“Bound but Not Gagged”—Immobilizing Single-Site α-Olefin Polymerization Catalysts

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1. Introduction

The demand for low-cost high-performance materials has seen polyolefins’[1] share of total polymer production increase from approximately 30% to 60% over the last 30 years (1970[2] to 2002[3]). Polyolefins are finding new applications, replacing more expensive natural and synthetic materials, as well as materials or processes that are associated with health and environmental risks. This growth is expected to continue for the foreseeable future, because few materials can match their versatility and economy.[4]

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John Severn was born in 1971 in Doncaster, U.K. He attended the University of Sussex, where he received his B.Sc. (Hons, 1994) and D.Phil. (1998), under the supervision of Prof. M. F. Lappert. Since then he has worked as a postdoctoral researcher at Eindhoven University of Technology, The Netherlands, on several projects related to the immobilization of single-site α-olefin polymerization catalysts. His initial project with Dr. R. Duchateau and Prof. R. A. van Santen focused on silsesquioxanes as soluble models for silica supports and was funded by DSM Polyolefins (1999–2000). He then worked with Dr. J. C. Chadwick investigating supported activators based on $MgCl_2$ for the Dutch Polymer Institute (2000–2004). Finally, he worked with Prof. G.-J. Gruter developing high-throughput α-olefin polymerization workflows in conjunction with Avantium Technologies (2004–2005). At present he is a researcher at Borealis Polymers Oy, Porvoo, Finland, working on single-site polyethylene polymerization catalysts projects.

John Chadwick was born in 1950 in England and received his B.Sc. and Ph.D. degrees from the University of Bristol, after which he moved to The Netherlands, joining Shell Research in Amsterdam in 1974. Following the formation of Montell Polyolefins in 1995, he transferred from Shell to the Montell (now Basell) research center in Ferrara, Italy, where he was involved in fundamental Ziegler–Natta catalyst R&D. Since 2001, he has been at Eindhoven University of Technology on full-time secondment from Basell Polyolefins to the Dutch Polymer Institute (DPI), and he is DPI Program Coordinator for Polymer Catalysis and Immobilization. His main research interests involve heterogeneous olefin polymerization catalysis, including both Ziegler–Natta and immobilized single-site systems, and the relationship between catalyst and polymer structure.

Rob Duchateau (born 1966) grew up in Groningen, The Netherlands. After attending the University of Groningen, where he received his B.S. in chemistry in 1989, he joined the group of Prof. S. Gambarotta at the University of Ottawa (Canada) for one year, where he worked on low-valent titanium chemistry. He then returned to The Netherlands, where he did his Ph.D. on “Ancillary Ligand Effects in Organoyttrium Chemistry” in the group of Prof. J. H. Teuben at the University of Groningen. He continued his academic carrier by joining the group of Prof. M. Bochmann at the University of Leeds (U.K.) for one year as a postdoc working on zwitterionic olefin polymerization catalysts. In 1996 he went to the catalysis group of Prof. R. A. van Santen at the Eindhoven University of Technology to work as a research associate on immobilization of homogeneous olefin polymerization catalysts and silsesquioxane chemistry. Since July 2002, Duchateau has been Assistant Professor in the polymer chemistry group of Prof. C. E. Koning at the Eindhoven University of Technology and has been running his own research group in the field of catalytic olefin polymerization and developing new catalytic routes to engineering plastics and resins from basic (renewable) feedstocks.

Nic Friederichs was born in 1962 in Schinveld, The Netherlands. In 1986 he received his bachelor’s degree in organic chemistry at the Zuidlimburgse Laboratorium School in Sittard, The Netherlands, and in the same year he joined DSM as a research chemist on the development of both Ziegler and metallocene catalysts for DSM’s LLDPE solution process and for the slurry UHMwPE process. In 1989 he received his bachelor’s degree in chemical engineering. From 1996 until 2000, he was project coordinator for the pilot plant research for DEX-PLASTOMERS for the introduction of metallocene catalysts in the high-temperature solution process, targeting the production of ethene–octene plastomers. In 2000, he became project coordinator for Advanced Polyolefin Catalysis in the area of polyethylene, polypropylene, and EPDM at DSM Research. Since 2002, he has been project coordinator for Advanced Catalysis for SABIC–Europe and has been involved in the development and optimization of both conventional Ziegler–Natta and single-site catalysts for polyethylene and polypropylene.

The astronomical numbers involved are truly hard to imagine; for example, it is estimated that approximately 110 million tons of polyolefins (70 million tons of polyethylene (PE) and 40 million tons polypropylene (PP)) will be produced in 2005.[4a,5] If we approximate the density of polyolefins to be 1 g/cm^3, then 1 ton would have a volume of 1 m^3. Khufu’s great pyramid at Giza has an estimated volume of 2.5×10^6 m^3. We could, therefore, build 44 polyolefin pyramids each year. Couple to this a current market price in the region of 1000 euro per ton,[6] and it is easy to understand the scientific, social, and economic impact these polymers have.

Their impact and success has been intimately linked to the implementation of revolutionary discoveries and improved basic understanding within the fields involved (polymer science, process technology, catalysis, inorganic and organometallic chemistry).[7] As a result, unique mutually beneficial collaborative research, between industry and academia, as well as among the various scientific disciplines, has been established, ensuring that the study of polyolefins remains an intellectually stimulating field of research.

Breakthroughs in polymer catalysis by the likes of Ziegler,[8] Zletz,[9] and Hogan and Banks[10] revolutionized the polyolefin industry. Their scientific contributions led to the successful commercial production of HDPE, while the seminal work of Natta[11] on the stereoselective polymerization of propylene pioneered its commercialization. The following 50 years of research and development has simplified and maximized the production process in terms of resources and energy savings. Several generations of highly active and stereospecific Ziegler–Natta catalysts have eliminated the need for removal of catalyst residue (de-ashing) and atactic polypropylene and in some cases the whole pelletization steps.[12] In general, the polymers produced by these heterogeneous catalysts are themselves heterogeneous in nature. Multiple catalytic sites lead to polymer resins with broad molecular weight distributions and nonhomogeneous comonomer incorporation. Heterogeneous catalysts are also restricted in terms of stereocontrol and ability to incorporate comonomers containing functional groups. Despite these shortcomings, traditional heterogeneous catalysts are expected to remain the dominant catalytic route for the production of polyolefins, particularly for large-volume, low-cost resins.[2] In fact, overcoming these shortfalls continues to be a field of intense industrial research, and as a consequence, heterogeneous Ziegler–Natta catalysts with increasing single-site characteristics are being developed.

The evolution of single-site catalysts started when Breslow[13] and Natta[14] combined Cp_2TiCl_2 with alkylaluminum compounds, polymerizing ethylene with low activity and stability. These systems did, however, prove to be effective models for the mechanistic study of heterogeneous Ziegler–Natta catalysts.[15] Further studies on the abovementioned titanocene[16] and analogous zirconocene[17] systems demonstrated an enhancement in activity upon addition of water. This serendipitous discovery led to a revolution in the early 1980s when Kaminsky and Sinn combined metallocene catalysts with methylaluminoxane (MAO), the latter proving to be a much more potent activator for single-site catalysts than traditional alkylaluminum complexes, AlR_nCl_{3-n}.[18] This discovery re-ignited scientific interest in the field of single-site catalysis, with metallocenes[19] at its vanguard. The ability to tailor the steric and electronic environment of the ubiquitous cyclopentadienyl moiety, allied with developments within the field of complex activation,[20] such as the perfluoroaryl group 13 complexes[21] has influenced activity, molecular weight, comonomer incorporation,[22] stereoselectivity,[23,24] polymer microstructure,[24] and macroscopic properties.[25]

The search for new catalysts with interesting properties has led to the development of alternative ancillary ligands. These non- or post-metallocene single-site catalysts,[26] exemplified by early transition metal constrained geometry,[27] phenoxyimine (FI),[28] boraaryl,[29] amino-ether,[30] phosphinimide[31] catalysts, and late transition metal α-diimines[32] and bis(imino)pyridine[33] complexes, have opened the door to new and interesting polymer resins. The late transition metal systems have been of particular interest. In the α-diimine systems unique polymer microstructures such as short chain branching (SCB) have been produced without the need for comonomer. The extent and type of short chain branching can be controlled via modification of the α-diimine ligand, the metal, or the polymerization conditions. In the bis(imino)pyridine complexes, such tuning can result in catalytic polymerization or linear α-olefin oligomerization.[33e,f] Additionally, late transition metals have a low oxophilicity, which provides a higher tolerance to polar groups, leading to the opportunity to polymerize polar monomers[34] and operate in unconventional diluents such as aqueous emulsions[35] or supercritical CO_2.[36]

The commercialization of single-site technologies started just over a decade ago. It is now well established and regarded as a crucial technology for the future development of the polyolefin industry.[37] As a result, considerable research and investment, estimated by some to be in the region of $4 billion, has been undertaken in all areas of single-site α-olefin polymerization catalysis.[38] Commercialization, however, has been slower than first anticipated. Some of this delay was due to early processing difficulties and higher catalyst costs, a major part of which was the cost of cocatalysts such as MAO. Nevertheless, these processing difficulties have been overcome and the price of cocatalyst continues to fall as larger production capacity benefits from economies of scale.

A major reason for the slow penetration of single-site catalysts has been the intense legal wrangling over intellectual property. Essentially all major developers of these technologies have been involved in legal suits spanning continents. Legal jurisdictions and protracted litigation impeded third party licensing until clear ownership of the catalyst, process technologies, or both could be determined. However, the resolution of lingering legal issues, by settlement, judgment, or merger, and the increased collaborative agreements and third party licensing have seen commercialization of single-site polyolefin catalysts accelerate.[3,37]

A number of commercial, solution-based polymerization processes exist for single-site catalysts. These processes rely on the polymer either being soluble in the polymerization medium or operating at a temperature above the melting point. The latter, however, places arduous requirements on the catalyst in terms of thermal stability and the ability to achieve high molecular weights and stereoselectivity at elevated temperatures. As a result, solution-based processes are predominantly used for the lower crystalline polymers such as ULDPE, VLDPE, EPDM, elastomers, and plastomers.[39] However, developments in catalyst design, aided by the implementation of high-throughput experimentation, have eluded to the possibility of commercial solution polymerization of polymers having increased crystallinity such as *i*PP.[40]

At present, however, the vast majority of production capacity for high-density or crystalline polyolefins (HDPE, LLDPE, *i*PP, and *s*PP) is based on gas- or slurry-phase processes. These processes, typically employing traditional heterogeneous catalysts, have been refined over the last 50 years and are extremely efficient and well-understood technologies.[5a] All of these processes rely on the catalyst particles forming morphologically uniform polymer particles of the appropriate size and shape for continuous trouble-free operation. Such controlled particle growth eliminates reactor fouling and produces polymer particles whose shape mirrors the starting catalyst particles but that are at least 20 times their size with a relatively high bulk density. For single-site catalysts to successfully exploit the enormous process resource that gas-, slurry−bulk-, and slurry-phase polymerizations represent, they must not only fulfill the same particle-forming requirements as traditional heterogeneous catalysts but also retain their single-site characteristics, such as high activity, narrow molecular weight distributions, stereoselectivity, and uniform comonomer incorporation. The realization of all these criteria is a difficult challenge. Although an increasingly large number of successful examples of supported single-site catalysts have been commercialized,[41] in depth understanding of the processes occurring on the support surface is lacking. The development of new support/catalyst/cocatalyst combinations remains a fruitful field of research.

Immobilized single-site polymerization catalysis has been the subject of several reviews varying in both length and scope.[42] To date the only comprehensive review of this discipline has been performed by Hlatky.[43] This 2000 publication, covering developments up until 1998, proved both invaluable and inspirational to many in the field, the current authors included. The six years since then, however, have seen an even greater research and development effort in the field of immobilized single-site polymerization catalysis, spurred on by industrial challenges and scientific developments. With this review, we aim to comprehensively cover the substantial body of research within this field, focusing particularly on the requirements, challenges, protocols, and ingenious solutions to the successful immobilization of single-site catalysts.

2. Background

2.1. Source Material

The reference literature that forms the basis of this review was extracted from searches on numerous online databases, in particular, the excellent SciFinder 2004 search engine with patent material taken from Espacenet, the European Patent Offices online database. Because successful immobilization of single-site α-olefin catalysts is primarily of industrial importance, the majority of literature cited in the review will be in the form of patents or published patent applications where the immobilization rather than the precatalyst is the state of the art. When a published patent application has appeared as a U.S. Patent, the U.S. Patent number will invariably be cited; one should also remember that the references cited within refer to the publication date and not the filing date; therefore, detailed discussions of priority will not be undertaken. Additionally, an abundance of Japanese patents exist in this field; regrettably, only those that have an English language version, Kokai with unambiguous abstracts as to the invention within, or previously translated patents will be cited.

2.2. Polymerization Processes

The push to immobilize single-site polymerization catalysts on an inert carrier is to utilize them in slurry- or gas-phase processes, which are the major metal-catalyzed process technologies for the production of polyolefins. It is important to understand the range of processes and, in particular, their scope and limitations regarding product range capabilities when immobilizing a single-site catalyst. It is also important to understand the crucial role that development within the field of process technology has played in the success of polyolefins. This section provides a brief overview of the major polyolefin process technologies.[44]

Commercial production of polyolefins utilizes four main process types: high-pressure, solution-phase, gas-phase, and slurry-phase. Each process is able to produce particular resins with certain performance advantages. The oldest of these methods is the high-pressure production of low-density polyethylene (LDPE) by free radical polymerization, and although its invention dates back more than 70 years, it continues to be an economically viable process.[45] The polymerization is carried out in an autoclave or tubular reactor, generally operates at pressures of 1000−3000 bar and a temperature of 150−300 °C, and is initiated by oxygen or more commonly peroxide. LDPE resins contain both long- and short-chain branches, which can be varied to some extent depending on whether the resins are produced in an autoclave or tubular reactor. No additional diluent is required, and films of exceptional clarity, having no catalyst residues and low volatile organic contents (VOCs), are produced. Additionally, an advantage is the ability to copolymerize a variety of polar functional monomers to produce interesting resins such as poly(ethylene-*co*-vinyl acetate) (EVA).

Solution polymerization processes for polyolefins were first used industrially for Ziegler−Natta catalysts. Though mostly replaced by slurry- and gas-phase processes, several solution-based technologies still exist for the production of polyethylene (homo- and copolymers).[46] Typically, the process operates in a continuous stirred tank reactor (CSTR) using an aliphatic hydrocarbon as solvent. The reactions are typically adiabatic processes operating at temperatures of 130−250 °C, sufficient to keep the polymer in solution. Short residence times (1−10 min) lead

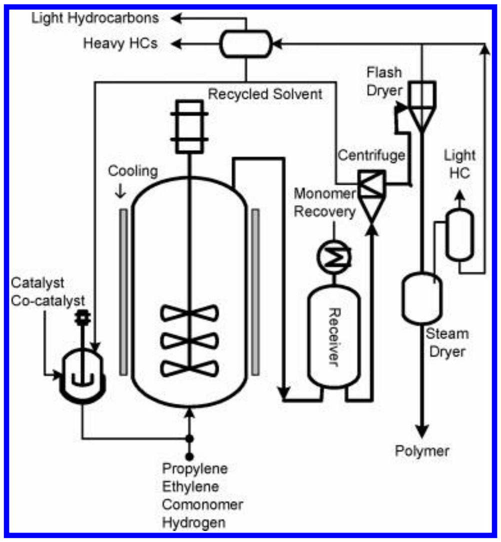


Figure 1. Schematic representation of the CSTR polymerization process.

to rapid grade transitions, a major advantage when compared to the other metal-catalyzed processes. Following polymerization, the hot polymer solution is discharged from the reactor, and the solvent is vaporized and recycled, a high-energy-consuming process and hence a cost disadvantage. Additionally, to maximize the reactor throughput, precooling of the reactor feed to temperatures below 0 °C is commonly employed. Another major disadvantage is that solution viscosity increases rapidly with molecular weight, making it difficult to achieve high molecular weight polymers in this process. Solution processes are, however, extremely flexible and operate best for polymer resins having a low softening point, high solubility, or both. They are capable of producing polyethylene in the density range of 0.86−0.96 g/cm^3, in particular, LLDPE, VLDPE, ultra-low-density polyethylene (ULDPE), EPDM, and plastomers, where the very homogeneous nature of the process benefits random comonomer incorporation. Additionally, the commercial production of ethylene-*co*-1-octene polymer resins is almost exclusively limited to the solution process.

2.2.1. Slurry

Traditional slurry polymerization reactors are CSTRs employing heterogeneous catalysts and typically operate at temperatures around 70−90 °C and pressures of 2−24 bar with an aliphatic hydrocarbon (hexanes) as a diluent, Figure 1. The high miscibility and solvent-induced swelling that low-molecular weight or low-density polyethylene has in such diluents, along with the limited solubility of the chain transfer agent, hydrogen, lead to a narrow product range capability.

Because the polymerization of α-olefins is an inherently exothermic process, the heat generated has to be effectively removed from the growing polymer particle; otherwise, "hot" spots may form leading to a softening of the polymer. The subsequent formation of agglomerated polymer particles or chunks may cause blockages, while sheeting of the reactor walls forms an isolating layer between the reaction medium and the cooled wall, further aggravating the problem. Slurry CSTRs are typically fitted with a cooling jacket to remove the heat of polymerization, but this alone is usually an insufficient means of cooling. In these reactors, additional cooling is provided by passing the slurry through external zones consisting of a heat exchanger or a section for vaporization and condensation of the diluent. Heat transfer from the polymer particles to the diluent and from the diluent itself is, however, more effective than that in a gas-phase process, leading to a higher capacity per volume, shorter catalyst residence times (0.5−1 h), and quicker grade transitions. Generally, these reactor systems are simple and robust technologies. They are, however, relatively expensive to build and operate, because removal of the "heavy" solvent from the polymer via centrifugation or other techniques and subsequent recycling must be undertaken.

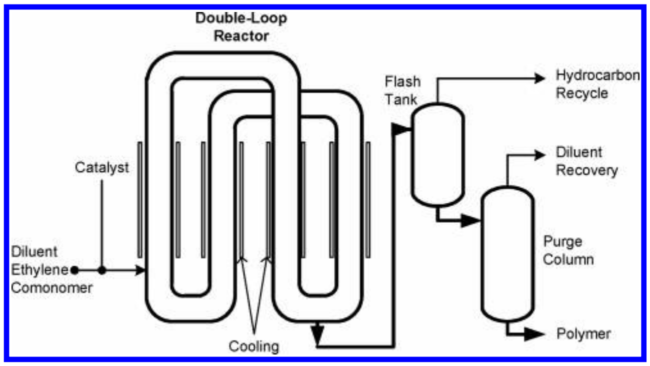


Figure 2. Schematic representation of the Phillips (double) slurry loop process.

Slurry-phase polymerization can also be performed in a slurry loop reactor. The reactors may have horizontal or vertical configurations and can consist of multiple loops. An example of this is the ubiquitous Phillips slurry loop process, Figure 2, the largest of which is Phillips-BP/Solvay "Unit 1799" at Cedar Bayou, TX, with a capacity of 350 kton/yr.[47]

In slurry loop reactors, the typically long circular pipes are cooled via a jacket and as a result of the loop's high surface area-to-volume ratio very efficient cooling is achieved. In this case polymerization occurs in a "light solvent" (isobutane), the polymer being driven around the loop by a large capacity pump. Although the problem of solubility and solvent-induced swelling of the polymer particle is still a problem with a light solvent, it is considerably less so than in the heavy solvents used in CSTR slurry processes. This allows loop reactors to operate between 85 and 110 °C and 30−45 bar. The conditions are chosen to keep the reaction system in the liquid full phase for efficient heat transfer and slurry recirculation. Slurry loops are capable of producing polyethylene products with a density range between 0.93 and 0.97 g/cm^3.

The polymer produced can be extracted continuously, although in general the polymer is removed at intervals from multiple settling legs, where the polymer partially sediments, locally increasing the solid content of the slurry. The polymer is then separated by flashing off the volatile diluent, which is then recycled. Removal of the polymer product from

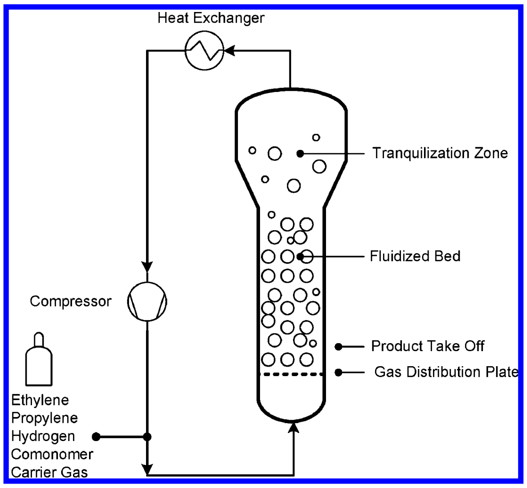


Figure 3. Schematic representation of a gas-phase polymerization process.

the settling legs does, however, present several problems. The polymer is removed periodically through the operation of valve mechanisms, which require frequent maintenance. The dumping of the polymer-rich slurry also interferes with slurry flow within the reactor.

2.2.2. Gas-Phase Polymerization

Gas-phase polymerization processes typically employ either a mechanically stirred or a gas fluidized bed as the polymerization reaction zone. Fluidized bed reactors typically consist of a vertical cylindrical reactor containing a fluidized bed of polymer particles supported or suspended above a perforated plate (fluidization grid or gas distribution plate) by a gas with a velocity high enough to fluidize the bed, Figure 3. However, the velocity also has to be low enough to prevent particle entrainment from the reactor. The fluidizing gas employed comprises the monomer or monomers to be polymerized, an inert carrier gas, usually N_2, and a chain transfer agent such as hydrogen. It is assumed that this fluidizing gas is perfectly mixed and evenly distributed throughout the bed. For polyethylene production, typical operating temperatures are between 70 and 115 °C with pressures of 20−30 bar, and products having a density range of 0.91−0.97 g/cm^3 can be produced.

At the start of the reaction, a bed, consisting of polymer particles similar to the target polymer, is introduced. The bed is then dried with an inert fluidization gas (N_2) prior to the introduction of the polymerization components. The polymerization catalyst can then be added continuously or semicontinuously to the fluidized bed. Such catalysts are usually supported species, which have frequently been subjected to a prepolymerization step. The monomer or monomers are introduced, part of which is polymerized on the bed with unconverted monomer emerging from the reactor as part of a hot gas stream. This mixture of hot gases emerges from the top of the reactor, normally via a zone having a wider diameter than the fluidized bed (velocity reduction zone or tranquilization zone). In this area, the fine particles carried by the gas stream have the opportunity to fall back, under gravity, to the fluidized bed.[48] The polymer produced is then discharged continuously or intermittently via a conduit in the lower portion of the reactor, close to the gas-distribution plate.

Cooling is provided by the fluidizing gas stream, which serves as a heat exchange medium. The gas is recycled to the bed by means of a compressor or blower, via one or more heat exchangers. Additional cooling can be provided by injecting a volatile liquid (e.g., isopentane) into the bed. The evaporative cooling effect, often referred to as operating in the "(super)-condensed" mode, is frequently used for highly active immobilized single-site and traditonal Ziegler−Natta catalysts. If the monomer or monomers are volatile liquids or can be condensed, further evaporative cooling is provided. The volatile liquids that evaporate in the hot fluidized bed form a mixture with the fluidizing gas medium. If the temperature within the heat exchangers is reduced below the dew point, liquid condenses from the gas stream. This liquid is then continuously recycled as liquid droplets carried in the recycle gas stream or is separated from the recycle gas stream and re-injected directly into the bed as fine droplets.

Mechanically stirred gas-phase reactors operate in a similar way to fluidized beds in terms of cooling and recycling of reactor gases. As the name suggests, the main difference is that the gas bed is mechanically stirred above the gas distribution plate by an agitator, in either a horizontal or vertical reaction chamber. In all gas-phase processes, cooling the reaction gas is less effective than cooling a reaction liquid. This leads to a lower capacity per volume reactor than is obtained in a slurry reactor, which in turn leads to longer residence (hours) and grade transitions times. However, due to the efficiency and product flexibility of this process, approximately 60% of all new production plants are based on gas-phase technology, with "world-scale" plants capable of producing 660 kton of polyolefins each year.[49]

2.2.3. Bulk Polymerization

In the manufacture of polypropylene, modern bulk (liquid monomer) and gas-phase processes have largely replaced the earlier slurry processes in which polymerization was carried out in a hydrocarbon diluent. The most widely adopted process for PP is Basell's Spheripol process. Homopolymer production involves a prepolymerization step at relatively low temperature, followed by polymerization in a loop reactor using liquid propylene; random copolymers are produced by introducing small quantities of ethylene into the feed. The prepolymerization step gives a prepolymer particle with the capacity to mechanically withstand or reduce the reaction peak, which occurs on entering the main loop reactor. The addition of one or two gas-phase reactors for ethylene/propylene copolymerization makes it possible to produce heterophasic copolymers containing up to 40% of E/P rubber within the homopolymer matrix.[50]

2.2.4. Recent Developments

Since its inception, the main drivers of applied research and development, within the field of polyolefin process technology have been optimization and

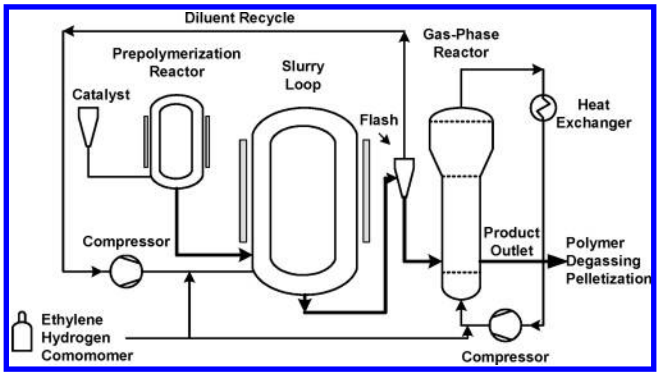


Figure 4. Schematic representation of the Borstar PE process.

cost reduction, while at the same time a drive for quality improvement is present ("quality up−cost down"). Such developments, allied with advancements in catalyst technology have allowed the removal of as much "steel" (columns, evaporators, pumps, etc.) as possible from a process, reducing investment and operational costs. Additionally, for low-cost general-purpose polyolefins, most producers have simplified the process further by developing general grades of polyolefins that replace two or three other grades, reducing the number of grades per process. Recently however, process technology developments have been driven by product versatility and innovation and have allowed the production of value-added products, able to compete in nontraditional polyolefin markets.

The development of the Spheripol process was based on the use of $MgCl_2$-supported Ziegler−Natta catalysts having spherical particle morphology. Further catalyst and process development, including the manufacture and use of catalysts having different degrees of porosity, led to the Catalloy process. This is a highly sophisticated modular technology, based on three mutually independent gas-phase reactors in series. Random PP copolymers containing up to 15% comonomer can be obtained, as well as heterophasic alloys containing high proportions of multimonomer copolymers. The feasibility of producing reactor-grade polymer blends containing up to 65% rubber phase arises from the use of a controlled porosity catalyst and the ability to control the porosity of the growing polymer particle during the early stages of polymerization. Again, prepolymerization is applied to give particles with sufficient mechanical strength to withstand injection into a gas-phase polymerization step.

The development of the Borstar PE process, by Borealis, is a relatively recent development in multireactor processes. The foundation of this process is the utilization of supercritical propane as diluent in the slurry loop reactor. The slurry loop(s) is connected in cascade to a fluidized gas bed reactor, as illustrated in Figure 4. Operating the slurry loop in a supercritical condition provides several advantages over the traditional diluent (isobutane). The solubility of PE drops markedly at the supercritical point of propane, allowing the process to operate at higher temperatures and reduce the risk of reactor fouling. Additionally, higher hydrogen concentrations can be used. As a result the process has a broad product range capability. Utilizing supercritical propane also reduces the phenomena of solvent-induced swelling of the polymer particles. The increase in polymer to diluent density ratio affords an improved sedimentation of the polymer in the settling leg, while its higher compressibility provides less pressure fluctuations in the reactor. These features all contribute to increased throughput.[51]

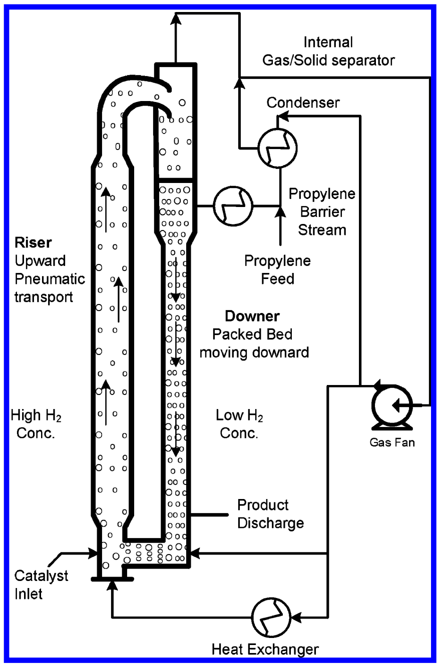


Figure 5. Schematic representation of a multizone circulating reactor gas-phase process.

