Heterogeneous Single-Site Catalysts for Olefin Polymerization

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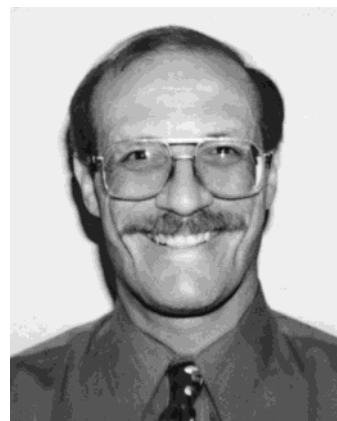
Contents

I. Introduction

Breakthroughs in single-site catalysis have completely transformed our view of alpha-olefin polymerization catalysis. The conventional Ziegler−Natta catalysts used in industrial production of polyolefins

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Gregory Hlatky was born in 1956 near Philadelphia, PA. He received his B.S. degree in 1978 from Rider University, studying chemistry and history, and his Ph.D. degree in 1983 from Yale University, where he worked under Robert Crabtree. After postdoctoral research at the University of Cambridge with Sir Jack Lewis and Brian Johnson, he joined Exxon Chemical Company in 1984 at the Baytown Polymers Center in Baytown, TX. In 1996 he moved to Lyondell Petrochemical Company, now part of Equistar Chemicals, LP. His research interests are in inorganic and organometallic complexes for homogeneous catalysis, intellectual property analysis, and chemical information. Otherwise he helps his wife breed, raise, and show Borzoi (Russian Wolfhounds) under the kennel name Soyara.

are heterogeneous systems, referring not only to the insolubility of the catalyst in the polymerizing medium, but also to its multisited nature. The result is catalysts which are difficult to study and understand that produce complex polymer mixtures with widely varying molecular weights and microstructures.

The first homogeneous polymerization catalyst, $Cp_2TiCl_2−AlEt_2Cl$ ($Cp = \eta^5\text{-}C_5H_5$), was reported within a few years of Ziegler's discovery of low-pressure metal-catalyzed alpha-olefin polymerization.[1] Although they are useful for model studies and kinetics, these titanocene catalysts were of no commercial interest because of their low activity, propensity to decompose to inactive species, and inability to polymerize higher alpha-olefins. The discovery that partially hydrolyzed aluminum alkyls,[2] in particular methylalumoxane (MAO),[3] as cocatalysts vastly increased catalyst activity, especially of zirconocene complexes, revived interest in these systems. Commercial interest was heightened by the disclosure that judicious substitution of the zirconocene framework could influence activity, polymer molecular weight, comonomer incorporation,[4] and stereospecificity in alpha-olefin polymerization.[5] The discovery of fluoroaryl-based activators such as [R$_3$NH]-

$[B(C_6F_5)_4]$,[6] $[Ph_3C][B(C_6F_5)_4]$,[7] and $B(C_6F_5)_3$ [8] led to comprehensively characterizable catalysts with commercially significant activities. The search for new polymerization-stable ancillary ligands has spurred the development of "non-metallocene" single-site catalysts,[9] the polymers from which can have unusual structures, such as the hyperbranched polyethylene homopolymer produced from nickel diimine catalysts.[10]

Regardless of the virtues these new catalysts possess, they would remain mere playthings of the laboratory if they could not be adapted to run in commercial polymerization processes. Single-site catalysts are almost all homogeneous, not only, as their name suggests, having a uniform polymerizing species, but also soluble and active in non-nucleophilic organic solvents such as toluene or aliphatic hydrocarbons.

Commercial polymerization processes using soluble catalysts are mostly those in which the lower-crystallinity polymers produced are soluble in the reaction diluent (e.g., elastomers and very low-density ethylene copolymers) or which operate at temperatures above the melting point of the polymer. In these solution processes, the reaction diluent is volatilized and the polymer recovered for compounding and pelletization.

In slurry, bulk-monomer, or gas-phase processes, the polymer is usually of higher density or crystallinity (e.g., high-density polyethylene, linear-low-density polyethylene, isotactic polypropylene) and is thus insoluble in the reactor diluent or fluidizing gas stream. The continuous operation of these processes suggests the use of morphologically uniform catalyst particles which can be fed into the reactor smoothly without clumping, which in turn implies fixing the solution-soluble catalyst on an insoluble carrier.

A continuous and gradual expansion of the particle, especially in the early stages of polymerization, ensures a uniform expansion and avoids overheating of the particle and melting of the polymer, which could result in the particles adhering to form sheets on the reactor walls and agitator, or large chunks which disturb fluidization or product discharge. Premature fragmentation of the polymer particle forms fines which can be carried into recycle lines.[11] The catalyst should polymerize the monomer to produce a polymer product of high bulk density which mirrors the particle size distribution of the catalyst despite a 25- to 200-fold increase in volume.[12]

A tall order! Yet single-site catalysts have been successfully supported using numerous methods on many different types of carriers and have been used in commercial plants to produce with high catalyst activities polymers with narrow particle size distributions and high bulk densities. This review examines catalyst and cocatalyst families, methods of heterogenization, and process considerations in hetereogeneous single-site catalysts. Although this is the first comprehensive survey of the subject, the reader's attention is drawn to a number of short reviews which have appeared recently.[13]

II. Source Materials

The literature to be reviewed was taken from searches on a number of online databases, including *Chemical Abstracts*, Derwent World Patent Index, European Patents Online, and the full text U.S. Patent database.[14] The author has endeavored to encompass all the literature at least to the end of 1998.

Because of the widespread industrial interest these catalysts have engendered, the majority of the literature to be cited is in the form of patents or published patent applications.[15] When a published patent application has been subsequently issued as a U.S. Patent, the U.S. Patent number will be cited. When an equivalent application appears to a published PCT International Application in Japanese, the English-language version will be cited. Japanese laid-open applications (Kokai) will be addressed to the extent that the abstract gives a clear picture of the unique aspect of the invention. *Chemical Abstracts* accession numbers will be provided for all cited patent literature.

Patents are not journal articles. They are legal documents which contain scientific information. Applicants are obliged to set forth the best means of practicing the claimed invention. They are not obliged to lay out their reasoning; indeed, a sensible applicant will avoid such theorizing. Instead of attempting to reconcile observations conflicting with those in the literature, the patent literature delights in presenting unanticipated and unexpected results, which are rarely explained. The author is aware that some of the disclosures in this review may be contradictory; whenever possible these will be reconciled, but there will be many cases in which, regrettably, there is not enough information provided to do so.

III. Supported Catalysts Activated by Trialkylaluminums

Since its discovery, the attractiveness of the Cp_2-$TiCl_2$–AlR_2Cl catalyst lay in its solubility, unlike the commercial heterogeneous Ziegler–Natta systems. This solubility facilitated kinetics and active site characterization. The inherently low activity of the titanocene catalyst *vis à vis* conventional Ziegler catalysts provided no impetus for adapting it for continuous commercial processes. Some research indicated that the titanocene catalyst was not inhibited by adsorbants. Ethylene is polymerized in the presence of carbon black, the activity roughly mirroring the surface area of the carbon black used.[16] Cp_2TiCl_2 supported on 1,2-polybutadiene affords a heterogeneous metallocene which, when allowed to react with $Al(i\text{-}Bu)_2Cl$, forms a catalyst which polymerizes ethylene at a rate of 240 g/g Ti·h.[17] Chien and Hsieh reacted Cp_2ZrMe_2 and $CpTiMe_3$ on $Mg(OH)Cl$ to form supported complexes which, when activated by $AlEt_2Cl$, polymerized propylene, albeit with quite low activities.[18]

Silica-supported Cp_2TiCl_2–$AlEt_nCl_{3-n}$ catalysts afford quite different polyethylene products depending on the preparation procedure. When the alkylaluminum is contacted with silica prior to reacting with

the titanocene, the polyethylene formed has a higher molecular weight and broader molecular weight distribution ($\bar{M}_w/\bar{M}_n$) than that produced from the homogeneous catalyst. Supporting Cp_2TiCl_2 on silica and reacting with alkylaluminum gives polyethylene with a bimodal distribution, one component of which has a molecular weight similar to that produced from the soluble catalyst. Apparently, desorption of active catalyst from the support in the latter case is the reason for this observation.[19]

Even though they are largely overshadowed by the more widely used MAO and fluorinated borate anion activators, single-site catalysts activated by simple alkylaluminums continue to be studied because of the low cost, stability, and wide availability of the co-catalyst. Much of this research focuses on modifying the activator or support to improve catalyst activity, especially with respect to zirconocene catalysts.

Using $MgCl_2$ as the support for a titanocene dichloride catalyst affords a catalyst which, when activated by $AlEt_2Cl$, has a higher activity than the homogeneous system, as well as a longer lifetime: the homogeneous catalyst ceases polymerization after 10 min, whereas the supported system remains active after an hour.[20] Supporting a $Cp_2TiCl_2-AlEtCl_2$ catalyst on silica treated with butyl ethylmagnesium gives a system with high activity (102 kg/g Ti) and bulk density (0.32 g/cm^3),[21] whereas the same catalyst on $Mg(OEt)_2$ has inferior performance (6.9 kg/g Ti and 0.23 g/cm^3).[22]

In some cases a greater range of alkylaluminums can be used. $Al(i\text{-}Bu)_3$ is not a useful cocatalyst for Cp_2TiCl_2 but functions more effectively when the titanocene is supported on $MgCl_2$, with a catalyst activity of 142 kg/g Ti and polymer bulk density of 0.37 g/cm^3.[23] Although $AlMe_3$ fails to activate silica-supported Cp_2ZrCl_2, a combination of $AlMe_3$, Bu_2Mg, and CCl_4 at an aluminum-metal ratio of 500–1000 gives an active catalyst.[24]

Soga and co-workers have studied extensively supported zirconocenes activated by simple alkyl-aluminum compounds. In solution, alkylaluminums are ineffective activators for zirconocenes, but when supported on alumina or $MgCl_2$ activity improves dramatically in propylene polymerizations, though it is still less than the homogeneous MAO-activated variant (Table 1).[25] Trialkylaluminums work well, but chlorine-containing compounds such as $AlEt_2Cl$ and $AlEtCl_2$ suppress activity completely. Silica, the most commonly used support for heterogenized single-site catalysts, is a poor choice as a carrier when trialkyl-aluminums are to be used as cocatalysts; only by pretreating the silica with a small amount of MAO does activity improve. In ethylene copolymerizations with propene or 1-hexene, mixtures of homopoly-ethylene and copolymer were formed from the Et-$(H_4-Ind)_2ZrCl_2-MgCl_2-Al(i\text{-}Bu)_3$ (Et$(H_4-Ind)_2$ = 1,2-ethylenebis(tetrahydroindenyl), but copolymer was the only product when $AlMe_3$ was the cocatalyst. The composition of the polymers resembled that from homogeneous systems, but molecular weights were higher.[26]

In olefin polymerization, $CpTiCl_3$ with MAO is a relatively poor catalyst and with $Al(i\text{-}Bu)_3$ virtually

Table 1. Propylene Polymerization with Supported Zirconocene Catalysts Activated by Simple Alkylaluminums
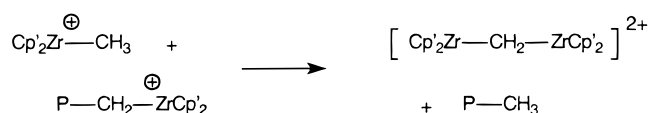
metallocene	support	cocatalyst	activity (kg of PP/mol Zr)	ref
Cp_2ZrCl_2	Al_2O_3	$AlMe_3$	47	25b
Cp_2ZrCl_2	$MgCl_2$	$AlMe_3$	172	25b
Cp_2ZrCl_2	none	MAO	132	25b
$Et(H_4-Ind)_2ZrCl_2$	Al_2O_3	$AlMe_3$	259	25a
$Et(H_4-Ind)_2ZrCl_2$	none	$AlMe_3$	negligible	25a
$Et(H_4-Ind)_2ZrCl_2$	none	MAO	2,070	25a
$Et(H_4-Ind)_2ZrCl_2$	Al_2O_3	$AlEt_3$	158	25a
$Et(H_4-Ind)_2ZrCl_2$	Al_2O_3	$AlMe_2Cl$	negligible	25a
$Et(H_4-Ind)_2ZrCl_2$	Al_2O_3	$AlMeCl_2$	negligible	25a
$Et(H_4-Ind)_2ZrCl_2$	$MgCl_2$	$AlMe_3$	139	25a
$Et(H_4-Ind)_2ZrCl_2$	$MgCl_2$	$Al(i\text{-}Bu)_3$	138	25a
$Et(H_4-Ind)_2ZrCl_2$	MgF_2	$AlMe_3$	264	25a
$Et(H_4-Ind)_2ZrCl_2$	CaF_2	$AlMe_3$	167	25a
$Et(H_4-Ind)_2ZrCl_2$	AlF_3	$AlMe_3$	13	25a
$Et(H_4-Ind)_2ZrCl_2$	silica	$AlMe_3$	negligible	25a
$Et(H_4-Ind)_2ZrCl_2$	MgO	$AlMe_3$	negligible	25a
$i\text{-}Pr(Cp)(Flu)ZrCl_2$	Al_2O_3	$AlMe_3$	52	25b
$i\text{-}Pr(Cp)(Flu)ZrCl_2$	$MgCl_2$	$AlMe_3$	51	25b
$i\text{-}Pr(Cp)(Flu)ZrCl_2$	MgF_2	$AlMe_3$	61	25a
$i\text{-}Pr(Cp)(Flu)ZrCl_2$	SiO_2	$AlMe_3$	negligible	25a
$i\text{-}Pr(Cp)(Flu)ZrCl_2$	MgO	$AlMe_3$	negligible	25a
$i\text{-}Pr(Cp)(Flu)ZrCl_2$	none	MAO	758	25a

inactive, but it functions far better when supported on silica, alumina, or $MgCl_2$.[27] The catalyst activity increases in propylene polymerization when higher alkylaluminums such as $Al(n\text{-}C_{10}H_{21})_3$ are used as cocatalysts.[27a] The polypropylene produced is atactic, but isotactic polymer is formed when an external donor such as ethylbenzoate is added.[28] A similar pattern is observed when bis(diketonato) metal dihalides are supported on $MgCl_2$.[29] The titanium-based catalysts are far more active than the zirconium analogues: $(acac)_2TiCl_2-MgCl_2-Al(i\text{-}Bu)_3$ (acac = acetylacetone) has an activity of 310 kg/mol M·h vs 1.1 kg/mol M·h for $(acac)_2ZrCl_2-MgCl_2-Al(i\text{-}Bu)_3$. Adding ethylbezoate or silane donors improves the percentage of hepane insolubles from 25% to as high as 94%, but at the cost of most of the catalyst activity.

IV. Supported Catalysts Activated by Alumoxanes

Single-site catalysts activated by alumoxane, in particular MAO, and supported on inorganic oxides form the vast majority of heterogeneous single-site catalysts for olefin polymerization. Silica predominates among support materials. Silicas with a wide range of particle sizes, surface areas, and pore volumes have been used. Most commonly, these have had a particle size of about 50–100 μm, but single-site catalysts were supported on silica with an average particle size as low as 0.012 μm; improvements in film properties were claimed.[30] Numerous techniques have been disclosed for supporting and finishing the catalyst in order to optimize catalyst activity, particle morphology, and particle bulk density without seriously affecting polymer properties.

As a lagniappe, the ratio of alumoxane to metal can be reduced considerably. It has been suggested that large excesses of MAO (aluminum-to-metal ratios of 1000–10 000) are needed in homogeneous polymerizations with metallocene catalysts in order to prevent bimolecular deactivation processes (Scheme 1).

Scheme 1

$$\text{Cp}'_2\text{Zr}\overset{\oplus}{-}\text{CH}_3 \quad + \qquad \qquad \left[\text{Cp}'_2\text{Zr}-\text{CH}_2-\text{ZrCp}'_2\right]^{2+}$$

$$\overset{\oplus}{\text{P}-\text{CH}_2-\text{ZrCp}'_2} \qquad\qquad\qquad + \quad \text{P}-\text{CH}_3$$

Immobilizing the polymerizing centers on a carrier itself suppresses any interaction of polymerizing sites. Accordingly, the ratio of aluminum to metal component can be reduced to a far lower and more economical level of 50–300.[31]

Examination of the literature suggests there are three basic methods of supporting alumoxane-activated single-site catalysts: (1) supporting the alumoxane, then reacting with the metal complex; (2) supporting the metallocene, then reacting with the metal complex; and (3) contacting the alumoxane and metal complex in solution before supporting.

A. Supported Alumoxanes

Supporting the alumoxane first, followed by reaction with the metal complex, was among the earliest methods used for preparing heterogeneous single-site catalysts. Welborn[32] and Takahashi[33] reacted silica with a toluene solution of MAO and decanted the solution to isolate the MAO-containing solids. These were reacted with $\text{Cp}'_2\text{ZrX}_2$ (Cp = substituted or unsubstituted cyclopentadienyl; X = Cl, Me) to form the finished catalyst, which was used in stirred-bed gas-phase ethylene polymerizations and copolymerizations. Dilute solutions of MAO (<5 wt % Al) gave inferior catalyst performance. Precipitating the MAO onto the silica by adding n-decane to the silica–MAO slurry in toluene is reported to narrow particle size distribution as well as improve activity.[34]

The metallocene is added to the supported MAO as a solution in toluene or aliphatic hydrocarbon. Subsequently subjecting the mixture to microwaves has been claimed to fix the metal component on the support and reduce reactor fouling (adhesion of polymer to reactor surfaces).[35] The metallocene can also be dry-blended with the support, avoiding solubilization of the finished catalyst.[36]

A number of mono(cyclopentadienyl) complexes of the group 4 metals were supported by reaction with MAO on silica. The "constrained-geometry" trivalent titanium complexes $\text{Et}(\text{Cp}')(\text{NMe}_2)\text{TiCl}_2$ were combined with MAO supported on silica to form catalysts used in slurry or gas-phase ethylene copolymerizations.[37] Cosupporting the mono(cyclopentadienyl) titanium amine complexes with bis(cyclopentadienyl) zirconium complexes on MAO–silica gave polymers with broad molecular weight distributions. CpZrCl_3 was contacted with MAO on silica to prepare a catalyst for gas-phase ethylene polymerization.[38] The inventors obtained the best results when an Al/Zr ratio of 200 was used, and no further scavenger needed to be added to the polymerization environment.

