. Additional single component catalyst is added as a liquid into this mineral oil suspension on the way to the reactor, and is supported/activated onto the particles of the binary system. This trim system often uses the alkylated version of the LMW metallocene component to fine tune the molecular weight and split control of the polymer being made [367, 368]. Fine tuning it appears can also be done via an asymmetric response to condense mode operation [369, 370]. The system, when utilized in a single reactor, can make impressive PE100+ pipe material. However, somewhat of a drawback of these systems is that production of several grades with varying degrees of split between the molecular weights is challenging. To overcome this, more recent developments have seen the use of a component (LMW or HMW complex) that can be considered unresponsive to hydrogen. In case of the HMW component the "O_4" complexes described above have been employed (Fig. 1.40) [371, 372], while for the LMW a modified phenoxyimine complex has been utilized (Fig. 1.41) [373].

These catalysts all form extremely pronounced bimodal material which make excellent pipe products, but for some applications like blow molding a very broad distribution is required that would make the split too pronounced, leading to such issues as melt fracture. In this concept there needs to be an additional mode to fill the valley, so to say. So, proving that three is not a crowd, three-component hybrid catalysts have been disclosed to tackle this issue (Fig. 1.42) [373, 374].

In terms of disclosure the main rival to the Univation hybrid crown is CPChem., which is also the substantial licensor of the unimodal Phillips slurry loop technology. They have concentrated mainly on the combinations of two or more metallocenes on their proprietary supported activators previously discussed [375–379]. More recent disclosures have appeared to settle on one main system based on a unbridged and a bridged metallocene for the LMW phase and HMW phase, respectively [380]. As above, the addition of a third component really does assist in broadening the Mw distribution (Fig. 1.43).

As for split control it appears that the addition of an alcohol such as isopropyl alcohol can be used to selectively poison the LMW site, shifting the split to high

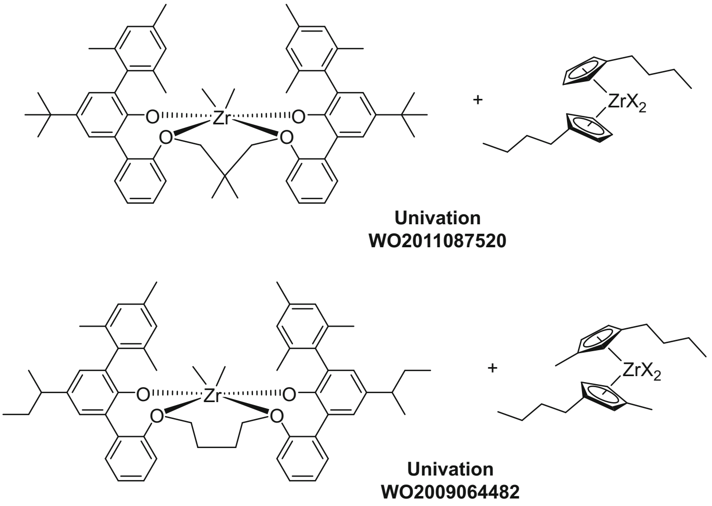


Fig. 1.40 Example of bicomponent hybrid catalyst with poor hydrogen response on the HMW component

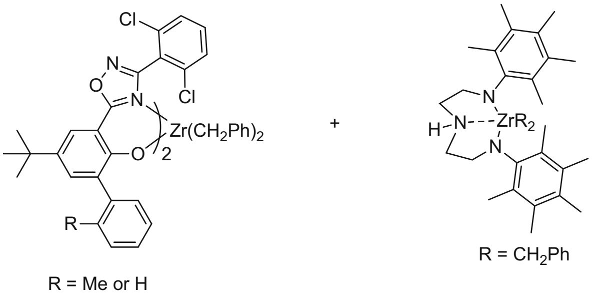
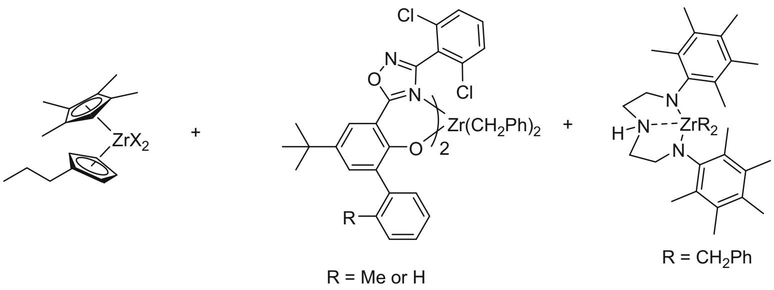