The use of multiple reactors in series or tandem is now commonplace in the production of polyolefins, providing flexibility in the production of unimodal homo- and copolymers, as well as bimodal and heterophasic resins.[52,53] Multiple reactor technologies are not, however, the only way to produce bimodal PE resins. The recent advances in bimodal catalyst technologies by Univation (Prodigy bimodal catalysts) have provided a route to bimodal resins using a single gas-phase reactor.[54]

The most recent major development in polyolefin process technology has been the introduction of the Spherizone process, based on a gas-phase multizone circulating reactor.[55] In this process, the growing polymer granule is continuously circulated between two polymerization zones: upward, by fast fluidization, in the "riser" leg and downward, by means of gravity in a packed bed, in the "downer" leg. The monomer composition and the hydrogen concentration in the two legs can be different, and multiple short passes of the growing particle between the two zones leads to intimate and effective mixing of very different polymers, Figure 5. For example, it is possible to obtain broad molecular weight distribution even with a "single-center" catalyst.

2.3. Polymer Particle Growth

An important aspect of olefin polymerization using heterogeneous catalysts concerns the characteristics of particle growth during the course of polymerization, taking into account such aspects as mass and

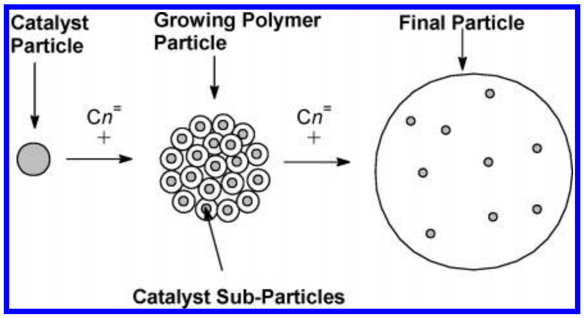


Figure 6. Polymer particle growth.

heat transfer. Ineffective monomer mass transfer can limit the catalyst productivity, while ineffective removal of heat of polymerization from the growing particle in the early stages of polymerization can cause the formation of hot spots, which may in turn lead to catalyst decay. In the absence of prepolymerization, exotherms of up to 20 °C have been measured for individual catalyst particles in the early stages of polymerization.[56]

Various models describing particle growth during olefin polymerization have been developed and have been recently reviewed by McKenna and Soares.[57] It is important that the mechanical strength of the catalyst particle is high enough to prevent disintegration leading to fines formation but low enough to allow controlled progressive expansion during polymerization. As polymerization proceeds, the initial catalyst support becomes fragmented and dispersed within the growing polymer matrix (Figure 6). The morphology of the starting support is replicated in the final polymer so that a spherical support in the size range 10−100 μm will give spherical polymer morphology with particle size generally in the range 100−3000 μm, dependent on the catalyst productivity. Extensive fragmentation and uniform particle growth are key features in the replication process and are dependent on a high surface area, a homogeneous distribution of catalytically active centers throughout the particle, and free access of the monomer to the innermost zones of the particle. In the case of ethylene polymerization, the latter is not always the case, and it is frequently observed that polymer growth starts at and near the particle surface, leading to the formation of a shell of polyethylene around the catalyst particle. This imposes a diffusion limitation, preventing free access of the monomer to active sites within the particle. Polymerization then takes place layer by layer, as the monomer gradually diffuses through the outer layers to the core, resulting in an onion-type internal morphology.[58] This mechanism of particle growth is associated with a kinetic profile in which an initial induction period is followed by an acceleration period, after which, in the absence of chemical deactivation, a stationary rate is obtained. Each polymerizing particle can be considered as a microreactor with its own mass and heat balance.[59] Ethylene polymerization activity can be greatly increased by first carrying out a prepolymerization with propylene, which results in a significant lowering in the monomer diffusion barrier in the subsequent ethylene polymerization.[60] In a further refinement of particle growth models, effects of not only diffusion but also monomer convection have been taken into account, the convection being driven by a pressure gradient created by monomer consumption within the particle.[61]

Serious mass transfer limitations are less common in propylene polymerization. Studies with $MgCl_2$-supported Ziegler−Natta catalysts have revealed uniform polymer particle growth in the early stages of polymerization, the catalyst support undergoing even and progressive fragmentation.[62] Recently, evidence for polymer subglobule formation in propylene polymerization with $MgCl_2$-supported catalysts has been reported, these subglobules within each particle originating from clusters of primary crystallites of $MgCl_2$, which are themselves pushed to the surface of each subglobule as the polymer forms.[63] Evidence for drifting of catalyst microparticles to the surface of polymer (sub)globules has been provided by scanning electron microscopy studies of prepolymerized catalyst particles.[64] Very different particle growth characteristics have been found in propylene polymerization with SiO_2-immobilized metallocenes. Using *rac*-$Me_2Si(Ind)_2ZrCl_2$ immobilized on SiO_2/MAO, Fink observed a shell by shell fragmentation with gradual break up from the outside to the inside of the particle.[65] The polymerization kinetics showed a slow build up in activity, the time to reach maximum rate decreasing with increasing concentration of the Al(i-Bu)$_3$ added to the polymerization medium. Subsequent studies revealed high initial activity, followed by a drastic decrease in activity, then after an induction period of approximately 10 min a gradual increase in activity, reaching a maximum after about 1 h.[66] During the induction period, a continuous filling of the catalyst pores from the outside to the interior took place, presenting a diffusion barrier for the monomer. The polymer molecular weight and melting points showed maxima after several minutes of polymerization, consistent with high monomer concentration at the active centers in this early stage of polymerization. The induction period could be reduced or eliminated by prepolymerization with 1-octene or by the addition of hydrogen and was greatly reduced when polymerization was carried out in liquid monomer rather than in toluene slurry. A mathematical model describing olefin polymerization with supported metallocene catalysts was developed.[67]

Another example of diffusion limitation in olefin polymerization with a silica-supported metallocene is the formation of a copolymer having broad compositional distribution in ethylene/1-hexene copolymerization with *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}PhInd)_2ZrCl_2$ immobilized on SiO_2/MAO.[68] Both homo- and copolymerization of ethylene took place, explained by the formation of a copolymer envelope around the particle, this envelope acting as a filter to restrict diffusion of the larger monomer (1-hexene), resulting in ethylene homopolymerization in the inner reaches of the particle.

It will be apparent from the above that different particle growth characteristics apply to different types of supports and different polymers and polymerization conditions. For example, the fragmentation behavior of SiO_2 supports, containing a branched pore network, is different from that of $MgCl_2$ comprising an agglomeration of small crystallites and is also influenced by the viscoelastic properties of the polymer formed.[69] A further important factor is the degree to which the catalyst is anchored on the support; Ray pointed out that catalyst extraction into the pores of the particle during polymerization can lead to plugging of the pores, thereby limiting monomer mass transfer through the particle.[70]

2.4. Lights, Camera, Action

The combination of video microscopy and minireactors has led to the optical observation of growing polyolefin particles in the gas phase and has proved to be an effective tool in studying several different polymerization parameters. The technique was first applied by Reichert and co-workers to study the gas-phase polymerization of butadiene using a heterogeneous catalyst at relatively low pressures.[71] Further development by the group[72] and others[73] enabled kinetic studies to be performed on single resting polymerizing polybutadiene particles. On-line optical and infrared observation of growing polypropylene particles has been used to study the propylene polymerization behavior of traditional Ziegler−Natta catalysts,[74] Weickert et al. having developed a reaction cell capable of operating at industrially relevant pressures (35 bar).[56]

Recently, Fink and co-workers have successfully applied the technique to supported metallocene/MAO catalyst systems, providing microkinetic data on their polymerization of ethylene.[75] A custom-built reactor, equipped with a clean window located under an optical microscope, which is in turn connected to a high-resolution digital camera, was used to study polymerization behavior of a heterogeneous zirconocene/MAO/silica system. Individual snapshots taken during polymerization were analyzed automatically by image-processing software, enabling simultaneous detection and evaluation of a large number (40) of individual growing catalyst particles. As a result, kinetic data on the growing "microreactor" particles during prepolymerization and main polymerization could be gathered. The group also claimed that video microscopic analysis, due to its sensitivity and the small amounts of catalyst required, would prove a suitable technique for combinatorial catalyst optimization.

The application of microscopy to combinatorial screening of supported metallocene catalyst has also been reported by Klapper et al.[76] The group consecutively treated silica with MAO and Me_2Si(2-Me-Benz-[*e*]Ind)$_2ZrCl_2$, $^{bu}Cp_2ZrCl_2$, or Et(Ind)$_2ZrCl_2$ to form a supported catalyst. The catalysts could then be either used as they were or additionally "tagged" by contact with a UV fluorescent rylene dye. The tagged and untagged systems were then mixed together and used simultaneously to polymerize ethylene. Exposure of the resultant polymer beads to UV-light clearly revealed different kinds of particles under fluorescence microscopy and allowed the fluorescent "tagged" particles to be physically separated from the untagged particles and separately analyzed. Recently, the Fink and Klapper groups reported the use of a combination of video and laser scanning confocal fluorescence microscopy to study the fragmentation of dye-labeled supported metallocene/MAO systems.[77]

Reichert and co-workers have also reported the use of video microscopy as an effective tool in the fast screening of supported α-olefin polymerization catalysts.[78] Six catalyst systems derived from three different methods of heterogenization were prepared by admixing various concentrations and volumes of a $^{bu}Cp_2ZrCl_2$/MAO/toluene solution to a silica support (600 °C calcined). Three different volumes of catalyst solution were chosen relative to the pore volume of the support to give a "slurry" ($V_{\text{cat. solution}} \gg V_{\text{support pore}}$), "mud" ($V_{\text{cat. solution}} > V_{\text{support pore}}$), or "dry" ($V_{\text{cat. solution}} = V_{\text{support pore}}$) mixed supported catalyst, while two different solution concentrations were also used. Video microscopy allowed the group to quantify the fraction of active catalyst particles in a given sample. Additionally, the growing polymer particles were also found to suffer from overheating due to the static nature of the polymer particle.

One of the most fascinating results to arise from the use of video microscopy is the effect that illumination has on polymerization activity.[79−82] Kallio and co-workers set out to perform kinetic studies on silica-supported metallocene/MAO catalyst in the gas-phase polymerization of ethylene, using video microscopy. However, the group found that the illumination light caused reproducibility problems in their kinetic measurements. Investigating the phenomena further, they found that polymerization activity was strongly dependent on the wavelength of the illuminating light as well as the type of transition metal. The highest activity was achieved under a blue light (300−480 nm) and was about 45% higher when compared to polymerization performed under red light (>600 nm). Furthermore, the activation effect of light irradiation was reported to be reversible.[79] The phenomena became more pronounced when the polymerization systems were treated with small amounts of dioxygen or carbon dioxide. The activity of the poisoned system reduced rapidly but totally recovered after approximately 20 min of irradiation.[80] Such experiments led the group to postulate that irradiation dissociates dioxygen or carbon dioxide from the metal center while having little to no effect on the coordination of ethylene. Subsequent UV−vis studies on the supported systems indicated that light irradiation may, however, favor olefin coordination.[81] UV−vis spectroscopy has been used to extensively study the activation of metallocenes in homogeneous solution[83−86] and has recently been extended to silica-supported systems in an attempt to elucidate the interactions between the metal center and the monomer[81] or supported cocatalyst.[87]

FT-Raman spectroscopy has also been used to study silica-supported MAO/metallocene systems. Van der Pol and co-workers studied silica-supported 2,2′-biphenyl-(2-Ind)$_2ZrCl_2$ in the presence of MAO and were able to correlate spectral features to ethylene polymerization activity and Al/Zr ratio. Specifically, a "fairly linear" correlation was found between

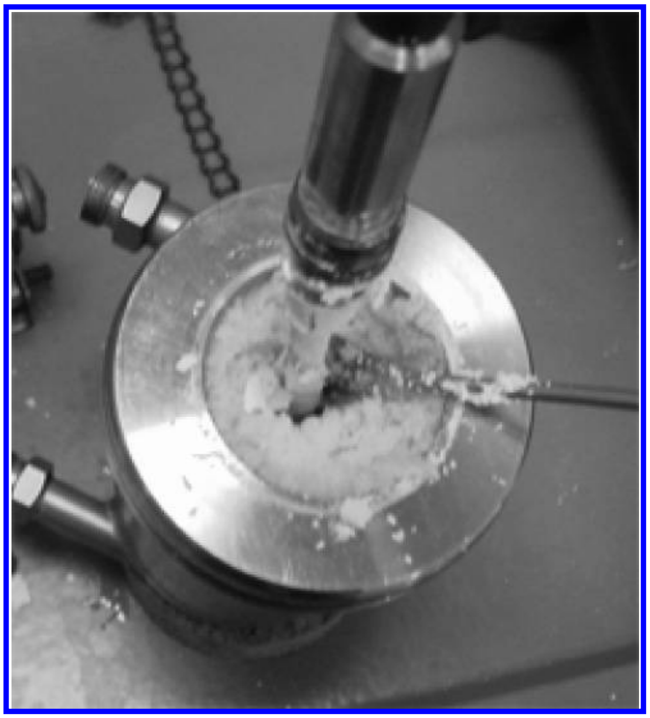


Figure 7. Example of severe reactor fouling.

the signal intensity due to M−Me bonds (M = Al or Zr) and the productivity (kg of PE/mmol of Zr) for a series of samples of differing Al/Zr ratios.[88] A similar correlation between spectroscopy and catalyst performance has recently been disclosed by Brintzinger and co-workers, who have developed a method for determining the activity of a supported metallocene catalyst using UV−vis spectroscopy.[89]

2.5. Leaching and Reactor Fouling

Avoiding catalyst leaching in all forms of immobilized “homogeneous” catalytic systems is of crucial importance. However, it is imperative to understand the different implications this term has for immobilized α-olefin polymerization catalysts, when compared to other immobilized systems. Outside the field of olefin polymerization, the commercial application of countless homogeneous catalysts will depend, in part, on their effective immobilization onto a carrier support. The ability to recycle the catalyst in batch or continuous processes without loss of activity, along with the removal of catalyst residue from the final product, are the driving forces for supportation.[90] To achieve this the solid particle should preferably remain intact throughout the reaction, without the catalytic metal, in either its activated or its deactivated form, leaching from the surface of the support.

In contrast, α-olefin polymerization catalysts are exclusively “one-shot” systems, with the catalytic metal remaining within the polymer matrix,[91] and are not recycled in the strictest sense of the word.[92] Polymer morphology, high bulk density, and avoidance of reactor fouling are the main driving forces for immobilization (Figure 7). As illustrated in the previous section on particle growth, the catalyst particle should fragment evenly to produce good product morphology and bulk density. It should also be noted that deactivated catalytic metal leaching from the surface has little effect, so long as the deactivated species are not reactivated by the polymerization environment (scavenger or cocatalyst in diluent).

Choosing the appropriate solvent and condition when performing a polymerization or leaching experiment cannot be overstated.[43] Immobilized single-site catalysts were developed as “drop-in technologies” for industrial slurry and gas-phase processes. Invariably these processes use liquid monomer, fluidizing gas streams, or aliphatic hydrocarbons as diluents. To the best of our knowledge, aromatic solvents such as toluene are not used in these processes. Cost and environmental issues are not the sole concerns; commercial processes operate at the highest possible process temperature for maximum efficiency. At these elevated temperatures, the solubility and solvent-induced swelling of the polyolefin particles produced become important considerations for slurry-phase processes. These phenomena are aggravated by the use of toluene, when compared to aliphatic hydrocarbons. Additionally, the removal of residual high-boiling solvent from the polymer resin is a costly process. The solubility of MAO and single-site precatalyst/cocatalyst combinations is also much greater in toluene than in aliphatic hydrocarbons. As a result, catalytic systems, especially those that are physisorbed to the carrier surface, may leach in an aromatic solvent but operate successfully in aliphatic hydrocarbon. This property can be utilized to produce heterogeneous catalysts without the use of a support and is discussed in the subsequent section. In general, polymerization data obtained in toluene are extremely difficult to translate to industrial slurry processes.

One should, however, be aware that attaining good morphology with an absence of reactor fouling does not entirely depend on the leaching characteristics and particle fragmentation of a certain protocol, particularly in gas-phase processes. Because the polymerization of α-olefins is an inherently exothermic process, the heat generated has to be effectively removed from the growing polymer particle; otherwise, “hot” spots may form, leading to a softening of the polymer and possible fouling. In a gas-phase process, the build up of static charge, caused by the movement of the polymer in the bed, may also lead to sheeting and fouling. The excessive static or heat build up or both is often suppressed or eradicated by the addition of antistatic, antifouling, or inhibiting agents before or during polymerization,[93] while the use of argon as a carrier gas[94] or circulating the discharging polymer through an integrated Faraday drum have also been reported to reduce static build up.[95]

2.6. Challenges in Catalyst Performance and Characterization

Comparing the performances of single-site α-olefin polymerization catalysts is a confusing and often complicated affair. Reasons for this include a non-standardized means of expressing parameters such as pressure (bar, atm, psi, MPa, etc.) and amount of catalyst (moles of active metal, grams of active metal, or grams of precatalyst) and the various combinations of these parameters that can and have been used, making quick comparison quite difficult. A further major complication arises when one considers precatalyst sensitivity and stability relative to changes in activator, reaction medium, conditions, or polymerization time. For example, the activity of a precatalyst is often expressed in terms of kg of polymer/(mol of metal·bar·h), which implies that activity has a linear dependence on pressure and polymerization time at a certain temperature, which is often not the case. The performance of traditional heterogeneous catalysts, on the other hand, is usually expressed in terms of productivity, by relating the mass of polymer produced to mass of solid catalyst or active metal used (kg of polymer/g of catalyst or kg of polymer/g of active metal), giving an idea as to the metal and halide residue in the polymer. One can imagine how difficult it is then to evaluate the performance of supported single-site catalysts, because one would like to compare their catalytic performance in terms of activity to the homogeneous systems and in terms of productivity to the more traditional heterogeneous catalysts. Obviously, a supported single-site system with a high activity and productivity is desirable, but with this in mind the reader is reminded that high activities reported in this review do not necessarily mean that the solid catalyst has a high productivity, especially at low loadings of precatalyst on support. High productivities are extremely important because the amount of catalyst residue (ash content) inside the polymer resin plays a major role in determining the application in which the resin can be used, for example, high strength and clarity film, microelectronics, optical media, and pharamaceutical packaging require low levels of catalyst (which includes the support) residue.

It is important to consider what we mean by the term single-site catalyst. A better term is single-center catalyst, taking into account that a single-center catalyst for olefin polymerization requires two sites, one of which is (alternately) occupied by the polymer chain and the other by the coordinated monomer. A true single-center catalyst produces polymers with a Schulz−Flory molecular weight distribution ($M_w/M_n = 2$ and $M_z/M_w = 1.5$) and copolymers with uniform comonomer distribution. In practice, even if single-center characteristics are retained during catalyst immoblization, supported systems may give somewhat broader distribution as a result of nonuniform monomer concentrations within the particle.

As mentioned in the Introduction, one of the advantages of a homogeneous single-site α-olefin polymerization catalyst is the ability to rationally improve and tailor its polymerization performance. However, throughout this review, there are numerous examples where the immobilization of a single-site catalyst dramatically alters the catalyst performance and resultant polymer resin, when compared to the corresponding unsupported system. Therefore, for supported systems, a thorough understanding of the interactions and mechanisms at work on the support surface during the immobilization, activation, and polymerization steps and the effects of local environments (pore size, etc.) is required. However, comprehensive characterization of the catalytically active species on a support, especially at low catalyst loadings on supports with a high porosity and surface area, is a challenging task, requiring an in depth knowledge of the chemistry involved, along with application of advanced surface science techniques. The difficulties in characterizing a supported single-site α-olefin polymerization catalyst are exemplified when one considers the ubiquitous activator MAO. MAO solutions have proved to be extremely effective at imparting high activity to a precatalyst, fulfilling several crucial roles (alkylation and alkyl abstraction, counterion, and scavenger). However, despite helping to ignite the field of single-site α-olefin polymerization catalysis, MAO has remained a relative “black box” consisting of “multiple equlbria between different $(AlOMe)_n$ oligomers coupled with the interaction of MAO and TMA”.[20d] That said, there is increasing experimental and theoretical evidence to suggest that three-dimensional cagelike structures provide the best description of the “active” component of MAO.[20] One can therefore imagine how complicated the immobilization of a solution of MAO is on a support surface, given the relative reactivities of the $(AlOMe)_n$ oligomers, reactive support species, free TMA, and steric structural effects and how difficult it is to analyze the resultant surface products.

2.7. “Inert Carrier-Free” Polymerization

This review focuses on the immobilization of single-site α-olefin polymerization systems on solid inert carriers to form uniform polymer particles with high bulk density and no reactor fouling. It should, however, be stated from the outset that polymer resins boasting good bulk density and uniform particle morphology have been obtained without the need for an inert carrier. The following section discusses the use of single-site polymerization catalysts in particle forming polymerization processes free from an inert carrier. The somewhat related concept of “self-immobilizing” catalyst systems will be discussed in a later section.

Strictly controlled prepolymerization of a homogeneous metallocene/MAO solution under depleted monomer conditions affords solid polymer, which encapsulates the catalyst. These solid particles can be polymerized in a further step operating under more rigorous conditions.[96] Prepolymerization of ethylene or propylene using $Me_2Si(2\text{-}Me\text{-}4\text{-}PhInd)_2ZrCl_2$/MAO solutions under ultrasonic irradiation applied to the outside walls of the reactor vessel resulted in no reactor fouling in the initial prepolymerization step. These prepolymers were successfully used in the heterogeneous polymerization of propylene and ethylene. In the case of propylene, spherical pre- and final polymer particles were obtained, whereas for ethylene, the “cotton-like aggregates” formed in the prepolymerization step produced agglomerated particles in the final step.[97]

The prepolymerization of metallocene/MAO solutions, however, is not necessarily required to accomplish good polymer morphology. Workers at Union Carbide successfully utilized metallocene/MAO solutions, part of which consisted of a highly volatile component (ethane) in a gas-phase polymerization process. Vaporization of these solutions directly into a gas-phase reactor produced a metallocene/MAO aerosol that subsequently formed uniform polymer particles of good bulk density[98] and has been technically demonstrated on a commercial scale.[98a] Judicious addition of an antistatic/antifouling agent aided the smooth operation of this process.

The solidification of various metallocene/MAO solutions has recently been described by workers at Borealis. The metallocene is activated by a toluene MAO solution.[99] This solution forms an emulsion when added to cooled (ice bath) perfluoroctane containing a "surfactant−MAO" solution prepared by addition of dodecafluoroheptanol to MAO. Addition of this cooled emulsion to a larger volume of hot perfluoroctane induces solidification, yielding spherical catalyst particles (average particle diameter 22 μm) that could be used to copolymerize ethylene and 1-hexene in a slurry process.

Solid methylaluminoxanes can also be exploited as a supporting cocatalyst. The general preparation involves the chemical or physical precipitation of MAO from solution. Geerts and co-workers at Phillips obtained solid cross-linked MAO via chemical precipitation of commercial MAO solutions.[100−102] Addition of catechol borane,[100] boroximes,[101] epoxides, organic peroxides or carbonates[101] to toluene solutions of MAO afforded solid MAO, which was then used to activate Cp_2ZrCl_2[100,101] or $^{bu}Cp_2ZrCl_2$[102] for the slurry polymerization of ethylene. Solid cross-linked MAO has also been obtained via addition of water,[103] 1,6-hexanediol,[104] and bisphenol A[105] to commercial toluene solutions of MAO. While addition of *p*-hydroquinone[106] produced a solid cross-linked MAO that was suitable as a support, activation only occurred after further addition of a trialkylaluminum compound. Solid MAO supports have also been obtained by isolating the often superfluous insoluble gel fraction of a MAO solution.[107] Finally, "quasi-spherical" particles of solid MAO (5−20 μm) have been produced by hydrolysis of a hexane solution of $AlMe_3$, in the presence of a sorbitan monooleate emulsifier. The solid MAO was then used to activate Cp_2ZrCl_2. This system proved surprisingly effective at polymerizing ethylene in a toluene diluent or propylene (bulk) to granular polymer particles, without reactor fouling or fines generation.[108]

As mentioned in a previous section, the insolubility of MAO in aliphatic hydrocarbons can be utilized to produce solid MAO supports. Kashiwa and Kioka at Mitsui were able to precipitate MAO via addition of *n*-decane to a toluene solution of MAO. The toluene was then removed in vacuo to afford a "finely divided" aluminoxane (average particle size 29 μm), which was isolated and subsequently prepolymerized in *n*-decane (ethylene). The solid prepolymer was then introduced to a stirred bed (NaCl) gas-phase reactor and effectively polymerized ethylene.[109] Mixtures of hexanes[110] or isopentane[111] have also been used to precipitate MAO from toluene solutions. In these cases, the precipitate is filtered directly without removal of toluene, affording a solid MAO containing ca. 60% of the original Al content.[111]

A highly surprising and unexpected catalytic system that produced polyethylene resin with controlled particle morphology in the absence of an inert support has recently been claimed. The catalyst system in question is formed by the micronization of Cp_2TiCl_2, via deposition from supercritical CO_2, which yielded uniform precatalyst particles that were used in a hexane slurry along with MAO.[112]

The disclosure by Jacobsen and co-workers at Dow provides the only example of carrier-free, borate-cocatalyzed polymerization of α-olefins. Controlled precipitation of borate salts of a general formula $[NHMe(C_nH_{2n-1})][(C_6F_5)_3BC_6H_4OH]$ ($n = 14, 16, 18$) in hydrocarbon solvents provided spherical particles, which when used in combination with a metallocene and an alkylaluminum to form a particulate system operable in slurry phase processes, afforded polymer resins with good spherical morphology.[113]

3. Inorganic Oxide Supported

3.1. Silica and Alumina Supports

Silicas are by far the most common support to be utilized in the heterogenization of single-site α-olefin polymerization catalysts. Silica exists in many phases, including anhydrous crystalline phases (quartz, tridymite, cristobalite, etc.), but the phase most commonly used to prepare supported catalysts is the common amorphous form, which includes anhydrous amorphous silica and surface-hydroxylated amorphous silica. Common amorphous silica is usually prepared by sol−gel or condensations involving $Si(OH)_4$, which is usually generated in situ by hydrolysis of a silicon tetra-alkoxide species such as TEOS ($Si(OEt)_4$) in saturated aqueous solutions or in the vapor phase if water is present in the system. Alternatively, the commercial production of silica polymerization supports involves the combination of silicate and acid to form either an acidic or a basic hydrosol. The hydrosol is then transformed into a "raw" hydrogel, which in turn is washed ("washed" hydrogel) and dried to form the silica support material. The particles formed can be of various sizes and morphology depending on the preparation conditions. In the preparation, micrometer-sized agglomerates of submicrometer particles may form, resulting in porous aggregates with large surface areas.

Typical "polymerization grade" silicas are usually unmodified and fully hydroxylated forms, requiring some form of thermal treatment to remove H_2O, reduce the number of silanol groups on the surface, or both. In its unmodified and fully hydroxylated form, the surface is saturated in silanol groups. Three different hydroxyl groups can be distinguished, isolated (**I**), geminal (**II**), and vicinal (**III**), Figure 8. Water molecules can easily adsorb on this type of surface through hydrogen bonds to the silanol groups or through physical adsorption. Generally speaking, physically adsorbed water molecules desorb at 25−105 °C and hydrogen-bonded water at 105−180 °C. At temperatures above 180 °C, the adjacent vicinal

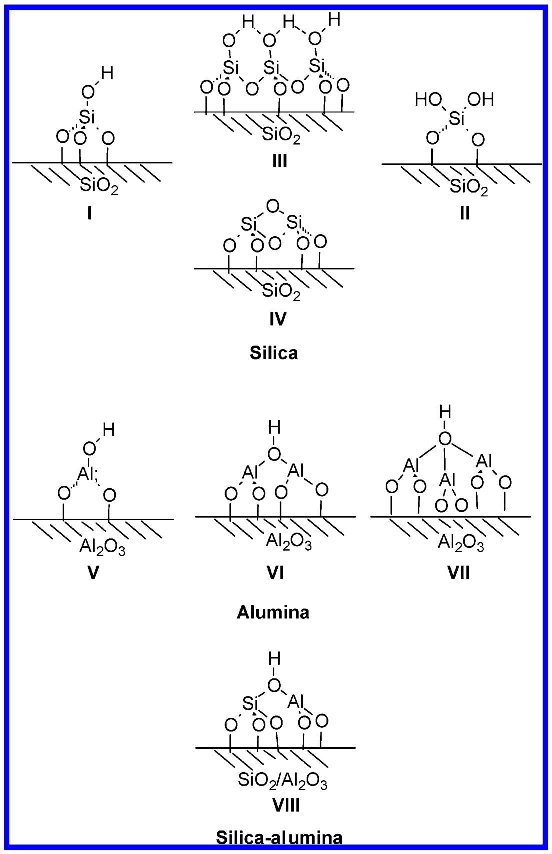


Figure 8. Surface hydroxyl species.

silanol groups begin to condense with each other forming a surface siloxane (silyl ether, Figure 8, **IV**) with the final density of silanol groups depending on the dehydration (calcination) temperature but usually ranging between 1 and 5 OH/nm^2. The full range of hydroxylated, dehydroxylated, or partially dehydroxylated silicas have been employed in the preparation of heterogeneous single-site α-olefin polymerization catalysts, and while some degree of thermal treatment is usually required, the exact calcination temperature of the support may depend on several factors such as polymerization process, cocatalyst or precatalyst combination, or target properties of the polymer resin.