Among the techniques used for fixing the alumoxane to the support surface are heating the MAO solution to 50–85 °C prior to supporting; this is claimed to remove gels deemed deleterious to catalyst performance.[39] Heating the toluene slurry of MAO and silica at superatmospheric pressures (closed vessel) evenly distributes the aluminum through the silica particles.[40] Heating the dry MAO–silica material fixes the alumoxane to the surface more thoroughly; whereas toluene washes a third to a half of the supported aluminum from a support heated to 125 °C, scarcely any is lost when the support is heated to 200 °C.[41] A catalyst formed when these supports are reacted with $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(N\text{-}t\text{-Bu})\text{TiMe}_2$ exhibits higher activities and superior bulk densities with the latter formulation.

An alternative method of generating alumoxanes in situ hydrolyzes alkylaluminums with water in the presence of the support, either in a hydrocarbon suspension,[42] in a spray dryer,[43] or with the reactive components in the gas phase.[44] A toluene solution of the metallocene is added to the mobile powder to form the finished catalyst. The elemental distribution of aluminum on a silica-supported MAO from the gas-phase process shows that all of the MAO is located on the particle surface with no aluminum present in the pores of the particle. The supported MAO was reacted with $(n\text{-BuCp})_2\text{ZrCl}_2$ and polymer growth in ethylene polymerization was examined by electron microscopy. No particle fragmentation occurred and polymer formed irregularly on the surface.[45] Alumoxanes are also generated when solutions of trialkylaluminums are reacted with boric acid supported on silica. Reaction with metallocene dichlorides generates a catalyst, which can be generated and used in situ or isolated as a solid.[46]

The supported MAO may be chemically modified when supported. MAO supported on silica or alumina was taken up in tetrahydrofuran (THF) and reacted with a cross-linking agent such as bisphenol A (4,4′-isopropylidenediphenol).[47] A one-step method reacts the MAO and modifier simultaneously in the support step.[48] The modified MAO support, reacted with Et-$(\text{Ind})_2\text{ZrCl}_2$, polymerizes propylene to spherical polymer particles while the unmodified support forms coarse agglomerates. Pentafluorophenol has also been used to modify the supported alumoxane, probably converting it to $(-\text{Al(O)}(\text{OC}_6\text{F}_5)-)_n$.[49]

B. Supported Metal Complexes

Supporting the metal complex on the carrier first, then reacting with alumoxane, is more common for complexes chemically tethered to the carrier (Section VII) and rarer for $\text{Cp}_n\text{MX}_{3-n}$ complexes. As inorganic oxides, especially silica, have been overwhelmingly used as supports for single-site catalysts, residual hydroxyl groups on the surface can react with the metal complex, sometimes in a deleterious manner (Section IV-D). Blitz and co-workers studied the adsorption of Cp_2MCl_2 complexes on bare silica, silica heated to 600 °C-heated silica, and silica treated with the dehydroxylating agent hexamethyldisilazine (HMDS).[50] The order of reactivity is $\text{Cp}_2\text{HfCl}_2 > \text{Cp}_2\text{ZrCl}_2 > \text{Cp}_2\text{TiCl}_2$. Metallocenes react with silica surfaces to form $\equiv\text{Si}-\text{O}-\text{MClCp}'_2$ groups, which are converted to catalytic species on reaction with MAO (Scheme 2).

While examining the dependence of calcination temperature on metallocene loading, dos Santos and

Scheme 2
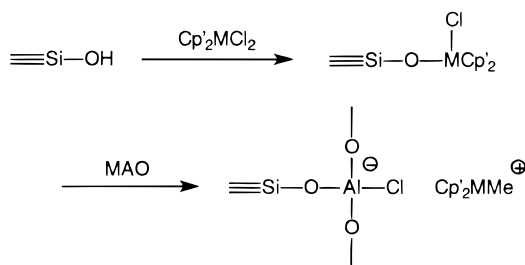
co-workers noted that while silica treated under vacuum at room-temperature adsorbed the most (n-BuCp)$_2$ZrCl$_2$, the catalyst activity was quite low.[51] They attributed this to the formation of the unreactive chloride-free zirconium species **1**. Supports with
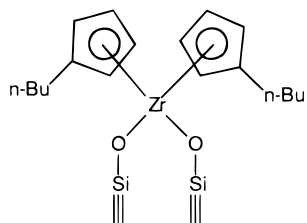
1

higher surface area adsorb more metallocene.[52] A study on the effect of calcination temperature, grafting times and temperatures, and solvent effects on grafting (n-BuCp)$_2$ZrCl$_2$ on Grace 948 silica shows a great deal of scatter through the data, but the authors suggest that intermediate grafting times on silica dried at 450 °C with nonpolar solvents gave the best activity in ethylene polymerization and narrowest molecular weight distribution.[53] At equal surface areas and zirconium loadings, an Et(Ind)$_2$ZrCl$_2$ catalyst (Et(Ind)$_2$ = 1,2-ethylenebis(indenyl)) on nonporous Aerosil is twice as active as than the same metallocene on porous Crossfield silica.[54] This was attributed to easier access to cocatalyst and monomer in the nonporous carrier.

Kaminsky reacted Et(Ind)$_2$ZrCl$_2$ with silica (heated at 100 °C in vacuo) and exhaustively extracted the toluene with toluene before contacting the support with 35−200 equivalents of MAO. Polymerization of propylene at 50 °C with this catalyst afforded isotactic polypropylene with melting points of 157−161 °C and molecular weights of 500,000−800,000 Da far higher than the 122 °C melting point and molecular weight of 20,000 Da observed with the homogeneous catalyst. Adsorbing the MAO on silica first, then reacting with metallocene afforded a catalyst which produced i-PP resembling that from the homogeneous catalyst.[55] This difference was attributed to a closer interaction of the cationic center with the silica when the metallocene is supported first, and a more "homogeneous" behavior when the MAO was supported first.

A later study by Sacchi and co-workers using essentially the same method and polymerization conditions employed by Kaminsky found the i-PP produced from the supported and homogeneous catalysts to be quite similar.[56] Although the unbridged

metallocene (Ind)$_2$ZrCl$_2$ produces atactic PP in solution, when supported on silica and subsequently reacted with MAO, it afforded a moderately isotactic polymer with broad molecular weight distribution (12.6); the authors attributed this to the decomposition of the metallocene framework and conversion of the metal complex to a stereospecific form.

CpTiCl$_3$ supported on silica calcined at 800 °C was contacted with MAO and used to copolymerize ethylene and propylene. The characteristics of the copolymer (composition, comonomer reactivity ratios, differential scanning calorimetry profiles) closely resemble those of a copolymer formed from a commercially used VOCl$_3$−Al$_2$Et$_3$Cl$_3$ catalyst.[57] In the polymerization of styrene, however, the same catalyst does not produce exclusively the syndiotactic polymer of the homogeneous catalyst.[58] The fraction of 2-butanone soluble material increases with increasing concentration of the titanium component on the support. Two titanium species were detected in the electron spin resonance (ESR) spectrum, one of which corresponded to a soluble Ti(III) catalyst. Indeed, a strong ESR signal is observed in the soluble component after the supported CpTiCl$_3$ is allowed to react with MAO in toluene.

Using the silsequioxane complex (c-C$_5$H$_9$)$_7$Si$_8$O$_{12}$-OH, a model system for (1,3-SiMe$_3$−C$_5$H$_3$)TiCl$_3$ (**2**)

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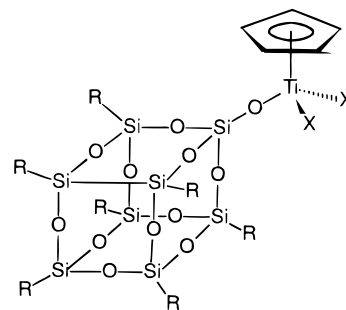
supported on silica was synthesized and tested in ethylene polymerization.[59] With MAO (X = Cl) or B(C$_6$F$_5$)$_3$ (X = CH$_2$Ph), active catalysts of the type [(c-C$_5$H$_9$)$_7$Si$_8$O$_{12}$O)Cp′TiR]$^+$ are formed. However, an active catalyst is also formed from MAO (1,3-(SiMe$_3$)-C$_5$H$_3$)TiCl((c−C$_5$H$_9$)$_7$Si$_8$O$_{12}$O)$_2$, suggesting that the Si−O−Ti unit in CpTiCl$_3$ on silica may not be polymerization stable with respect to MAO; there is no reaction with B(C$_6$F$_5$)$_3$.

To remove reactive surface hydroxyl groups, the support may first be treated with compounds such as simple alkylaluminums. Silica treated with alkylaluminums serves to fix metallocene complexes bearing polar substituents such as Et(2-(t-BuMe$_2$-SiO)Ind)$_2$ZrCl$_2$[60] and bis(2-tetrahydrofuranylmethyl-Cp)$_2$ZrCl$_2$.[61] Reacting the metallocene with a trialkylaluminum before supporting is reported to lead to catalysts of higher activity than when metallocene dichlorides are supported alone.[62] The metallocene is usually added to the silica as a solution in toluene, but a solvent-free vapor deposition method has also been disclosed to support mono- and bis(cyclopentadienyl) complexes on calcined silica or alumina.[63] The

amount of metallocene supported is dependent on the calcination temperature of the support: 6.5 wt % zirconium is deposited on silica calcined at 300 °C, whereas only 1.1% is found on silica calcined at 900 °C.

One means of preparing a heterogeneous "metallocene" catalyst is to assemble the components on the support. A silica–$MgCl_2$ supported "titanocene" catalyst is formed when Cp_2Mg is contacted with silica, reacted with $TiCl_4$, and treated with gaseous HCl. Activation is by MAO or alkylaluminums.[64] Comparison of the gel permeation chromatograph (GPC) traces of a conventional Ziegler–Natta catalyst and a catalyst modified by Cp_2Mg shows a narrower molecular weight distribution for the latter catalyst. MCl_4 (M = Ti, Zr) supported on silica or alumina and reacted with Cp′-$SiMe_3$ (Cp′ = Cp, Ind, $^1/_2$ Et(Ind)$_2$) forms a heterogeneous "metallocene" catalyst which can be activated by MAO, alkylaluminums, or borate salts to polymerize ethylene.[65] No GPC data were reported, however, and it is difficult to say whether this functions as a single-site catalyst or as a modified Ziegler–Natta system, but in a similar process using Cp′Li (Cp′ = Cp, Ind) on $ZrCl_4$ on silica, the molecular weight distributions were quite narrow (M_w/M_n = 2.5–3), suggesting single-site behavior.[66] When $TiCl_4$ was used, much broader distributions (4.8) were observed, though still less than unmodified $TiCl_4$ on silica (7.8).[67] Similarly, adding Cp′–$SiMe_3$ [68] or Cp′–Li[69] reagents to conventional commercial Ziegler–Natta catalysts gave polymers with distributions no narrower than the unmodified catalyst. Supported titanium halides, it seems, are more prone to the formation of secondary active species.

C. Supporting Metal Complex–MAO Solutions

The third most common method of supporting single-site catalysts is to combine the metal component and alumoxane in a solvent, then add the solution to the support material. There are several advantages to this method. The process maximizes the number of active centers by activating the metal component in solution, instead of carrying out the process with one or the other component in an immobilized state. Highly active catalysts can be produced even at low Al/Zr ratios. Techniques have also been developed to reduce the amount of solvent used, thereby speeding the catalyst preparation process and avoiding large amounts of solvent byproducts.

In this method, the metal component and MAO are combined in a solvent, usually toluene. Metallocenes of low solubility dissolve in MAO solutions and impurities can be removed by filtration.[70] Allowing a toluene solution of Me_2Si(2-Me-4-PhInd)$_2ZrCl_2$–MAO to stand for 18 h before adding to the silica support is claimed to improve the activity in propylene polymerizations (193 kg of PP/g of metallocene·h) over catalysts in which the solution was added to the carrier immediately (103 kg of PP/g metallocene·h).[71]

The solution is then added to the support; a method of vacuum impregnation has been described wherein the catalyst solution is added to the support held

under low pressure in order to improve penetration into the pores of the support.[72] In the final step, the slurry is dried in a vacuum, by a nitrogen purge or by spray drying,[73] to form the finished product as a free-flowing solid. It has been suggested that the presence of gels in MAO is a cause of poor particle morphology in catalysts supported by this method. The use of filtered MAO solutions dramatically improves the particle size distribution of the final polymer product.[74]

A very useful refinement of this supporting technique is the "incipient wetness" method, in which the pore volume of the support is measured and a volume of catalyst solution is added which only just fills the pores of the support.[75] The volume of the catalyst solution can exceed the pore volume of the support as long as the ratio of aluminum to metal is low (<300) and the catalyst–support mixture does not form a slurry, but remains dry or has the consistency of a paste.[76]

There are two perceived advantages to this method: the catalyst occupies the pores of the support and less of the surface—leading to improved particle morphology—and a greatly reduced volume of liquid solvent need be used, thus decreasing preparation time and lowering effluents and disposal costs. Equipment has been described which is suitable for preparing 25–50 kg of supported catalyst by incipient impregnation.[77]

D. Influence of Hydroxyl Groups

Silica, the most commonly used support for heterogeneous single-site catalysts, contains Si–OH groups of varying structures and concentrations depending on the dehydration temperature. These Si–OH groups may be geminal (undehydrated silica), hydrogen bonded (dehydrated at temperatures up to 600 °C), or isolated (dehydrated above 600 °C) (**3A**–**3C**). As described above, these can react with metal

3A   **3B**   **3C**
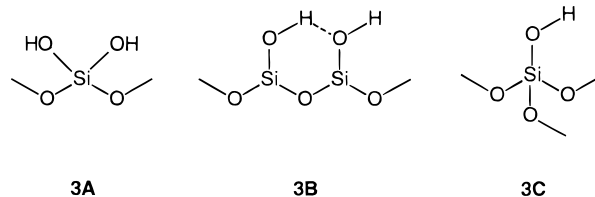
dichloride complexes to form Si–O–M functionalities which can be converted to active catalysts when a cocatalyst is added. In some cases, though, these hydroxyl groups can have a deleterious effect on the catalyst. For example, Et(Ind)$_2ZrCl_2$ contacted with hydroxylated silica or alumina then reacted with MAO has no activity in propylene polymerization, an effect which is attributed to decomposition of the catalyst (Scheme 3).[78] The diastereomeric zirconocene (1′S, 2′R, 5′S-menthoxy)$_2$Si((R, R)−(+)−Ind)$_2ZrCl_2$ supported on silica and activated by MAO had poor activity in ethylene polymerization and was inactive in propylene polymerization.[79] Rather more dramatically, Me_2Si(Cp)(Flu)$ZrCl_2$ (Flu = η^5-$C_{13}H_8$), which as a homogeneous catalyst produces syndiotactic polypropylene, forms *isotactic* polypropylene (T_m = 158 °C,

Scheme 3
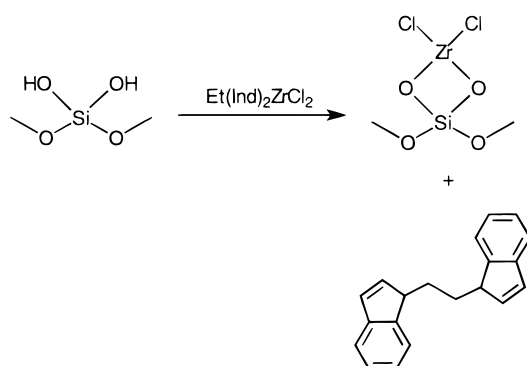
mmmm = 90%) when supported on silica and activated with MAO.[80]

These surface hydroxyl groups can be removed by treatment with a variety of agents. An IR spectroscopic study of the action of $AlMe_3$ and $AlMe_3$-rich and -lean MAO on 400 °C dried silica showed that the silanol groups reacted preferentially with $AlMe_3$ and less rapidly with the alumoxane oligomer.[81] The aforementioned $Et(Ind)_2ZrCl_2$–SiO_2 (Al_2O_3)–MAO combination[78] polymerizes propylene with much improved activity when partially dehydroxylated silica or alumina is first treated with $AlMe_3$; $AlMe_2Cl$ has also been used as the passivating agent.[82] The activity of a $Me_2Si(2$-Me-4-$PhInd)_2ZrCl_2$–MAO catalyst increases from 67 to 242 kg/g of metallocene·h and the melting point increases from 156 to 160 °C when the silica is treated with $AlMe_3$ before supporting the catalyst.[83]

Similar beneficial effects of $AlMe_3$ treatment were observed for (i-$PrCp)_2ZrCl_2$–MAO[84] and $MePhSi(C_5$-$Me_4)(N$-t-$Bu)TiCl_2$–MAO[85] catalysts. Failure to treat silica with $AlMe_2Cl$ before supporting a Cp_2ZrCl_2–MAO catalyst results in product with a much lower bulk density (0.15 vs 0.36 g/cm³).[86] Other surface passivating agents used include $Me_2(n$-$octyl)SiCl$[87] and (c-$C_6H_{11})_2Si(OMe)_2$.[88] The reaction of hexamethyldisilazine with was found to cap the isolated Si–OH groups (**5**) leaving the hydrogen bonded silanols unreacted; virtually all silanols are eliminated from silica dried at 600 °C and treated with HMDS.[50]

Surprisingly, other disclosures indicate that the presence of surface hydroxyl groups is beneficial, possibly by fixing an increased amount of aluminum to the carrier. Such apparently contradictory results may depend on the type of metal complex used or the procedure employed for supporting the catalyst. An (n-$BuCp)_2ZrCl_2$–MAO catalyst supported on silica free of adsorbed water (<0.1 wt %) but with surface hydroxyl groups (2.7 wt %) copolymerizes ethylene and 1-butene to a morphologically uniform product with fewer fines (0.8 wt %) than a similar catalyst supported on silica dried at a higher temperature.[89] MAO was allowed to react with silica containing 1–5 wt % water; metallocenes were then contacted with these supported activators. Ethylene–butene copolymers from these catalysts showed higher melt tension than those from catalysts on more rigorously dehydrated supports.[90]

Table 2. Polymerization Performance of Metallocene Catalysts Based on Support Dehydration Temperature

metallocene	dehydration temp (°C)	productivity (g/g of cat·h·100 psi $C_2^=$)	melt index
(n-$BuCp)_2ZrCl_2$	20	2300	18.7
(n-$BuCp)_2ZrCl_2$	110	2700	1.16
(n-$BuCp)_2ZrCl_2$	300	2500	1.19
(n-$BuCp)_2ZrCl_2$	600	1300	0.72
$Cp^*_2ZrCl_2$	200	300	1.8
$Cp^*_2ZrCl_2$	600	150	2.0
$(Ind)_2ZrCl_2$	200	1700	6.5
$(Ind)_2ZrCl_2$	600	1500	5.5
$(MeCp)_2ZrCl_2$	200	600	0.4
$(MeCp)_2ZrCl_2$	600	500	0.8

Table 3. Ethylene Polymerization by $Et(Ind)_2ZrCl_2$–MAO on Various Supports

support	activity (kg/mmol Zr·h)	molecular weight ($M_w \times 10^{-3}$)	molecular weight distribution (M_w/M_n)
none	400.0	111	2.4
Davisil-645	8.9	197	2.9
PQ silica	5.1	150	3.0
Dispal 18N4	5.6	132	2.4
Ketjen G	5.4	150	2.3
sol–gel alumina	114.0	97	2.3

At Al/Zr = 200, a variety of metallocene–MAO catalysts were supported on silicas dried at various temperatures (Table 2).[91] Supports dried at lower temperatures afforded catalysts of higher activities; pretreating the support with $AlMe_3$ also diminished activity.[92] Analysis of the distribution of aluminum and silicon indicates a very even distribution of cocatalyst on the support, with no more catalyst on the outer surface than within the pores.[93]

High surface area sol–gel aluminas with large concentrations of hydroxyl groups (0.5 mmol/mmol support) were prepared by calcining a bohemite precursor, heating to 600 °C, and passing water-laden helium over the solid at 300 °C. Allowed to react with MAO, these supports can carry more aluminum than conventional silica supports.[94] Heterogeneous metallocene catalysts based on these supports have much higher activity than the silica supports examined (Table 3), but the morphology of the product appears to be poor.