Fig. 1.41 Example of bicomponent hybrid catalyst with poor hydrogen response on the LMW component

HMW with relatively little drop in the productivity [380]. Recent patenting has seen the company disclose multiple loop technology [381], opening another route to multimodal polymers.

Japan Polyethylene have also started to look at combinations of bridged metallocenes to form similar multimodal applications [382–384].

The iron-based Brookhart–Gibson catalyst has been utilized and finally commercialized by Mihan and coworkers at LyondellBasell (Fig. 1.44). In the numerous disclosures there are several combinations, but judging by the scale of the disclosed examples and also the application for patents protecting transitions between catalysts, one would expect that the combination outlined above is the leading combination [385–389]. Similar combinations were also reported by Repsol [390, 391].



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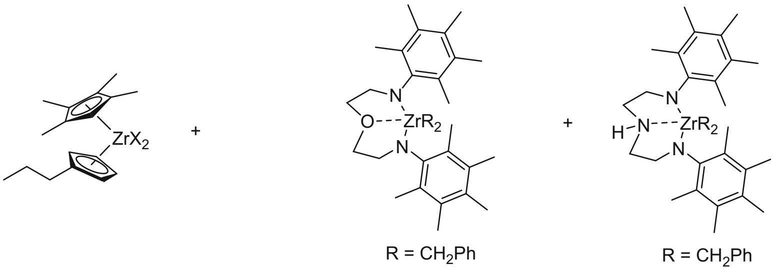

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Fig. 1.42 Examples of tri-component hybrid catalysts

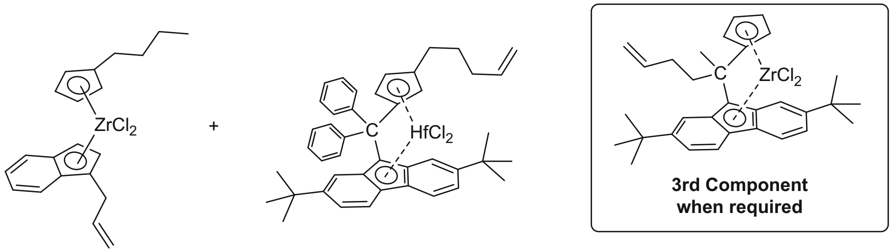
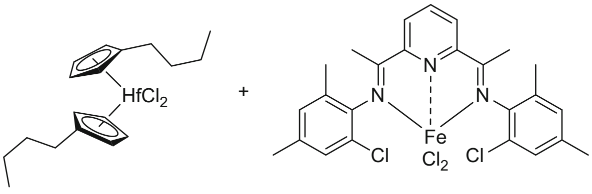


Fig. 1.43 Example of CPChem bi- and tri-component hybrid catalyst

Fig. 1.44 Mixed metallocene and Brookhart/Gibson hybrid catalyst



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1.4 Conclusion

In this chapter the author tries to cover the latest industrial developments in the area of supported catalysts. From the vast number of references one can see that this area is still seeing significant developments. The reader should also be aware that what is missing from this review is the tremendous work being carried out towards multimodal products via solution processes. Taking the above into account, one can see the tremendous opportunities that catalysis continues to bring to the polyolefin industry and why it remains a healthy area for research, at least within an industrial environment.

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