Alumina-supported polymerization catalysts are usually based on γ-Al_2O_3, an industrially important alumina, which is formed by heating hydrated $Al(OH)_3$ and is a metastable member of the binary aluminum oxide family. γ-Al_2O_3 has a spinel ordering with the oxygen atoms in a cubic close-packed arrangement with the aluminum cations situated partially in tetrahedral and octahedral positions and can be represented by the general formula $H_{1/2}Al_{1/2}[Al_2]O_4$ with the octahedral cations between the brackets and with the protons representing the surface OH groups. Therefore 12.5% of all oxygen atoms are situated on the surface leading to a high OH density (10−12 OH/nm^2). Three different types of surface OH groups are present on alumina, isolated (**V**) and two types of bridged species containing either two (**VI**) or three (**VII**) aluminum atoms, Figure 8. Species **V** and **VI** can also exist in two different forms depending on the aluminum geometry (tetrahedral or octahedral). Calcination of the alumina creates surface aluminum cation species, which act as Lewis acids.

Mixed silica−alumina supports are formed by co-condensation of $Si(OH)_4$ with $Al(OH)_3{\cdot}H_2O$. The resultant solid may contain zones of pure Al_2O_3 and SiO_2, especially at high Al contents due to the limited isomorphous substitution of Al^{3+} for Si^{4+}, which culminates in the formation of hetero-bridged hydroxyl species, Si−O(H)−Al (Figure 8, **VIII**). These bridging hydroxyls groups are responsible for the Brønsted acidity of the surface. The total amount of OH-groups on silica−alumina is around 5−8 OH/nm^2, while the surface areas are approximately 300 m^2/g.

An example of just how intimately related the physical properties of a support are to the polymerization process and resultant resin properties can be seen in the supports for Phillips catalysts. These intricacies were comprehensively and expertly covered in a recent review on the field by Zecchina et al.[10b]

3.2. Grafted Precatalysts

Precontacting an inorganic oxide with a precatalyst, prior to the addition of methylaluminoxane is not a common procedure for immobilizing a catalyst. One of the main reasons for this is predicting how the various surface hydroxyl groups will interact with the metal center and how the resultant species will interact with MAO. Soga and co-workers reacted $CpTiCl_3$ with calcined silica (800 °C) in refluxing toluene for 3 h, obtaining a metal loading of 0.63 wt %. Contacting the solid with MAO yielded an active catalyst system for the copolymerization of ethylene and propylene.[114] Analysis of the resultant resins indicated a copolymer composition similar to that formed by the commercial $VOCl_3$−$Al_2Et_3Cl_3$ catalyst. The system was also used by others to polymerize styrene.[115] The resultant resins did not exclusively form syndiotactic polystyrene, unlike the corresponding homogeneous system, and the fraction of *s*PS decreased with increased metal loadings. Electron spin resonance (ESR) analysis of the catalyst indicated the presence of two or more titanium species.

The effect of silica calcination temperature and grafting reaction conditions on the performance of silica-supported zirconocenes has been extensively studied by dos Santos and co-workers.[116] The group dehydroxylated silica in vacuo at various temperatures between rt and 450 °C and reacted these with solutions of $^{bu}Cp_2ZrCl_2$ at different contact temperatures and times. Silica pretreated at higher temperature led to lower catalyst loadings but when contacted with MAO afforded catalyst systems with higher activities and produced resins of higher molecular weight and narrower molecular weight distributions. High grafting temperatures and long contact times led to higher metal contents but reduced the activity of the system. The polarity of the metallocene solution seemed to have little effect on metal loading or final activity, while a coordinating solvent such as tetrahydrofuran led to a more active system, albeit with lower metal contents. Analysis of the supported zirconocenes indicated the presence of two different surface zirconocene species,

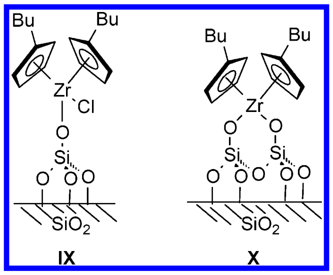


Figure 9.

Table 1. Metal Loading and Polymerization Performance of Various Supported Metallocenes

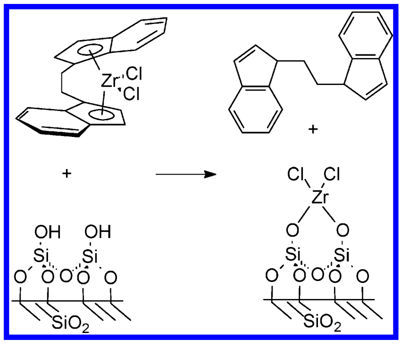
	M/SiO$_2$		M/MAO/SiO$_2$	
metallocene	*M* (wt %)	activity[a]	*M* (wt %)	activity[a]
MeCp$_2$ZrCl$_2$	1.0	58.3	1.4	91.8
^{i}BuCp$_2$ZrCl$_2$	0.8	52.8	1.1	23.9
^{n}BuCp$_2$ZrCl$_2$	0.8	26.0	1.2	48.9
Cp$_2$ZrCl$_2$	1.0	27.6	1.3	54.0
Cp$_2$TiCl$_2$	0.4	10.0	0.5	15.3
Et(Ind)$_2$ZrCl$_2$	1.5	traces	2.5	4.9
Et(Ind)$_2$HfCl$_2$	1.2	traces	1.1	traces
Et(Ind-H$_4$)$_2$ZrCl$_2$	0.7	28.8	0.9	43.2
Me$_2$Si(Ind)$_2$ZrCl$_2$	0.7	traces	0.8	traces

[a] 10^5 g of PE/mol of M·h (M = Ti, Zr, or Hf).

IX and **X** (Figure 9). Species **IX** is believed to form an active species with MAO, presumably by metathesis of the surface Si−O−M bond, which can be considered as the leaching of the precatalyst from the surface, which may complicate discussions on structure−property relationships. Species **X**, however, is believed to be inactive possibly due to a combination of steric and electronic considerations. Additionally, the amount of residual silanol groups on the support following contact with the zirconocene was believed to affect the catalytic performance of the system. The group also studied the grafting reaction of several other metallocenes on silica dehydroxylated at 450 °C in vacuo in the hope of understanding how the steric bulk on the metallocene affected the grafting process.[117] The metal contents were found to depend on the metal center (Ti < Hf < Zr), the coordination sphere, and the support. Alkyl substitution of the cyclopentadienyl ligand had no significant effect on the metal loadings of the catalyst and the inductive effect of the substituent had a greatly reduced effect on the activity in ethylene-*co*-1-hexene polymerization, when compared to the corresponding homogeneous systems. Furthermore, the ethyl-bridged indenyl derivatives gave higher metal contents than the more bulky dimethylsilyl-bridged analogues. The grafted systems were also compared to the same metallocene contacted with MAO-modified silica, Table 1.[117a]

Silica supports whose surfaces have been chemically modified by a chlorosilane,[118] alkoxysilane[119] or hexamethyldisilazane[119] have also been used as supports for the grafting of a metallocene. The catalytic systems, when activated by MAO, produced polyethylene resins with narrower molecular weight distributions at higher activities than those grafted onto untreated silica. The adsorption of metallocenes onto untreated, calcined, and hexamethyldisilazane-treated silica and their use in ethylene polymerization, activated by MAO, has also studied by several other groups.[120−124]

Scheme 1



Kaminsky and co-workers contacted Et(Ind)$_2$ZrCl$_2$ with silica previously dried in vacuo at 100 °C.[125] The grafted precatalyst was then contacted with MAO and utilized in the polymerization of propylene. The grafted catalytic system afforded isotactic polypropylene resins with high molecular weight and increased stereoregularity, when compared with the corresponding homogeneous system, while precontacting the silica with MAO prior to the addition of the metallocene afforded polypropylene resins similar to those produced by the homogeneous systems. Sacchi et al. contacted Et(Ind)$_2$ZrCl$_2$ and Ind$_2$ZrCl$_2$ with silica, using virtually the same grafting procedure as Kaminsky. In their case, however, the resins produced by the supported systems were similar to those produced by the homogeneous system.[126] Interestingly, Ind$_2$ZrCl$_2$, which produces atactic polypropylene under homogeneous conditions, produced moderately isospecific polypropylene when grafted onto silica, albeit with an exceptionally broad molecular weight distribution. The authors attributed the increased isospecifity to the decomposition of the metallocene coordination sphere and conversion to an isospecific form. In comparison, the report by Janiak and Rieger on Ind$_2$ZrCl$_2$ activated by MAO/SiO$_2$ and in solution resulted in waxy aPP for both systems.[127] Isotactic enrichment of polypropylene has, however, been observed when the aspecific precatalyst Ind$_2$ZrCl$_2$ is immobilized onto zeolite HY previously contacted with MAO.[128] A more pronounced example of the effect that grafting can have on stereocontrol can be seen when Me$_2$Si(Flu)(Cp)ZrCl$_2$ is precontacted with silica prior to activation by MAO. In the absence of silica, the homogeneous precatalyst produces syndiotactic polypropylene, while in the presence of silica isotactic polypropylene is formed.[129]

Decomposition of the metallocene coordination sphere to form inactive surface species has been reported by Collins et al.[130] They noted that the absorption of Et(Ind)$_2$ZrCl$_2$ onto silica afforded appreciable amounts of bis(indenyl)-ethane in the grafting solvent. The decomposition is believed to come from the reaction of the metallocene framework with one or more surface silanol groups, Scheme 1. Decreased decomposition was, however, observed when the precatalyst was contacted with alumina rather than silica, and surprisingly no decomposition was reported with Et(Ind-H$_4$)$_2$ZrCl$_2$ on either silica or alumina. The supported precatalysts were found to be 10−100 times less active than the corresponding homogeneous system, and interestingly, an increased calcination temperature of the silica led to an increase in catalytic activity, while the reverse was true for the alumina-supported systems. Decomposition of a metallocene coordination sphere has also been proposed to explain the inactivity of the silica-supported systems derived from *rac*-$MeO_2Si(Ind)_2ZrCl_2$ and di[(1′*S*,2′*R*,5′*S*)-menthoxy]silylene-bis[1(*R*,*R*)-(+)-indenyl]zirconium dichloride.[131]

Examples of grafted post-metallocene complexes are extremely rare, possibly due to the instability of the ancillary ligand of the complex toward protolysis, when compared to metallocenes. One example that does exist is the grafting of ethylenebis(salicylideneiminato)zirconium dichloride onto calcined silica (500 °C).[132] The supported systems were activated with MAO and compared to the homogeneous systems in the slurry polymerization of ethylene. The supported system showed higher activities than the homogeneous systems yet resulted in polyethylene resins with similar properties. Utilizing heptane as a polymerization diluent rather than toluene led to a resin with increased molecular weight and molecular weight distribution.

A related approach to grafting a metallocene onto a support surface has been to form heterogeneous metallocene catalysts by assembling them on a support or by the modification of a traditional Ziegler−Natta catalyst. Soga et al.[133] synthesized titanocenes supported on silica by first grafting titanium tetrachloride onto the silanol groups and then exchanging the remaining chloride ligands for cyclopentadienyl groups. The resultant catalyst showed some stereospecificity in propylene polymerization but at very low activities. The group also tried to modify $TiCl_4$ supported on $MgCl_2$ with cyclopentadienyl groups, which resulted in a catalyst with low activities in ethylene polymerization.[134] Modification of conventional Ziegler−Natta catalyst with LiCp′[135] or Cp′-$SiMe_3$[136] has also proved unsuccessful in producing a more single-site catalyst. However, Cp′-$SiMe_3$ (Cp′ = Cp, Ind, or $^1/_2Et(Ind)_2$) modification of silica- and alumina-supported MCl_4 (M = Ti or Zr) afforded heterogeneous metallocenes that produce resins with relatively narrow molecular weight distribution when activated by MAO or an alkylaluminum complex.[137] Similarly, silica contacted with Cp_2Mg has also been reacted with $TiCl_4$ followed by gaseous HCl to form a modified Ziegler−Natta catalyst. The modified catalyst system, when activated by MAO or an alkylaluminum complex, produced polymer resins with narrower molecular weight distribution than a more traditional unmodified Ziegler−Natta catalyst.[138]

Dupuy and co-workers grafted $TiCl_4$[139] or $ZrCl_4$[140] onto silica and alumina. The species thus formed were then modified by contacting with LiCp′ (Cp′ = Cp or Ind) to form a heterogeneous metallocene catalyst that could be activated by MAO, alkylaluminum complexes, or borate salts. The heterogeneous zirconocene precatalysts when used in conjunction with MAO formed polyethylene resins with a surprisingly narrow molecular weight distribution for such a procedure (M_w/M_n = 2.5−3),[141] while for the corresponding titanocene analogues, a broader distribution was observed (M_w/M_n = 4.8).[139] The group also formed heterogeneous metallocene catalyst by reacting silica, previously modified with $MgCl_2$, with $ZrCl_4$ in the gas phase.[141] The supported zirconium species was then modified with lithium indenyl to form a highly reproducible supported catalyst, which when activated by MAO proved to be effective in the slurry and gas-phase homo- and copolymerization of ethylene. Once again, the resins produced possessed narrow molecular weight distributions (M_w/M_n = 2.4−2.5). Heterogeneous metallocenes have also been constructed by the addition of various derivatives of cyclopentadiene to solid mixtures of magnesium and zirconium alkoxides.[142] Finally, heterogeneous metallocenes have also been formed on the surface of MAO-modified silica, following consecutive treatments of $Zr(CH_2Ph)_4$ and indene or pentamethylcyclopentadiene.[143]

3.3. Interactions of an Alkylaluminum Complex with Silica

The interactions of MAO, TMA, and TMA-depleted MAO with a silica surface and the performance of the finished catalyst system have been studied by several groups using various analytical, spectroscopic, and theoretical techniques. Soga and Kaminaka reported the possibility of quantitative reaction between TMA/MAO and the surface silanol groups,[144] while Bartam et al. proposed a chemisorption model for the interaction of MAO with a silica surface based on Si−Me and Al−Me population ratios. In the model, a monomethyl−aluminum complex and methyl groups bound to silica are proposed to be the major surface species at room temperature.[145] More recently, infrared studies on TMA/SiO_2 and MAO/SiO_2 interactions led Zakharov et al. to propose that the terminal surface silanol groups react rapidly with TMA via protolysis to yield methane, with a slower reaction and chemisorption of the MAO to the surface.[146] Determination of adsorption isotherms for TMA and MAO on silica, as well as in situ monitoring of the interaction, via infrared and diffuse reflectance infrared spectroscopy (DRIFTS)[147] have been used by dos Santos et al. The study showed that MAO plays a steric role during the surface reaction, shielding the unreacted surface silanol groups from further reaction.

Further studies on the interaction of a MAO with silica have included elegant NMR spectroscopic analysis on the diffusion and reaction of methylaluminoxane within a silica membrane[148] and development of a theoretical model for the reaction of MAO or MAO/TMA with silica.[149]

Tao and Maciel have used ^{13}C and ^{29}Si solid-state CP/MAS NMR to analysis the effect that methylating agents (MeLi, MeMgBr, and TMA) have on a dried and $SiMe_3$ capped silica surface.[150] Their interest was to study the generation of Si−Me groups resulting from the cleavage of surface (Si)−O−(Si) or (Si)−O−$SiMe_3$ linkages, rather than the actual alkylaluminum species. Their result indicated that TMA cleav-

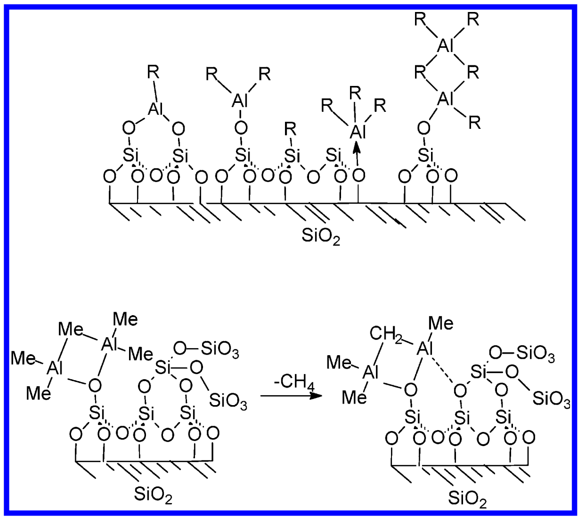


Figure 10. Proposed surface alkylaluminum species.

age of the (Si)−O−(Si) linkage occurs to only minor extent, while the (Si)−O−$SiMe_3$ linkage remains significantly intact. In contrast, MeLi induces severe cleavage of the (Si)−O−(Si) or (Si)−O−$SiMe_3$ linkages.[150b] This is an important point and has implications to several of the synthetic proceedures used throughout this review.

A recent paper by Scott and co-workers challenges many of the proposed structures formed when TMA is contacted with a silica surface, in their case Aerosil 380 (calcined at 500 °C).[151] In this disclosure, based on quantitative (analysis of volatiles and surface organometallics) and spectroscopic (IR, ^{13}C, and ^{29}Si solid-state CP/MAS NMR) analysis, the main product is believed to result from the reaction of an isolated surface silanol and the dimeric form of TMA (Figure 10) with a further C−H activation reaction to form a methylene-bridged complex (Figure 10).

It should be noted that all these studies on the interaction of silica and alkylaluminum are intimately related to the physical properties and calcination temperature of the silica as well the alkylaluminum used. The range of proposed species formed when silica is contacted with AlR_3 is illustrated in Figure 10. For convenience, the subsequent alkylaluminum silica species in this review have been drawn in their most simplistic proposed form. The reader is cautioned not to over-interpret these structures as being the predominant surface species.

3.3.1. Aluminoxanes Generated in Situ

Supported aluminoxane activators have been generated by the in situ hydrolysis of an alkylaluminum compound, usually TMA, in the presence of the support. Chang prepared silica-supported aluminoxanes via the hydrolysis of TMA and or AlR_3 (R = Et or ^{i}Bu) with “undehydrated” or hydrated silica (ca. 5−35 wt % H_2O) suspended in a hydrocarbon diluent.[152] The silica-supported aluminoxanes were then treated with a metallocene to form a catalyst system that out-performed those prepared via adsorption of MAO onto the same “undehydrated” supports. Improvements in activity were noted when the supported aluminoxanes were either aged,[153] heat-treated,[154] or prepared by the impregnation of the “unhydrated” silica with a solution of TMA and metallocene.[155] Fink and co-workers used the gas-phase impregnation of a fluidized bed of silica with water, TMA, and a metallocene to produce a supported catalyst for the polymerization of ethylene.[156] Analysis of ultracut-microtome images of the catalytic particles and resultant resins by SEM and SEM-EDX techniques clearly showed that the active sites were situated on the outer surface of the support and not within the particle pores. Little to no particle fragmentation was observed, and while this was not essential for gaining a high and consistent level of polymerization activity, it did result in polymer particles with a poor irregular morphology. Additional hydrocarbon suspension,[157−160] spray-drying,[161] and gas-phase[162] impregnation procedures have also been reported to generate silica-supported MAO, in situ.

3.3.2. Supporting an Aluminoxane

Precontacting a toluene or aliphatic hydrocarbon solution of MAO with a calcined silica, followed by washing, drying, and reaction with an appropriate precatalyst, is one of the earliest and most frequently used and commercially available means to facilitate the immobilization of single-site α-olefin polymerization catalysts. Welborn[163] and Takahashi[164] contacted silica with a toluene solution of MAO. Isolation and treatment of the silica-supported MAO with a dichloride or dialkylmetallocene yielded a supported single-site catalyst that was effective in the homo- and copolymerization of ethylene in a stirred-bed gas-phase process. The activity of the supported catalyst can often be augmented by the addition of an alkylaluminum or aluminoxane complex. Similar procedures, including large commercial scale production,[165] have also been reported for the immobilization of metallocene,[166] half-metallocene,[167] constrained geometry,[168] and late transition metal[169] precatalysts, while detailed investigations of their kinetic behavior in various processes have also been reported.[170−173] Additionally, precipitating the MAO from a toluene solution onto the silica surface by addition of *n*-decane has been reported to result in an effective system.[174]

Employing a heat treatment regime in a particular step(s) of the supportation procedure has been reported to improve the fixation of MAO to the silica surface as well as the performance of the finished catalyst. Heating a toluene suspension of silica/MAO at an elevated temperature (ca. 95 °C) prior to filtration, cold washing, and contact with a metallocene solution has been reported by Tsutsui and co-workers at Mitsui to improve the catalyst performance in the gas-phase copolymerization of ethylene and 1-butene. Improvements in the morphology of the polymer resins and an absence of reactor fouling were all noted as additional benefits.[175]

Razavi and Debras[176] and colleagues[177] at Fina found that refluxing the silica/MAO toluene suspension for approximately 4 h prior to contact with a C_2- or C_1-symmetric metallocene improved the stereoselectivity and activity of the finished catalyst and yielded polymer resins with good bulk density and

Table 2. Aluminum Loadings of MAO/SiO$_2$ Following Heat Treatment and Washing

temp (°C)	wt % Al heating	wt % Al washing (20 °C)	wt % Al washing (90 °C)
125	31	20	16
150	31	26	24
175	31	30	29
200	31	31	29

morphology. Catalyst efficiency was also strongly related to the temperature used in supporting the metallocene onto the MAO-treated silica. Higher catalytic activities of the finished catalysts were observed when low contact and washing temperatures (−20 to 0 °C) were employed during the fixation of the metallocene. The finished catalysts were then dispersed in a TIBA-treated mineral oil prior to polymerization.[177] The group also reported that the TIBA-treated catalyst dispersions were unstable and resulted in a steady, predictable decrease in activity on aging.[175a,d] This steady decrease in activity has been claimed to allow one to select the activity of a catalyst without affecting final polymer properties.[177d] Heat treating the toluene suspension of MAO/silica at 130 °C for 3 h under pressure (ca. 2 bar) in a closed vessel, prior to contact with a precatalyst, has also been said to encourage an even distribution of aluminum throughout the catalyst particle.[178]

A highly effective means of thoroughly fixing the MAO to a silica surface was reported by Jacobsen and co-workers at Dow.[179] The procedure involved room-temperature treatment of a calcined silica (250 °C, 3 h) with a toluene solution of MAO overnight. The toluene was then removed in vacuo, rather than being filtered or decanted, to afford a dry solid silica/MAO mixture that was subjected to a heat treatment step (125−200 °C, ca. 2 h) prior to being washed with toluene (20 or 90 °C) and dried in vacuo (120 °C, ca. 1 h). Analysis of the various supports showed that heating the dry solid silica/MAO leads to a more thorough fixation of the MAO to the surface of the support, Table 2. The heat-treated supports (200 °C), when used in conjunction with $Me_2Si(C_5Me_4)(^tBuN)TiMe_2$ for the copolymerization of ethylene and 1-octene, exhibited high activities and resulted in polymer resins with high bulk densities. Removal of the diluent from the MAO/silica suspension in vacuo has also been reported by others to form effective supported activators.[180]

Heating a toluene solution of MAO (30 wt %) at an elevated temperature (50−80 °C) for prolonged periods (1−7 h), prior to contact with vacuum-dried silica (200 °C), is believed to provide a more stable MAO with a reduction or removal of gels that lead to variable catalyst performances. Diefenbach and co-workers at Albemarle compared such supported activators to samples prepared without heat treatment in the copolymerization of ethylene and 1-hexene, using *rac*-Et(Ind)$_2$ZrCl$_2$. The results showed that heat-treating the MAO solution prior to contact with silica leads to an appreciable improvement in catalytic activity (ca. 25%) and product morphology.[181]

Knuuttila and co-workers at Borealis reported a dry mixing procedure, which was claimed to reduce reactor fouling and improve catalyst performance.[182] The silica-supported MAO was formed by impregnating a calcined silica (600 °C) with a toluene solution of MAO so that only the silica pores were filled with the MAO solution, followed by dry mixing and removal of residual toluene in vacuo. The metallocene, (Ind)$_2$ZrCl$_2$, is then dry mixed as a solid with the silica-supported MAO at 130 °C for approximately 1.5 h to form a finished catalyst that was utilized in the ethylene homo- or copolymerization.

Silica-supported MAO has been treated by Rytter et al. with $(^{Bu}Cp)_2ZrCl_2$ dissolved in a liquid α-olefin (1-hexene, 1-octene, or styrene) using the pore-filling technique described above for the impregnation of MAO onto silica.[183] Instead of evaporation, the solvent is allowed to polymerize, affording catalyst particles that were protected from oxidation. For example, when 1-hexene was used as a solvent and prepolymerization monomer, the catalyst system retained 70% of its original activity following exposure to air for 5 h. A similar procedure involving the pore-filling impregnation of silica with a cooled (−40 °C) 1-hexene solution of an aluminoxane and $(^{Bu}Cp)_2ZrCl_2$ has also been reported to afford a catalyst system robust toward exposure to air.[184] Alternatively, pore-filling the finished catalyst system with a hydrocarbon solution of poly(4-methyl)styrene, low molecular weight waxes,[185] styrene,[186] paraffin wax,[187] heptane,[188] or a high-boiling aromatic solvent[189] has led to catalytic systems that are safer,[188] more robust, or more active and possess improved product morphology.

The in-situ immobilization of the precatalyst onto silica-supported MAO within the polymerization reactor, followed by the introduction of an alkylaluminum complex and (co)monomer, has been reported by Soares et al.[190,191] and others[192] to produce a more efficient catalyst, when compared to isolated ex situ prepared catalysts in ethylene[190,192] and propylene[191] polymerization. Other physical modifications reported to reduce reactor fouling or improve activity or fixation of MAO or metallocene to the support have included subjecting the metallocene MAO/SiO$_2$ suspension to ultrasonic[193] or microwave[194] irradiation.

Chemical modification of MAO before or after supportation has been reported to lead to specific improvements in a supported catalyst performance. Isolating solid MAO via evaporation and vacuum-drying of commercial MAO solution, followed by washing and drying in vacuo (120 °C),[195a] yielded an aluminoxane that was alkylaluminum (usually TMA) poor or depleted.[195] The solid MAO was then redissolved in toluene and added to calcined silica or added as a solid to a stirred toluene suspension of calcined silica. An example of how effective this procedure can be was disclosed by Meijers et al.[195a] The group added solid MAO prepared as above to a suspension of dried silica (150 °C, 10 h, N$_2$ flow) at room temperature. Immediate evolution of gas was observed on contact with the silica surface, and the reaction was continued until no further gas evolved. A solution of the low-valent catalyst Et(Cp″)(NMe$_2$)TiCl$_2$ (Cp″ = 2,4-(SiMe$_3$)$_2$Cp) was then added and allowed to react with the SiO$_2$/MAO prior to the removal of solvent in vacuo. The isolated catalyst,

Table 3. Polymerization Performance of a Supported Precatalyst[a]

support	Al/Ti	press. (MPa)	prod (kg of PE/g of cat.·h)
DMAO/SiO_2	75	0.5	346
	75	2.0	2244
	100	0.5	1014
	100	2.0	3434
	150	0.5	1505
	284	0.5	669
	284	2.0	1277
MAO/SiO_2	75	0.5	285
	75	2.0	1504
	100	0.5	311
	100	2.0	1014
	150	0.5	364
	284	0.5	347
	284	2.0	616

[a] Precatayst = Et(Cp″)(NMe_2)$TiCl_2$; *D*MAO = TMA depleted MAO.

when used to homopolymerize ethylene at various pressures and Al/Ti ratios, was considerably more active than a comparative example synthesized using the commercial MAO (Table 3). Coulter and co-workers at Nova Chemicals reported that addition of cellulose to MAO afforded "sweet" MAO, which when contacted with calcined silica (600 °C) and used in conjunction with (Ind)($^tBu_3P{=}N$)$TiCl_2$ yielded a catalyst that was more active than the corresponding cellulose-free protocol in ethylene-*co*-1-hexene polymerization.[196] Treatment of MAO with a long-chain alcohol prior to supportation[197] or contacting MAO-modified silica and alumina with the cross-linking agent bisphenol A[198] have also been disclosed to lead to improvement in the performance of the finished catalyst.

Alternatively, the chemical modification of the inorganic oxide support with an organic, inorganic, or organometallic (covered in the subsequent section) complex has been used to remove the surface hydroxyl groups, produce a more uniform surface species, add an additional functionality, or alter the electronic properties of the support.