Surface functionalities can be modified in order to influence catalyst performance. Silica modified by Me_2SiCl_2, reacted with MAO, then with Cp_2ZrCl_2 has a higher catalyst activity than the same catalyst on unmodified silica.[95] Silica can also be modified by $(MeO)_3Si(CH_2)_3X$ agents (X = SH, OMe) before supporting *ansa* metallocenes for propylene polymerization.[96] When X = Cl, the catalyst performace suffers considerably.

E. Prepolymerization of Supported Catalysts

The vigorous activity of the catalyst in the early stages of polymerization can cause uncontrolled fracturing of the catalyst particle. The particle size distribution of the polymer formed suffers accordingly. Very small particles (fines) do not fall back into the fluidizing bed and are all too easily caught in recycle lines. Large chunks can be formed from

polymer particles melting and fusing together. These are too heavy to be fluidized and fall to the distributor plate. Further adhesion of polymer to the walls of the reactor interferes with heat transfer, and the bulk density of the product is reduced as well. Microstructurally, the temperature spike in the initial phase of polymer growth could lead to broadening of molecular weight and composition distributions or lowering of the polymer melting point in propylene polymerizations. With the long residence times used in most continuous-slurry, bulk-monomer, or gas-phase processes, a rapid decrease in catalyst productivity is an undesirable consequence of reaching the diffusion limit too quickly.

To moderate the initial burst of activity in a supported catalyst, the catalyst is prepolymerized by adding monomer at ambient or subambient temperatures and low pressures. This coats the catalyst particle with 1−50 g of polymer per gram of catalyst. The diffusion barrier to monomer reacting with the catalyst can lead to smoother polymerization profiles and improved particle morphology. Ethylene−propylene copolymers prepared in bulk propylene slurry from a silica-supported $Me_2Si(Ind)_2ZrCl_2$−MAO catalyst form individual spherical particles without reactor fouling, even at relatively high propylene compositions (ca. 50%),[97] and a silica-supported $Me_2Si(2$-MeInd$)_2ZrCl_2$−MAO catalyst similarly prepolymerized with ethylene has high activity to produce polymer in a bulk propylene slurry process with high bulk density (0.36 g/cm³).[98]

Investigators at Mitsui have synthesized prepolymerized catalysts by isolating dry metallocene−MAO on silica, slurrying in n-decane, and prepolymerizing with ethylene in the presence of Al(i-Bu)$_3$,[99] Al(i-Bu)$_2$H,[100] or Al(i-Bu)$_2$(OMe).[101] They found that leaving out the aluminum reagent in the prepolymerization step led to a polymer of lower molecular weight when the catalyst was used in the polymerization and copolymerization of ethylene. Failing to remove all the toluene from the catalyst before prepolymerization in a slurry process can cause the catalyst to agglomerate in the prepolymerization step,[102] although the prepolymerization can be carried out in a vapor phase process, which moistens the catalyst with a volume of an aliphatic solvent approximately equal to the pore volume of the supported catalyst.[103] Insufficient drying of the prepolymerized catalyst (>2 wt % volatiles) can also lead to poor flowability of the solids and problems feeding the catalyst into a gas-phase polymerization process.[104]

Although prepolymerization using supported Cp_2-$ZrCl_2$−MAO proceeds without incident, prepolymerizing supported catalysts of metallocenes affording polymer of higher molecular weight (e.g. (1,3-Me-BuCp)$_2ZrCl_2$, rac-$Me_2Si(2$-Me-4,5-BenzoInd)$_2ZrCl_2$) can result in severe fouling. Addition of hydrogen to reduce the molecular weight of the prepolymer avoids this problem.[105]

As an alternative to prepolymerizing with a gaseous monomer such as ethylene, Brant added hydrocarbon-soluble poly(4-methyl)styrene or low molecular weight waxes to the supported catalyst to fill the pores of the support.[106] Using a pore-filling technique to add $(n$-BuCp)$_2ZrCl_2$ in 1-hexene, 1-octene, or styrene to MAO on silica at low temperatures, then warming to ambient temperatures fills the pores of a silica support with polymer.[107] Melting paraffin wax with a $Me_2Si(2$-Me-4,5-BenzoInd)$ZrCl_2$−MAO catalyst on silica and pouring the mixture into pentane produces a solid which not only polymerizes propylene with high activity, but also is essentially air-stable.[108]

V. Alumoxane-Free Supported Single-Site Catalysts

Supporting single-site catalysts activated by non-aluminum agents—principally borate anions such as $[B(C_6F_5)_4]^-$ or $B(C_6F_5)_3$—is far more problematic than supporting those activated by alumoxane-based analogues. These systems are highly prone to deactivation by adventitious impurities. Even silica treated at 800 °C has sufficient surface hydroxyl groups to render a $[Cp_2ZrMe][B(C_6F_5)_4]$ catalyst inactive (Scheme 4).

Scheme 4

$$\equiv Si-OH \ + \ Cp'_2MR^+ \ \longrightarrow \ \equiv Si-O-M^+Cp'_2 \ + \ RH$$
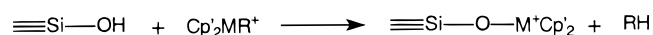
Treatment of the support material with alkylaluminums passivates the support surface to make it compatible with $Cp'_2MMe_2-[Ct][B(C_6F_5)_4]$.[109] The alkylaluminum-treated support itself is not an effective cocatalyst. The supported catalysts can be used in slurry, bulk-monomer, or gas-phase processes.[110] Similarly pretreated alumina, $MgCl_2$, and cross-linked polystyrene are also suitable support materials for these ionic catalysts. Partially or fully hydroxylated supports can also be capped by deprotonating the Si−OH groups with butyllithium or butylethylmagnesium followed by reaction with BrC_6F_5;[111] or by reacting silica with NH_4F[112] or chlorodimethyloctylsilane.[113] Surprisingly, nonfluorinated borate activators, ordinarily not compatible in solution with most metallocenes, can be used when the catalyst is supported. Cp_2ZrMe_2 and $[n$-Bu$_3NH][B(p$-tolyl)$_4]$ decompose to inactive materials in solution, but when supported on silica the combination forms an active catalyst, though no productivity data were provided.[114]

"Constrained-geometry" titanium dialkyls such as $Me_2Si(C_5Me_4)(N$-t-Bu)TiMe$_2$ form active catalysts when reacted with alkylaluminum-treated silica containing $[HNMe_2Ph][B(C_6F_5)_4]$[115] or $B(C_6F_5)_3$.[116] Separate addition of alkylaluminum-treated silica without metallocene to the supported ionic catalyst has been claimed to improve catalyst activity, probably by scavenging of reactor impurities.[117] Diene complexes such as $Me_2Si(C_5Me_4)(N$-t-Bu)Ti(η^4-C_5H_8), converted to zwitterionic complexes when contacted with $B(C_6F_5)_3$ (Scheme 5), may also be adsorbed on pretreated silica to form an active supported catalyst.[118] The use of functionalized dienes such as 1-phenyl-4-(4-N,N-dimethylaminophenyl)-1,3-butadiene was reported to give a modest improvement in catalyst activity; the inventors imply that the amino group affords improved adsorption of the metal complex to the support.[119]

Scheme 5

Me_2Si ... Ti ... N ... t-Bu $\xrightarrow{B(C_6F_5)_3}$ Me_2Si ... Ti$^\oplus$ ... N ... t-Bu ... $\ominus B(C_6F_5)_3$
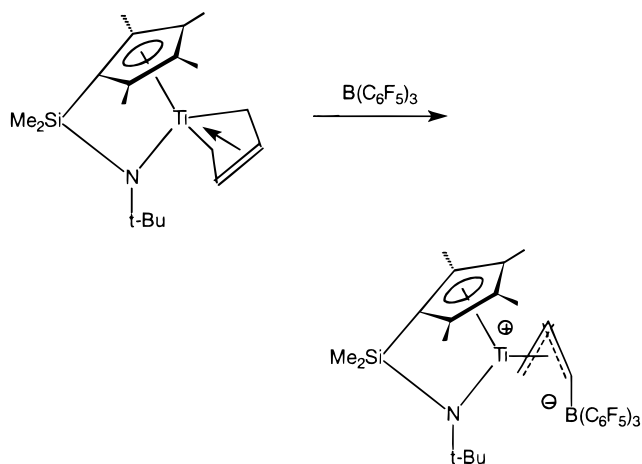
The $Me_2Si(C_5Me_4)(N\text{-}t\text{-Bu})TiMe_2\text{-}B(C_6F_5)_3$ catalyst supported on polyethylene or silica was used in the fluidized-bed gas-phase polymerization of ethylene and interpolymerization of ethylene and 1-olefins and/or dienes; the densities of the copolymers can be as low as 0.898 g/cm^3.[120] Prepolymerization at low temperatures (<40 °C) was shown to improve catalyst activity significantly.[121] A catalyst comprising the dimethyl or diene complex activated by $[Ct][B(C_6F_5)_4]$ ($Ct^+ = Ph_3C^+$, $HNMe_2Ph^+$) or $B(C_6F_5)_3$ and supported on silica with a particle size less than 15 μm can be dispersed in a hydrocarbon solvent. Settling is slow enough that the slurry can be pumped into a solution process.[122]

Because metal alkyl complexes can be unstable and in order to remove one step from the synthetic process, an alternative method of generating cationic metal alkyls was developed. The metal halide is alkylated in situ using common trialkylaluminums, then converted to the cation by contacting with $[Ct]$-$[B(C_6F_5)_4]$ or $B(C_6F_5)_3$. This technique has been used widely in the preparation of supported single-site catalysts. For example, Cp'TiCl$_3$ complexes supported on silica are catalytically inert when combined with AlMe$_3$, but addition of $[Ph_3C][B(C_6F_5)_4]$ or $B(C_6F_5)_3$

activates the metal complex to form a catalyst for the atactic polymerization of propylene.[123] Metallocenes bearing polar groups (e.g., Et(2-t-BuMe$_2$SiO−Ind)$_2$-ZrCl$_2$) were reacted with AlMe$_3$ on silica to fix the metallocene to the surface and alkylate the metal center. This catalyst copolymerizes ethylene and 1-butene in the presence of $B(C_6F_5)_3$ or $[Ph_3C]$-$[B(C_6F_5)_4]$.[124]

Matsumoto generated group 4 metal catalysts by cosupporting bis(cyclopentadienyl)-, mono(cyclopentadienyl)-, or cyclopentadienyl-free compounds with ferricinium or dimethylanilinium tetrakis(pentafluorophenylborate) on a variety of carriers. Triisobutylaluminum can be added in the support step or added to the reactor with the catalyst. Spherical particles with bulk densities as high as 0.36 g/cm^3 are formed using this technique.

Scrubbing the carrier surface free of residual hydroxyl groups improves catalyst activites. Solutions of mono- or bis(cyclopentadienyl) metal dichlorides reacted with alkylaluminums can be evaporated onto passivated silica and activated by $B(C_6F_5)_3$,[126] $[HNMe_2Ph][B(C_6F_5)_4]$,[127] or $[Ph_3C][B(C_6F_5)_4]$.[128] Cross-linked polystyrene−divinylbenzene is claimed to be a superior support to even alkylaluminum-passivated silica for an $(Ind)_2ZrCl_2$-$[Ph_3C][B(C_6F_5)_4]$−$Al(i\text{-}Bu)_3$ catalyst, though, rather surprisingly, catalyst activities were essentially the same when $B(C_6F_5)_3$ was the activator.[129]

Simple alkylaluminums are customarily used as the alkylating component, but other agents can be used. Metallocene dichlorides reacted with MAO are supported and prepolymerized before contacting with $[HNMe_2Ph][B(C_6F_5)_4]$; final activities are low without the boron component.[130] Butylethylmagnesium and even butyllithium have been successfully used as alkylating agents, giving catalysts with activities comparable to those when $Al(n\text{-}C_6H_{13})_3$ was used.[131]

Although the usual method of preparing supported single-site catalysts is to combine the metal component and activator on a support, another means of activation is to combine separately supported metal component and activator. For example, $Me_2C(Cp)$-

Table 4. Supported Zirconium Catalysts Activated by Trialkylaluminums and Borate Salts

| metal complex	activator	support	pre- or post-support activation by Al(i-Bu)$_3$	monomer	activity (g/mmol Zr·h)
Cp$_2$ZrCl$_2$	[HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]	silica	pre- and post-support	ethylene	69 300
Cp$_2$ZrMe$_2$	[HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]	silica	post-support	ethylene	67 300
Cp$_2$ZrMe$_2$	[HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]	silica	none	ethylene	14 000
Cp$_2$ZrCl$_2$	[HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]	MgCl$_2$	pre- and post-support	ethylene	64 000
Cp$_2$ZrCl$_2$	[HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]	alumina	pre- and post-support	ethylene	59 300
Cp$_2$ZrCl$_2$	[HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]	Mg(OEt)$_2$	post-support	ethylene-1-octene	64 000
CpZrMe$_3$	[Cp$_2$Fe][B(C$_6$F$_5$)$_4$]	silica	post-support	ethylene	78 600
CpZrMe$_3$	[Cp$_2$Fe][B(C$_6$F$_5$)$_4$]	silica	none	ethylene	13 300
CpZrCl$_3$	[HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]	silica	post-support	ethylene	65 300
CpZrCl$_3$	[HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]	MgCl$_2$	post-support	ethylene-1-octene	28 700
CpZrCl$_3$	[HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]	alumina	post-support	ethylene-1-octene	30 300
CpZrCl$_3$	[HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]	Mg(OEt)$_2$	post-support	ethylene-1-octene	56 700
Zr(CH$_2$Ph)$_4$	[HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]	silica	post-support	ethylene	74 000
Zr(CH$_2$Ph)$_4$	[HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]	silica	none	ethylene	127
ZrCl$_4$	[HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]	silica	post-support	ethylene	653
ZrCl$_4$	[HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]	MgCl$_2$	post-support	ethylene-1-octene	784
ZrCl$_4$	[HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]	alumina	post-support	ethylene-1-octene	767
ZrCl$_4$	[HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]	Mg(OEt)$_2$	post-support	ethylene-1-octene	2730
Et(Ind)$_2$ZrCl$_2$	[HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]	silica	post-support	propylene	1600
Me$_2$C(Cp(Flu)ZrCl$_2$	[HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]	silica	post-support	propylene	1000

(Flu)ZrX$_2$ (X = Cl, Me) on silica[132] or MgCl$_2$[133] is combined in liquid propylene with separately supported [Ph$_3$C][B(C$_6$F$_5$)$_4$] as the sole component of another fraction of carrier. The reactor walls are not fouled by the syndiotactic polypropylene produced therefrom.

VI. Supported Catalysts without Cocatalysts

Marks and co-workers examined the solid-state ^{13}C NMR spectra of Cp*$_2$ThMe$_2$ (Cp* = η^5-C$_5$Me$_5$) adsorbed on dehydroxylated alumina. Comparison against model compounds suggested that the alumina surface was sufficiently Lewis acidic to abstract a methyl group, forming a three-coordinate [Cp*$_2$-ThMe]$^+$ cation which interacted weakly, if at all, with the oxygen functionalities of the surface (Scheme 6).[134] Ethylene pulsed into a helium stream was

Scheme 6
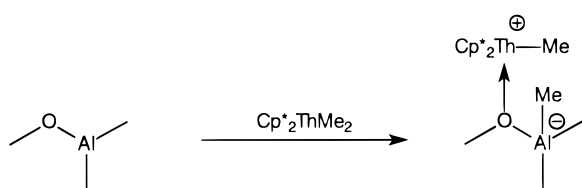
consumed as it passed over this catalyst or one based on Cp*$_2$UMe$_2$−Al$_2$O$_3$.[135]

Polymerization also takes place when Cp′$_2$ZrMe$_2$ (Cp′ = Cp, Cp*) or Cp*ZrMe$_3$ are supported on dehydroxylated alumina.[136] While only some 4% of Cp$_2$ZrMe$_2$ centers are active, about 12% of the Cp*ZrMe$_3$ is converted to cationic centers. The order of polymerization activity is Cp*ZrMe$_3$ > Cp$_2$ZrMe$_2$ ≈ Cp*$_2$ZrMe$_2$. Unlike the actinide compounds, Cp*-ZrMe$_3$ exhibits ethylene polymerization activity even on partially dehydroxylated alumina.

Similar results were observed when MgCl$_2$ was used as the support. Although only some 10% of thorocene centers supported on alumina polymerize ethylene, about 50% are active when MgCl$_2$ is the support.[137] Extending these results to group 4 metallocenes, slurrying MgCl$_2$ with Me$_2$C(Cp)(Flu)ZrMe$_2$ or Et(Ind)$_2$ZrMe$_2$ affords an active catalyst for the syndiospecific or isospecific polymerization of propylene.[8b]

Solid-state ^{13}C NMR analysis of Cp*$_2$ThMe$_2$ adsorbed on dehydroxylated silica suggests that there is a stronger interaction between the oxygen atoms of the silica and the three-coordinate thorium fragment (Scheme 7), and indeed this combination is

Scheme 7
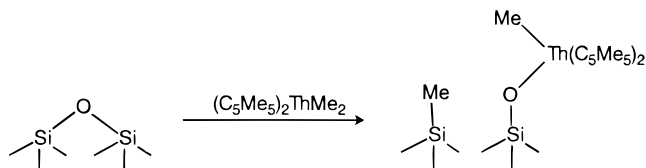
catalytically inactive at low ethylene pressures.[138] However, at 80 °C and 10 bar ethylene pressure, Cp$_2$-ZrMe$_2$ supported on silica dehydroxylated with Me$_3$-SiCl, AlEt$_3$, or Al(i-Bu)$_3$ exhibits some activity.[139]

Remarkably, (n-PrCp)$_2$ZrCl$_2$ supported on silica has limited polymerization activity, though the mechanism by which an active center is generated was not explained.[140]

Sulfated zirconias, prepared by thermal decomposition of Zr(SO$_4$)·4H$_2$O, have strongly Brønsted acidic hydroxyl groups on the surface. Even though these hydroxyl groups on alumina or silica deactivate Cp*$_2$-MMe$_2$ cations, active catalysts are generated from these metallocenes on sulfonated zirconia.[141] Extensive charge-delocalization of the conjugate base was deemed the reason for this phenomenon (Scheme 8).

Scheme 8
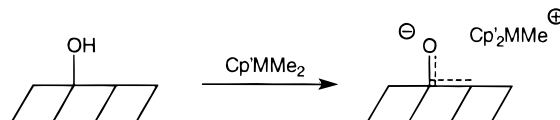

VII. Chemically Tethered Metal Complexes

The frequent reason given for tethering single-site catalysts to the support is to prevent the catalyst from leaching from the surface during polymerization and causing fouling in the reactor. Whether the catalyst is actually desorbed from the support during the polymerization process is not totally clear. It is, after all, entirely possible to polymerize olefins with heterogeneous single-site catalysts while maintaining excellent particle morphology and narrow particle size distribution without tethering the metal complex to the support. Nor is leaching of the catalyst from the support the sole reason for poor morphology, which can occur in fluidized-bed gas-phase processes as well as solvent-based processes.

Furthermore, the solvent used in many leaching experiments[78,142] has been toluene, in which many metallocene−MAO catalysts have some solubility, especially at high Al/M ratios. However, to the best of the author's knowledge, few if any commercial polymerization processes use toluene as a diluent. Aliphatic hydrocarbons, bulk monomers, and fluidizing gas streams are used in large-scale plants. Especially at the lower excess of aluminum used in many supported catalysts (50−200:1), metallocene−MAO catalysts are insoluble in hydrocarbon solvents.[143] The heptane extracts from a Cp$_2$ZrCl$_2$−MAO catalyst supported on silica showed no activity in ethylene polymerization, even when additional MAO was added.[144]

The most common techniques for tethering single-site catalysts to supports are by contacting a reactive support with a substituent on the metal complex, constructing all or part of the ancillary ligand set on the carrier, then reacting with a metal component; or by polymerizing through the substituents on the metal complex. The carrier can be tethered through a substituent on the cyclopentadienyl ring, through a substituent on the bridge in *ansa*-metallocene complexes, or through a heteroatom, principally in mono(cyclopentadienyl) metal complexes and non-metallocene procatalysts.

Binding the metal complex to silica through a substituent on the cyclopentadienyl ring can be done by reacting a substituent on the ring with the

Scheme 9
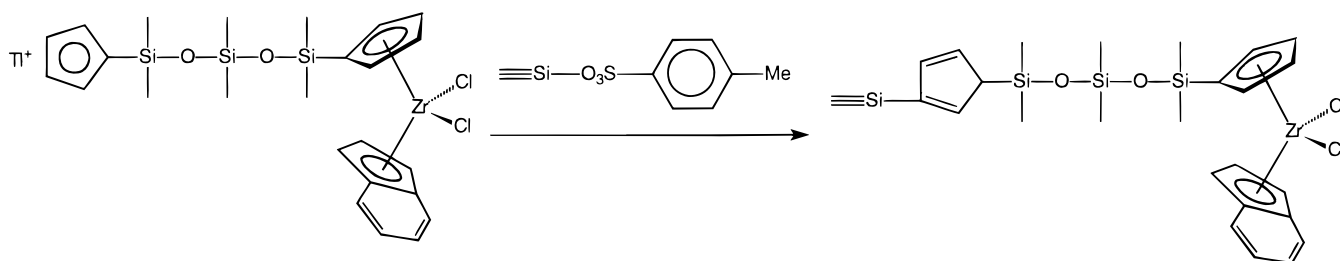
hydroxyl groups of the silica. A variety of mono- and bis(cyclopentadienyl) complexes bearing hydroxyl-reactive substitutents on one or two rings, including $((MeO)_3Si(CH_2)_3Ind)ZrCl_3$,[145] $((MeO)_3Si(CH_2)_3Ind)_2$-$ZrCl_2$,[146] $(MeO)_2MeSiCpTiCl_3$,[147] and $((MeO)Me_2SiCp)$-$CpZrCl_2$,[148] have been prepared and contacted with silica to produce catalysts which are catalytically active in the presence of MAO.

The thallium salt of (1,5-bis(cyclopentadienyl)-hexamethyltrisiloxyl)(indenyl)zirconium dichloride reacts with *p*-tolylsulfonyl-treated silica to form a tethered metallocene with a cyclopentadiene group bound to the surface (Scheme 9). This catalyst polymerizes ethylene in the presence of MAO with activities much higher than those of $Cp(Ind)ZrCl_2$ supported on silica, but still less than that of the homogeneous catalyst.[149]

Partially hydroxylated silica substituted with $ClCH_2$-$PhSi(OMe)_3$ quaternizes the amino groups in Me_2Si-$(2-Me_2NInd)_2ZrCl_2$ yielding an ionic metallocene procatalyst which is active in propylene polymerization when contacted with MAO (Scheme 10).[150]

Scheme 10
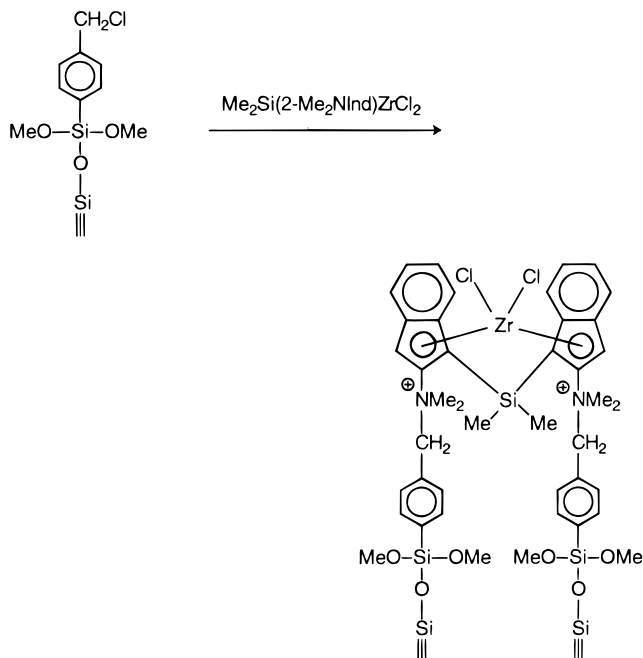
Ansa-metallocenes tethered to a silica surface through the bridging group have been prepared by reacting $ClMeSi(Cp)_2MCl_2$ (M = Zr, Hf) with partially dehydroxylated silica, either by itself[151] or modified by agents such as $(MeO)_3Si(CH_2)_3NH_2$.[152] The catalyst activity in ethylene-1-hexene copolymerization is

reduced by about 75% over the homogeneous variant. It has also been suggested that $(i\text{-PrO})MeSi(C_5Me_4)$-$LMCl_2$ complexes (L = C_5Me_4, M = Zr;[153] L = *N-t*-Bu, M = Ti[154]) also react with silica to form supported procatalysts, though no specific examples were supplied.

Assembling the metallocene complex on the support is a second method of preparation. Silica can be modified using $(EtO)_3Si(CH_2)_3C_5H_5$ to give a cyclopentadiene-bearing silica surface. Deprotonation with BuLi and reaction with $CpZrCl_3$ affords $\equiv Si-O-$(EtO)_2Si(CH_2)_3C_5H_4(Cp)ZrCl_2$. The activity of this catalyst in ethylene polymerization is twice as high as that of a homogeneous $CpZrCl_3-MAO$ catalyst, though still only a third as active as the Cp_2ZrCl_2 analogue.[155] Similarly, $(MeO)Me_2Si-C_9H_7$ can be reacted with the surface hydroxyl groups of silica to afford $\equiv Si-O-SiMe_2-C_9H_7$. This is then allowed to react with $M(NMe_2)_4$ or $Cp'M(NMe_2)_3$ to form the tethered metallocene.[156] A silica-bound cyclopentadiene is also the result of the reaction of NaCp with chlorinated silica. Subsequent treatment with $M(NMe_2)_4$ or $Cp'M(NMe_2)_3$ results in a supported metallocene procatalyst.[157]

Ansa-metallocenes attached to silica through the bridging atom were prepared by reaction of $ClMeSi$-$(Cp)(Flu)$ with partially dehydroxylated silica. Deprotonation and reaction with $ZrCl_4$ affords a supported catalyst active in ethylene polymerization when combined with MAO.[158] Reacting Cl_2SiCp' (Cp = Cp[159] or Ind[160]) with silica produces a tethered *ansa* ligand set from which a zirconocene complex can be synthesized and used in ethylene polymerization to form polyethylene particles with good bulk density ($0.38-0.39$ g/cm³) and no adhesion of polymer to the reactor. A similar synthetic methodology is used to react the $Li(TMEDA)$ salt of cross-linked polystyrene with $Cl_2Si(Ind)_2$ or $PhClSi(Ind)_2$.[161]

Soga and co-workers assembled ancillary ligand sets by reacting partially dehydroxylated silica with $SiCl_4$, $SnCl_4$, or 1,1,2,2-tetrabromoethylene followed by substitution with indenyl or fluorenyl anions.[162] These are used to create tethered metallocenes (Scheme 11). The indenyl-based catalysts polymerize propylene to isotactic PP with melting points as high as 164 °C, but a substantial amount of atactic material is also formed from the meso isomer. Neodymocene catalysts synthesized from the surface-bound dianion and $NdCl_3$ and activated by $Al(i\text{-Bu})_3$ polymerize ethylene with modest activity (7.72 g of PE/mmol Nd·h).[163] In a similar synthetic methodology, silica was treated with $MeSiCl_3$ and indenyllithium to form $\equiv Si-O-SiMe(Ind)_2$. This was deprotonated
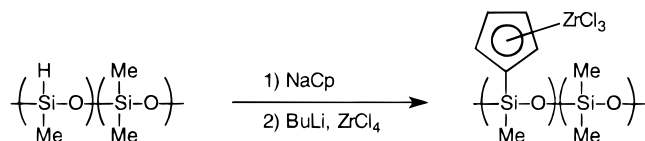
Scheme 11
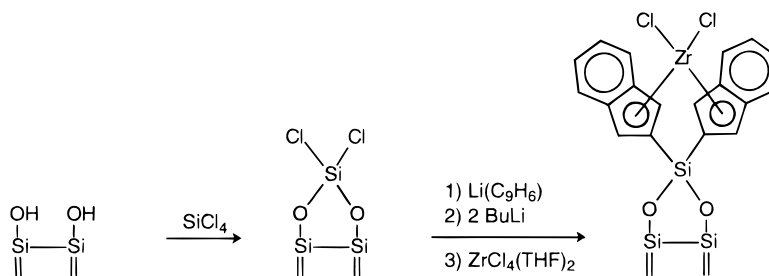
by BuLi and metalated with ZrCl$_4$. Polyethylene of high molecular weight and narrow molecular weight distribution is formed when this material is activated by MAO.[164]

Polysiloxane-supported tethered metallocenes have been synthesized by reaction of brominated poly-(methylhydrogen)siloxane−poly(dimethylsiloxane) with NaCp and subsequent reaction with ZrCl$_4$ (Scheme 12).[165] Cohydrolysis of Cl$_2$Si(Cp′)(Flu) and Me$_2$SiCl$_2$
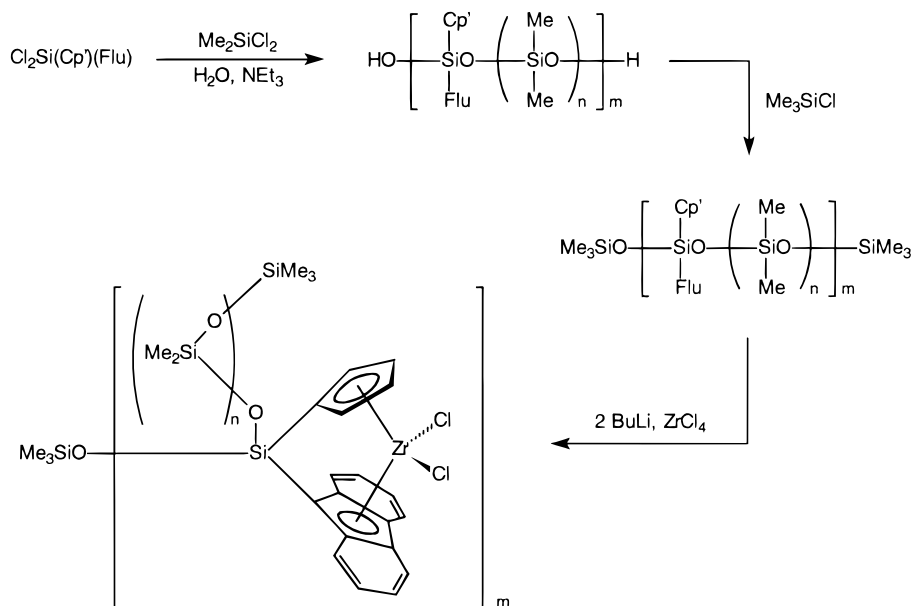
Scheme 12

forms a ligand−dimethylsiloxane copolymer which can be deprotonated and reacted with ZrCl$_4$ (Scheme 13).[166] The MAO-activated catalyst formed when Cp′ = C$_5$Me$_4$ is only feebly active in propylene polymerization, but when Cp′ = Cp, a more vigorous system is formed which produces syndiotactic polypropylene.

Synthesizing the metallocene on a polymeric support can be done by reacting a chlorinated polymer such as chloromethylated polystyrene with cyclopentadienide. This can be deprotonated to form the polymer-bound Cp anion, which can react with CpZrCl$_3$ to form polystyrene-bound Cp$_2$ZrCl$_2$.[167] A more elaborate metallocene was constructed when

the polymer-bound Cp anion is allowed to react with ClMe$_2$(Flu), followed by deprotonation and metalation with ZrCl$_4$ (Scheme 14).[168] Activated by MAO, this metallocene polymerizes ethylene in a hexane slurry.

A polystyrene-supported *rac*-Ph$_2$Si(Ind)$_2$ZrCl$_2$ was prepared by the procedure indicated in Scheme 15.[169] Combined with MAO (Al/Zr = 5000), this catalyst polymerizes ethylene at temperatures as high as 150 °C. Elemental mapping indicates that the catalyst is evenly distributed and located only on the surface of the polystyrene bead, and no Zr is contained inside the bead; polymer growth occurs, then, only on the surface.[170]

Ethylene−methyl acrylate (EMA) copolymers react with sodium cyclopentadienide yielding a polymer-bound Cp anion, which forms an EMA-bound metallocene when combined with CpZrCl$_3$ or ZrCl$_4$(THF)$_2$ (Scheme 16).[171] Both catalysts polymerize ethylene in isobutane or toluene slurries to polyethylene of relatively narrow molecular weight distribution ($M_w/M_n = 2.3$−3.0) when activated by MAO.