The most common organic surface modifiers have been chloro- or alkoxysilanes. Soga et al. described the use of Me_2SiCl_2-modified silica to support MAO.[199] The solid activator when contacted with Cp_2ZrCl_2 had a higher activity in ethylene homopolymerization than the "unmodified" system. Similarly, Chao et al.[200] and Jongsomjit et al.[201] found that catalytic systems generated by silane-modified silica-supported MAO and Et(Ind)$_2$$ZrCl_2$ resulted in higher polymerization activities than the corresponding "unmodified" system in the copolymerization of ethylene with proplyene[200] or a higher α-olefin (1-hexene, 1-octene, or 1-decene).[201] In the latter report, the vacuum-dried silica (400 °C, 6 h) is modified with $SiCl_4$, followed by treatment with aqueous $NaHCO_3$ and in vacuo drying prior to contact with MAO.[201] In this system, the increase in activity became less pronounced when higher α-olefins were used as comonomer. However, the silane-modified supports did result in polymer resins with a narrower molecular weight distribution than the "unmodified" system. Silica has also been chemically modified by $(MeO)_3Si(CH_2)_3X$ (X = SH, OMe, or NH_2[200a]),[202] 2-(3,4-epoxycyclohexyl)ethyltrismethoxylsilane followed by coupling with poly(ethylene oxide),[203] or $(MeO)_3Si(CH_2)_3NH_2$ followed by coupling with poly(styrene-*co*-4-vinylpyridine),[204] prior to contact with MAO, while other unfunctionalized silane modifiers have included (*c*-Hex)$_2$Si(OMe)$_2$[205a] and Me_2(Oct)SiCl.[205b]

Recently, Chisholm and co-workers disclosed a convenient method for preparing fluorinated[206] or sulfated[207] modified inorganic oxide supports (silica or alumina), by contacting the inorganic oxide with an aqueous solution of NaF or $[X]_2[SO_4]$ (X = H or NH_4), respectively. Drying (135 °C, overnight; 200 °C for 2 h) the modified support in air, followed by calcination (600 °C, 6 h) under N_2, afforded a fluorinated or sulfated support, which when consecutively contacted with MAO and (Ind)($^tBu_3P{=}N$)$TiCl_2$ afforded supported catalysts with higher activities than the corresponding "un-fluorinated or un-sulfated" systems. Chemical modification of an inorganic support with $AlCl_3$[208] or $Al(OBu)_3$[209] has also been suggested to lead to suitable supports for the immobilization of a MAO/metallocene system.

The Lewis base ethyl benzoate has been contacted with a preformed Et(Ind)$_2$$ZrCl_2$/MAO/$SiO_2$ system in a 5:1 molar ratio of ethyl benzoate/Zr. The ethyl benzoate acts as an external chemical modifier/donor.[210] The resultant catalyst, along with the unmodified system, was used to polymerize propylene in continuous and semibatch processes. The systems derived from the ethyl benzoate modification resulted in increased catalytic activities, albeit with reduced stability, and afforded polymer resins with a higher stereoregularity.

Unconventional aluminoxane activators, such as MAO derived partly from $AlMe_2OSiMe_3$,[211] hydrocarbylhaloaluminoxane,[212] dimethylaluminum methylaluminoxanate[213] and hydroxyaluminoxane,[214] have also been successfully supported on silica. Supporting hydroxyaluminoxane onto a silica surface has the additional benefit of improving the stability of the Al−OH, a species that is vital in the generation of the aluminoxanate anion and relatively unstable in solutions.

3.3.3. Supporting Precatalyst–Methylaluminoxane Solutions

Combining a solution of the precatalyst with MAO prior to contact with the inorganic oxide support has become a frequently utilized and successful technique for producing a supported single-site α-olefin polymerization catalyst. The process has several advantages in that it reduces the amount of solvent used and byproducts produced, allows contact with MAO to solubilize and purify a poorly soluble precatalyst,[215] and finally allows a more effective activation of the metal center to be carried out in a homogeneous solution rather than a heterogeneous phase where problems with diffusion or side reaction may occur.

An early and highly successful example of the above procedure was disclosed by Burkhardt and co-workers at Exxon.[216] In this protocol, a metallocene precatalyst was initially contacted with a solution of MAO prior to contact with calcined silica (800 °C, 8

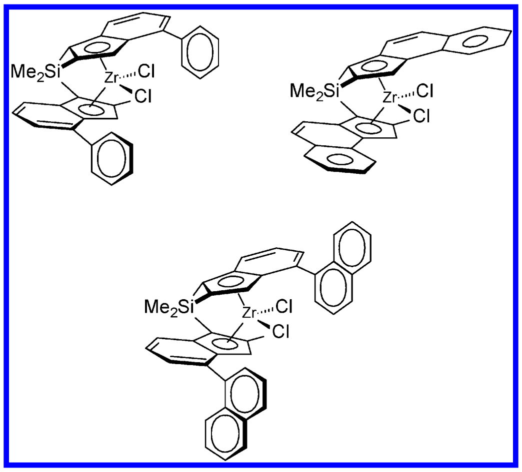


Figure 11. C_2-symmetric metallocene precatalysts.[217]

h, N_2 flow). The slurry of metallocene/MAO/SiO_2 was then mixed together, while the temperature was gradually elevated (ca. 50 °C). During heating a vacuum is applied above the suspension, while a slight N_2 purge is applied below to remove the solvent and afford a viscous mixture. At this point, the heating was gradually increased and the temperature held at ca. 65 °C for an additional 3 h to afford a dry free flowing catalyst. The catalyst was then reslurried in isopentane and carefully prepolymerized to yield the finished catalyst.

At approximately the same time, workers at Hoechst were searching for an effective means of immobilizing the highly active and stereoselective C_2-symmetric metallocene precatalysts, such as $Me_2Si(2\text{-}Me\text{-}4\text{-}PhInd)_2ZrCl_2$, $Me_2Si(2\text{-}Me\text{-}4\text{-}(1\text{-}Naphth)Ind)_2ZrCl_2$, and $Me_2Si(2\text{-}Me\text{-}Benz[e]Ind)_2ZrCl_2$ (Figure 11).[217] Although these precatalysts performed exceptionally well in the solution polymerization of propylene,[217,218] their immobilization proved to be difficult. The search resulted in collaborative research between Exxon and Hoechst and led to the successful combination of the respective precatalyst and immobilization technologies.[219−221]

The difficulty in supporting the Spaleck family of precatalysts was illustrated in a subsequent study by Mülhaupt et al.[222] The study investigated and compared the isoselective polymerization of propylene using a supported catalyst SiO_2/MAO/$Me_2Si(2\text{-}Me\text{-}Benz[e]Ind)_2ZrCl_2$[223] and the corresponding homogeneous system, concentrating particularly on the influence of monomer concentration, polymerization medium, temperature, and scavenger on polymerization kinetics and polypropylene properties. The supported systems possessed lower activities and yielded resins of lower molecular weight and lower melting point, resulting from an increased number of stereo- and regio-errors, all of which led the group to conclude that mass and heat transfer was important for a supported catalyst when high bulk density polypropylene was formed. Similar results were also reported by Kaminsky and co-workers for the polymerization of propylene using $Me_2Si(2\text{-}Me\text{-}4\text{-}(1\text{-}Naphth)Ind)_2ZrCl_2$ as a precatalyst in conjunction with MAO or MAO/SiO_2.[224] In addition, the group studied the supported catalyst in various polymerization processes, such as toluene slurry, bulk monomer, and gas phase (NaCl and PE mechanically stirred fluidized bed). The latter gas-phase process resulted in a more stable polymerization, especially at elevated temperatures.

Modifications to the basic procedure of adding a MAO/precatalyst solution to a silica support have been reported to afford dramatic improvements in activity, morphological control, or both. Removal of the gel fraction of a MAO-solution via decantation or filtration prior to contact with the metallocene precatalyst has been claimed to lead to polymer resin of superior morphology and particle size distribution when compared to its gel-containing counterpart.[225] Allowing a solution of MAO and $Me_2Si(2\text{-}Me,4\text{-}PhInd)_2ZrCl_2$ to stand in the dark overnight before addition to silica is also reported to lead to an almost doubling of activity over catalysts derived from an immediate contact with the support.[226] Finally, additional physical procedures such as N_2 purge drying[227] or spray drying[228] of the MAO/metallocene/silica slurry have all been claimed to be beneficial to catalytic performance.[229]

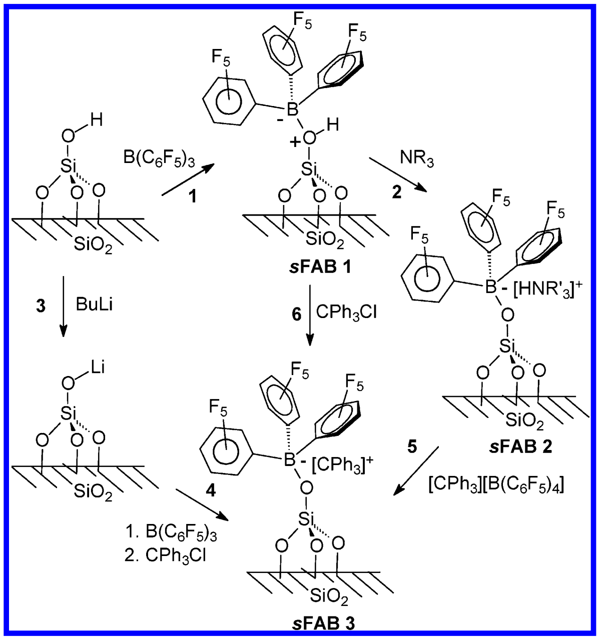
A major advance in the field of immobilized single-site α-olefin polymerization catalyst has been the development of controlled pore-filling or "incipient wetness" techniques for impregnating the silica support by the metallocene/aluminoxane solution. In these procedures, the volume of the catalyst solution can be less than (ca. 60−95%),[230,231] equal to (100%),[231,232] or slightly higher than (ca. 125−150%)[233] the pore volume of the support. The catalyst solution, in the majority of cases, is added slowly or incrementally to a stirred sample of calcined silica,[230−233] and reports describing large (ca. 120 kg) scale catalyst preparation have appeared.[234] Alternatively, Chang reported the use of vacuum impregnation, where the silica was held under a slight vacuum (ca. 0.33 atm) while an aliquot of the catalyst solution equal to the pore volume was added.[235] Other interesting and large scale[236] variations on the "incipient wetness" procedure have been the impregnation of the support via aspirating the catalyst solution onto a mechanically fluidized bed of support material[236,237] and the use of a liquid/liquid two-phase system in which the silica was slurried in perfluorooctane and a toluene solution of the catalyst (equal to the pore volume of the silica) added.[238] The immiscibility of the two liquids forced the catalyst solution into the pores of the support. Prepolymerization of the resultant perfluoroalkane slurry by ethylene afforded the finished catalyst following isolation.

MAO, metallocene, or solutions of both have also been added to silica surfaces that have been modified by an alkylaluminum complex. In these cases, the alkylaluminum "pacifies" the silica surface prior to immobilization of the precatalyst.[239−245] The pacification step reacts away or blocks the surface species (water, silanol, and silyl ether functions) that may poison or interfere with the active center of the final catalyst. For example, Jejelowo and Bamberger treated a solution of $(^{bu}Cp)_2ZrCl_2$ and MAO with a TMA-pacified silica (dried at 200 °C, prior to pacification) affording a catalyst system that was more active and yielded higher molecular weight ethylene-*co*-1-hexene resins than a catalyst prepared by treating $(^{bu}Cp)_2ZrCl_2$ with a silica-supported MAO.[240] The copolymer resins produced by the TMA-pacified catalyst did, however, possess broader molecular weight distribution than the unpacified samples, $M_w/M_n = 3.1$ and 2.4, respectively. The improvements in catalyst activity appear to be related to the calcination temperature of the silica prior to TMA pacification, as Lo and Pruden reported a reduction in activity with increased reactor fouling for the catalyst system prepared by treatment of a TMA-pacified silica (calcined at 600 °C, prior to pacification) with a $(^{bu}Cp)_2ZrCl_2$/MAO solution when compared to the unpacified counterpart.[241] Gas-phase pilot plant runs on the two systems afforded some unexpected results for the unpacified system with respect to the effect that comonomer concentration, temperature, scavenger, carbon monoxide concentration, and in particular operating in condensed mode (injection of isopentane) has on the melt flow index of the resultant resins.[242] TMA-pacified silica has also been used to support metallocene/hexaisobutylaluminoxane combinations.[243]

Pacification of silica by an alkylaluminum complex has also been reported to improve final catalyst performance in the bulk-phase polymerization of propylene. Fritze and co-workers used TEA and TIBA treatments to pacify various commercial silica supports that had previously been dried in vacuo at 140 °C. The pacified silica was then treated with a solution of *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}PhInd)_2ZrCl_2$ and MAO, followed by isolation. The catalysts were then compared in the bulk phase homopolymerization of propylene to catalyst systems prepared by contact of the precatalyst with commercial or preparative MAO/SiO_2 activator. Higher activity was reported for the catalyst prepared on the pacified supports, affording polymer resins with fewer stereo- and regio-errors, a higher melting point, and similar molecular weight and molecular weight distribution compared to the unpacified system.[244] Similar benefits have also been reported for systems formed via treatment of MAO-pacified silica with *rac*-$Me_2Si(2\text{-}Me\text{-}Benz[e]Ind)_2ZrCl_2$/MAO, which afforded highly active systems (up to 12.5 kg of PP/(g of catalyst h)) that produced polypropylene resin of narrow molecular weight and particle size distributions.[245]

As we have seen earlier, there has been a recent effort to support metallocene/MAO catalyst on silica chemically modified by an inorganic complex. Speca,[246] for example, reported the chemical treatment of silica by solid $[NH_4][X]$ ($X = F, SiF_6, PF_6$, or BF_4), which followed a heat treatment regime to afford a modified silica. The modified silica was then treated with a metallocene/MAO solution, affording catalysts that were up to three times more active than comparative "unmodified" examples in the bulk polymerization of propylene. Similarly, Welch and co-workers pretreated uncalcined silica with Borax in methanol.[247] The support was then dried, calcined at 800 °C, and treated with TMA prior to contact with a solution of MAO/$Me_2Si(2\text{-}Me\text{-}Benz[e]Ind)_2ZrCl_2$ to give systems that were more active in the homopolymerization of propylene. Additional examples of chemically modified silica as supports for metallocene−MAO combinations have also been reported.[248]

Scheme 2

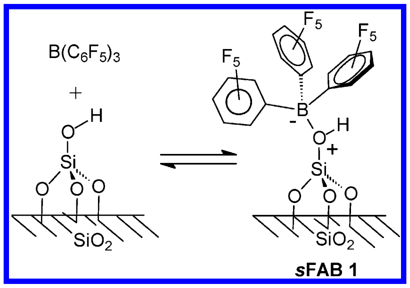


3.4. Grafted Perfluorinated Group 13 Complexes

The ability of group 13 complexes, containing perfluorinated aryl ligands, to cocatalyze the homogeneous polymerization of α-olefins is well documented.[21] These weakly coordinating anions are attractive cocatalysts for a number of reasons. First, they generate catalytic systems with comparable activities to MAO, and although relatively expensive, their efficient activation of the precatalyst leads to low cocatalyst to metal ratios, making them cost competitive to MAO. One of the most interesting features is the discrete nature of such cocatalysts, which has led to the unambiguous characterization of numerous catalytic systems.[20b] It is hardly surprising therefore that the development of the corresponding supported species has become an area of increased academic and industrial interest. Generally, immobilized perfluorinated aryl group 13 cocatalysts can be divided into three groups: grafted, physisorbed, or tethered. The following section concentrates on grafted and physisorbed species, while tethered species will be covered in a separate section.

Grafted group 13 complexes containing one or more pentafluorophenyl groups are supported cocatalysts in which the group 13 atom is chemically linked to the surface of the support. Utilizing trispentafluorophenyl borane, Walzer[249] along with Ward and Carnahan[250] was able to prepare three examples of grafted boron species (*s*FAB-1,[249] *s*FAB-2,[249,250] and *s*FAB-3,[250] Scheme 2) that were capable of generating a catalytically active species in conjunction with a dimethylmetallocene complex. Walzer used the interaction of $B(C_6F_5)_3$, acting as a Lewis acid toward the surface silanol group (step 1, Scheme 2), to yield the Brønsted acid *s*FAB-1, which was claimed to activate $Cp^*_2ZrMe_2$ in the slurry-phase polymeriza-

Scheme 3



tion of ethylene.[251] Treatment of *s*FAB-1 with a tertiary amine (Et_2NPh) or the admixing of $B(C_6F_5)_3$ and Et_2NPh with partially dehydroxylated silica formed the anilinium borate species *s*FAB-2. This species, in conjunction with several dialkylmetallocenes, was used to homo- or copolymerize ethylene to HDPE, LLDPE, or VLDPE in slurry- or gas-phase processes and to homopolymerize propylene to *i*PP in a bulk phase process, producing resins of relatively narrow polydispersities ($M_w/M_n = 2.5-2.9$).

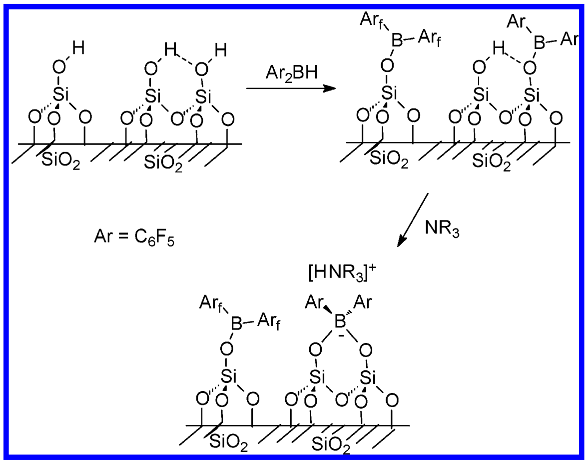
Ward and Carnahan on the other hand treated silica or alumina with ^nBuLi (step 3, Scheme 2) followed by addition of $B(C_6F_5)_3$ and metathesis with trityl chloride (step 4, Scheme 2) to form the supported trityl borate *s*FAB-3.[250] Solid-state ^{11}B NMR spectroscopic experiments resulted in sharp resonance patterns with a chemical shift that indicated the presence of four-coordinate boron species. The supported borate species were tested in the homopolymerization of ethylene, utilizing Cp_2ZrMe_2 as a precatalyst. The catalytic systems afforded higher activities than the corresponding silica-supported dimethylanilinium borate system.

The interaction of $B(C_6F_5)_3$ with silica and alumina supports was studied by Collins and co-workers.[252] The reactions were indirectly monitored by ^{19}F NMR spectroscopy in toluene-d_8 suspensions containing an internal standard to determine incorporation of borane. The results, when compared to the elemental analysis of the solid cocatalyst, indicated that the Brønsted acid, *s*FAB-1, is in equilibrium with free borane and silica, Scheme 3. A higher loading of the borane was noted for the alumina support compared to silica.

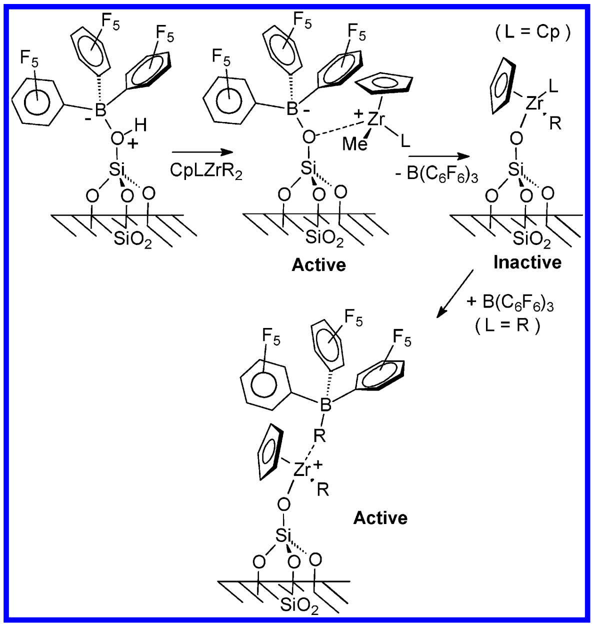
Solution ^{19}F NMR spectroscopic experiments also indicated an absence of borane hydrolysis products, C_6F_5H, $[B(C_6F_5)_2]O$, or $HOB(C_6F_5)_2$. It should be noted, however, that complexes such as $[B(C_6F_5)_2]O$ and $HOB(C_6F_5)_2$,[253] along with $XB(C_6F_5)_2$ ($X = Cl$[252,254] or H[252,254,255]), have themselves been shown to interact with a silica surface (Scheme 4) to produce supported boron cocatalysts.

Studies of the supported bis-perfluorinated phenyl borane silica systems revealed the presence of $MeB(C_6F_5)_2$ in solution, following contact with Cp_2ZrMe_2.[252] The result indicates that Cp_2ZrMe_2 cleaves the boron−siloxy bond to form a grafted zirconocene and $MeB(C_6F_5)_2$ (Scheme 5). Such a reaction has implications for the Brønsted acid *s*FAB-1, mentioned earlier. If the cleavage of the boron−siloxy bond were to take place for *s*FAB-1, then the choice of dialkyl or trialkyl zirconium precatalyst may lead to an inactive or active system. Consequently a possible misinterpretation as to the nature of the active site may occur.

Scheme 4



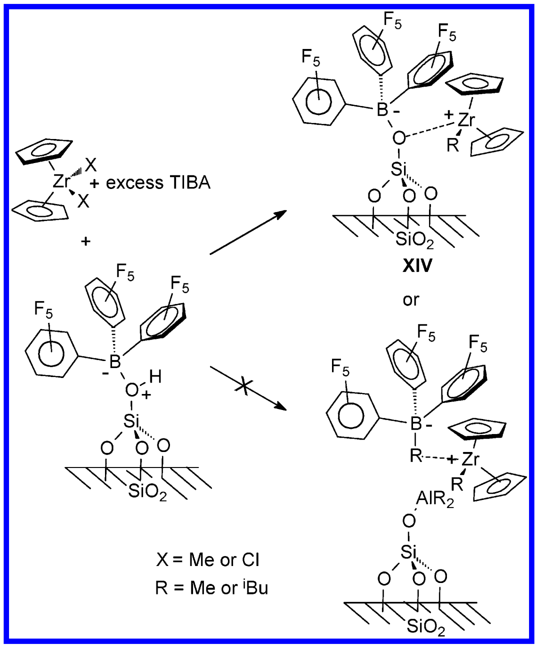
Scheme 5



Bochmann and co-workers provided the first examples in open literature of silica-supported anilinium and trityl borates.[256] The anilinium borate was synthesized as previously mentioned (Scheme 2), while the trityl borate was produced by ion exchanging the supported anilinium borate with $[CPh_3][B(C_6F_5)_4]$ (step 5, Scheme 2). The heterogeneous cocatalysts, in combination with $AlMe_3$ and a dimethyl-metallocene, Cp_2ZrMe_2, or $Me_2Si(Ind)_2ZrMe_2$, showed reasonable activities in ethylene polymerization. However, the polymers produced showed exceptionally broad molecular weight distributions, possibly due to the ratio of B/Zr/Al used (1:12:60).

Recently, a third synthetic route to heterogeneous trityl borates has been reported.[257] Gulari and coworkers found that the Brønsted acid *s*FAB-1 reacts with trityl chloride under facile conditions, room temperature, and in the absence of light (step 6, Scheme 2), eliminating HCl to form the supported trityl borate. In addition, $B(C_6F_5)_3$ was also found to form Brønsted acid sites on partially alkylaluminum-pacified (AlR_3; R = Et or ^iBu) silica. The Brønsted

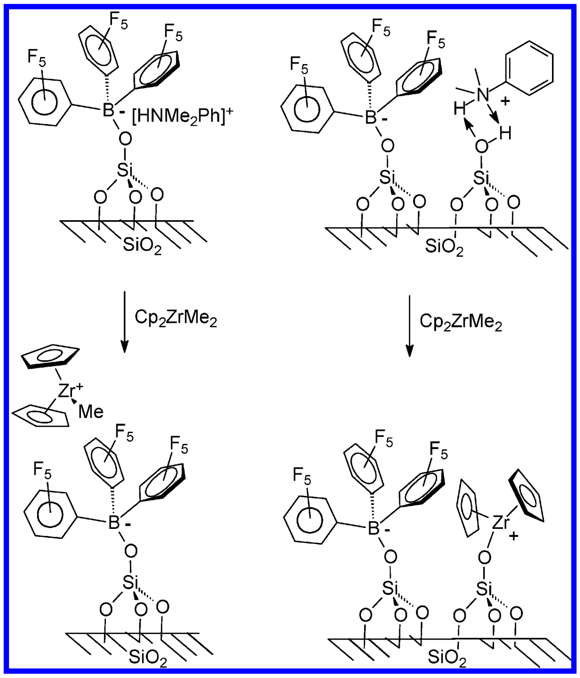
Scheme 6



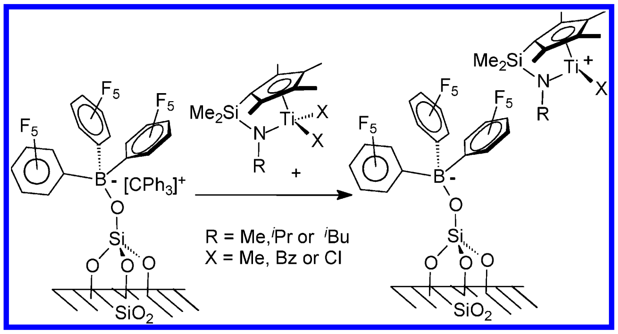
acid sites could also be converted to the trityl borate following contact with trityl chloride. The heterogeneous cocatalysts produced were used to activate a Cp_2ZrCl_2/TIBA solution (Al/B/Zr ratio = 1500:6.5:1), for the homopolymerization of ethylene. The Brønsted acid supported on unpacified silica was also used to activate solutions of Cp_2ZrCl_2/TIBA (Al/Zr = 625:1) or Cp_2ZrMe_2/TIBA (Al/Zr = 500:1), forming the supported catalyst **XIV**, depicted in Scheme 6. The excess TIBA used to generate or protect the dialkyl zirconocene was believed to be unreactive toward the Brønsted acid function.

As mentioned previously, one of the main advantages of single-component cocatalysts is the opportunity to fully characterize the cocatalyst and activated species. The discrete nature of these cocatalysts, along with ^{13}C enrichment of specific functions on a metallocene complex, allowed Basset and co-workers to use IR, CP-MAS ^{13}C NMR, and solid-state ^{11}B and $^{1}H-^{13}C$ HETCOR spectroscopic techniques to comprehensively characterize the catalyst systems formed by reaction of a silica-supported diethylanilinium borate with $Cp^{*}ZrMe_3$.[258] The study of such systems also provided an insight into the interaction between $B(C_6F_5)_3$ and NR_2Ph (R = Me or Et) in the presence or absence of a protic function such as a surface silanol group.[258d] Recently, a similar silica-supported anilinium borate has been characterized by DRIFT spectroscopy. The results highlighted the possible formation of two types of silica-supported borate species, Scheme 7. This view is supported by collorary evidence on catalyst loading and its effect on polymerization activity.[259]

Scheme 7



Scheme 8



Further examples of grafted trispentafluorophenyl borate activators have been reported.[260,261] Of note are the disclosures by Vizzini and Chudgar[260a] on the silica-supported diethylanilinium borate, which when treated with *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}PhInd)_2ZrMe_2$ polymerized propylene to relatively high activities, 8.6 kg of PP/g of catalyst, and narrow polydispersities, $M_w/M_n = 2.44$, and Jacobs and co-workers' communication on an immobilized dimethylanilinium borate/Cp_2ZrMe_2 system that produced a heterogeneous propylene oligomerization catalyst, affording 90% 1-alkenes with a Flory−Schulz carbon number distribution and an activity comparable to the homogeneous system.[261]

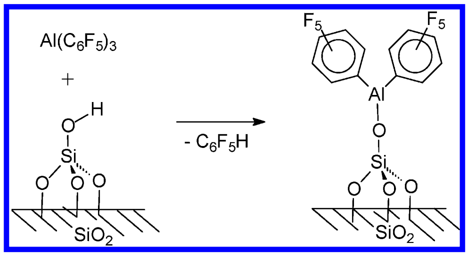
The previous examples of olefin polymerization cocatalyzed by supported trispentafluorophenyl borates have focused on the activation of zirconocenes. To date, only one example of their application as supported activators for non- or post-metallocene precatalysts has been published. Okuda and co-workers prepared supported trityl borates on two types of silica (Sylopol 948 and MPS5) and used them to activate several titanium-based "constrained geometry" catalysts having various bonding patterns, Scheme 8.[262] Interestingly, polymerization activities comparable to (MPS5) or even higher than (Sylopol 948) the homogeneous $[CPh_3][B(C_6F_5)_4]$-activated systems were observed. Additionally, the polymer resins produced were of higher molecular weight and narrower molecular weight distribution than the aforementioned homogeneous system, Table 4. The productivity of the heterogeneous catalysts in terms of kg of PE/g of catalyst is, however, less impressive. The morphology of the polymer resins differed greatly between the two silicas, the Sylopol- and MPS5-

Table 4. Comparative Polymerization Data and Polymer Properties

	B−Sylopol	B−MPS5	$[CPh_3][B(C_6F_5)_4]$
Ti (μmol)	5	5	5
B (μmol)	10	10	10
B content (mmol/g)	0.15	0.18	na
solid cat. (mg)	66	55	na
yield (g)	1.501	0.324	0.843
activity (kg of PE/mol of Ti·h)	600.4	129.6	337.2
prod. (kg of PE/g of cat.·h)	0.045	0.012	na
M_w	738 000	859 000	144 600
M_w/M_n	2.2	1.9	3.1

Ti = $Me_2Si(C_5Me_4)N(^tBu)TiBz_2$, 70°, 5 bar $C_2^=$, t = 30 min., toluene, TIBA (Al:Ti = 200:1).

Scheme 9



supported borates producing fines or spherical particles, respectively.

Research groups at Univation[263] and Dow[264] have treated silica surfaces with trispentafluorophenyl-alumane, $Al(C_6F_5)_3$. Holtcamp studied the interaction and found that $Al(C_6F_5)_3$ did not form a Brønsted acid site when contacted with silica or fluorinated silica, unlike its boron analogue.[263a] Instead, the supported Lewis acid, bispentafluorophenyl-alumane, is produced via elimination of pentafluorobenzene, Scheme 9. The supported perfluorophenylaluminum complexes were capable of activating dialkylmetallocenes, but the storage stability of these supported cocatalysts was found to be strongly dependent on the silica calcination temperature. For example, Holtcamp and co-workers found that activity degraded rapidly when the silica was calcined at 600 °C, while a calcination temperature of 800 °C yielded a relatively stable cocatalyst. The addition of TEA to the supported bispentafluorophenyl-alumane led to an increase in activity of the stored catalyst over time (calcined 600 °C).[263c] The trispentafluorophenyl-alumane has also been treated with $[Me_2AlOCPh_3]_2$ prior to contact with a silica support. The pretreatment formed an ionic species consisting of a trityl cation and a methyl-pentafluorophenyl-aluminoxate.[263b]

A convenient synthetic route to trispentafluorophenyl-alumane involves the metathesis reaction between $AlMe_3$ and $B(C_6F_5)_3$.[265] Similar ligand exchange reactions between $B(C_6F_5)_3$ and TMA-[266] or MAO-pacified[267] silica have also been employed to produce supported perfluorinated phenyl aluminum species capable of acting as cocatalysts. Perfluoraryloxide-containing cocatalysts that are efficient activators for dialkylmetallocenes have been produced by contacting TMA-[268] or MAO-pacified[269] supports with C_6F_5-OH or by pretreating an alkylaluminum solution with 4,4′-dihydroxyoctafluorobiphenol monohydrate prior to contact with a diethyl aniline treated silica.[270] Additionally, alkylaluminum-pacified supports have been treated with 4,5,6,7-tetrahydroindole to give effective supported cocatalysts.[271]

The addition of boronic acids, boronic esters, or boroximes to MAO has been shown to enhance its activating properties.[272] Various boronic acids have since been contacted with trialkylaluminum complexes at varying stoichiometries to form ill-[273] or well-defined[274] boralumoxane cocatalyst systems. Recently, the immobilization of numerous examples of boralumoxane complexes has been reported. Kratzer, Fritze,[275] and others[276] have formed silica-supported boralumoxane or anilinium boralumoxate complexes capable of activating dialkylmetallocenes.

3.5. Physisorption of Pentafluorophenyl Group 13 Complexes

The physisorption of boron-activated systems on a silica surface previously pacified by an alkylaluminum or alkylaluminoxane complex has proved to be an efficient means of producing polymerization systems that operate very effectively in the particle forming processes. Good morphology, without leaching or reactor fouling, has been observed for the majority of these systems, despite the absence of an apparent link between the support and the pre- or cocatalysts. The active species are associated with the surface support via electrostatic or van der Waals interactions. As a result, the polarity of the synthesis solvent and polymerization medium is of critical importance. There are three synthetic protocols to physisorb boron-activated systems. These procedures differ in their order of addition, with either the boron-containing cocatalyst, the metal precatalyst, or an activated combination of the two being initially contacted with the pacified surface of the support.

Hlatky et al reported the use of calcined, TEA-pacified silica in conjunction with $[HNMe_2Ph][B(C_6F_5)_4]$ or $[CPh_3][B(C_6F_5)_4]$ and a dimethylhafnocene complex.[277] Calcined silica (800 °C) is treated with TEA to form a pacified silica containing approximately 2 wt % aluminum. Addition of a stoichiometric mixture of dimethylhafnocene and either $[HNMe_2Ph][B(C_6F_5)_4]$ or $[CPh_3][B(C_6F_5)_4]$ in toluene formed a supported ionic catalyst system, following removal of toluene in vacuo. However, it was reported to be preferable to first support the borate cocatalyst prior to contact with the dimethylhafnocene. In the latter route, the pacified silica is treated with a solution of the cocatalyst dissolved in either CH_2Cl_2 ($[HNMe_2Ph][B(C_6F_5)_4]$) or warm toluene ($[CPh_3][B(C_6F_5)_4]$). The solid activators were analyzed by low-voltage scanning electron microscopy, following the removal of the volatiles in vacuo, and were found to contain no crystallites of the borate complex (50 Å level) on the surface, suggesting even distribution throughout the support. Pentane slurries of the supported borate could then be treated with Cp_2HfMe_2 or *rac*-$SiMe_2(Ind)_2HfMe_2$, generating an active catalyst for the homopolymerization of ethylene or propylene, Table 5. The *rac*-$SiMe_2(Ind)HfMe_2$ system was also used to polymerize propylene with high activities in bulk monomer (80 kg of PP/(mmol of Zr·h)) or gas phase (440 g of PP/g of catalyst). The storage stability of

Table 5. Ethylene Polymerization with Supported Cp_2HfMe_2 Precatalysts

support	activator[a]	activity[b] (kg of PE/mol of Hf·atm·h)
SiO_2/TEA	A	577
SiO_2/TEA	B	987
SiO_2/TEA		5
SiO_2	A	55

[a] A = $[HNMe_2Ph][B(C_6F_5)_4]$, B = $[CPh_3][B(C_6F_5)_4]$. [b] 80 °C, hexane, 13.6 atm $C_2^{=}$, TEA, 30 min.

Table 6. Effect of Addition of NMe_2Ph on the Polymerization Performance

	mole ratio in system[a]			activity[b] (kg of PE/g of cat.)
	B	Zr	A	
SiO_2/TEA	1	1	1	2.4
SiO_2/TEA	1	1	1.5	2.8
SiO_2/TEA	1	1	2	5.1
SiO_2/TEA	1	1	4	0.6

[a] B = $[HNMe_2Ph][B(C_6F_5)_4]$, Z = $BuCp_2ZrCl_2$, A = NMe_2Ph. [b] 70 °C, 26 bar $C_2^{=}$, isobutane, BOMag, 90 min.

the supported catalysts was also reported to be far superior to the corresponding homogeneous system.

Brintzinger[278] and Stevens[279] along with their respective co-workers have also reported the formation of active ionic catalysts by consecutive addition of a borate cocatalyst and a precatalyst to pacified silica. In the latter approach, the ionic cocatalyst was treated with a TEA- or hexamethyldisilazane (HMDS)-modified silica prior to the addition of a constrained geometry titanium butadiene complex. When compared to the TEA-pacified silica, the silane-modified support achieved comparable or higher activities in ethylene-*co*-1-octene polymerization.[279]

Conscious of the sensitivity of metal alkyl complexes, Kristen et al. developed a procedure in which the immobilized ionic catalyst is formed in situ.[280] In a modified approach to Hlatky et al.,[277] the silica surface is treated with a stoichiometric mixture of $[HNMe_2Ph][B(C_6F_5)_4]$ and a metallocene dichloride. Samples of the isolated catalyst were analyzed by wavelength dispersive X-ray analysis. The results indicated that both boron and zirconium were distributed throughout the support. The isolated catalysts were then introduced into a polymerization reactor and an alkylating agent (LiR, MgR_2, or AlR_3) present inside the reaction medium was used to alkylate the metallocene, initiating activation of the metal center. The procedure resulted in a highly active and reproducible system for a range of metallocenes. The system's flexibility also provided the ability to homo- or copolymerize ethylene or propylene and has been up-scaled to operate beyond pilot plant scale (gas and slurry phases). The addition of 1 equiv of dimethylaniline to the reactor, above that produced by the activation process, led to a considerable improvement in ethylene polymerization activity of the system generated by $^{bu}Cp_2ZrCl_2$, $[HNMe_2Ph][B(C_6F_5)_4]$, and BOMag ($MgBu_{1.5}Oct_{0.5}$), while addition of higher levels led to a drastic reduction, Table 6.

Research groups at Basell have since extended this procedure to utilize iron dichloride precatalysts based on a diacetylpyridine-bis-pyrrol-1-ylimine backbone to produce a two-component catalyst system with a zirconocene complex[281] or a constrained geometry catalyst.[282] A similar preparation procedure to Kristen et al.[280] has also been reported for the gas-phase polymerization of Stephan's[31] trisalkylphosiphinimine-containing titanium precatalysts.[283]

The benefits of cocontacting a mixture of a dichloride precatalyst and an anilinium borate with a pacified surface to form in situ the active species has also been reported by workers at Equistar.[284−286] In the reports, a boroaryl-containing precatalyst, $(1\text{-}Me\text{-}BC_5H_5)(Cp)ZrCl_2$ or Cp_2ZrCl_2, and $[CPh_3][B(C_6F_5)_4]$ were cocontacted with TEA-,[284] HMDS-[285] or HMDS/BEt_3-pacified[285,286] silica. The storage and polymerization stability of the catalytic systems generated were superior to those generated by the analogous dimethyl precatalyst. Once again addition of a Lewis base was found to have a profound positive effect on catalyst activities with an appropriate amount of a fatty amine leading to a 2-fold increase in the productivity of ethylene and ethylene-*co*-1-hexene polymerization systems.[285] The use of fatty amines also proved beneficial to the operation of the gas-phase process, reducing the static charge generated in the reactor. Fatty ammonium cations have also been used as static charge modifiers by Patrick and co-workers, who utilized a catalyst system comprising $[N(C_{18}H_{37})_4][B(C_6F_5)_4]$, *rac*-$SiMe_2(Ind\text{-}H_4)_2ZrCl_2$, MAO, and SiO_2.[287] In addition, bis(trispentafluorophenyl group 13)-imidazole or -triazole cocatalyst systems containing a fatty ammonium cation have also been found to produce active polymerization systems.[288]

Improvements in activity when using the dichloride, rather than a dialkylmetallocene, were also reported by Fritze and co-workers.[289] Addition of TMA to *rac*-$SiMe_2(2\text{-}Me\text{-}4\text{-}PhInd)_2ZrCl_2$ prior to addition of dimethylanilinium bis(2,2′-octafluorobiphenyl)borate and subsequent admixing with a TIBA-pacified silica led to higher catalyst productivities (48 kg of PP/(g of metallocene·h)) in the bulk phase polymerization of propylene than the corresponding *rac*-$SiMe_2(2\text{-}Me\text{-}4\text{-}PhInd)_2ZrMe_2$ catalyzed species (37 kg of PP/(g of metallocene·h)).

Contacting the precatalyst with an alkylaluminum-pacified silica before activation by a borane[290−295] or borate[290,295,296] cocatalyst has been reported by various industrial research groups. The majority of these reports concentrate on the activation by $B(C_6F_5)_3$ of a supported constrained geometry precatalyst (dimethyl, butadiene, or Cl_2/TIBA).[290−292] Separate addition of an alkylaluminum-pacified silica to the aforementioned supported ionic catalyst has been shown to improve catalyst activity.[294] Presumably the alkylaluminum-pacified silica acts as a supported scavenger for impurities in the polymerization medium. The catalytic systems were found to form polymer resin with good morphology, but one might question the morphology of a reported polymer resin that could not be stirred after only 10 g of PE was produced in the reactor (1 L of toluene slurry polymerization).[291]

Knuuttila and co-workers studied the preimpregnation of *rac*-$Et(2\text{-}^tBuMe_2SiO{-}Ind)_2ZrCl_2$ on a TMA-pacified silica or alumina support prior to contact with $B(C_6F_5)_3$ or $[CPh_3][B(C_6F_5)_4]$ cocatalyst.[295] Various combinations of the above components were utilized in polymerization with the TMA−alumina $[CPh_3][B(C_6F_5)_4]$ systems producing active species with good molecular weight distributions (M_w/M_n = 2.1−2.8), while the TMA−silica $B(C_6F_5)_3$ systems gave exceptionally broad distributions ($M_w/M_n \leq 8.5$).

Surprisingly, the admixing of separately supported precatalyst and cocatalyst within the reactor has been shown to produce an active species. Silica-supported $Me_2C(Flu)(Cp)ZrX_2$ (X = Cl or Me) was mixed with silica-supported $[CPh_3][B(C_6F_5)_4]$. The resultant solid mix was then introduced into a bulk propylene polymerization experiment to produce syndiotactic polypropylene. The fact that an active species is formed may indicate that either the pre- or cocatalyst is able to leach from its silica surface, while an absence of reactor fouling implies that only one of these species is leaching.[297]

An early example of a preactivated ionic catalyst contacted with pacified supports was reported by Krause and co-workers.[298] The dialkyl zirconocene Ind_2ZrMe_2 was preactivated with either $[CPh_3][B(C_6F_5)_4]$ or $B(C_6F_5)_3$ before contact with a TMA-, TIBA-, HMDS- or BuLi-pacified silica. Surprisingly, the supported borane-activated system was approximately five times more active in slurry polymerization than the trityl borate-based systems and was unexpectedly active when supported on unpacified silica calcined at 600 °C. The productivities of the systems were as high as 9.8 kg of PE/(g of catalyst·h) for ethylene-*co*-1-hexene polymerization with the relative productivity of the individual systems dependent on the silica pacification agent used: HMDS > TMA > BuLi > none > TIBA. Silica supports pacified by NH_4F or $RSiMe_2Cl$ (R = Oct) have also been used to produce immobilized polymerization systems in conjunction with a dialkylmetallocene−borate combination.[299] Further examples of such systems can be found in the reports by Bingel,[300] Fritze,[301] and Yang.[302]

Supported ionic late transition metal catalysts have been utilized in the polymerization of α-olefins.[303,304] Ionic nickel complexes in their unalkylated form have been immobilized by workers at Eastman. The silylated silica surface was further pacified by treatment with $AlMe_3$, BEt_3, or $ZnEt_2$.[304] The support was then treated with an ionic nickel α-diimine complex, $[(CH_2SC{=}NAr)_2Ni(acac)][B(C_6F_5)_4]$ (Ar = 4-Ph-2,6-^{But}-$Ph_2C_6H_2$) to form a supported ionic catalyst able to polymerize ethylene. The most productive systems were formed when the ionic precatalyst was used in conjunction with the BEt_3-modified support.

An early and interesting example of an immobilized ionic α-olefin polymerization cocatalyzed via a borate was presented by Takahashi and Yano.[305] In the disclosure, Cp'_2ZrCl_2 (Cp′ = Cp, ^{bu}Cp, or Ind) or *rac*-$Et(Ind)_2ZrCl_2$ was immobilized onto a silica−MAO support. The immobilized system is then prepolymerized with ethylene to a productivity of 6−30 g of PE/g of catalyst. A sample of the prepolymer is then treated with $[HNMe_2Ph][B(C_6F_5)_4]$ and polymerized under more arduous conditions. The polymerization behavior of the MAO-activated prepolymer, without contact with $[HNMe_2Ph][B(C_6F_5)_4]$, was also examined and was found to lead to a 5−10-fold decrease in activity, implying that $[B(C_6F_5)_4]^-$ had undergone cation exchange with $[Me\text{-}MAO]^-$.

Table 7. Ethylene Polymerization Data[a]

	yield (g)	M_w	M_n/M_w
$MnCl_2$	7.0	75600	2.0
$FeCl_2$	2.07	75400	1.6
$NiBr_2$	1.75	78500	1.6
NaCl	0.48	134000	2.6
NaI	0.63	74300	1.6
SiO_2/TIBA	8.39	74900	1.9
Fe_2O_3	1.87	82250	2.1
C1	7.75	74220	1.8
C2	2.69	72750	1.8

[a] 5 μmol of $[CPh_3][B(C_6F_5)_4]$, 1 mmol of TIBA, 10−15 mg of support, 10 bar $C_2^=$, 1 h; C1 and C2 = montmorillonite and synthetic saponite, respectively.

Finally, two rather unusual borate-containing systems have been reported to produce active polymerization catalysts. The first was formed by a non-fluorinated borate complex, $[^nBu_3NH][B(C_6H_4\text{-}4\text{-}Me)_4]$, which produced an inactive catalyst in combination with Cp_2ZrMe_2 in homogeneous solution but was found to produce an active species when contacted with support.[306] One of the most unusual and possibly important disclosures within the field of supported α-olefin polymerization catalysis is the claim by Seki and Hirahata that $[CPh_3][B(C_6F_5)_4]$/TIBA (B/Al = 1:200) forms an active species when used in conjunction with various carrier materials.[307] Some of the results for homopolymerization of ethylene are illustrated in Table 7. As one can see, exceptionally narrow molecular weight distributions are achieved, the molecular weights of the polymer resins indicating that the same active species is formed on each carrier surface. The systems based on $MnCl_2$ and SiO_2/TIBA were also shown to effectively copolymerize ethylene and 1-hexene, again to narrow molecular weight distributions and with relatively high comonomer incorporations (11% 1-hexene). It is also interesting to note that the melting points of the PEs (all 136 °C) are indicative of linear HDPE, signifying that supports such as $FeCl_2$ and especially $NiBr_2$ do not themselves oligomerize or polymerize ethylene under these conditions. $[CPh_3][B(C_6F_5)_4]$/TIBA contacted with SiO_2/TIBA also afforded an active propylene polymerization catalyst, producing PP with a narrow molecular weight distribution (M_n/M_w = 1.73) and some degree of stereoregularity (*mm* 0.930, T_{m_2} = 142 °C). The report does not describe the nature or mechanism of the active species formed, and no mention is given to the morphology of the polymer resins produced.

4. Zeolites and Mesoporous Materials

Zeolites are crystalline aluminosilicates with a framework structure based on the three-dimensional arrangement of tetrahedral Al^{3+} and Si^{4+} (MO_4; M = Al or Si). These arrangements form cavities or supercages with connecting channels of specific dimensions. Unlike amorphous silica, these supports possess well-defined pore structures with a narrow pore size distribution. The electronic properties of the support surface are governed by the aluminosilicate's Brønsted acidity, which in turn is dependent on the coordination state of the aluminum after calcination and on the type of counterion, which can be tailored by ion exchange.[308] Mesoporous silicates, such as SBA-15 or MCM-41 and -48 belong to the family of mesoporous molecular sieves[309] and consist of cylindrical, hexagonal, or cubic ordered pores and can be modified by the incorporation of other elements such as aluminum.[310]

Woo and co-workers studied the homo- and copolymerization of ethylene with catalytic systems generated by metallocenes supported on faujasite zeolite NaY or MCM-41, which were precontacted with MAO or TMA.[311,312] The group observed a large decrease in activity when compared to the corresponding homogeneous system but an increase in polymer molecular weight. The authors attributed the increased molecular weights and stable polymerization activity to a reduction in the rate of chain transfer and prevention of active sites forming bimolecular species, due to the steric constraints of the zeolite pores.[311] However, the ability to polymerize an olefin within the mesopores of a zeolite has been questioned.[311b] The copolymerization of ethylene with propylene, 1-hexene, 1-octene, or 1-octadecene indicated that the catalyst systems exhibit a monomer shape and diffusion controlled copolymerization mechanism that is strongly dependent on the molecular structure of the comonomer and its size.[312] Additionally, Ciardelli and co-workers have postulated that for zeolite-immobilized systems the size and location of metallocene can affect comonomer incorporation.[313] In comparative tests with the homogeneous systems, the group observed similar or decreased comonomer incorporation for $Et(Ind)_2MCl_2-MAO$ (M = Zr or Hf) or Cp_2ZrCl_2-MAO zeolite-supported systems, respectively. In Cp_2ZrCl_2-MAO systems, the metallocene is thought to be able to penetrate the pores of the zeolite and reside inside the pores where comonomer diffusion is restricted, while the larger steric bulk of the $Et(Ind)_2MCl_2-MAO$ systems prevents such penetration resulting in the metallocene residing on the exterior of the support where it is more readily accessible to the comonomer. Marques et al., however, found the catalytic activities and comonomer contents of zeolite- and mordenite-supported Cp'_2ZrCl_2 ($Cp' = Cp$ or ${}^{bu}Cp$) systems to be similar to those of the homogeneous system.[314]

The initial bulk Si/Al ratio of a zeolite has also been reported to have a major influence on the catalyst loading and final polymerization activity of a supported species. Altomare et al. noted that a reduction in the bulk Si/Al ratio in various zeolites prior to contact with MAO led to a decrease in the productivity of supported metallocene,[315] while Marques and co-workers reported that de-alumination of zeolite NaY, prior to contact with Cp_2ZrCl_2/MAO led to a reduction in the pore volume, total surface area, and number of Brønsted/Lewis acid sites, while increasing the external area and polymerization activity of the final supported catalyst.[316] These groups and others[317] have postulated that the concentration of framework aluminum is the dominant factor in a zeolite's performance as an olefin polymerization catalyst support. In all the above reports,[315−317] an increase in the molecular weight of the resultant polymer resins was observed, when compared to the corresponding homogeneous system. Controlled partial alumination of MCM-41, on the other hand, has been reported to improve the catalytic activity and metal loading of immobilized metallocene systems in comparison to the corresponding siliceous MCM-41 analogue.[318]

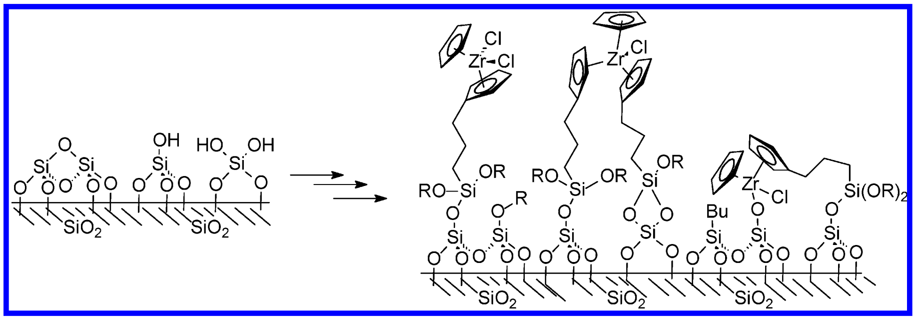
It has been reported that the in situ generation of a methylaluminoxane via reaction of TMA with surface adsorbed H_2O leads to a more effective and accessible activator for dialkylmetallocene species supported on MCM-41[319] and ZSM zeolites.[320] In addition, Jacobs and co-workers' study of the cooligomerization of ethylene and propylene with $Et(Ind)_2ZrMe_2$ supported on the aforementioned MCM-41/MAO system revealed a clear pore size effect, with narrow pore sizes leading to increased molecular weights, an effect more pronounced at lower Al/Zr ratios.[319]

C_2-symmetric metallocenes confined inside the pores of zeolites (VPI-5) and mesoporous silica (MCM-41) have been used to prepare isotactic polypropylene with higher stereoregularities, molecular weights, and melting points than the corresponding homogeneous and silica-supported system.[321] The pore size of the support has also been shown to strongly influence polymerization stability, molecular weights and stereoregulaties. Similar increases in stereoregularity, melting points and molecular weights have also been observed for syndiotatic polypropylene formed with MCM-41-supported $Me_2C(Cp)(Flu)ZrCl_2$/MAO systems.[322] Once again the initial aluminum content of the MCM-41 has a considerable influence on the catalytic performance.[322b] Various MCM-41 and SBA 15 materials have been used in the absorptive separation of MAO. Interestingly, the stereoregularity of the polypropylene resins formed by a homogeneous solution of $Et(Ind)_2ZrCl_2$ and absorbent (MCM-41s or SBA-15)-filtered MAO were markedly dependent on the pore size of the absorbent material.[323]

Zirconium-,[324] vanadium-,[325] iron-,[326] and nickel-based[327] post-metallocene precatalysts have been supported onto zeolites and mesoporous materials. In supported nickel α-diimine precatalysts, the supporting method and particle morphological parameters, such as pore size and length, were shown to significantly affect catalyst impregnation and chain-walking ability.

Grafting titanocene within the pores of a mesoporous silica (MCM-41) has been used by Aida et al.[328] to produce polyethylenes with a novel fibrous morphology. The fibrous morphology is attributed to directed growth down the narrow channels of the honeycomblike support. The narrow channels restrict the folding of the nascent polymer chains and, with relatively low productivity ensuring that particle fragmentation does not occur, the growing polymer chain is "extruded" out of the pores of the support,

Scheme 10



leading to the fascinating concept of oriented nanoreactors. Analysis of the PE fiber samples by XRD and DSC showed additional peaks, which were claimed to have arisen from the extended chain structure of the polyethylene. However, recent work by Turunen et al.[329] on samples of fibrous polyethylene prepared by Cp_2TiCl_2 supported on a novel MAO-treated MCM-41 silica fiber[330] has indicated that the additional peaks in the XRD and DSC studies may have been misinterpreted for aluminum ($[Al(H_2O)_6][Cl]_3$) residue resulting from the acid termination (HCl) of the polymerization or washing of the resin sample.

Extrusion polymerization using grafted titanocene within the pores of MCM-41 has recently been reported by Wang et al.[331] and Zhu et al.[332] In the latter case, three levels of fibrous morphologies were identified in the fiber samples by extensive scanning electron microscopy studies. Extended-chain PE nanofibrils (diameter ca. 60 nm) were the major morphological units present. These nanofibrils were parallel packed into individual microfibers (1−30 μm), which were further aggregated into bundles. The mechanical properties of the nascent polyethylene fibers were also compared to commercially available PE fibers. The phenomenon of extrusion polymerization has also been reported for bis(imino)pyridyl iron dichloride precatalyst grafted onto SBA-15[332] and in the initial stages of ethylene polymerization on $Cr(acac)_3$ modified MCM-41.[334]

5. Tethering to Inorganic Oxides

Tethering a catalytic complex via a covalent link between the support and the ancillary ligand framework of the pre- or cocatalyst represents one of the largest and most varied techniques employed in the immobilization of single-site α-olefin polymerization catalysts. In this way, the active centers are firmly anchored to the support at all times in the hope that the catalyst will not leach or have enough freedom to deactivate via a bimolecular species during polymerization. Tethers not only serve as ties to bind the catalyst to the support but also function as an isolator from the steric and electronic effects of the support. The disadvantage of the technique for precatalysts in particular is that the catalyst's steric and electronic environment is always different from the homogeneous cousin it is trying to mimic, which complicates the catalyst synthesis and translates into a more expensive catalyst.

Silica is a relatively versatile and robust material and has the additional advantage of a history of varied chemistry being performed on it.[335] Consequently it has become the most extensively studied support for tethering. Two main synthetic strategies have been developed to immobilize the catalyst. The first is to construct the ligand and subsequently the catalyst on the support, and the second is to deposit a catalytic component containing a selective reactive tether that targets a specific function on the support. In theory, selective reactive tethers should give the best hope of forming uniform single active sites, because constructing the complex on the surface usually involves steps that are nonselective or that eliminate potential catalyst poisons or need rigorous purification to remove byproduct from the support. Characterization is also difficult.[42a]

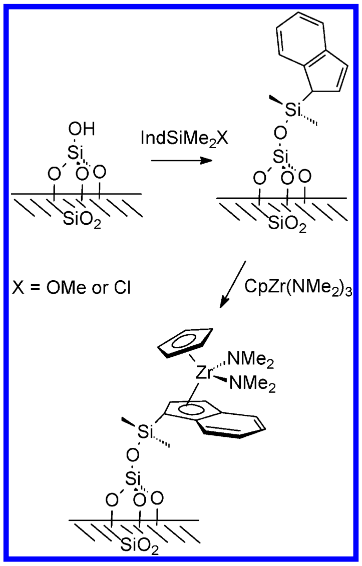
The ubiquitous group 4 metallocenes are particularly difficult to selectively tether due to their electron-deficient, highly oxophilic, and in some cases easily accessible metal centers. Once a tether has reacted with a support, the support itself forms part of the ancillary ligand, affecting the symmetry as well as the steric environment of the final complex. Careful consideration of the type, length, and placement of the tether as well as the monomer(s) to be polymerized is therefore crucial. Extensive studies on homogeneous catalysts have illustrated the consequence of altering the steric or electronic properties of a precatalyst with respect to activity, but especially stereoselectivity.

5.1. Tethering Precatalyst

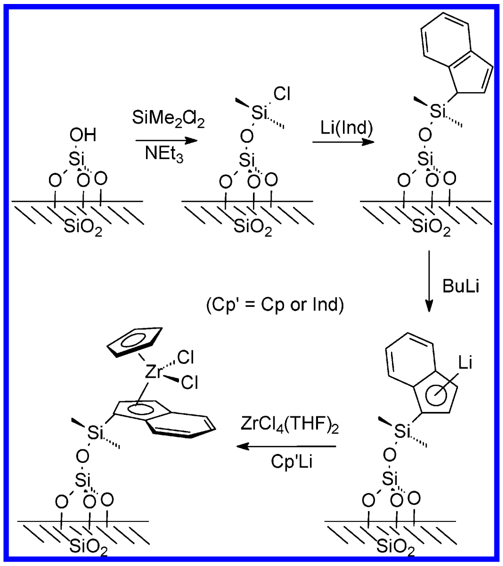
5.1.1. Metallocenes Constructed on a Surface

Pakkanen and co-workers utilized the stepwise construction method to tether an α-olefin polymerization precatalyst onto silica.[336] The silica surface was modified by $Cp(CH_2)_3Si(OEt)_3$ or $Cp(CH_2)_3SiMe_2$-OE, using ALCVD (atomic layer chemical vapor deposition) with the reagent reacting with the surface silanol or strained silyl-ether groups to form the tethered species. The cyclopentadiene modified silica[337] could then be treated with ^nBuLi to form the cylopentadienyl anion, and reacted with either $ZrCl_4\cdot(THF)_2$,[336e] $CpZrCl_3$,[336a] or $CrCl_3(THF)_3$[336d] to form the appropriate starting material. These studies highlighted the various side reactions that can occur when such harsh metallating agents are used (Scheme 10).[336e,] Reaction of the cyclopentadiene with a zirconium amide,[338] however, was thought to provide a less evasive procedure.[336c] All the above systems proved to be active in ethylene polymerization when contacted with MAO (Al/Zr 1500−2000), producing

Scheme 11



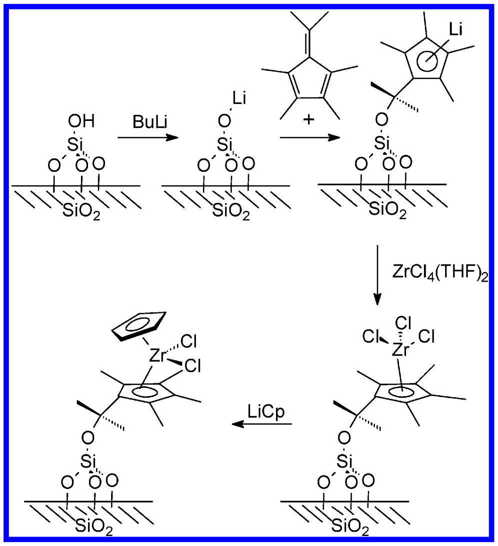
Scheme 12



polymer resins with relatively narrow polydisperisties, with the exception of the chromium species.