All or part of the ligand set can be homo- or copolymerized prior to metalation. 2-vinylfluorene is homopolymerized or copolymerized with styrene using 2,2′-azobisisobutyronitrile (AIBN) or BF$_3$·OEt$_2$ as initiators. The polymer, with a molecular weight of 5000−20 000 daltons, is then deprotonated and reacted with CpZrCl$_3$ to form the polymeric procatalyst.[172] The substituted styrene complex is copoly-

Scheme 13
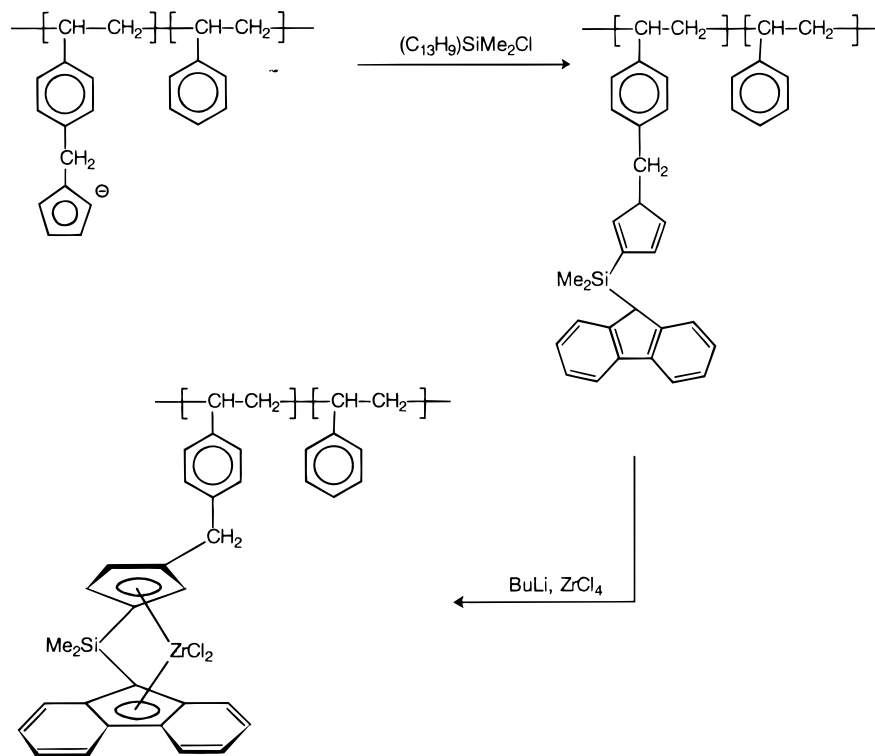
Scheme 14

Scheme 15
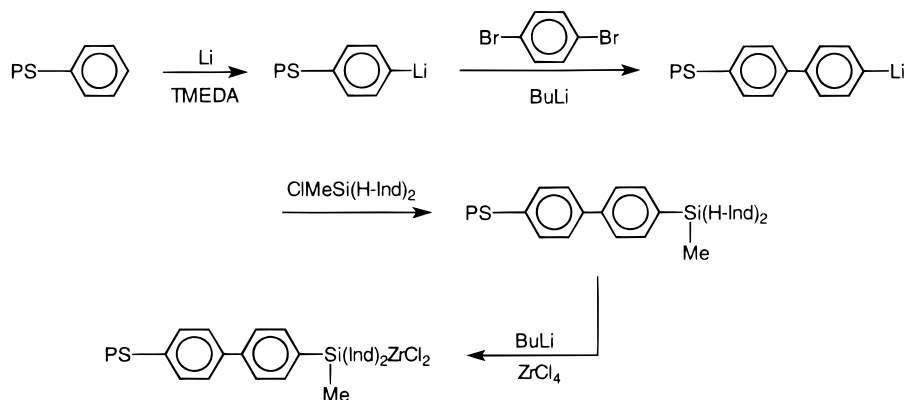
Scheme 16
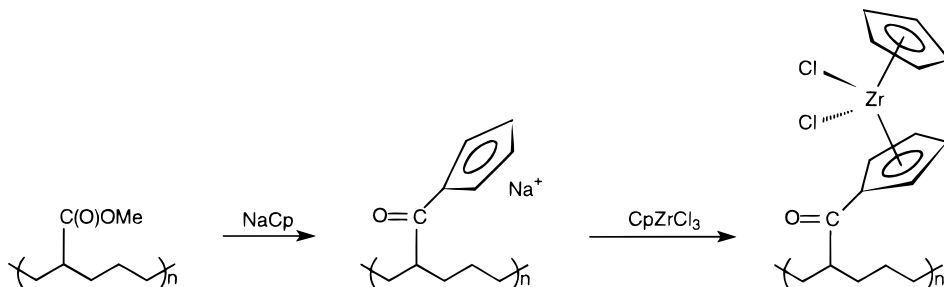
merized with styrene in the presence of AIBN yielding a polymeric ligand set (Scheme 17).[173] The zir-conocene dichloride derived from this copolymer polymerizes propylene to syndiotactic polypropylene with relatively high stereospecificity (rrrr = 0.86–0.89 at 40 °C).

Polymer-bound metallocenes are also prepared by polymerizing through a group on the cyclopentadi-enyl ring or the bridge.[174] Alkenyl- and alkynyl-

substituted metallocenes such as $(H_2C=CHCp)_2$-$ZrCl_2$,[175] $(H_2C=CHCH_2Cp)_2ZrCl_2$,[176] 1,2-$C_2H_4(H_2C=CH(CH_2)_n$Ind)(Flu)$ZrCl_2$ ($n=1, 4$),[177] 1,2-$C_2H_4(H_2C=CH(CH_2)_4SiMe_2$Ind)(Flu)$ZrCl_2$,[178] and $Cp(2,7$-$(PhC=C-)_2$Flu)$ZrCl_2$[179] can be reacted with MAO and prepolymerized with ethylene under low-pressure conditions to form heterogeneous cross-linked met-allocene polymers with or without silica as a filler. These can be used under more demanding conditions

Scheme 17
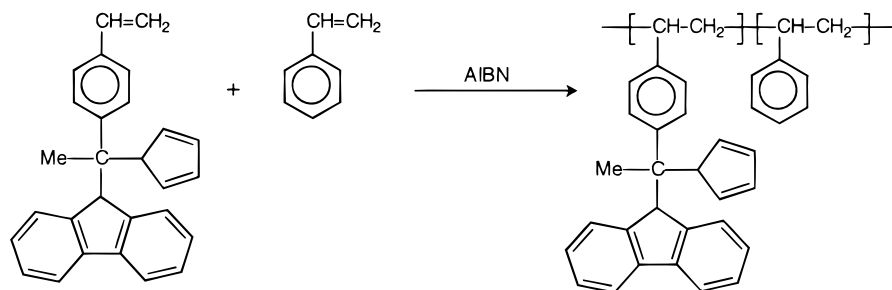
for slurry or gas-phase polymerizations free of reactor fouling. Metallocenes bearing olefinic groups in the bridge, such as **4**[180] and **5**,[181] are self-immobilized

R = H, Me
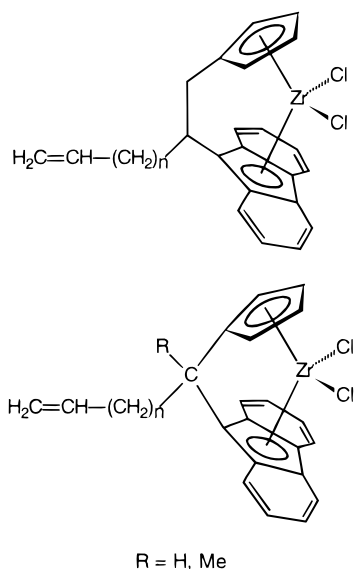
when copolymerized with ethylene in the presence of MAO.

Metallocenes bound to polysiloxanes through the Cp ring were prepared by reacting (H$_2$C=CH−R−Cp′)$_2$ZrCl$_2$ complexes (Cp′ = Cp, Ind) with poly-(methylhydrogensiloxane) in the presence of H$_2$PtCl$_6$·6H$_2$O (Scheme 18).[182] *Ansa*-metallocenes bound to

Scheme 18
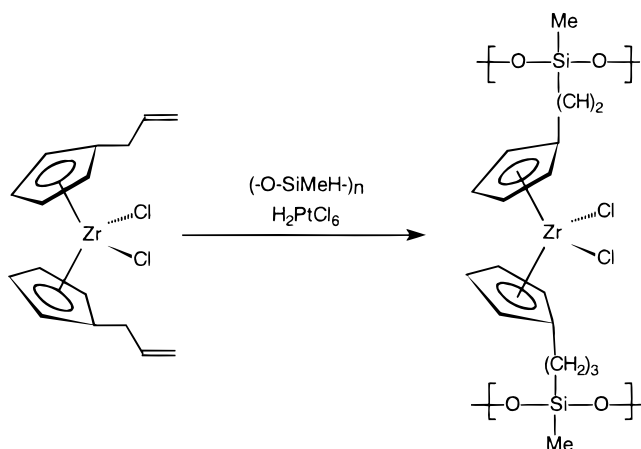
polysiloxanes through the bridging atom are formed from hydrolysis of Cl$_2$Si(Cp)$_2$ZrCl$_2$ (Scheme 19).[183]

Scheme 19
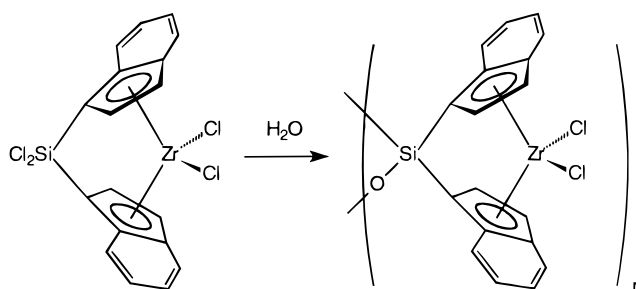
Alt and co-workers attached metallocenes to poly-(methylsiloxane) microgels by reacting these supports with cyclopentadienides bearing long-chain silyl chloride substituents on the ring or in the bridge. Deprotonation and metalation with ZrCl$_4$ affords the tethered metallocene (Scheme 20).[184] These are ethylene polymerization catalysts in the presence of MAO with activities ranging from 0.14 to 1.44 kg/g Zr·h.

Binding the metal complex to the support through a heteroatom is done in the cases of mono(cyclopentadienyl) metal complexes or nonmetallocene single-site catalysts. An amine-functionalized support is produced from the reaction of silica with 3-amino-propyltrimethoxysilane. This is then allowed to react with Cp*TiCl$_3$, affording a supported metal complex (Scheme 21).[185] When contacted with MAO, a catalyst is formed which copolymerizes ethylene with 1-octene to polymers with narrow molecular weight distribution and high comonomer content. Styrene-4-amino-styrene copolymers react with L(*N-t*-Bu)VCl$_2$ complexes (L = Cp, Cl) to form supported imidovanadium procatalysts (Scheme 22).[186] With an AlEt$_2$Cl cocatalyst, the Cp derivative polymerizes ethylene with 10−50 times the activity of unsupported Cp(*N-t*-Bu)VCl$_2$.

A polymeric support material is prepared by reacting α,ω-amines with 1,5-dichlorohexamethyltrisiloxane. This is deprotonated and allowed to react with CpZrCl$_3$ to afford a procatalyst which, when contacted with 1000−1500 equivalents of MAO, polymerizes ethylene with activities as high as 1100 kg/g Zr·h (Scheme 23).[187]

Eisen and co-workers attached a "constrained-geometry" titanium complex to silica or alumina through a pendant trimethoxysilyltrimethylene group bonded to the nitrogen atom (Scheme 24).[188] Unlike many supported single-site catalysts, the ethylene and propylene polymerization activity of the supported compound cocatalyzed by MAO is quite similar to that of the homogeneous analogue.

Scheme 20
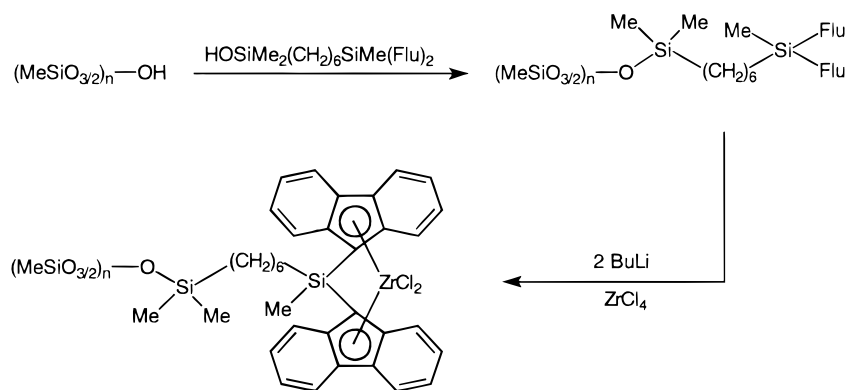
Scheme 21
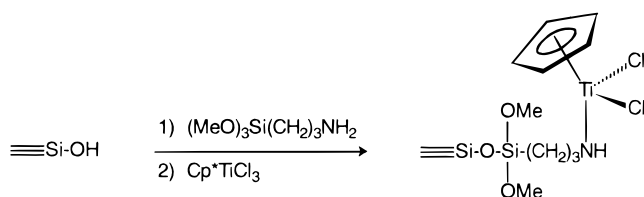
Catalyst libraries for combinatorial screening of diimine-based nickel and palladium catalysts can be developed by attaching a diketone to a Merrifield resin, reacting with a variety of anilines in the presence of a dehydrating catalyst, and complexing with the metal (Scheme 25). After each variant is activated with MAO or borate salt, the 96-well microtiter plate is exposed to ethylene and polymerization activity is qualitatively determined by infrared imaging.[189]

Solid-phase supports used in combinatorial chemistry were used to prepare a cross-linked polystyrene bead containing a tetraethylene glycol spacer. The p-nitrosulfonate derivative of the polymer was substituted with NaC_5HMe_3Et to form a supported cyclopentadiene, which was allowed to react with $CpTiCl_3$, making a tethered titanocene (Scheme 26).[190] With MAO, this polymerizes ethylene with relatively low activity (41 g/mmol catalyst·h) forming polymer with a noodle-like morphology.

VIII. Chemically Tethered Activators

A. Alumoxanes

Chemically tethering the activator component, instead of the metal complex, allows for flexibility in the choice of metal complex while retaining some of the advantages that chemically tethered catalysts exhibit. This technique was one of the earliest sup-

ported metallocene disclosures. Kaminsky reacted $AlMe_3$ with starch and lignin to form a surface-supported alumoxane. This was allowed to react with Cp_2ZrMe_2 to form a catalyst with rather low activity in ethylene polymerization (3,000−13 000 g/g M; toluene slurry).[191] Simple trialkylaluminums can be used to form supported alumoxanes by contacting $AlMe_3$ with silica containing from less than 3 to 40% water.[192] Addition of metallocene dichloride and evaporation affords a solid polymerization catalyst, although another method uses separately supported metallocene and MAO to form the active catalyst.[193] Alternatively, a metallocene/$AlMe_3$ mixture can be added to undehydrated silica.[194] Other materials such as $Mg(OH)_2$,[192b] clays and zeolites,[195] $MgCl_2·6H_2O$,[196] or $Al(O)OH$[197] can also be used as the solid hydrolysis agent. $AlEt_3$ can be used as a substitute, with a metallocene/$AlMe_3$ mixture added to the surface-bound ethylalumoxane.[198] Mixtures of $AlMe_3$ with $AlEt_3$ or $Al(i\text{-}Bu)_3$ mixtures are also effective for generating the alumoxane.[199] The amount of alumoxane bound to the silica can be adjusted by altering the amount of water on the silica, the ratio of water to trialkylaluminum,[200] or by washing the supported metallocene catalyst after preparation.[201] Aging of the supported cocatalyst for 2 weeks to 3 months is claimed to impart a modest increase in catalyst activity.[202]

Investigators at BASF have noted that (n-BuCp)$_2$-$ZrCl_2$ contacted with $AlMe_3$-treated "wet" silica and used to polymerize ethylene in an isobutane slurry results in severe reactor fouling. Addition of a small amount of n-butyllithium to the autoclave eliminates this fouling and allows for smooth continuous reactor operations.[203]

A study of the relative performance of metallocenes, alkylaluminums, and variously hydrated silicas shows that the activity of the surface-generated alumoxanes rivals that of supported MAO or

Scheme 22
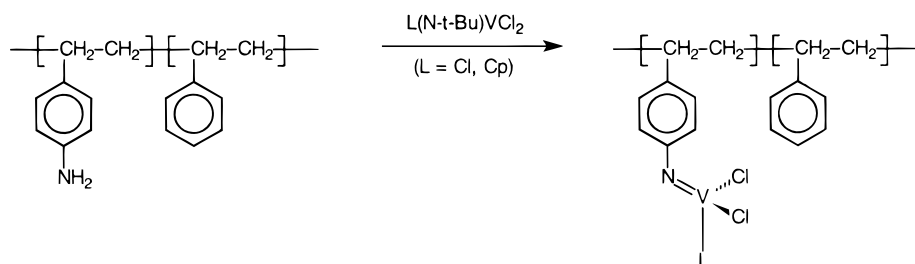
Scheme 23
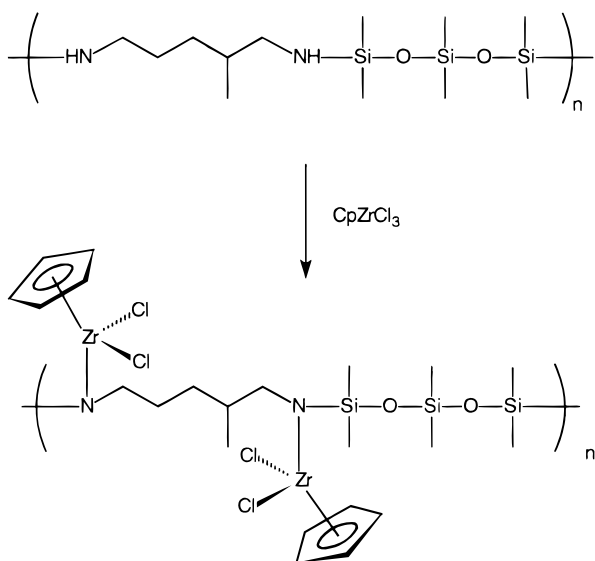
modified MAO (MMAO) catalysts (Table 5).[204] Trimethylaluminum on calcined silica shows negligible activity, whereas triethylaluminum and tributylaluminum are effective cocatalysts only at higher levels of silica hydration. Cp_2ZrCl_2 activated by surface-hydrolyzed diethylaluminum chloride has only feeble activity.
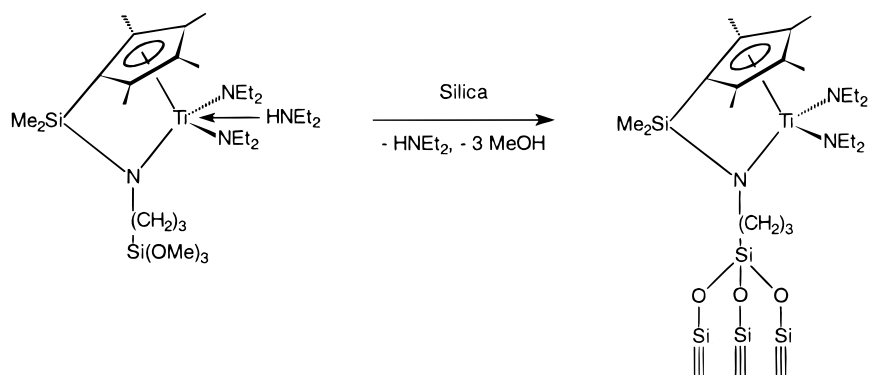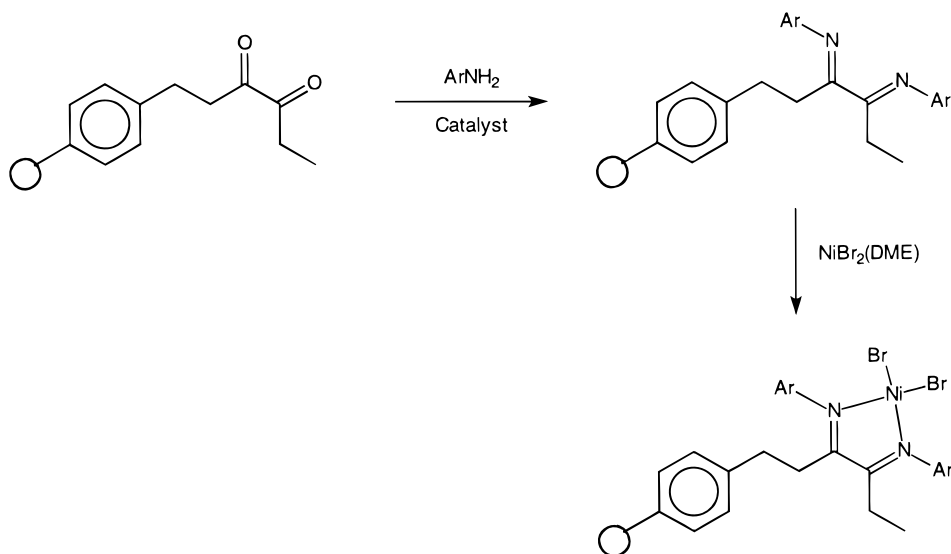
Table 5. Ethylene Polymerization with Zirconocenes Supported on Water-Laden Silicas

metallocene	cocatalyst	water content (wt %)	activity (g of PE/mmol Zr)
Cp_2ZrCl_2	$AlMe_3$	0	0
Cp_2ZrCl_2	MAO	0	811
Cp_2ZrCl_2	MMAO	0	709
Cp_2ZrCl_2	$AlMe_3$	16	895
$(MeCp)_2ZrCl_2$	$AlMe_3$	16	1007
$(n\text{-}BuCp)_2ZrCl_2$	$AlMe_3$	16	2400
$(Ind)_2ZrCl_2$	$AlMe_3$	16	400
Cp_2ZrCl_2	$AlMe_3$	45	581
Cp_2ZrCl_2	$AlEt_3$	16	11
Cp_2ZrCl_2	$AlEt_3$	45	440
Cp_2ZrCl_2	$Al(i\text{-}Bu)_3$	45	487
Cp_2ZrCl_2	$AlEt_2Cl$	45	17