A variety of synthetic procedures can often be used to form the same intended tethered precatalyst. For example, three groups have utilized different synthetic routes to form virtually the same tethered precatalyst, on similarly treated silica supports.[339−341] Gila and co-workers at Enichem reacted silica with $IndSiMe_2OMe$ to form an immobilized substituted indene, which when metalated with $Ti(NMe_2)_4$ or $CpZr(NMe_2)_3$ formed a tethered precatalyst (Scheme 11).[339] Herrmann and co-workers on the other hand contacted silica with $IndSiMe_2Cl$. Metalation of the supported indene by $CpZr(NMe_2)_3$ was again used to form the tethered precatalyst.[340] In the third route, Boisson and co-workers initially contacted silica with $SiMe_2Cl_2$ in the presence of NEt_3, before metathesis with either LiCp or LiInd.[341] The tethered ligand was then lithiated, reacted with $ZrCl_4(THF)_4$, and finally reacted with LiCp or Li(Ind) to form a tethered precatalyst (Scheme 12). Different catalyst loadings for the three routes were observed (1.99,[339] 3.11,[340] and 2.5[341] wt %), and all were found to be active in

Scheme 13



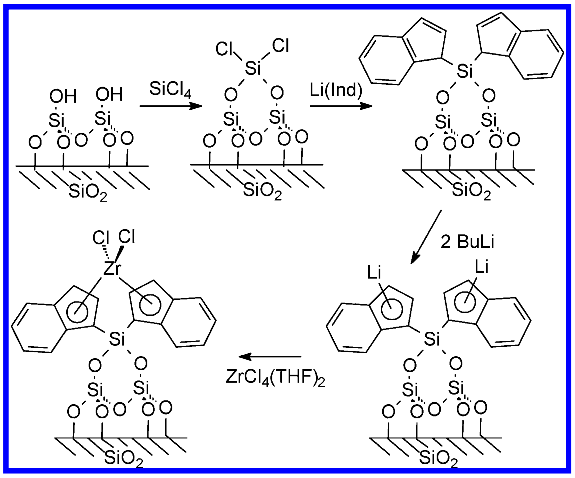
ethylene polymerization when used in combination with MAO (629,[339] 1360,[340] and 243[341] kg/(mol of Zr·b·h)). Analysis of the polymer produced showed slightly broad molecular weight distributions (M_w/M_n = 2.9[340] and 3.3[341]) indicating the existence of several active centers, arising from nonselective or competitive reaction on the silica surface.[340]

A novel multistep route to a tethered precatalyst was recently report by Spitz and co-workers.[342] The four-step procedure involved lithiation of the surface silanol groups and then reaction with 6,6-dimethylfulvene, $ZrCl_4(THF)_2$, and LiCp to form the final tethered precatalyst (Scheme 13). This product when used in combination with TIBA and $[HNMe_2Ph][B(C_6F_5)_4]$ (Al/B/Zr = 285:10.7:1) formed a highly active ethylene polymerization catalyst (22.4 kg/(g of catalyst·h) or 7200 kg/(mol of Zr·bar·h)). The disclosure also illustrates the laborious purification needed when constructing a complex on a surface, for example 15 wash cycles are used in this four-step synthesis. Silica-bound cyclopentadienyl moieties can also be constructed by chlorination of a silica surface via high-temperature treatment with CCl_4. The chlorinated silica surface is then treated with NaCp, followed by $CpM(NMe_2)_3$ or $M(NMe_2)_4$ (M = Ti or Zr), to form the tethered precatalyst.[343]

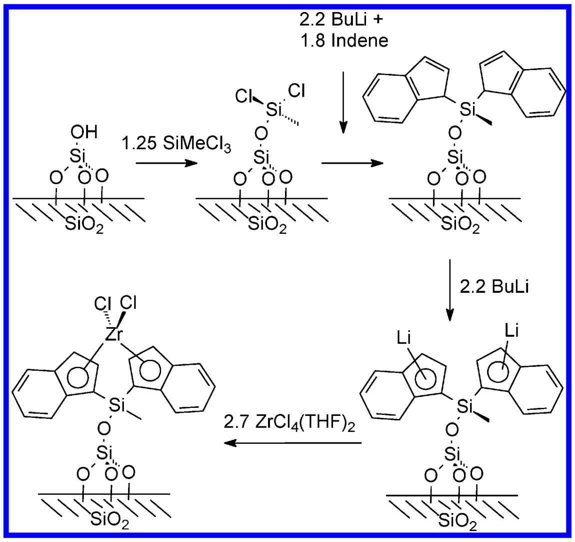
Soga and co-workers constructed bis-indenyl and fluorenyl *ansa*-metallocenes tethered via the bridging atom(s). Partially dehydroxylated silica was initially contacted with $SiCl_4$, $SnCl_4$, or 1,1,2,2-tetrabromoethane. Subsequent treatment with the indenyl or fluorenyl anion afforded the *ansa*-ancillary ligand, which could be converted to the corresponding metallocene complex via lithiation and subsequent metathesis with $ZrCl_4(THF)_2$ [344] (Scheme 14) or $NdCl_3$.[345] Propylene polymerization with the bis-indenyl zirconium complexes yielded isotactic and atactic PP, highlighting the need, when constructing on a surface, to consider how racemic enrichment and or separation of the mesomeric form is to take place. For the neodymocene catalysts, the activity and M_w of the polyethylene produced was strongly dependent on the cocatalyst employed.[345]

Using a similar approach, Spitz and co-workers disclosed a synthetic route involving initial contact

Scheme 14



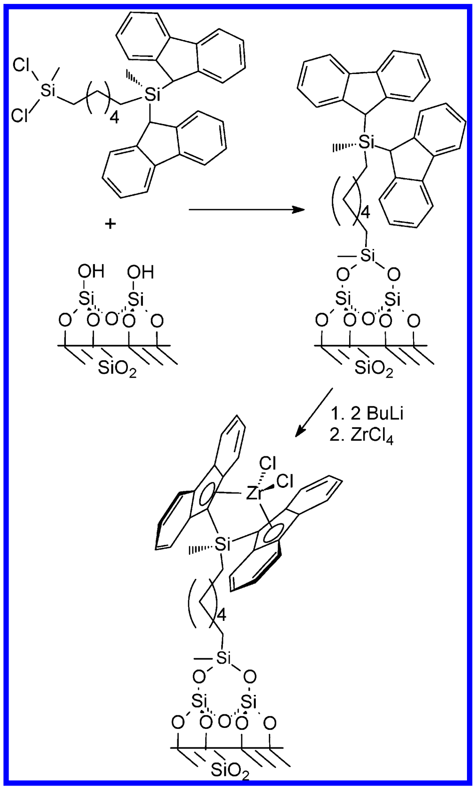
Scheme 15



of the silica surface by $SiMeCl_3$ (Scheme 15). The final tethered precatalyst, when activated with MAO, produced polyethylene with a polydispersity index equal to 2.1.[346] Such a narrow molecular weight distribution is surprising when one considers the numerous possible side reactions that can occur on the silica surface, especially when excess organolithium complexes are employed. Comparable tethered precatalysts have also been prepared by reacting Cp'_2SiCl_2 (Cp' = Ind[347] or Cp[348]) with silica and subsequently converting to the zirconium complexes. This procedure afforded an active catalyst system in conjunction with MAO and produced polyethylene of good bulk density without reactor fouling.

The construction of *ansa*-metallocene precatalysts tethered via their bridging atom has also been reported by Alt[349] and Osamu.[350] Alt and co-workers reacted dehydroxylated silica with either CpFluSiMeCl,[349a−c] $Flu_2SiMe(CH_2)_2SiCl_3$,[349a−c] $CpFluCMe(CH_2)_4SiMe_2Cl$,[349a−c] $Flu_2SiMe(CH_2)_6SiMe_2Cl$,[349d] or $Flu_2SiMe(CH_2)_6SiMeCl_2$.[349d] The corresponding tethered metallocenes were obtained by deprotonation and metathesis with $ZrCl_4$ (Scheme 16). The complexes formed, however, showed low activities and productivities in ethylene polymerization, when used in combination with MAO. The tethered complex illustrated in Scheme 16, for example, displayed

Scheme 16

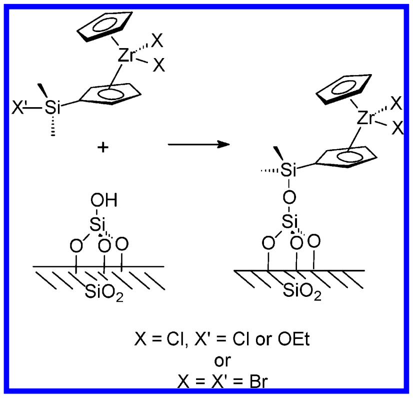


an activity of 144 kg/(mol of Zr·b·h) and a productivity of 34 g of PE/(g of catalyst·h) and was approximately 60 times less active than the homogeneous model compound $SiMe_2(C_6H_{13})Flu_2ZrCl_2$.[349d] Osamu et al. reacted silica with $SiMe_2Cl_2$ and treated this with (HOEt)(Me)C(Cp)$_2$, followed by MeLi and MCl_4 (M = Ti or $ZrCl_4$) to form a tethered ansa-bridged metallocene.[350]

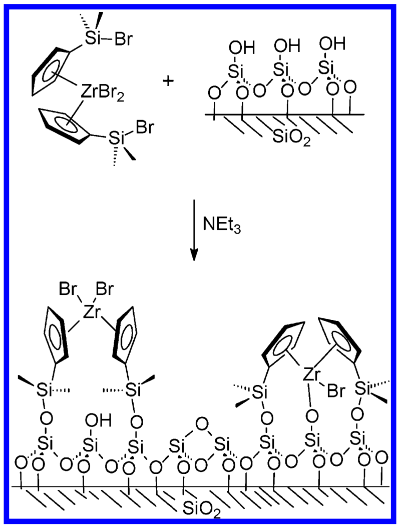
5.1.2. Metallocenes with Reactive Functional Groups

Metallocenes containing a chemically reactive alkoxysilyl tether, such as $\{Cp(CH_2)_3SiOMe_3\}MCl_2$ (M = Ti or Zr), were initially immobilized onto silica to form supported catalysts for the hydrogenation, rather than polymerization, of α-olefins.[351] Antberg and co-workers at Hoechst were one of the first to report the use of reactive alkoxylsilyl tethers for the formation of tethered α-olefin polymerization precatalysts.[352] The functionalized metallocene $(CpSiMe_2OEt)CpZrCl_2$ was reacted with dehydroxylated silica (0.88 mmol of OH per gram of SiO_2), eliminating ethanol to form the silica-tethered metallocenes (Zr 2.7 wt %), Scheme 17. The tethered precatalyst proved effective at polymerizing ethylene (1.25 kg/g of catalyst) when contacted with MAO at relatively low Al/Zr ratios (22:1). Virtually the same tethered precatalysts have been formed by the reaction of halosilyl reactive tethers. Vega and co-workers at Repsol[353] and Deck and co-workers[354] have illustrated the use of $(CpSiMe_2Cl)CpZrCl_2$ and $(CpSiMe_2Br)CpZrBr_2$, respectively, in conjunction with dehydroxylated silica (Scheme 17). In all cases, the polyethylene produced possessed high polydispersities (M_w/M_n = 3.5−5.1), indicative of multiple active species, while for the $(CpSiMe_2Br)CpZrBr_2$ tethered species considerable leaching was reported, albeit in

Scheme 17



Scheme 18

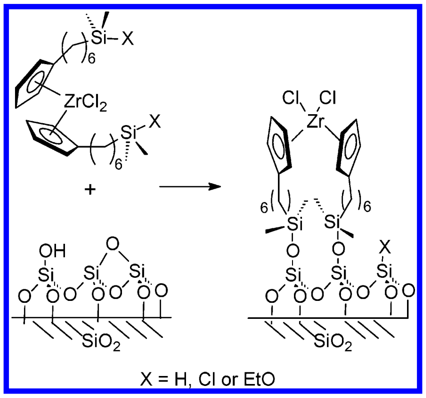


toluene and with high MAO concentration (Al/Zr = 5000:1).

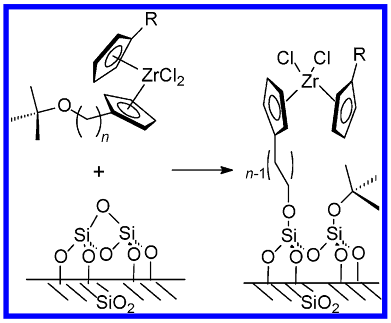
Deck and co-workers also utilized metallocenes with multiple reactive tethers, such as $(CpSiMe_2Br)_2ZrBr_2$, $(CpSiMeBr_2)_2ZrBr_2$, and $(Cp\{SiMe_2Br\}_2)_2ZrBr_2$. A decrease in activity and leaching was observed with increasing number of tethering points, while the PE resins produced showed an increase in molecular weight distribution. The decrease in activity was attributed to either the reduction in the amount of leached (higher activity) homogeneous precatalyst, restriction of conformational freedom on the surface, which hindered monomer uptake, or the presence of an irreversibly locked "face-down" configuration, Scheme 18.[354a] Improved catalytic performance was claimed when the same precatalysts are immobilized in sol−gel networks.

The polymerization precatalysts above contain relatively short tethers to the surface. To increase the conformational freedom of a catalytic species, Oh and co-workers at LG Chemicals synthesized several metallocenes containing a hexamethylene spacer between the cyclopentadienyl moiety and the functional tether, $[(X)SiMe_2(CH_2)_6Cp]_2ZrCl_2$ (X = H, Cl or OEt). Silica samples, calcined at four different temperatures (200, 400, 600, and 800 °C) were employed and provided active tethered polymerization catalysts with MAO as cocatalyst. Increasing the calcination temperature resulted in higher activities and produced PE resins with decreasing polydispersities (3.37−2.64) and molecular weights but had a relatively small effect on catalyst loading (1.1−0.85 wt %), indicating that the functional tether reacts with the both the strained silyl-ether and silanol surface functions (Scheme 19).[355] The authors have subsequently gone on to produce numerous metallocenes that contain various functionalities, $[(X)O(CH_2)_nCp]_2ZrCl_2$ (X = ^tBu, $MeOCH_2$, MeCH(OEt), $Me_2(MeO)C$, Me_3Si, $(EtO)Me_2Si$, or Me_2HSi) that specifically target the reactive surface silyl-ether moiety (Scheme 20).[356] The resultant tethered precatalysts were active in olefin polymerization when contacted with a toluene solution of MAO. In some reports, the MAO solution could then be recycled back into a subsequent batch polymerization.[357] Trimethylsiloxyl functionalized metallocenes, including several *ansa*-metallocenes have also been reported to react with the surface silyl-ether and silanol moieties.[358]

Scheme 19



Scheme 20



The synthesis of *ansa*-metallocene precatalysts containing a reactive functionality has been extensively studied by several research groups.[359,360] Early examples of such were provided when Aulbach and co-workers at Targor disclosed the use of trichlorosilyl-functionalized *ansa*-metallocenes $Cl_3Si(CH_2)_4SiMe(2\text{-}Me\text{-}Ind)_2ZrCl_2$, $(2\text{-}Cl_3Si(CH_2)_4Ind)(2\text{-}Me\text{-}Ind)_2ZrCl_2$, and $Cl_3Si(CH_2)_4SiMe(Cp)_2ZrCl_2$.[359] The latter, when contacted with silica, was moderately active in the polymerization of ethylene (0.65 kg PE/g of catalyst), while workers at Repsol provided an example of a poorly active polymerization catalyst (0.03 kg PE/g of catalyst) when $ClSiMe(Cp)_2ZrCl_2$ was treated with silica.[360]

In a detailed communication, Collins and co-workers demonstrated the use of hydrosilylation chemistry to form tethered *ansa*-metallocenes.[361] In one approach (route A, Scheme 21), Me_2SiHCl-treated silica

Scheme 21

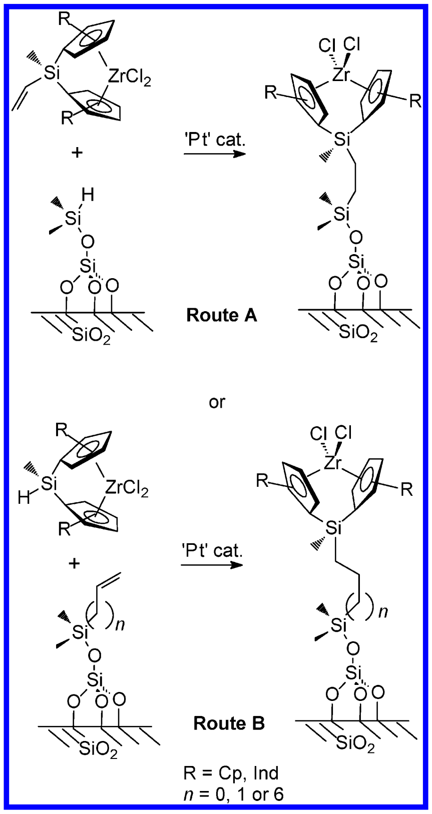


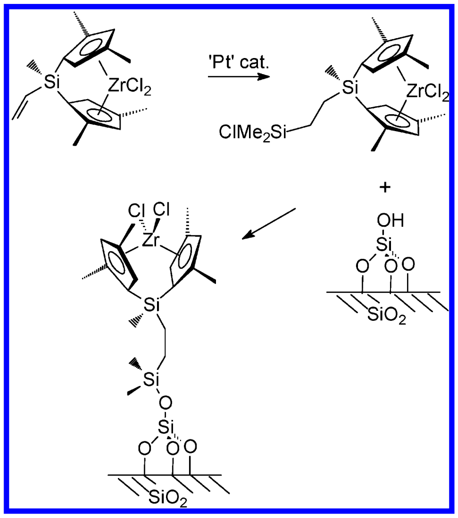
Table 8. Olefin Polymerization Data Using Supported Metallocenes

method	Cp	n	Zr (wt %)	Zr (μmol)	activity	PDI	% pentad
$C_2$$^{=}$ [c]							
A	Cp	2	2.62	3.42	3.9	3.4	
B	Cp	8	0.79	0.86	50	2.1	
B	Cp	8	1.14	0.72	33	3.1	
C	*a*			0.86	40	2.9	
D	*a*		3.45	3.74	21	2.9	
$C_3$$^{=}$ [c]							
A	Ind	2	2.11	1.00	8.8	2.1	86.2
B	Ind	8	2.85	1.00	23.4	2.0	85.3
C	*b*			1.00	30.6	1.8	85.7
D	*b*		4.32	1.00	11.0	1.9	87.2

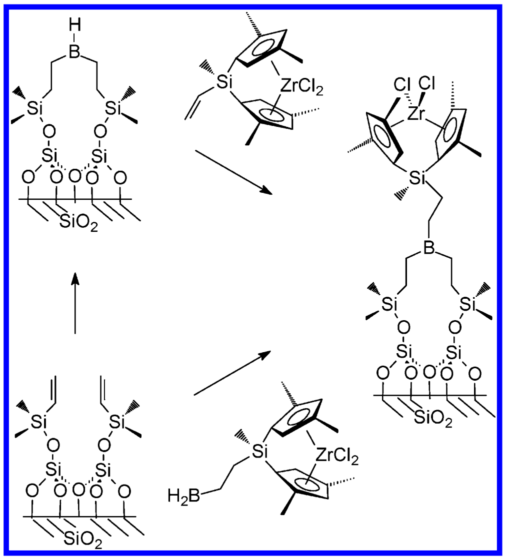
[a] Cp_2ZrCl_2. [b] $Me_2Si(Ind)_2ZrCl_2$. [c] MAO, toluene, 70 °C, 5 bar $C_2^{=}$ or 40 °C, 3 bar $C_3^{=}$.

was used in combination with an *ansa*-metallocene bearing a vinyl group on the bridging silicon atom. A second, more useful approach involved reaction of an *ansa*-metallocene compound with a MeSiH moiety as the bridge with a suitable vinyl- or alkene-functionalized silica (route B, Scheme 21). Route B afforded the opportunity to study the effect of tether length on catalytic performance, longer tethers (C_8) providing increased activity. Catalyst loading, however, was found to play the principal role in determining catalytic activity, high Zr loadings leading to a decrease in activity. The systems compared favorably with Cp_2ZrCl_2 and *rac*-$SiMe_2(Ind)_2ZrCl_2$ activated with MAO (method C, Table 8) or commercially available SiO_2/MAO (method D, Table 8). Leaching, however, was observed in the majority of systems with the stability of SiO_2–$OSiMe_2R$ toward MAO also being called into question. A reduction in leaching was observed when a prepolymerization step was used.

Scheme 22



Scheme 23



Suzuki and co-workers produced a pseudo C_2-symmetric silyl-bridged zirconocene compound with a chlorodimethylsilylethyl functional group on the bridging silicon via hydrosilylation of the vinyl-substituted starting material, $(CH_2{=}CH_2)MeSi(1,3\text{-}Me_2Cp)_2ZrCl_2$, Scheme 22.[362] The chlorosilyl functional group is believed to react selectively with the surface silanol, and this was supported by a model study carried out using $^{t}BuMe_2SiOH$ instead of silica, which obtained the expected modified zirconocene compound with a Si–O–Si linkage. Hydroboration of $(CH_2{=}CH_2)MeSi(1,3\text{-}Me_2Cp)_2ZrCl_2$ with BH_3 and subsequent reaction with a vinyl-coated silica, or vice versa, also produced immobilized precatalysts, Scheme 23. The precatalyst formed via the hydroboration procedure when utilized in propylene polymerization gave higher activity, higher stereoregularity, and a narrower polydispersity than those produced via the hydrosilylation route. A chain transfer reaction to boron, similar to those proposed by Chung et al., may have some influence if residual B–H functionalities are present.[363]

Recently, Miller and O'Hare synthesized a pseudo-C_2-symmetric zirconocene bearing a chlorosilyl function, tethering it to a series of supports, MCM-41,

Scheme 24

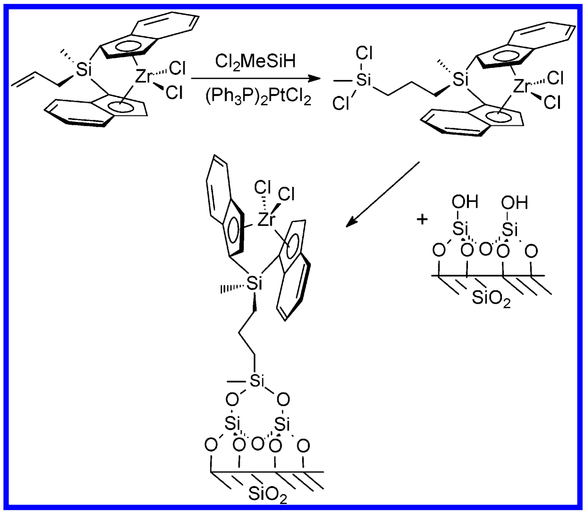


Table 9. Olefin Polymerization Data Using a Supported Metallocene

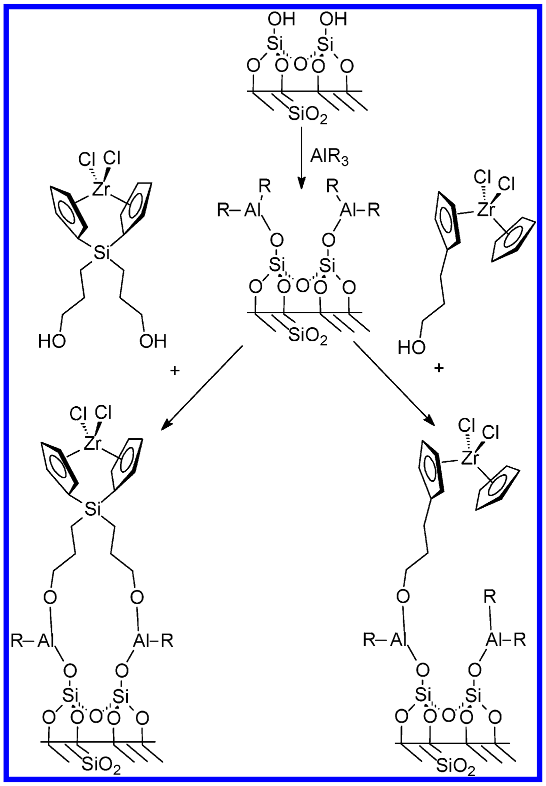
	Zr (wt %)	activity[a]		PDI	
		$C_2^=$	$C_3^=$	$C_2^=$	$C_3^=$
MCM-41	3.5	29.3	4.93	21.5	2.6
MCM-48	4.4	234	0.3	7.0	2.3
SBA-15	3.5	25.2	2.56	20.1	3.4
DMS	3.7	99.5	9.2	4.2	2.6
SiO_2	4.6	317	8.9	10.7	3.5
$SBIZrCl_2$		533	506	8.2	8.4

[a] MAO, toluene, 5 bar, temp and time not reported.

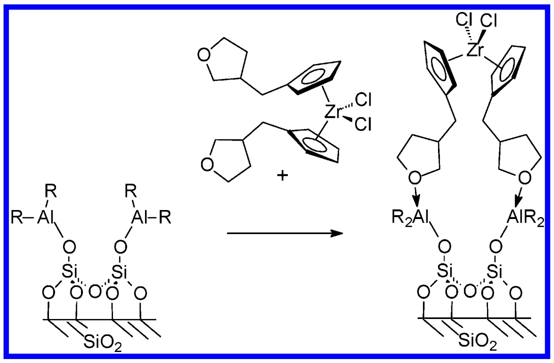
MCM-48, SBA-15, SiO_2, and a disordered mesoporous phase silica (DMS).[364] Great pains were taken to control the synthesis of the precatalyst, using Jordan's racemic directing route,[365] as well as to characterize the final tethered precatalyst (XRD, EDX, ^{13}C, and ^{29}Si CP-MAS NMR spectroscopy). The results were consistent with the presence of a surface-grafted zirconocene species, depicted in Scheme 24. However, when the immobilized precatalysts were used in ethylene homopolymerization, the resultant PE resin possessed exceptionally high polydispersities, indicative of multiple active sites, Table 9. The polydispersities, however, narrow dramatically when propylene is homopolymerized. Striking differences in ethylene and propylene polymerization activities are also reported; for example, the precatalyst immobilized on MCM-48 provides one of the most active precatalysts for ethylene polymerization, while the same system has the lowest activity for propylene polymerization. It should however be noted that the reported performance of *rac*-$Me_2Si(Ind)_2ZrCl_2$ ($SBIZrCl_2$, Table 9) under identical conditions is also a little unusual.

One of the major drawbacks of reactive tethering is the generation of reactive side products (alcohols and HCl) that can interfere with the metal center. To combat this, synthetic procedures involving the initial pacification of the silica surface with an alkylaluminum (MAO, DEAC, or TEA) and reaction with a metallocene carrying a protic functional group were developed. The side products formed in this protocol are benign alkanes. One of the first examples of such a procedure was reported by Nakajima and co-workers, who contacted an alkylaluminum-pacified silica with the amine- and hydroxyl-functionalized metallocenes $(H_2N(CH_2)_3)_2Si(Cp)_2ZrCl_2$ and $(HO(CH_2)_3)_2Si(Cp)_2ZrCl_2$ (Scheme 25).[366] Contact of an alkylaluminum-pacified silica with unbridged monohydroxy-[367] (Scheme 25) and tetrahydrofuranyl-functionalized[368] metallocenes has also been reported (Scheme 26).