B. Boron Activators

Another means of ensuring that the ionic catalyst formed from the metal component and the activator in non-alumoxane systems is not leached from the support has been to covalently bind the activator, instead of the metallocene, to the support material. Initial efforts used strongly acidic ion-exchange resins bearing $-SO_3H$ groups to generate active catalysts when allowed to react with $Cp'_2ZrCl_2-Al(i\text{-}Bu)_3$.[205] An $(Ind)_2ZrCl_2-Al(i\text{-}Bu)_3$ was also successfully activated by an ionic $[Ph_3C][(polymer)-SO_3]$ support material and used in ethylene-1-hexene copolymerization with an activity of 1000 g of polymer/g of catalyst·h.[206]

Scheme 24

Scheme 25

Scheme 26

Scheme 27

$$\equiv Si-OH + Li[(C_6F_5)_3B-R-SiR'_2Cl] \xrightarrow{R_3N} \equiv Si-O-R'_2Si-[R-B(C_6F_5)_3][R_3NH]$$
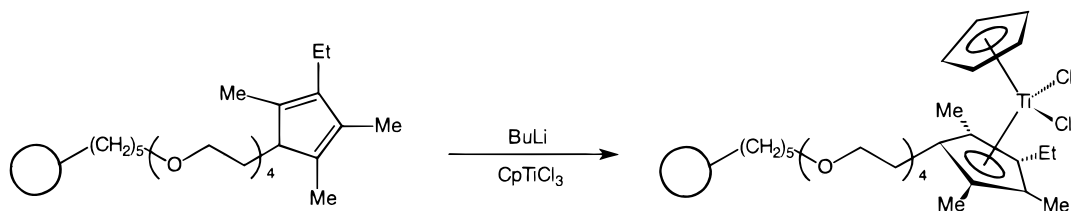
Scheme 28
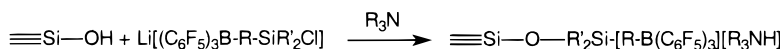
R = SiCl$_3$, SiMe$_2$Cl, ClMe$_2$Si(CH$_2$)$_8$
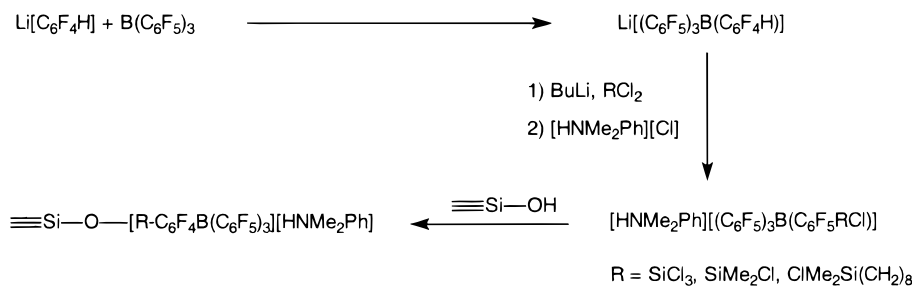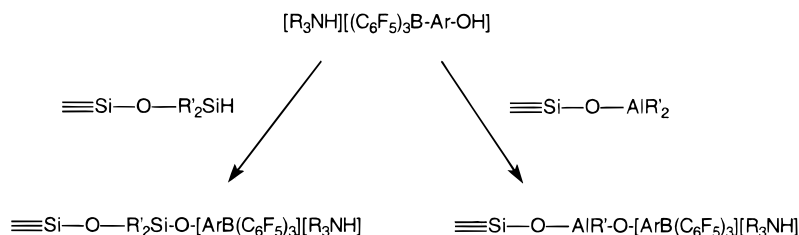
Scheme 29

Turner postulated, but did not specifically exemplify, using a partially hydroxylated silica surface to bind a polyfluorinated tetraphenylborate anion bearing a reactive group (Scheme 27).[207] The essence of this idea was later put into practice by investigators at Dow and Nippon Polyolefins. Partially hydroxylated silica reacts with [HNMe$_2$Ph][(C$_6$F$_5$)$_3$B(C$_6$F$_4$-RCl)] (RCl = SiCl$_3$, SiMe$_2$Cl, (CH$_2$)$_8$SiMe$_2$Cl) to form a surface-bound activator for Cp$'_2$ZrCl$_2$−Al(i-Bu)$_3$ systems with improved control of fines (Scheme 28).[208] The reaction of silane-modified silicas with [R$_3$-NH][(C$_6$F$_5$)$_3$B−Ar−OH] salts (Ar = phenyl, biphenyl, naphthyl) also affords supported activators for Me$_2$-Si(C$_5$Me$_4$)(N-t-Bu)TiMe$_2$ complexes in slurry polymerization processes (Scheme 29).[209] The same ammonium salts may be reacted with AlR$_3$-treated silicas and used as activators for Me$_2$Si(C$_5$Me$_4$)(N-t-Bu)Ti-(η^4-diene) complexes.[210]

Noninterfering anions covalently bound to polymers have been prepared by the AIBN-initiated copolymerization of styrene with trialkylammonium 4-styryltris(pentafluorophenyl)borate (Scheme 30). High-density polyethylene prepared from Cp$_2$ZrCl$_2$−Al(i-Bu)$_3$ and this activator shows no signs of reactor fouling in a slurry polymerization.[211]

The reaction of neutral bis- and tris(pentafluorophenyl)boranes with silica surfaces can also lead to supported ionic activators. B(C$_6$F$_5$)$_3$ acts as a Lewis acid toward the surface hydroxyl groups of silica,

Scheme 30
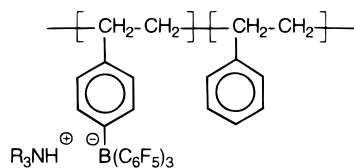
affording a Brønsted acid capable of reacting with Cp$'_2$ZrMe$_2$ procatalysts. Ammonium salts, which also function as ionic activators, are formed on reaction with tertiary amines.[212] Ward and Carnahan deprotonated the hydroxyl groups with butyllithium prior to reaction with B(C$_6$F$_5$)$_3$; methathesis of the lithium salt with Ph$_3$CCl generates the supported trityl complex (Scheme 31).[213]

Research at Hoechst has led to the fixing of neutral triarylborane activators to silica surfaces. This was achieved by reacting HB(C$_6$F$_5$)$_2$ with silica modified by vinyltriethoxysilane (Scheme 32) or substituted tris(polyfluorophenyl)boranes with partially dehydroxylated silica (Scheme 33). The supported neutral activators can also be quaternized by reaction with Li(C$_6$F$_5$).[214]

The anion, even if noninterfering, can have a profound effect on the performance of the catalyst.[215] Another method of chemically anchoring ionic boron-based activators is to bind the cationic component to the surface. This has been done by reacting (MeO)$_2$Si-

Scheme 31
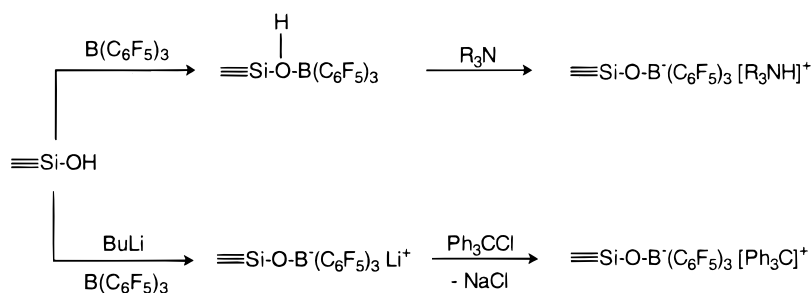
Scheme 32
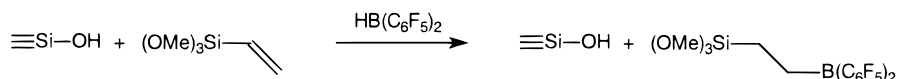
Scheme 33
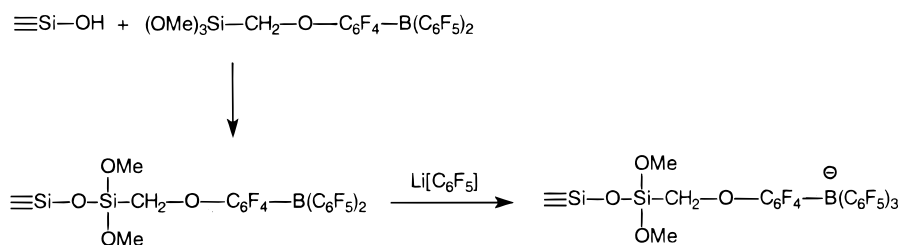
Scheme 34
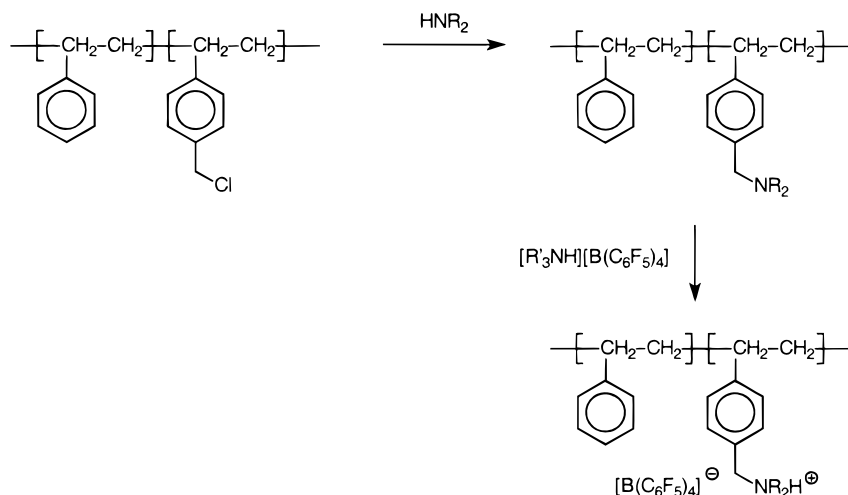
$(C_6H_4NMe_2)_2$ with silica, protonating with HCl, and metathesizing with $Li[B(C_6F_5)_4]$.[216] Polymer-bound cations are prepared by reaction of secondary amines with chloromethylated styrene, followed by reaction with $[R_3NH][B(C_6F_5)_4]$ salts (Scheme 34).[217] Although the active ionic catalyst produced from the reaction of the support with Cp'_2ZrMe_2 is not chemically bound to the support, the higher dielectric of the support with respect to the polymerizing environment (1-hexene in hexane) discourages leaching of the catalyst from the support and promotes good particle morphology.

IX. Supported Group 3 and Lanthanide Single-Site Catalysts

Soga synthesized the surface-bound *ansa*-neodymocene complex **6** which was activated by a number
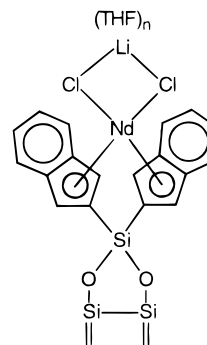
6

of alkylating agents to generate active ethylene polymerization catalysts.[218]

Alkylaluminum cocatalysts such as $AlMe_3$ and MAO generate less active catalysts (1−8 kg PE/mol

Nd·h) than do butyllithium (19 kg PE/mol Nd·h) or butylethylmagnesium (91 kg PE/mol Nd·h). The BuEtMg-activated catalyst exhibits even higher activity at elevated temperatures: at 150 °C, the catalyst rate goes up to 219 kg PE/mol Nd·h. Cp^*_2-SmMe(tetrahydrofuran(THF)) supported on MgO polymerizes ethylene in the absence of a cocatalyst, but the activity appears to be poor (1.5 kg PE/mol Sm·h).[219]

X. Supported Group 5 Single-Site Catalysts

Compared to studies on single-site catalysts of the Group 4 metals, research on heterogenized Group 5 single-site catalysts is very limited. Apart from the polymer-supported vanadium complexes noted above,[186] $CpVCl_3$ and alumoxanes have been supported on silica for the vapor-phase polymerization of butadiene. The finished catalyst was prepared by a variety of methods: supporting a $CpVCl_3$–MAO mixture on silica,[220] prepolymerizing with butadiene in a slurry before isolating the final catalyst,[221] and generating the alumoxane by treating silica with a $AlMe_3$–$Al(i\text{-}Bu)_3$–H_2O mixture, isolating the supported alumoxane, and reacting with $CpVCl_3$.[222] Polybutadiene of principally cis-1,4 microstructure is formed with molecular weights over 3 000 000.

XI. Supported Group 6 Single-Site Catalysts

Of course, the first supported group 6 metallocene catalyst which comes to mind is Cp_2Cr on silica, developed in the early 1970s.[223] This should be considered a heterogeneous catalyst and not a true supported single-site catalyst; the nature of the active site remains unclear even after 25 years of research, and the polymer produced from this catalyst has a broad molecular weight distribution, suggesting the presence of multiple polymerizing sites.

Other chromium-based catalysts have been explored which, when supported, afford polyethylene with relatively narrow molecular weight distribution. These are based on mono(cyclopentadienyl) chromium alkyl complexes first explored by Theopold.[224] These may be Cr(II) compounds such as $[Cp^*$-$CrMe]_2$,[225] Cr(III) oxo compounds such as $Cp^*Cr(O)$-Me_2,[226] neutral and cationic Cr(III) compounds such as $Cp^*CrMe_2(THF)$ and $[Cp^*CrMe(THF)_2][BPh_4]$,[227] mixed valence dimers such as $Cp^*Cr(\eta^1\text{-}CH_2Ph)(\mu\text{-}\eta^3\text{:}\eta^6\text{-}CH_2Ph)CrCp^*$,[228] or even anionic complexes such as $[Li][Cp^*Cr(CH_2Ph)_3]$ (Table 6).[229]

Aluminum phosphate and alumina–aluminum phosphate supports are preferred for producing catalysts with high activities and relatively narrow molecular weight distributions ($M_w/M_n = 2$–4). Silica-supported catalysts afford polymers with much broader distributions. Isobutylalumoxane was used as the cocatalyst; some catalytic activity was observed even in the absence of cocatalyst, and $AlMe_3$ and BEt_3 led to inferior performance. Striking as well is the vast *increase* in catalyst activity when the chromium complexes are supported. This is contrary to the general trend in group 4 complexes, where heterogenization of the complex diminishes activity.