Scheme 25



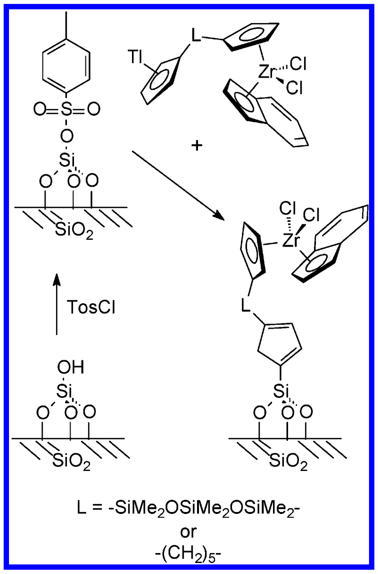
Scheme 26



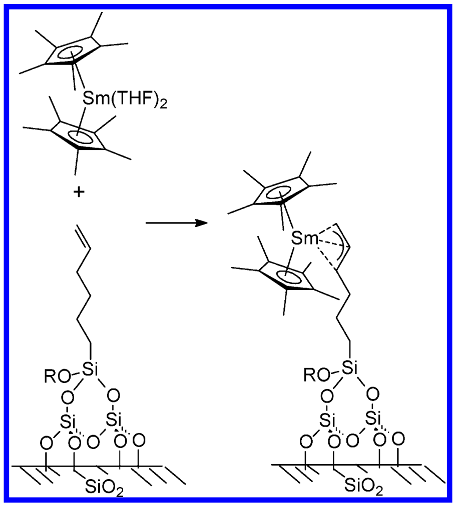
Brintzinger and co-workers reported the pretreatment of dehydroxylated silica with $4\text{-}ClCH_2C_6H_4Si(OMe)_3$ yielding a silica that quarternizes the amino group(s) in $Me_2Si(2\text{-}NMe_2{-}Ind)_2ZrCl_2$ to form an ionic metallocene, which was active in the polymerization of propylene in combination with MAO.[369]

Perhaps the most unusual example of a reactive tethering is the use of the thallium cyclopentadienyl salts. Lee and co-workers reacted the thallium salt, $TlCp\text{-}L\text{-}CpZr(Ind)Cl_2$ (L = hexamethyltrisiloxane or pentamethylene) with a *p*-tosylated silica surface, eliminating thallium tosylate to form a silica-substituted cyclopentadiene tether (Scheme 27). The tethered precatalysts formed moderately active po-

Scheme 27



Scheme 28



lymerization catalysts when treated with MAO, the most active system employing the pentamethylene spacer (658 kg/(mol of Zr·h·bar)). The activities are, however, approximately four times higher than those of $CpIndZrCl_2$ contacted with silica. However, in all cases, high polydispersities were observed for the polymer produced ($M_w/M_n = 3.9-5.2$).[370]

Although not intended to be an immobilized catalyst for large-scale production, the immobilization of $Cp^*{}_2Sm(THF)_2$ on a silica surface with pendant alkene functions and subsequent polymerization is noteworthy, being a rare example of a metallocene tethered via the alkyl moiety (Scheme 28).[371]

5.1.3. Constrained-Geometry Catalysts

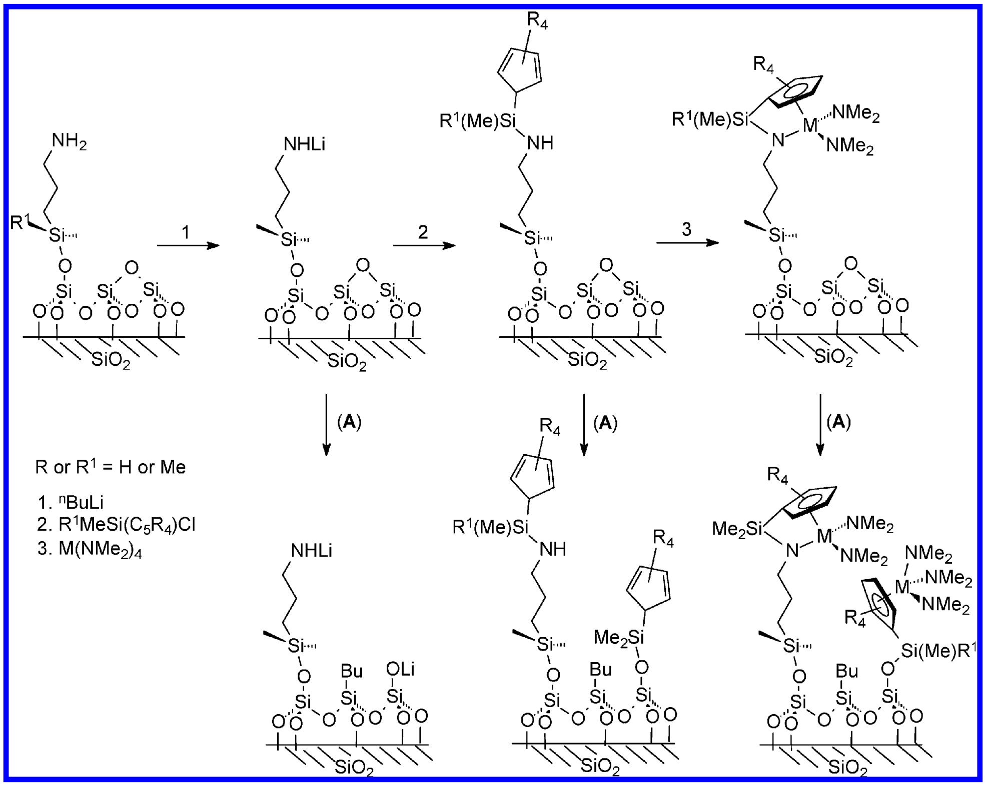
Several groups have attempted to immobilize constrained geometry inspired precatalysts (CGC) via tethering techniques, the majority employing a 3-aminopropyl link to the silica surface. The first such species was synthesized by Uozumi et al. Immobilization of 3-aminopropyltrimethoxysilane onto a silica surface and subsequent contact with Cp^*TiCl_3 formed a poorly active system for the polymerization of ethylene (1.2 kg/(mol·b·h) or 0.24 g of polymer/g of catalyst) and ethylene-*co*-1-octene polymerization (2.57 kg/(mol·b·h) or 0.51 g of polymer/g catalyst). However, it did produce polymers of a narrow molecular weight distribution and random comonomer incorporation.[372]

Pakkanen and co-workers used the construction on a surface approach (Scheme 29) to produce a more "accurate" CGC mimic. The silica surface was modified by $(EtO)Me_2Si(CH_2)_3NH_2$ using ALCVD. The immobilized amino group was lithiated with ^nBuLi and contacted with either $CpSiMe(R^1)Cl$ or $Me_4CpSiMe(R^1)Cl$ (R^1 = H or Me). Analysis of the resultant material indicated the possibility of different cyclopentadiene species on the surface due to side reactions of the ^nBuLi and silica surface (Scheme 29, A).[373] Metalation of the cyclopentadiene starting materials was achieved with $M(NR_2)_4$ (Ti, Zr, or Hf).[374] For the tetramethyl-substituted cyclopentadiene only the zirconium and hafnium precatalyst were successfully synthesized.[374b] In polymerization studies, the activities of the less sterically hindered unsubstituted cyclopentadienyl complexes were higher than those of the corresponding tetramethyl-substituted complexes, while the latter produced narrower polydispersity. A comparable titanium analogue was successfully produced when $(MeO)_3Si(CH_2)_3NH_2$ modifed silicas were used. Hlatky directly reacted 3-aminopropyl-modified silica with $Me_4CpSiMe_2Cl$ in the presence of NEt_3. Metalation with $Ti(NMe_2)_4$ and activation with MAO appears to be successful, although no data were given.[375]

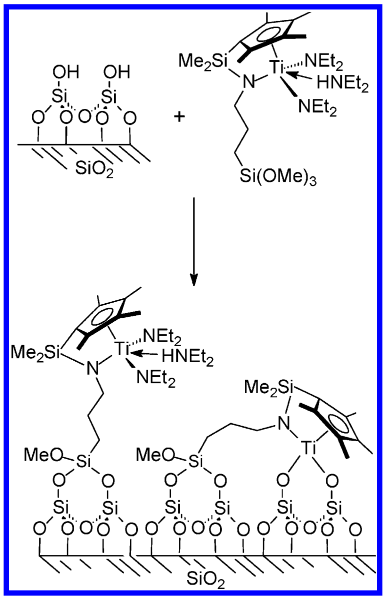
The use of an alkylsiloxyl-containing compound as a reactive tether has also been studied by Eisen.[376] The complex is thought to produce multiple sites, immobilized either through the tether or through the metal or both (Scheme 30). However, once activated via MAO, the active species are probably the same. The presence of MeOH released as side product from the surface may also interfere. The supported catalyst produced polymers with higher M_w than those produced by the homogeneous starting material.

Comparative studies of "constrained geometry inspired" tethered catalysts have recently been published by Jones and co-workers.[377] Active systems produced via stepwise construction or reactive tethers are compared to their ingenious stepwise construction of the precatalyst. In an attempt to produce a more well-defined and isolated species, Jones et. al. first contacted the silica surface with the sterically bulky imine $(Ph_3C)CH_2CHN(CH_2)_3Si(OMe)_3$. The imine's bulk "patterns" the surface like parasols on a sandy beach. After several further steps (Scheme 31), a tethered substituted cyclopentadiene is formed, which can be metalated by $Ti(NMe_2)_4$ and chlorinated with $SiMe_3Cl$, producing isolated uniform species. The benefits of such a rational approach and the absence of steps involving ^nBuLi can be seen in improved activity, reduced leaching, and narrower molecular weight distributions when compared to samples that they made with procedures similar to Pakkanen et al.[373,374] and Eisen et al.[376] Some leaching is reported in the majority of the above cases when MAO is used as an activator. Jones et al. have reported that catalyst leaching was not noticeable

Scheme 29



Scheme 30



when borane activators were used.[377b] It should be noted however that the catalyst productivities, as for most of the above cases, are extremely poor. For example, the highest activity reported for the borane-activated systems was 28 kg of polymer/(mol·h) from a catalyst that had a titanium loading of 0.38 mmol of Ti/g of catalyst. That equals a productivity per hour of just 11 g of polymer/(g of catalyst·h). When one considers that the polymerization time was only 10 min, the actual productivity is just 1.8 g of PE/g of catalyst.

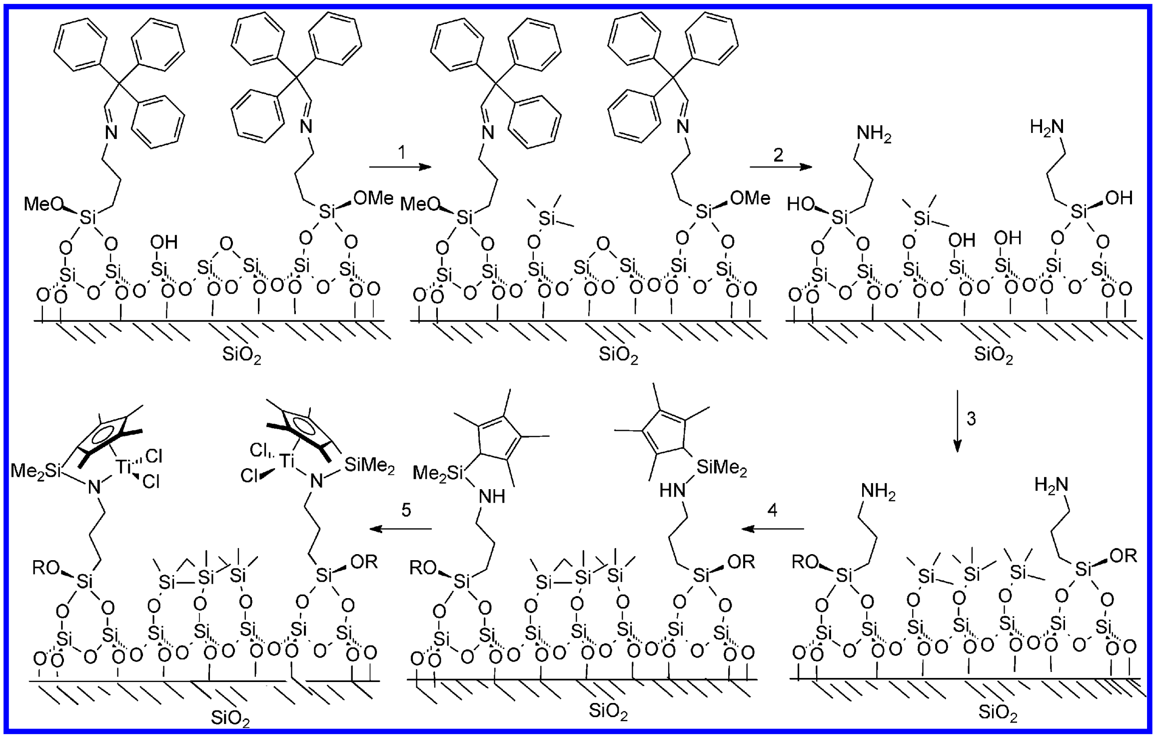
The importance that the spacing of the amine groups has on the final precatalyst can also be seen in another of Jones et al.'s disclosures.[378] In this report, the group compared the immobilization of $ClMe_2SiCpZrCl_3$ onto a support that contained either densely populated or spaced amine functionalities, as described above. In the case where the precatalyst was contacted with the densely populated surface, the resultant catalyst is tethered through the silicon atom and the zirconium atom by two different amine functions, and thus a CGC catalyst is not formed, whereas on the spaced out surface the desired CGC catalyst is formed (Scheme 32).

The use of reactive tethers to form immobilized "constrained geometry inspired" precatalysts has been limited. In addition to Eisen et al.[376] and Jones et al.,[378] Royo and co-workers synthesized $ClMeSi(CpMe_4)N(^tBu)TiCl_2$, then reacted it with silica to produce an immobilized titanium species. The polydispersity indices of the polymers produced in this approach (PDI = 3.0−3.6) indicate the existence of multiple sites, possibly due to competitive reaction of the metal−chloride bond and the silica surface or the acidic side product (HCl).[379]

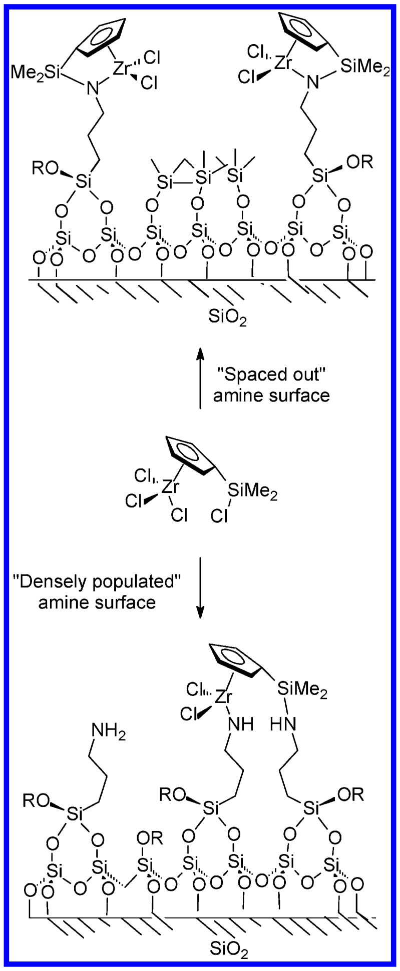
5.1.4. Late Transition Metal Catalysts

Relatively few examples of tethered late transition metal catalyst exist; however, the synthetic procedures used cover the full range of tethering strategies. Mendez Llatas and co-workers at Repsol produced mono- and bis-trimethylsiloxypropyl functionalized α-diimines via the lithiation of the standard α-diimines ligand and reaction with $ICH_2CH_2OSiMe_3$ (Scheme 33). The resultant α-diimines were contacted with silica and $NiBr_2(dme)_2$ to form a series of tethered precatalysts that were active in the polymerization of ethylene, producing PE resins with predominantly methyl branches.[380]

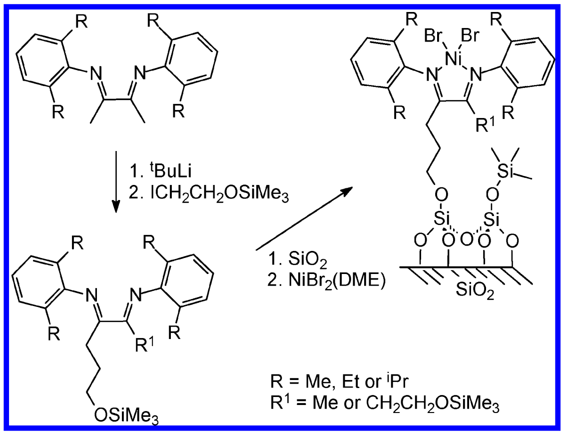
Scheme 31



Scheme 32



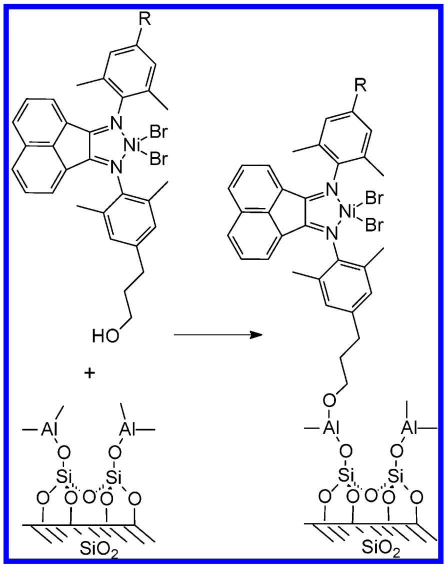
Scheme 33



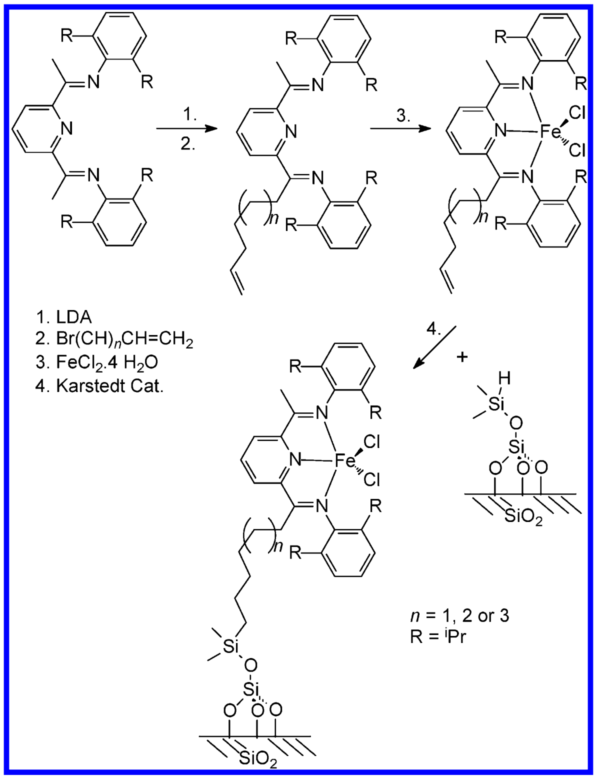
Brookhart and Preishuber-Pflugl synthesized a variety of nickel α-diimines containing amine or hydroxy functional groups, which were reacted with TMA-pacified silica to form tethered precatalysts (Scheme 34).[381] These tethered complexes could be used to polymerize ethylene to very high activities, up to 10.5 kg of PE/g of catalyst, when used in combination with relatively inexpensive alkylaluminum chloride cocatalysts at low Al/Ni ratios with no reactor fouling. The activities were an order of magnitude higher than those formed by treating the unfunctionalized nickel α-diimine with MAO/SiO_2. Grubbs and co-workers have also utilized various hydroxy-functionalized ancillary ligands; β-ketoamines, β-diketimines, and iminoamino-tropolones, which were contacted with phenylsilane-modified silica. These ligands were deprotonated and reacted with $(Ph_3P)_2Ni(Ph)Cl$ to form tethered neutral nickel chelates, which could be activated for ethylene polymerization by contact of a phosphine scavenger such as $Ni(COD)_2$. However, no details of activity and polymer characterization are presented.[382]

Bis(imino)pyridine iron(II) complexes have been prepared via two synthetic strategies. Herrmann and co-workers modified the standard bis(imino)pyridine

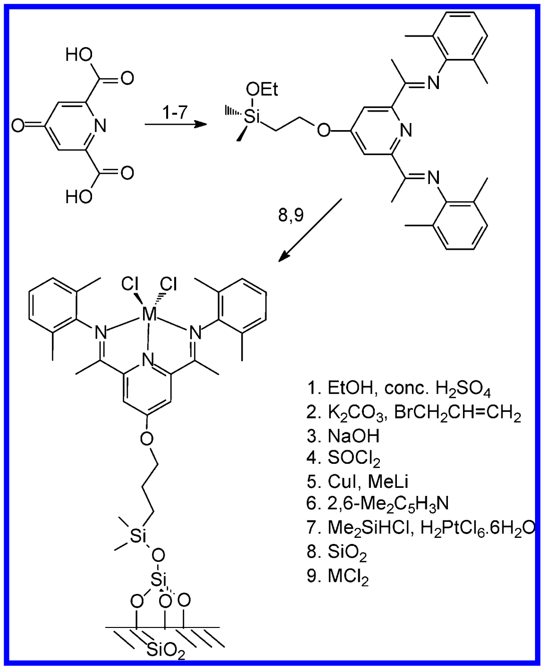
Scheme 34



Scheme 35



Scheme 36



via lithiation with LDA and reaction with a linear bromoalkene of varying lengths, Scheme 35. The alkene-functionalized bis(imino)pyridines were tethered to a silane-modified silica via hydrosilylation.[383] Activation with MMAO produced catalytic systems that were prone to deactivation, especially at elevated temperatures, with the length of tether having little effect on the catalytic activities. The polymer resins produced possessed multimodal polydispersities that narrowed markedly above a polymerization temperature of 60 °C. Kim and co-workers reported an elaborate multistep synthetic protocol to produce an ethoxysilyl-functionalized bis(imino)pyridine, Scheme 36, which was subsequently converted to the corresponding Fe(II) or Co(II) complexes. The tethered precatalyst, when activated by MAO, showed activities drastically lower than the homogeneous unfunctionalized analogues.[384]

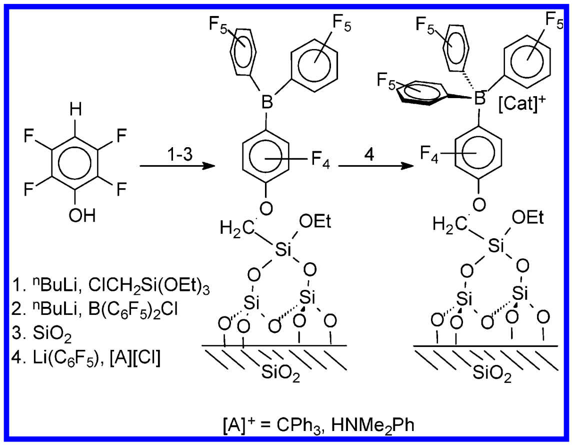
5.2. Tethered Cocatalysts

Tethering a cocatalyst to an inert carrier allows one to use different precatalysts for a single support preparation, making it a considerably more flexible protocol than tethering the precatalyst. Additionally, the use of known precatalysts provides a more realistic comparison to the homogeneous systems, as tethered precatalysts are, in the majority of cases, sterically or electronically different from the precatalysts they are “inspired” to mimic.

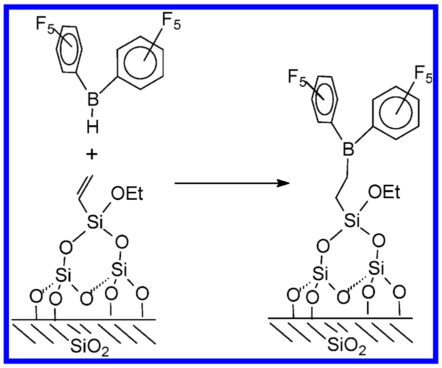
To some extent, supported MAO may be considered the archetypal example of a tethered cocatalyst and its extensive use has been outlined in previous sections. However, until recently surprisingly few examples of tethered perfluoroaryl group 13 cocatalyst systems existed. The tethering of perfluoroaryl group 13 complexes is performed using similar immobilization protocols to tethered precatalysts. As a consequence, they suffer from the same problems of nontrivial alteration of the ancillary ligand or competitive–nonselective reactions occurring when a complex is constructed on a support surface. Additionally, discoveries made by Bochmann[385] and Götz[386] and their respective co-workers may also need to be taken into consideration. The facile degradation of the $[B(C_6F_5)_4]^-$ anion, by reaction of AlR_3 (R = Me, ^{i}Bu) with $[CPh_3][B(C_6F_5)_4]$[385] or $[HNMe_2Ph][B(C_6F_5)_4]$,[386] respectively, leads to the formation of a transient “$[AlR_2][B(C_6F_5)_4]$” species and subsequent decomposition to mixtures of heteroleptic and homoleptic alanes and boranes. Such reactions may impinge on the sequence of addition or the choice of components to be used in the immobilization procedure.

The first proposed procedures for tethering a perfluoroaryl boron-containing cocatalyst were schemati-

Scheme 37



Scheme 38

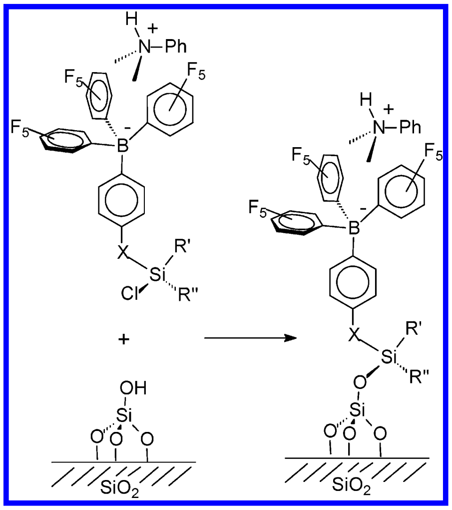


cally outlined by Turner in a 1995 patent.[387] It described either the use of a reactive tether or the construction on a surface of the desired activator. However, although this document contained schematic examples of alkylsiloxy, chlorosilyl, and hydroxy functionalized borates reacting with a silica surface, no specific examples were set forth. Subsequently, several research groups demonstrated the practical implementation of the above concepts.

Fritze and co-workers immobilized perfluoroaryl-containing boranes via a reactive alkoxysilane tether to a silica surface (Scheme 37).[388] The resultant, immobilized borane was used to activate *rac*-$SiMe_2(Ind)_2ZrMe_2$ in the slurry (bulk monomer) polymerization of propylene. However, from the examples outlined in the patent, some confusion arises as to which supported activator is actually used. On the face of it, a typical immobilization procedure contacts 10 mg (23 μmol) of metallocenes with 10 g of supported borane (20 mmol boron), which works out to be a B/Zr ratio of 870:1, a huge ratio when compared to the usual ratio of 1−2:1 and leads to an active species with a productivity of 110 kg/(g of metal·h) or 0.11 kg/(g of catalyst·h). The quarternization of the borane via addition of $Li(C_6F_5)$ and the resultant metathesis with CPh_3Cl to form the tethered borate is also disclosed (Scheme 37). The document also contains an example of an immobilized borane activator, formed by the hydroboration of vinylsiloxy-coated silica surface with $HB(C_6F_5)_2$ (Scheme 38).

Borates containing a chlorosilyl substituent as reactive tether have also been contacted with silica. Hinokuma and co-workers reacted dried silica with $[HNMe_2Ph][(C_6F_5)_3B(C_6R_4\text{-}X\text{-}SiR'_2Cl\text{-}4)]$ (R = H or F; X = O or $SiMe_2(CH_2)_8$; R′ = Me or Cl) in dichloromethane to form a silica-supported cocatalyst (Scheme 39) capable of activating various binary metallocene/TIBA precatalyst systems.[389]

Scheme 39

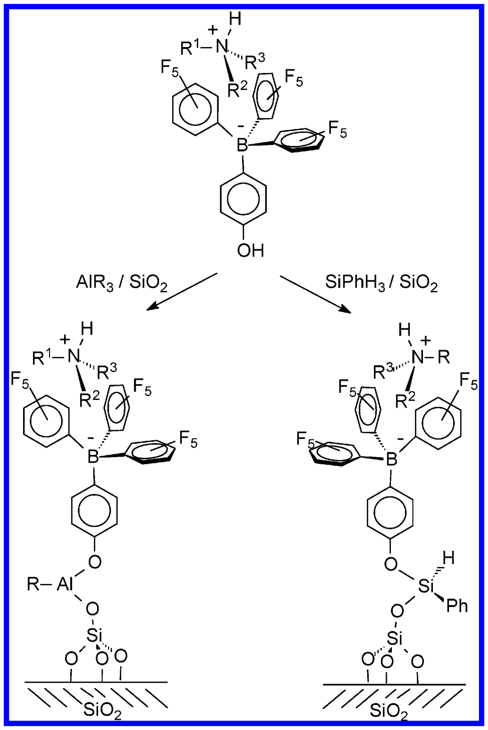


Borates containing a hydroxyl group are probably the most widespread examples of tethered borates. The reaction of a borate with the general formula $[NR^1R^2R^3H][(C_6F_5)_3BArOH]$ (R^{1-3} = alkyl, C_1-C_{+18}; Ar = phenyl, diphenyl, or naphthyl) with a silane-, alkylaluminum- or aluminoxane-“pacified” silica eliminates innocuous and gaseous byproducts (H_2, CH_4, or C_2H_4), providing an elegant immobilization protocol.

Carnahan and co-workers at Dow and W. R. Grace illustrated the first example of such a protocol.[390] In these disclosures, $[HNMe_2Ph][(C_6F_5)_3BArOH]$ (Ar = phenyl and naphthyl) is contacted with a silica or alumina[390a] surface previously treated with $PhSiH_3$ or $SiMe_2H_2$, Scheme 40. Rapid evolution of hydrogen was observed, to form an immobilized borate species capable of activating either a metallocene,[390a] constrained geometry,[390a] or iron bis(imino)pyridine[390b] precatalyst. Poor activity was, however, observed for the alumina-supported borate when compared to similar procedures carried out with silica.