Table 6. Ethylene Polymerization by Chromium Catalysts

chromium complex	support	cocatalyst	activity (g/g of Cr·h)	M_w ($\times 10^{-3}$)	MWD	ref
$[Cp^*CrMe]_2$	Al_2O_3·$2AlPO_4$	none	94 000	862	3.73	225
$[Cp^*CrMe]_2$	Al_2O_3·$2AlPO_4$	IBAO	638 000	791	2.23	225
$[CpCrH]_4$	Al_2O_3·$2AlPO_4$	IBAO	516 000	893	4.54	225
$Cr_4(CH_2SiMe_3)_8$	Al_2O_3·$2AlPO_4$	IBAO	145 000	384	144	225
$[Cp^*CrMe_2]_2O$	Al_2O_3·$2AlPO_4$	none	0			226
$[Cp^*CrMe_2]_2O$	Al_2O_3·$2AlPO_4$	IBAO	120 000	1123	3.08	226
$Cp^*Cr(O)Me_2$	Al_2O_3·$2AlPO_4$	IBAO	34 000	934	4.22	226
$Cp^*Cr(O)_2Me$	Al_2O_3·$2AlPO_4$	IBAO	58 000	961	13.58	226
$[Cp^*CrMe(THF)_2][BPh_4]$	none	none	510	125	5.8	227
$[Cp^*CrMe(THF)_2][BPh_4]$	silica	IBAO	48 400	252	12.8	227
$[Cp^*CrMe(THF)_2][BPh_4]$	silica	$AlMe_3$	3 700	236	34.2	227
$[Cp^*CrMe(THF)_2][BPh_4]$	Al_2O_3·$2AlPO_4$	IBAO	233 000	919	4.41	227
$Cp^*CrMe_2(THF)$	silica	none	0			227
$Cp^*CrMe_2(THF)$	silica	EAO	15 200	306	18.2	227
$Cp^*CrMe_2(THF)$	silica	IBAO	33 000	293	19.2	227
$Cp^*CrMe_2(THF)$	Al_2O_3·$2AlPO_4$	none	5400	805	2.68	227
$Cp^*CrMe_2(THF)$	Al_2O_3·$2AlPO_4$	IBAO	272 000	1130	2.75	227
$Cp^*Cr(CH_2SiMe_3)_2$	Al_2O_3·$2AlPO_4$	none	2 500	1124	2.02	227
$Cp^*Cr(CH_2SiMe_3)_2$	Al_2O_3·$2AlPO_4$	IBAO	372 000	1075	2.72	227
$Cp^*Cr(CH_2SiMe_3)_2$	Al_2O_3·$2AlPO_4$	BEt_3	0			227
$Cp^*Cr(CH_2SiMe_3)_2$	silica	IBAO	356 000	606	39.9	227
$Cp^*Cr(CH_2Ph)_2(Py)$	Al_2O_3·$2AlPO_4$	IBAO	794 000	1414	1.72	227
$Cp^*CrMe_2(Me_2NPy)$	Al_2O_3·$2AlPO_4$	IBAO	317 000	921	2.15	227
$Cp^*CrMe_2(Me_2NPy)$	$AlPO_4$	IBAO	401 800	801	2.11	227
$Cp^*CrMe_2(PMe_2Ph)$	$AlPO_4$	IBAO	1 229 000	850	3.20	227
$CpCrMe_2(PMe_2Ph)$	$AlPO_4$	IBAO	454 000	882	2.83	227
$CpCrMe_2(Py)$	Al_2O_3·$2AlPO_4$	IBAO	194 000	740	2.82	227
$Cp^*Cr(\eta^1\text{-}Bz)(\mu\text{-}\eta^1\text{:}\eta^6\text{-}Bz)CrCp^*$	$AlPO_4$	IBAO	403 000	897	2.68	228
$Li[Cp^*Cr(Bz)_3]$	none	none	5	171	9.54	229
$Li[Cp^*Cr(Bz)_3]$	Al_2O_3·$2AlPO_4$	IBAO	301 000	1408	2.61	229
$Li(TMEDA)[Cp^*Cr(Bz)_3]$	silica	IBAO	137 000	436	14.84	229

XII. Supported Late-Transition Metal Single-Site Catalysts

The nickel 1,2-diimine complexes $R_2C_2(=NR')_2NiX_2$ (**7**; R = H, R' = 2-isopropylphenyl, 2,6-diisopropyl-
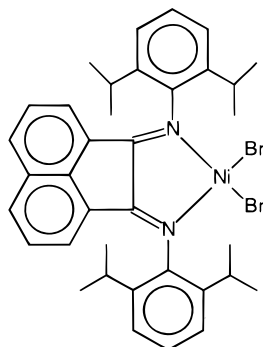
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phenyl) have been contacted with MAO on silica—either by itself[230] or prepolymerized with ethylene[231]—and used to polymerize ethylene in toluene or hexane slurry. Polymerization using the prepolymerized catalyst affords polymer with a high bulk density of 0.40 g/cm³.

Extrapolating from solution polymerization data in the literature, investigators at Exxon predicted that under gas-phase polymerization conditions employed (220 psi, 63 °C), polyethylene produced from acenaphthalenebis(2,6-diisopropylphenylimine)nickel dibromide—MAO would have a melting point of 66 °C and some 53 branches/1000 C. In a continuous fluidized-bed gas-phase polymerization, the polymer actually produced from this catalyst supported on silica had a melting point of 91 °C and only 34 branches/1000 C, suggesting that these catalysts can be used to prepare morphologically regular particles without risk of melting and fouling.[232]

Supported catalysts for the alternating copolymerization of ethylene and carbon monoxide are formed when palladium on alumina is reacted with [NO]-[BF₄] in an acetonitrile slurry. In the presence of 1,3-diphenylphosphinopropane, an active catalyst is generated which can be used in slurry or gas-phase processes.[233]

XIII. Other Support Materials

A. Magnesium Chloride

Magnesium chloride, a widely used support in conventional Ziegler—Natta catalysts, has been studied far less extensively than silica as a carrier for single-site catalysts. Reaction of dibutylmagnesium by *tert*-butyl chloride in a diisoamyl ether—hexane mixture produces $MgCl_2$ with very narrow particle size distribution. Toluene solutions of zirconocenes in the presence[234] or absence[235] of a proton donor such as *n*-butanol are supported, then reacted with MAO to form active catalysts. Highly porous $MgCl_2$ supports are prepared by the dealcoholysis of a $MgCl_2$·3EtOH adduct. These are allowed to react with zirconocene—MAO mixtures to form active supported

catalysts for ethylene homo- and copolymerizations.[236] Lin prepared $MgCl_2$-supported metallocene catalysts using a one-pot method: Bu_2Mg was added to a mixture of MAO and *i*-BuAlCl₂ or *n*-BuCl followed by reaction with $(n\text{-BuCp})_2ZrCl_2$. These catalysts exhibited twice the activity in ethylene polymerization as silica-supported analogues.[237]

$MgCl_2$·nTHF solutions, produced from the reaction of magnesium and 1,2-dichloroethane in THF, can be reacted with a THF solution Cp_2MCl_2 (M = Ti, Zr) and isolated as a solid[238] or supported on silica.[239] The Cp_2TiCl_2—MAO—$MgCl_2$ catalyst exhibits higher activity in the xylene slurry polymerization of ethylene than does the homogeneous catalyst.[240] Unlike the homogeneous catalyst, the catalyst activity increases with increasing temperature, but when hexane is the diluent, the activity declines above 50 °C. A Cp_2ZrCl_2—$MgCl_2$ adduct is more active in ethylene polymerization (heptane slurry) if treated with a trialkylaluminum before contacting with MAO. The number of active sites is only about 20% of those in the homogeneous catalyst.[241]

Soga and co-workers used the Lewis acidity of $MgCl_2$ to fix the metallocene complex $Cl_2Si(Ind)_2ZrCl_2$ (**8**).[242] Activated by MAO or Al(*i*-Bu)₃, this catalyst

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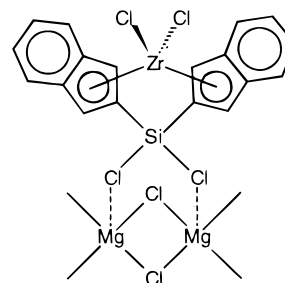
polymerizes propylene to isotactic polypropylene, but with an activity about 100 times less than that of $Me_2Si(Ind)_2ZrCl_2$—MAO. The $Me_2C(Cp)(Flu)ZrCl_2$—MAO—$MgCl_2$ catalyst was also used in the syndiospecific polymerization of propylene at 20 °C; in this case, the catalyst activity was somewhat higher than that of the homogeneous catalyst with less atactic product formed.[243]

B. Zeolites

Zeolites have begun to attract more interest as supports for single-site catalysts. Unlike silica, with its amorphous structure and wide distribution of pore sizes, zeolites have more regular structures, pore sizes, and supercages. Because the zeolite counter-cations (Na⁺, H⁺, NH₄⁺) can be ion exchanged, the possibility exists of electronically "tuning" the support.

The faujasite zeolite NaY can be treated with MAO or AlMe₃, then with Cp_2MCl_2 (M = Ti, Zr) to form the catalyst.[244] There is no activity in MAO-activated catalysts below Al/Zr = 186 and activity is negligible when AlMe₃ is used. Catalyst activities are lower than the homogeneous analogues, but the polymer molecular weights are higher.

Table 7. Ethylene Copolymerizations Using Zirconocenes Supported on HY Zeolite

catalyst	comonomer	activity (kg/mol·h·bar)	mol wt	% olefin
Cp$_2$ZrCl$_2$−MAO	1-hexene	652	7 000	20
Cp$_2$ZrCl$_2$−MAO−HY	1-hexene	228	63 000	8
Cp$_2$ZrCl$_2$−MAO	4-MP-1[a]	1160	3 000	8
Cp$_2$ZrCl$_2$−MAO−HY	4-MP-1[a]	270	25 000	2
Cp$_2$ZrCl$_2$−MAO	1-octene	616	9 000	16
Cp$_2$ZrCl$_2$−MAO−HY	1-octene	218	59 000	7
Cp$_2$ZrCl$_2$−MAO	1-dodecene	578	10 000	13
Cp$_2$ZrCl$_2$−MAO−HY	1-dodecene	196	68 000	5
(Ind)$_2$ZrCl$_2$−MAO	1-hexene	450	21 000	4
(Ind)$_2$ZrCl$_2$−MAO−HY	1-hexene	196	40 000	<1
Et(Ind)$_2$ZrCl$_2$−MAO	1-hexene	468	15 000	36
Et(Ind)$_2$ZrCl$_2$−MAO−HY	1-hexene	278	22 000	36
Et(Ind)$_2$HfCl$_2$−MAO	1-hexene	36	81 000	16
Et(Ind)$_2$ZrCl$_2$−MAO−HY	1-hexene	17	132 000	16

[a] 4-MP-1 = 4-methyl-1-pentene.

Dealumination of NaY by NH$_4$SiF$_6$ leads to a gradual decrease in total surface area and micropore volume, but an increase in the external surface area and Si/Al ratio. The gradual dealumination of NaY leads to an increase in activity of a supported Cp$_2$-ZrCl$_2$−MAO catalyst, though again the activity was lower and the polymer molecular weights higher than those of the homogeneous analogue.[245] Similar trends were observed in the conversion of NaY to HY by treatment with (NH$_4$)$_2$(SO$_4$).[246] Sodium mordenite has a higher Si/Al ratio than the Y zeolites and affords the highest catalyst activity.

The copolymerization of ethylene with 1-olefins catalyzed by homogeneous Cp$_2$ZrCl$_2$−MAO catalysts and catalysts supported on HY zeolite shows a loss in activity on heterogenization, an increase in molecular weight, and a decrease in comonomer incorporation (Table 7).[247] The *ansa*-metallocenes Et-(Ind)$_2$MCl$_2$ (M = Zr, Hf) display no attenuation of comonomer incorporation. The authors hypothesize that the smaller metallocenes are in the pores of the zeolite, into which diffusion of the comonomer is difficult, and the *ansa*-metallocenes, not adsorbed inside the pores, are located on the exterior and are therefore more accessible to comonomer.

To accommodate these larger metallocenes and polymerize larger monomers such as propylene, investigators have turned to the mesoporous molecular sieves MCM-41 and VPI-5. An X-ray absorption fine structure, extended (EXAFS) analysis of Et-(Ind)$_2$ZrCl$_2$−MAO catalyst shows that the indenyl framwork remains intact after supporting. No Zr−Cl bonds are observed but the presence of a Zr−C bond was suggested.[248] In the polymerization of propylene[244b,249] the melting point of the polymer is higher than that produced from the homogeneous analogue, though the catalyst activity suffers somewhat. Addition of AlMe$_3$ as a scavenger depresses catalyst activity as well.[249a] In the oligomerization of ethylene and propylene by Et(Ind)$_2$ZrMe$_2$, the alumoxane is best produced by in situ hydrolysis of AlMe$_3$ by the silanol groups of MCM-41; attempts to use commercial MAO resulted in insufficient adsorption of the aluminum cocatalyst for significant catalyst activity.[250]

C. Clays

Clays such as montmorillonite, hectorite, and mica have also been employed as carriers for single-site catalysts. Impregnating an aqueous suspension of clay particles averaging 10 μm with Brønsted acids such as HNMe$_2$Ph$^+$, drying, and reacting with a Cp$'_2$-ZrCl$_2$−AlR$_3$ mixture affords an active catalyst for olefin polymerization.[251] Catalyst activities are increased when longer-chain ammonium cations such as HNMe$_2$(n-C$_{18}$H$_{37}$)$^+$ are used.[252] The alkylaluminum acts only as an alkylating agent for the metal component: active catalysts are obtained when Cp$_2$-ZrMe$_2$ is contacted with clays impregnated with tertiary ammonium cations without further recourse to alkyating agents or scavengers.[253]

Investigators at Mitsubishi have taken another approach to using clay supports. Montmorillonite, vermiculite, and hectorite were allowed to react with AlMe$_3$, followed by a Cp$_2$ZrCl$_2$−AlMe$_3$ mixture.[254] The catalyst activity is proportional to the pore volume of the support. Ion-exchange reactions of montmorillonite with a variety of metal salts and mineral acids were used to modulate the activity of catalysts for ethylene[255] or propylene[256] polymerization. The treated support is heat-dried or spray-dried before contacting with a metallocene−AlR$_3$ mixture. Mixtures of mica and smectite afford catalyst and polymer particles of greater bulk density than does mica alone or mica mixed with silica.[257] Mixing TiO$_2$ with Me$_2$Si(H$_4$−Ind)ZrCl$_2$−AlEt$_3$ on HNO$_3$-treated smectite is reported to reduce adhesion of the polymer particles to the reactor wall.[258]

Comparing syndiotactic polypropylene from Ph$_2$C-(Cp)(Flu)ZrCl$_2$−MAO as a homogeneous catalyst and supported on silica and HY zeolite, the activity of the zeolite-supported catalyst was lower than that from the homogeneous catalyst or the catalyst supported on silica, but the syndiotacticity (82−83% rrrr pentads) was higher than the silica-supported catalyst (77.5%) and approximately equal to that from the homogeneous catalyst (83%).[259]

D. Polymers

Porous polyethylene powder, either by itself[260] or impregnated with Al(OEt)$_3$,[261] acts as a carrier for

metallocene–alumoxane catalysts for ethylene or propylene polymerization and copolymerization. Granulated polypropylene was used as the support for a $Me_2Si(H_4-Ind)_2ZrCl_2$–MAO catalyst to produce granular elastomer in the gas-phase copolymerization of ethylene and propylene.[262] A prepolymerization step was added in the bulk-monomer polymerization of propylene by a $Me_2Si(Me_3Cp)_2HfCl_2$–MAO catalyst on polypropylene; no scaling on the reactor walls was observed.[263] A $Me_2Si(Ind)_2ZrCl_2$–MAO catalyst supported on polypropylene granules loses none of its activity in propylene polymerization even after 2 months storage.[264]

Polymerization of propylene by an unsupported $Me_2Si(2-MeInd)_2ZrCl_2$–MAO catalyst results in extensive sheeting on the walls and stirrer of the reactor. When the same catalyst is supported on porous powdered high-density polyethylene, isotactic polypropylene, or nylon granules, morphologically uniform product is produced without fouling.[265] It has also been suggested that spray-drying microparticles of polystyrene formed in an emulsion polymerization agglomerate into regular macroparticles which can be used as supports for metallocene catalysts.[266] Styrene and divinylbenzene (DVB) were copolymerized in the pores of silica using AIBN as an activator. This polymer–silica support was treated with MAO, then $Me_2Si(2-Me-4-PhInd)_2ZrCl_2$ to form a catalyst for propylene polymerization.[267]

Polymers with polar groups can also be used as supports for single-site catalysts. Cross-linked polystyrene which has been chloromethylated, or acylated with CH_3COCl–$AlCl_3$ then reduced with $NaBH_4$ (Scheme 35), functions as a support for $Et(Ind')_2ZrCl_2$–

Scheme 35
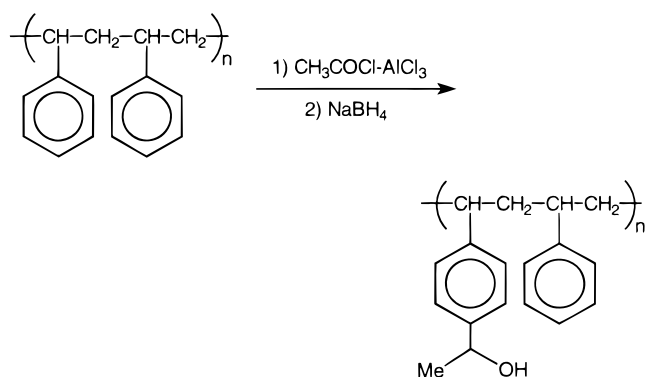
MAO catalysts (Ind′ = Ind, H_4–Ind).[268] In this study, unfunctionalized polystyrene or functionalized polystyrene with insufficient cross-linking (ca. 4% DVB) gave inferior activities and extensive reactor fouling.

With a Cp_2ZrCl_2–MAO catalyst, the nature of the functional group had a profound influence on the molecular weight of the ethylene-1-hexene polymer produced, ranging from a melt index (a measurement of molecular weight inversely proportional to M_w) of 1.9–1500 (Table 8).[269] When the metal component is $(n-BuCp)_2ZrCl_2$, the dramatic differences in molecular weight are largely moderated.[270]

Styrene, DVB, and acrylamide can be copolymerized using an AIBN initiator to form a functionalized terpolymer. This support is unreactive toward Cp_2-

Table 8. Ethylene Polymerization by Zirconocenes Supported on Cross-Linked Polystyrenes

metallocene	support	activity (g/g of cat·h·100 psi $C_2^=$)	melt index
Cp_2ZrCl_2	cross-linked PS	810	1.9
Cp_2ZrCl_2	hydroxy-PS	490	430
Cp_2ZrCl_2	acetoxy-PS	560	1500
Cp_2ZrCl_2	silica	500	34
$(n-BuCp)_2ZrCl_2$	acetoxy-PS	1000	1.0
$(n-BuCp)_2ZrCl_2$	cross-linked PS	920	0.52
$(n-BuCp)_2ZrCl_2$	silica	310	0.38

$ZrCl_2$, but forms a supported activator when contacted with MAO. This catalyst copolymerizes ethylene and 1-octene to a copolymer little different in its comonomer distribution from that prepared using a homogeneous catalyst.[271]

Porous acrylonitrile–DVB copolymer further reacted with diamines or triamines provides a support for Cp'_2ZrCl_2–MAO catalysts.[272] The catalyst activity rivals that of silica-supported analogues and no adhesion of polymer to the reactor walls or stirrer was observed. Polypropylene grafted with maleic anhydride allowed to react with MAO acts as a support for a variety of metallocenes.[273] The number of gels in the polymer is lower than when silica is used as the carrier. Porous vinylpyridine–DVB[274] and poly(vinyl chloride)[275] have also been reported as suitable support materials for metallocene catalysts.

Alt and co-workers used poly(methylsiloxane) microgels as substrates for supporting MAO (Scheme 36).[276] These supports are amenable to functional-

Scheme 36
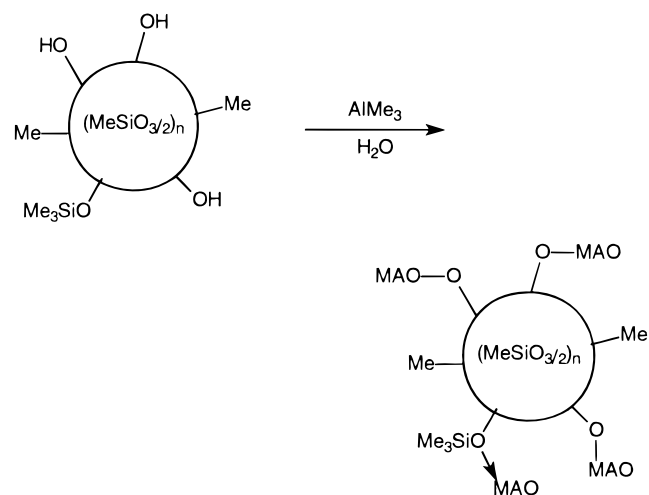
ization through surface $-SiHMe_2$ groups, thus changing the properties of the support and ultimately the catalytic performance.

E. Miscellaneous Supports

Cyclodextrins treated with MAO or $AlMe_3$ serve as supports for Cp_2ZrCl_2–$AlMe_3$ or Cp_2ZrCl_2–MAO catalysts in ethylene polymerization.[277] Additional alkylaluminum ($AlMe_3$, $AlEt_3$, or MAO) is needed to obtain meaningful activity from the catalyst. Polystyrene is formed when Cp^*TiCl_3 is the metal component. Talc treated with MgR_2 complexes, then with

n-butanol is contacted with Cp_2ZrCl_2 to form a supported metallocene. This is activated by MAO in an isobutane slurry for the polymerization or copolymerization of ethylene.[278]

Hollow $MgCO_3$ and $CaCO_3$ particles, either untreated or treated with alkylaluminums, were used as carriers for metallocene−MAO catalysts in ethylene[279] and propylene[280] polymerizations. *Rac*-Me_2Si-$(Me_3Cp)_2HfCl_2$ and $[HNMe_2Ph][B(C_6F_5)_4]$ can be cosupported on $CaCO_3$ and activated by $Al(i\text{-}Bu)_3$ to form an active catalyst for the isotactic polymerization of propylene.[281]

Fillers and pigments are added to polyethylene in the extrusion stage to change the color, stiffness, or magnetizability of the polymer. These same fillers−dyes, glass, ceramics,[282] or metals[283]−can function as supports for metallocene−MAO catalysts, improving the uniformity of filler distribution through the polymer.

XIV. Heterogeneous Single-Site Catalysts without Carriers

MAO is commercially available as a solution in toluene or aliphatic hydrocarbons. The solvent can be evaporated to produce a white pyrophoric solid that can be used as both a cocatalyst and a support. Evaporating and drying toluene solutions of MAO under high-shear conditions ensures that a particulate solid is formed.[284]

Finely divided particles of MAO are precipitated from a toluene solution by addition of *n*-decane followed by evaporation. Suspension of these particles in decane followed by reaction with toluene solutions of Cp'_2ZrCl_2 ($Cp'_2 = Cp_2$[285] or $Et(Ind)_2$[286]) affords a solid catalyst which can be used in solution or gas-phase polymerization processes using ethylene or propylene as the monomers. Solids also separate from a toluene solution of MAO on addition of an equal volume of hexane or isobutane.[287] Insoluble gels in toluene solutions of MAO, ordinarily a nuisance, can be filtered off, resuspended in aliphatic hydrocarbons, and reacted with metallocene dichlorides to produce active catalysts for olefin polymerization without reactor fouling.[288]

Alumoxane solids are precipitated from mixtures of toluene and aliphatic hydrocarbons by addition of methylboroxine or methoxyboroxine,[289] catechol borane,[290] and organic peroxides and carbonates.[291] Reaction with metallocene dichlorides affords a catalyst for olefin polymerization in an isobutane slurry. Cross-linking agents such as *p*-hydroquinone[292] and α,ω-diols such as 1,6-hexanediol[293] also precipitate MAO from toluene. In the former case, activation of $Et(Ind)_2ZrCl_2$ or Cp_2ZrCl_2 only occurred when additional trialkylaluminum was added.

In the presence of an emulsifier, water and $AlMe_3$ react in hexane to form MAO particles about 5−20 μm in diameter. When contacted with metallocene dichlorides, solid catalysts are formed which give good particle morphology and high bulk density in hexane−slurry polymerizations of ethylene or bulk monomer polymerization of propylene.[294]

In fact, it is not necessary to isolate solid MAO particles to achieve uniform polymer morphology. A precontacted metallocene−MAO catalyst can be atomized into a stirred-bed[295] or fluidized-bed[296] gas-phase reactor to give uniform particles of good bulk density. In the latter case, the catalyst is sprayed into the reactor into a particle-lean zone such as just above the distributor plate or in the expansion section at the top of the reactor. The catalyst solution, at least part of which consists of a highly volatile compressed or supercritical fluid such as ethane, is injected into the reactor using a spray nozzle.[297]

In solution, a metallocene−MAO mixture can be prepolymerized at low temperature (10−25 °C) and pressure to form catalyst-impregnated polymer particles. These are then polymerized in a second step at more demanding conditions to form the final polymer product.[298] The use of ultrasonic irradiation has been claimed to aid the prepolymerization of a $Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind)_2ZrCl_2$−MAO catalyst by propylene.[299] Addition of polyisobutylene as a viscosity modifier to a Cp_2ZrCl_2−MAO mixture in the prepolymerization process aids in the recovery of the polymer-supported catalyst.[300] Aging a toluene solution of $Me_2Si(Ind)_2ZrCl_2$ and MAO in the absence of daylight before addition to liquid propylene treated with MAO is claimed to give polypropylene particles with narrow particle size distribution.[301] Ethylene, propylene, and 1-butene are terpolymerized without reactor fouling by a $Et(H_4\text{-}Ind)_2ZrCl_2$−tetraisobutylalumoxane catalyst when the 1-butene fraction in the liquid phase is greater than 15 wt %.[302]

XV. Supported Mixed Single-Site Catalyst

Single-site catalysts characteristically produce polymers with narrow molecular weight and composition distributions. Although this leads to many improvements in physical properties (clarity, impact resistance, environmental crack resistance), it is also widely held that these narrow distribution polymers are more difficult to process and have a higher tendency to melt fracture, especially at higher molecular weights. Controllable broadening of molecular weight distribution and composition distribution using single-site catalyst is therefore desirable for making resins suitable for certain applications.

One method is to carry out the polymerization in a two-reactor system, in which the catalyst polymerizes monomer in a first reactor under one set of conditions (temperature, pressure, comonomer and hydrogen concentration) and then is transferred to a second reactor operating under a different set of conditions. Another method is to use in one or more reactors two catalysts producing polymers of different molecular weight and with different responses to hydrogen and comonomer.

Cp_2HfCl_2 and $Et(Ind)_2ZrCl_2$ were supported on silica individually and together to determine the influence of ethylene and hydrogen pressure on the molecular weight distribution of the polyethylene produced (Table 9).[303] Unimodal and bimodal polymers are produced depending on polymerization conditions. The relative contribution by the zirconium component to the molecular weight distribution curve increases with increasing ethylene pressure and temperature. The hafnium component is more reac-

Table 9. Effect of Ethylene Pressure and H_2 Concentration on Cp_2HfCl_2−$Et(Ind)_2ZrCl_2$−MAO Catalysts

catalyst A	catalyst B	ethylene pressure (kPa)	H_2 (mL)	M_w	M_n	MWD (M_w/M_n)
Cp_2HfCl_2	none	690	0	852 000	425 500	2.00
none	$Et(Ind)_2ZrCl_2$	690	0	89 600	40 000	2.24
Cp_2HfCl_2	$Et(Ind)_2ZrCl_2$	690	0	264 400	64 400	4.13
Cp_2HfCl_2	$Et(Ind)_2ZrCl_2$	140	0	274 000	67 500	4.06
Cp_2HfCl_2	$Et(Ind)_2ZrCl_2$	210	0	366 100	94 100	3.89
Cp_2HfCl_2	$Et(Ind)_2ZrCl_2$	280	0	283 600	63 700	4.45
Cp_2HfCl_2	$Et(Ind)_2ZrCl_2$	340	0	308 200	63 700	4.84
Cp_2HfCl_2	$Et(Ind)_2ZrCl_2$	480	0	389 000	74 400	5.24
Cp_2HfCl_2	$Et(Ind)_2ZrCl_2$	620	0	601 500	93 400	6.44
Cp_2HfCl_2	none	690	220	25 800	12 600	2.05
none	$Et(Ind)_2ZrCl_2$	690	220	90 700	43 200	2.10
Cp_2HfCl_2	$Et(Ind)_2ZrCl_2$	690	220	69 100	24 900	2.78
Cp_2HfCl_2	$Et(Ind)_2ZrCl_2$	690	25	183 700	54 900	3.35
Cp_2HfCl_2	$Et(Ind)_2ZrCl_2$	690	150	78 900	27 600	2.86
Cp_2HfCl_2	$Et(Ind)_2ZrCl_2$	690	180	53 800	5500	9.78

tive toward hydrogen, whereas the zirconium component is relatively unaffected. At high H_2 concentrations, Cp_2HfMe_2 forms the low molecular weight fraction while $Et(Ind)_2ZrCl_2$ forms the high MW fraction, opposite of the contributions in the absence of H_2.

Changes in just the ligand environment around the metal are sufficient to alter the molecular characteristics of the polymer produced. Syndiotactic polypropylene with a broadened molecular weight distribution (4.3−4.7) is formed when propylene is polymerized by $Ph_2C(Cp)(Flu)ZrCl_2$ and $Me_2C(Cp)(2,7-(t-Bu)_2Flu)-ZrCl_2$ co-supported on silica and activated by MAO.[304] In-reactor blends of isotactic and syndiotactic polypropylene are prepared from $Me_2Si(2-MeInd)_2ZrCl_2$ and $Me_2C(Cp)(Flu)ZrCl_2$ on silica treated with MAO.[305] Blends of isotactic and elastomeric polypropylene result from propylene polymerization using a catalyst prepared by adding an $Et(Ind)_2ZrCl_2$−MAO solution to tetra(neophyl)zirconium supported on alumina.[306] Polymers with molecular weight distributions as high as 32 are formed.

In the preparation and operation of mixed single-site catalysts, investigators at Exxon found that the best particle morphology in propylene polymerizations using a $Me_2Si(H_4−Ind)_2ZrCl_2$−$Me_2Si(2-Me-Ind)_2ZrCl_2$−MAO catalyst on silica resulted when a toluene solution of one of the metallocenes was supported first by a pore-filling method and dried, then contacted with a solution of the second metallocene with MAO and dried.[307] Other permutations in catalyst preparation resulted in reactor fouling. Gas-phase copolymerization of ethylene and hexene by a mixed $(n-BuCp)_2ZrCl_2$−$Me_2Si(2-MeInd)_2ZrCl_2$−MAO catalyst could be run with the components together on a silica support, injected into the reactor unsupported, or run with one of the components supported and the other unsupported.[308]

XVI. Comparison of Homogeneous and Heterogeneous Catalysts

It is, of course, most desirable that the molecular characteristics of the products produced from heterogeneous single-site catalysts resemble as closely as possible those of their homogeneous counterparts, mirroring the narrow molecular weight distribution, random distribution of comonomer and, in the case of stereospecific polymerization, high stereoregularity and melting point.

The most notable difference between the two families is catalyst activity. With few exceptions,[29,225−229] in myriad cases, the activity of the supported catalyst is half to a tenth that of the soluble catalyst. This is widely ascribed to diminished diffusion of monomer into the interior pores of the supported catalyst, but may also be the result of fewer active centers present in the heterogeneous variant. Catalyst centers could be deactivated when supported, or may not be generated in the metal−cocatalyst interaction. Tait and co-workers determined that 91% of zirconocene centers were activated by MAO in solution, but when the metallocene was supported on silica, the concentration of active sites generated by MAO was only 9% of the total zirconium supported.[309]

The molecular weight of the polymer is for the most part unaffected or somewhat higher when a single-site catalyst is supported. This suggests that the lower activity of the catalyst is due to a reduced number of active centers; were the propagation rate lower for a supported catalyst, the rate of termination would have to be reduced proportionately or more for these molecular weight observations to hold.

An extensive study of the effect of temperature on propylene polymerization using homogeneous and supported $Me_2Si(2-Me-4,5-BenzoInd)_2ZrCl_2$−MAO catalysts shows that changes in activity, molecular weight, isotacticity, and polymer bulk density were more moderate for the supported catalyst than the solution catalyst.[310] The melting point of i-PP from this metallocene is 147 °C for the homogeneous catalyst, declining to 144 °C when supported. Substituting $[HNMe_2Ph][B(C_6F_5)_4]$ as the activator affords polymer with the same melting point as the homogeneous catalyst.[311] Although the molecular weight of the polypropylene from rac-$Me_2Si(2,4-Me_2-Cp)(3',5'-Me_2Cp)ZrCl_2$−MAO catalyst increases when supported on silica (93 000 to 190 100), the melting point of the polymer is unaffected.[312]

The effect of heterogenization on response to comonomer is unclear. Comparing the composition of ethylene comonomers with 1-hexene or 1-octene, Collins and co-workers noticed a slightly less branched

copolymer when a metallocene–MAO catalyst is supported on sol–gel alumina than when the catalyst was used in solution; they attributed this to greater diffusion barriers for the supported catalyst.[94] No difference was observed in comonomer response toward 5-(*N,N*-diisopropylamino)1-pentene when co-polymerized with ethylene using homogeneous Me₂-Si(Ind)₂ZrCl₂–MAO and the same catalyst supported on silica.[313]

XVII. Other Process Considerations

Heterogeneous single-site catalysts have been run successfully in many large-scale plants using a variety of processes, including slurry, bulk-monomer, and fluidized-bed gas-phase. In the last case, the reactor can be run with hetereogeneous metallocene catalysts using "condensed mode" operation, in which a liquid such as isopentane is injected to run the reactor with at least some liquid present to aid heat transfer, thus improving the capacity of the reactor and the activity of the catalyst.[314] Because single-site catalysts have quite different responses to comono-mer and hydrogen than do conventional Ziegler–Natta catalysts, some care must be taken to avoid reactor fouling and process upsets. For example, AlEt₃ is injected into the reactor as an activator and scavenger for Ziegler–Natta catalysts. With sup-ported metallocene catalysts, the presence of a scav-enger can cause fouling. Either using very small amounts of AlEt₃, operating without added AlEt₃, or stopping addition after startup improves operability and allows for the preparation of copolymers with densities below 0.90 g/cm³.[315]

In transitioning between incompatible Ziegler–Natta catalysts and metallocene catalysts in a fluid-ized-bed gas-phase process, polymerization of the first catalyst must be fully stopped before introducing the second catalyst. Small amounts of a catalyst killer such as water or methanol, either injected directly into the gas stream or added as wet silica, are introduced to deactivate the catalyst in the reactor irreversibly. The second catalyst is added after adjustment of the feed streams.[316] Addition of CO above and below the distributor plate has also been used.[317] Leftover catalyst in addition vessels can be deactivated by heat treatment, followed by exposure to air.[318]

Reactor fouling can be reduced or eliminated by the judicious addition of antistatic agents such as poly-siloxanes,[319] long-chain amines, or 1,2-dimethoxy-benzene. This agent can be added to the catalyst before introducing the catalyst into the reactor[320] or injected as a solution into the polymerizing environ-ment.[321] The technique has also been used for unsup-ported catalysts in a fluidized-bed gas-phase pro-cess.[322]

The molecular weight and density of the polymer produced by a metallocene catalyst in a gas-phase process can be adjusted through the temperature or by injecting trace amounts of agents such as CO, CO₂, Al(*i*-Bu)₃, or acetylene.[323] Addition of acetone or methanol vapor has also been suggested to improve the flowability of the polymer product and prevent blockage of discharge lines.[324]

XVIII. Summary

"Modern Chemistry... is much, and yet it is very little. Much has been accomplished, for chemistry has learned to shrink before no difficulty; little, because what has been accomplished is as nothing compared with what remains to do. 'Tis a fair science, yet she owes much to chance." Honoré de Balzac, *The Quest of the Absolute*, 1831).

This review has attempted to survey the large body of research into supporting single-site catalysts, tracing the development of homogeneous single-site catalysts as they were supported, and used in labora-tory reactors, pilot plants, commercial trials, and full commercial production as highly active catalyst systems which operate efficiently in many different large-scale industrial polymerization processes. The number of announcements of commercial production of polyolefins produced by single-site catalysts has increased rapidly in the past few years. The learning curve continues, though, even into full commercial production: for example, in 1997 Exxon was forced to declare *force majeure* on metallocene polyethylene from its Mont Belvieu, TX, gas-phase polymerization plant.[325]

One area which continues to attract interest is increasing the activity of single-site catalysts when supported, making up some of the deficit from which they suffer compared to their solution-soluble cous-ins. In this vein, Collins recently described in broad terms the synthesis of and polymerization using tethered *ansa*-metallocenes, the activity of which is comparable to a homogeneous analogue; we await full details of catalyst structures and methods of prepa-ration.[326]

Another worthwhile area of endeavor is new sup-port materials, ones which are as "single-sited" as the catalysts they carry. For example, the zeolite carriers discussed above have more uniform pore sizes and volumes than the amorphous silicas hitherto widely used. The importance of single-site catalysts lies in the ability to characterize them comprehensively and alter them in a rational fashion in order to enhance desired polymer properties; extending this degree of understanding and control to their interaction with supports and their performance in numerous polym-erization processes could only be beneficial.

XIX. References

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