Jacobsen and co-workers at Dow were also successful in synthesizing an immobilized borate utilizing a similar ammonium borate, $[HNEt_3][(C_6F_5)_3BArOH]$, which was contacted with a silica surface pacified by treatment with TEA or MAO (Scheme 39).[391] The insolubility of $[HNEt_3][(C_6F_5)_3BArOH]$ salt in apolar solvents compatible with the alkylaluminum-pretreated silica is one of the main drawbacks for successful immobilization of these species. An elegant solution to increased solubility was found when ammonium cations derived from long-chain amines were employed.[392] However, unlike the above, the previous ammonium ($[NEt_3H]^+$) borate systems, species containing $[H(C_{18}H_{35})_2NMe]^+$, for example, were first contacted with a solution of TEA to form $[H(C_{18}H_{35})_2NMe][B(C_6F_5)_3(C_6H_4\text{-}4\text{-}OAlEt_2)]$.[392d] This species was then reacted with the precatalyst before being contacted with a TEA-pacified silica support, presumably forming some form of heteroleptic siloxy-, phenoxy-bridged aluminum species on the surface.

Scheme 40



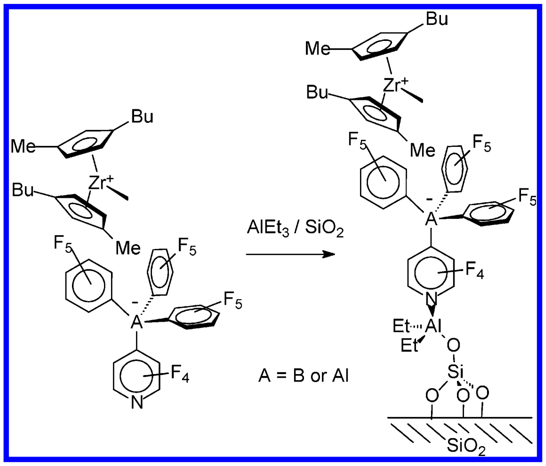
This area of research has recently seen a sharp increase in patent activity by the BP Chemicals company,[393] who have achieved at least pilot plant development of such systems.[394] As mentioned previously, the above precatalyst/cocatalyst solution can be used to form polymer particles with spherical morphology without the need for contact with a support.[113]

"Pacified" alkylaluminum supports have also been used by Holtcamp in the immobilization of [(1,3-Bu-MeCp)$_2$ZrMe][(C$_6$F$_5$)$_3$A(C$_5$F$_4$N)] (A = Al or B)[395] or a diborate activator bridged by an octamethyltetrasiloxane group.[396] The author contacted the activated species or diborate activator with TEA- or EAO-pacified silica, respectively. The supported diborate was then used in conjunction with (1,3-Bu-MeCp)$_2$-ZrMe$_2$ to copolymerize ethylene and 1-hexene in slurry (2.7 kg of PE/(g of catalyst·h)). The final active species are presumably attached to the surface aluminum species via a dative bond to either the pyridyl-function (Scheme 41) or the octamethyltetrasiloxane bridge.

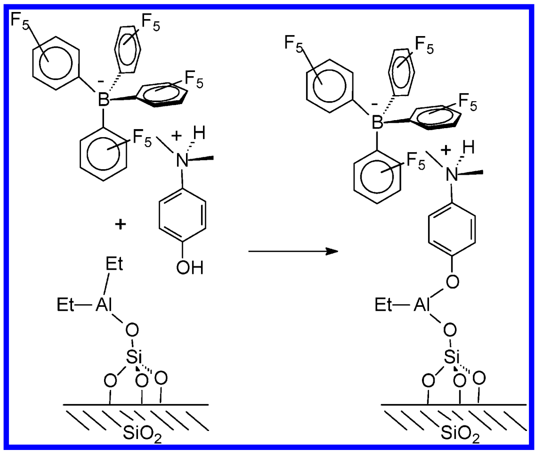
The immobilization of borate activators has also been achieved via tethering its ammonium anion.[397,398] This has been performed by reacting (MeO)$_3$SiC$_6$H$_4$NMe$_2$ with a silica surface, followed by addition of HCl then Li[B(C$_6$F$_5$)$_4$],[397] Scheme 42, or by contacting [HOC$_6$H$_4$NMe$_2$H][B(C$_6$F$_5$)$_4$] with a TEA-pacified silica (Scheme 43).[396] The free ionic species formed is held to the surface via electrostatic interaction or by the labile coordination of the supported amine.

A novel procedure for the immobilization of a borate anion can be seen in Vogel's disclosure, the starting point of which is again a TEA-pacified support.[399] Treatment of the pacified silica with *trans*-8,*trans*-10-dodecadiene-1-ol formed an immobilized diene. The CGC precatalyst, SiMe$_2$(C$_5$Me$_4$)(N^{t}Bu)-TiCl$_2$, is then reduced in its presence, yielding a diene-tethered Ti(II) species, and activated by addition of B(C$_6$F$_5$)$_3$ to form an immobilized borate (Scheme 44). During production of the initial chain it can be considered as a doubly immobilized species containing both a tethered precatalyst (metal−alkyl) and cocatalyst. Similarly, functionalized dienes such as 1-phenyl-4(4-*N,N′*-dimethylaminophenyl)-1,3-butadiene have been converted into zwitterionic complexes and immobilized onto silica with the implication that the amino group facilitates improved adsorption of the complex.[340] Similarly, vinyltrimethoxysilane has been treated with Cp$_2$ZrClH to form a zirconium alkyl that can be adsorbed onto a SiO$_2$/TIBA surface.[401]

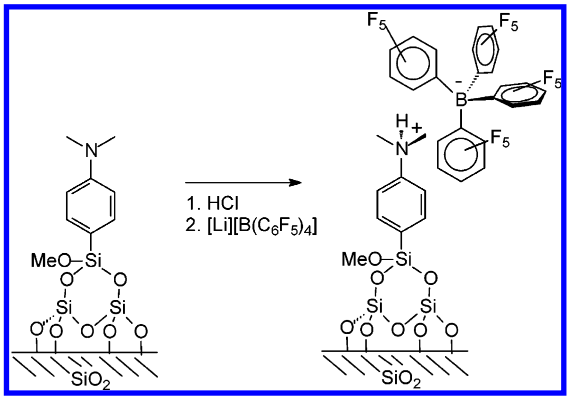
Scheme 41



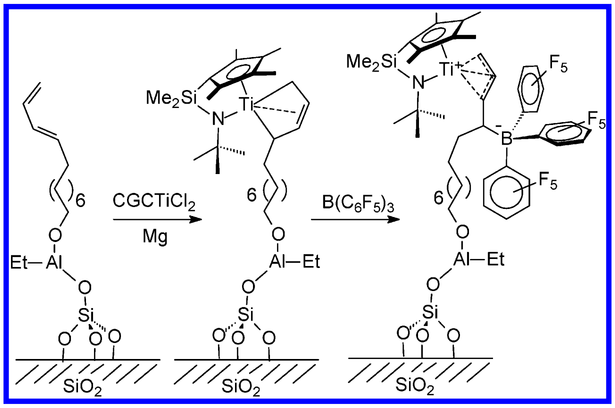
Scheme 42



Scheme 43



Scheme 44



6. Magnesium Chloride

In his review published in 2000, Hlatky[43] commented that magnesium chloride, although a widely used support in Ziegler–Natta catalysts, had been studied far less extensively than silica as a carrier for single-site catalysts. This is still the case, but in the past few years, there has been a notable increase in research on single-site catalyst immobilization and activation using $MgCl_2$-based systems. This interest stems partly from the development of controlled-morphology $MgCl_2$ supports for Ziegler–Natta catalysts. Spherical supports having controlled particle size can be produced by cooling emulsions of molten $MgCl_2 \cdot n$ROH adducts in paraffin oil, thus obtaining almost perfectly spherical supports, which are then converted into Ziegler–Natta catalysts by reaction with $TiCl_4$ and other components. Porous support materials can be prepared by partial dealcoholation of a $MgCl_2 \cdot 3EtOH$ adduct, followed by reaction with AlR_3 or MAO, and such supports have been used in conjunction with zirconocenes for ethylene homo- and copolymerization.[402] Similar supports, of composition $MgCl_2/AlEt_n(OEt)_{3-n}$, have recently been used in the absence of MAO for the immobilization and activation of a range of titanium-based single-site catalysts, leading to polyethylene having narrow molecular weight distribution and spherical particle morphology.[403,404] Particularly high activity (around 6000–9000 g/(mmol of Ti·h·bar)) was obtained using $CpTiCl_3$ and related compounds. Previous studies on propylene polymerization using systems of type $MgCl_2/CpTiCl_3/Al(i\text{-}Bu)_3$ have indicated that the Cp ligand remains bound to Ti after contact with the Al alkyl.[405] A particular advantage of $MgCl_2$ a as support for titanocenes, reported previously, is stabilization of the active species, avoiding catalyst decay during polymerization.[406] $MgCl_2/AlEt_n(OEt)_{3-n}$ supports have now also been used for the immobilization of chromium-[407] and vanadium-based[408] catalysts, giving polyethylenes with narrow molecular weight distribution. Late-transition metal catalysts such as nickel diimine and iron complexes have also been immobilized on similar supports derived from $MgCl_2$/ethanol adducts, and it is apparent that catalyst activities exceeding those obtained under homogeneous polymerization conditions can be achieved.[409,410]

Spherical adducts of $MgCl_2$ and ethanol have also, after dealcoholation, been utilized for impregnation with MAO (and a cross-linking agent to give greater MAO incorporation); the immobilized MAO was then mixed with a solution of *rac*-Et(Ind)$_2$ZrCl$_2$ and used in ethylene polymerization, giving spherical polyethylene morphology.[411] A further example of the use of zirconocenes with a $MgCl_2$-derived support is the reaction of $MgCl_2 \cdot n$EtOH with $AlEt_3$ and treatment of the product with $(n\text{-}BuCp)_2ZrCl_2$ to give an immobilized catalyst used in ethylene polymerization in combination with MAO.[412] Solid $MgCl_2 \cdot n$ROH supports have also been prepared by dissolving $MgCl_2$ in excess ethanol or methanol, adding decane, and then heating under vacuum to effect precipitation of the support.[413] Such supports were reacted with aluminum alkyls and used, together with zirconocenes and MAO, in ethylene/1-hexene copolymerization. The preparation of hybrid Ziegler–Natta/metallocene catalysts was also investigated, incorporating $TiCl_4$ together with the zirconocene.[414]

Effective $MgCl_2$-based activators for single-site catalysts have also been obtained starting from an adduct of $MgCl_2$ and 2-ethyl-1-hexanol. Again, the roots of this development can be traced to aspects of Ziegler–Natta catalyst preparation, the solubilization of a 1:3 $MgCl_2$/2-ethyl-1-hexanol adduct in decane being described in Mitsui Ziegler–Natta catalyst patents.[415] Activation of Ti-based FI catalysts using $MgCl_2/Al(i\text{-}Bu)_n(OR)_{3-n}$, obtained in situ via reaction of $Al(i\text{-}Bu)_3$ with a solution of $MgCl_2$ and 2-ethylhexanol, resulted in catalyst activities comparable with those obtained using MAO.[416] This approach also gave very high activities with zirconium- and vanadium-based FI catalysts and resulted in well-defined polymer particle morphology.[417] In the case of V–FI catalysts, stable ethylene polymerization kinetics were obtained even at 75 °C, in contrast to the frequently observed rapid decay in activity of vanadium-based catalysts in olefin polymerization.[418] In addition to the FI catalysts, it was also stated that these $MgCl_2$-based support/activators could be used in combination with late transition metal catalysts; ethylene polymerizations with iron catalysts are described in a patent application.[419] In situ precipitation of magnesium chloride as a component in the activation of single-site catalysts can also be effected by the use of mixtures of MgR_2 and AlR_2Cl, generating $MgCl_2$ and AlR_3.[420] Various metallocenes could be activated in this way, giving ethylene/1-hexene copolymers with narrow compositional distributions. In another approach, MgEtBu was mixed with ethylaluminum sesquichloride and then an iron complex to give a solid catalyst component for ethylene polymerization.[421]

An important feature of magnesium chloride as a support material for single-site catalysts is the presence of Lewis acidic centers, which in many cases enables catalyst activation without the use of MAO.[422] Highly dispersed magnesium chloride was prepared by reaction of $MgCl_2 \cdot nAlEt_3$ with CCl_4 and used to immobilize *rac*-Me$_2$Si(Ind)$_2$ZrCl$_2$. Ethylene polymerization activities were similar to those obtained using a SiO_2/MAO support, although much lower than were obtained in homogeneous polymerization using MAO as cocatalyst. The $MgCl_2$-supported zirconocene was found to be relatively insensitive to chain transfer with hydrogen[422a] and, in contrast to the SiO_2-supported catalyst, did not exhibit a comonomer activation effect in ethylene/1-hexene copolymerization.[422b]

Highly dispersed activated $MgCl_2$, prepared by reaction of magnesium with excess *n*-butyl chloride in refluxing heptane, has recently been used for the immobilization of a bis(imino)pyridyl iron dichloride. Stable kinetics were observed in ethylene polymerizations carried out at 70 or 80 °C, using trialkylaluminum cocatalysts.[423] An unusual feature of $MgCl_2$-supported iron catalysts was shown to be increased activity for ethylene polymerization in the presence of hydrogen, in contrast to what is observed, for example, with $MgCl_2/TiCl_4$-based systems.

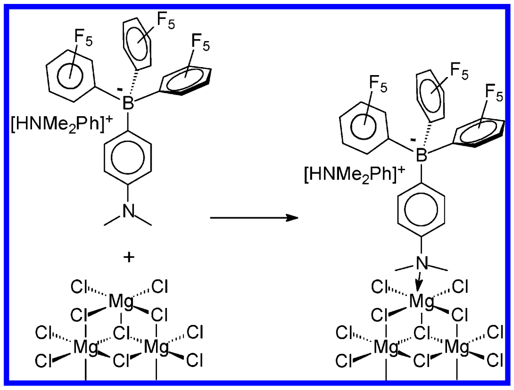
Magnesium chloride has also been used in combination with a silica support. Immobilization of $MgCl_2/Cp_2MCl_2$ (M = Ti or Zr) was carried out via the impregnation of silica with a solution of $MgCl_2$ and the metallocene in tetrahydrofuran (THF).[424] Ethylene polymerization was carried out in the presence of MAO. The polyethylene molecular weight distribution was significantly narrower than that obtained using silica alone. A related preparation not involving the use of silica involved the addition of a THF solution of $MgCl_2$ and metallocene to excess hexane to precipitate a solid catalyst.[425] Another example of the use of THF in catalyst immobilization using $MgCl_2$ involves treatment of $MgCl_2(THF)_2$ with an aluminum alkyl and subsequently Cp_2ZrCl_2.[426] Heterogenization of the metallocene was obtained using $AlEt_2Cl$, but was not effective when AlR_3 or MAO was used.

$MgCl_2$-supported metallocenes have also been prepared using the product of ball milling magnesium chloride with ethyl benzoate, one of the earliest methods used in the preparation of activated $MgCl_2$ as a support for Ziegler−Natta catalysts. Immobilization of Cp_2ZrCl_2 was carried out with and without first pretreating the support with MAO, which was also used as cocatalyst in polymerization.[427] Narrow molecular weight distribution was obtained, but catalyst decay during polymerization was apparent, similar to homogeneous polymerization. Very low activity was obtained when a bulkier zirconocene, Et-$(Flu)_2ZrCl_2$, was used. This negative effect of zirconocene steric bulk on activity in a $MgCl_2$-immobilized system is also apparent from other studies.[403]

Magnesium chloride has also been used for the immobilization of new manganese-based transition metal complexes.[428] MAO was found to be a poor cocatalyst in these systems, but moderate activities were obtained using $AlEt_2Cl$. Other alternatives to MAO as cocatalyst for $MgCl_2$-supported single-site catalysts have also been described. High ethylene polymerization activity was reported using *rac*-Et-$(Ind)_2ZrCl_2$ in combination with Ph_3CClO_4 and $MgCl_2$, although the presence of nonimmobilized active species was noted.[429]

The feasibility of using magnesium chloride as support for both Ziegler−Natta and single-site catalysts has, as indicated above, led to attempts to synthesize “hybrid” catalyst systems containing both a single-site component and a Ziegler−Natta component such as $TiCl_4$.[414,430] The broad polyethylene molecular weight distribution obtained on contacting $CpTiCl_3$ with the reaction product of $MgCl_2$, 2-ethyl-1-hexanol, $Ti(OEt)_4$, and $AlEt_2Cl$ is also likely to arise from formation of a hybrid system.[431] The development of catalysts classed as Ziegler−Natta systems but with uniform active species has also been investigated via the immobilization of a dichlorobis(β-diketonato)titanium complex on $MgCl_2$.[432]

Scheme 45



The use of magnesium chloride for the immobilization of single-site catalysts is also described in a number of recent patent applications, many of which describe the use of $MgCl_2$-based supports in combination with MAO. Polypropylene having narrow molecular weight distribution has been prepared using a catalyst obtained by contacting a $MgCl_2$/ROH adduct first with MAO and subsequently with a metallocene.[433] An alternative support preparation is via the reaction of *t*-BuCl and $MgBu_2$ in a hydrocarbon solvent and contact of the resulting precipitate with MAO and a metallocene.[434]

An approach for the tethering of a borate activator to a magnesium chloride support has recently been identified, involving activators containing a Lewis base functionality able to coordinate to the Lewis acidic support.[435] A chemically activated $MgCl_2$ support was treated with $[Ph_3C][B(C_6F_5)_3(C_6H_4NMe_2)]$ (Scheme 45) to give an immobilized borate, which was used in ethylene and propylene homopolymerization and in ethylene/1-butene copolymerization in combination with *rac*-$Me_2Si(Ind)_2ZrCl_2/Al(i\text{-}Bu)_3$.

Hydrated magnesium chloride, $MgCl_2 \cdot nH_2O$, has also been used as a support precursor, which after calcining at 200 °C was treated with MAO and a zirconocene.[436] It is likely that $Mg(OH)_nCl_{2-n}$ is formed during the calcination step, facilitating chemical tethering of MAO to the support.

7. Surface Organometallic Complexes and Superacids

The development of heterogeneous SOMC (surface organometallic complex) catalysts is of ongoing interest in various fields. The aspiration is to produce a heterogeneous catalyst system that preserves or enhances the activity and selectivity of a homogeneous catalyst, while benefiting from increased stability due to a reduction in bimolecular decomposition and the ease of process control that heterogeneous catalysts provide.[437]

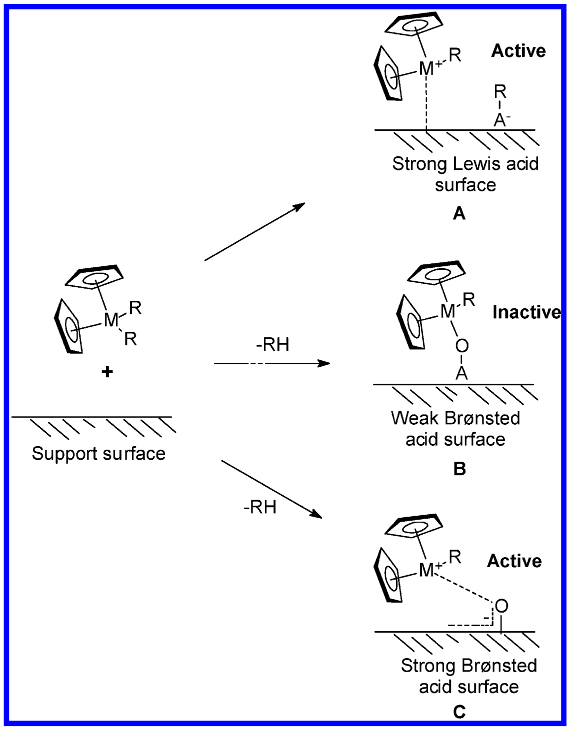
The most common SOMC α-olefin polymerization catalysts are those prepared by anchoring a homoleptic early transition metal hydrocarbyl complex onto inorganic oxide supports. For example, a number of studies on alkyl, alkylidene, or hydride complexes resulting from the reaction of homoleptic organozirconium[438−443] and organochromium complexes[444−449] (neopentyl, neopthyl, benzyl, methylsilyl, cyclopentadienyl, allyl, or arene) with silica or alumina have been reported by researchers at ICI/Du Pont,[438] Union Carbide,[444] and various other groups[439−449] to produce highly active polymerization systems in the absence of a cocatalyst and invariably produce polyolefin resins with broad molecular weight distributions, indicative of multiple active sites. It should be noted, however, that $Zr(CH_2Ph)_4$ in combination with MAO[450a] and $B(C_6F_5)_3$[450b] has been reported to produce polymer resins with narrow molecular weight distributions.

Marks and co-workers extensively studied the adsorption of well-defined organoactinide and organozirconium molecules onto various inorganic oxides.[451−454] The group studied, via ^{13}C CP-MAS NMR spectroscopy, the adsorption of ^{13}C enriched organoactinide complexes such as $Cp^*_2Th(^{13}CH_3)_2$ and early transition metal hydrocarbyls onto γ-alumina (dehydroxylated or partially dehydroxylated), silica (dehydroxylated or partially dehydroxylated), silica−alumina, MgO, or $MgCl_2$.[452] “Cation-like” species, with comparable spectral assignments to homogeneous analogues were identified and were believed to be responsible for the observed catalytic activity in arene hydrogenation and ethylene polymerization.[452] Subsequent kinetic studies,[452a,c,f] stoichiometric probe reactions,[452a,b] and poisoning experiments[452a−c,f] helped elucidate catalytic rate laws, active chemical functionalities and percentages of catalytically significant sites.

Marks et al. established that alkyl anion abstraction (Scheme 46, A) constituted the major adsorptive pathway for metallocenes on strong Lewis acidic surfaces (γ-alumina, dehydroxylated or partially dehydroxylated, or $MgCl_2$), while protonolysis (Scheme 46, B) was the major pathway for conventional weakly Brønsted acidic surfaces. For the strong Lewis acidic surfaces, the heterolytic M−C bond scission yielded a surface cationic species whose catalytic behavior is strongly dependent on the nature and possible coordination of the charge-compensating support, while the weakly Brønsted acidic surfaces produce μ-oxo structures that were chemically inert.

Polymerization studies on the heterogeneous catalyst formed by the adsorption of an organozirconium complex on a strongly Lewis acidic surface indicated that the number and nature of the active sites were highly sensitive to the ancillary ligation. Comparative polymerization studies of Cp_2ZrMe_2 ($Cp' = Cp$ or Cp^*) or Cp^*ZrMe_3 supported on dehydroxylated alumina yielded an order of activity $Cp^*ZrMe_3 > Cp_2ZrMe_2 \approx Cp^*_2ZrMe_2$. The order of activity is also in correlation with the percentage of catalytically significant sites calculated from CP-MAS and poisoning studies, previously mentioned (catalytically significant sites Cp^*ZrMe_3 ca. 12%; Cp_2ZrMe_2, ca. 4%).[452] For $Cp^*_2ThMe_2$, the nature of the support was also found to strongly influence the number of catalytically significant sites, with $MgCl_2$ (ca. 50%) generating five times the number of catalytically significant sites than were obtained with dehydroxylated alumina (ca. 10%).

Scheme 46



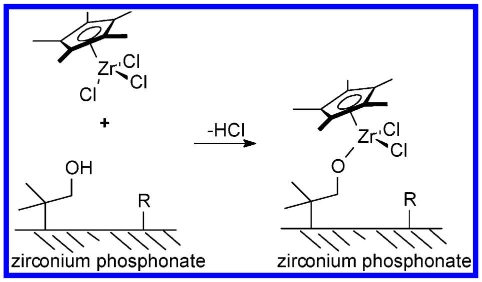
Similar, comprehensive investigation into the interactions of Cp^*ZrMe_3 and Cp_2ZrMe_2 with partially dehydroxylated silica, silica−alumina, and alumina surfaces have been carried out by Basset et al.[453] Careful identification of the resulting surface organometallic complexes was undertaken to probe the relationship between catalyst structure and polymerization activity. As above,[452] the activity of the supported species was dependent on the choice of support, with increased activity directly related to the number of Lewis acidic centers present on the oxides and to the strength of their Lewis acidity, as well as the ancillary ligation of the organozirconium complex. Addition of a cocatalyst complex ($B(C_6F_5)_3$ or MAO) to the surface organometallic complex was also investigated. Increased activity was noted on addition of the cocatalyst complex and was interpreted to result from an increased concentration of fully cationic zirconium surface complex. The activity, however, remained very low in comparison to the analogous homogeneous systems. The lowering in activity was proposed to arise from the steric nature of the support, which restricts monomer coordination or the reduction in the electrophilicity of the zirconium center resulting from the potentially efficient π-donation from the siloxy and aluminoxy ligands to the metal center.

Marks and co-workers have recently investigated the interactions and catalytic properties of metal hydrocarbyls adsorbed onto strongly Brønsted acidic surfaces, in particular “superacidic” sulfated metal oxides.[454,456−458] The initial studies concentrated on the chemisorption and interaction of organozirconium complexes with the strongly Brønsted acidic hydroxyl groups on the surface of sulfated zirconia, previously prepared by the thermal decomposition of $Zr(SO_4)\cdot 4H_2O$.[454] The resultant surface bound species were found to be highly active in ethylene and propylene polymerization, which was in stark contrast to the species formed on weakly Brønsted acidic surfaces, with the active species (Scheme 46, C) resulting from extensive charge delocalization of the conjugate base. The number of active sites generated by the adsorption of Cp^*ZrMe_3 on sulfated zirconia (ca. 65%) was also found to be much higher than that on dehydroxylated alumina (ca. 12%); for the former, this was approximately equal to the percentage of Brønsted acidic site population for sulfated zirconia activated at 300−400 °C.[455] The activity and number of catalytically significant sites were again found to be highly sensitive to the ancillary ligation and calcination temperature of the support. Additional “superacidic” sulfated metal oxides to be utilized as solid cocatalysts have included sulfated stannia,[456,457] titanium dioxide,[457] iron oxide,[457] and alumina,[458] all of which produced heterogeneous catalysts with a high percentage (and in the case of the latter virtually 100%) of catalytically significant sites. It should be noted, however, that the number of catalytically active sites does not always indicate the activity of these catalysts. The authors reported that the catalytic activity in ethylene polymerization appeared to be derived from the interplay between the electrophilicity of the Zr cation and the percentage of catalytically significant sites.[458] Finally, while the sulfated supports described above may be beneficial in terms of cost and synthetic simplicity when compared to traditional cocatalysts, their application as a “drop in technology” would strongly depend on their ability to form regular polymer particles of sufficient size and size distribution, which in turn is strongly dependent on the porosity and particle size and size distribution of the starting support. For example, traditional support sizes are on the order of tens of micrometers, while the sulfated stannia support was approximately 5 nm in size.

Jensen and co-workers at Chevron Phillips have recently demonstrated the use of activator/supports for metallocenes that were based on halogenated superacidic support surfaces.[459,460] The group pretreated silica, silica−alumina, alumina, and titania surfaces with a halogen-containing inorganic complex (e.g., $[NH_4][F]$, $[NH_4]_2[SiF_6]$) prior to calcination. The halogenated support was then contacted with a metallocene dichloride and an alkylaluminum prior to polymerization. A large proportion of the resultant solid catalysts proved to be highly active in the polymerization of ethylene. For example, silica−alumina pretreated with a 10 wt % loading of NH_4HF_2 and calcined to 450 °C yielded a catalytic system in conjunction with TEA and $^{bu}Cp_2ZrCl_2$ that achieved a productivity of 18.5 kg of PE/(g of catalyst·h).[460e]

Aluminum phosphates or alumina−aluminum phosphates have also proven to be efficient support/activator materials for a range of chromium-based precatalysts,[461] in particular, the Cr(II) ($[Cp^*CrMe]_2$), neutral ($Cp^*CrMe_2(THF)$) or cationic ($[Cp^*CrMe(THF)_2][BPh_4]$) Cr(III), and various anionic or mixed valence complexes developed by Theopold et al.[462] The activity of these systems was greatly improved when used in conjunction with IBAO, with the resultant polyethylene resins possessing narrower molecular weight distribution ($M_w/M_n = 2-4$) than the corresponding silica-supported systems ($M_w/M_n = 12.4-40$).

Scheme 47



Bochmann and co-workers recently reported the first application of homoleptic and mixed α-zirconium phosphonates as support material for metallocene precatalysts.[463] The supports were impregnated with zirconocene dichloride (sublimation or slurry methods), while Cp^*ZrCl_3 was covalently attached to a functionalized α-zirconium phosphonate $\alpha\text{-}Zr(O_3PR)_{2-n}(O_3PCMe_2CH_2OH)_n$ (Scheme 47). The resultant system when activated by addition of MAO or a combination of TIBA and $[Ph_3C][B(C_6F_5)_4]$ produced highly active (up to 9600 kg of PE/(mol of Zr·bar·h)) ethylene polymerization catalysts. The resultant resins, however, while being free flowing and showing good replication, did possess relatively broad molecular weight distributions. Additional examples of support/activators have been reported by Takahashi et al, who used alumina-coated silica in conjunction with a dimethyl zirconocene or hafnocene and dimethylaniline to form an active supported catalyst system.[464]

8. Clays

Mineral clay supports such as montmorillonite, hectorite, vermiculite, hydrotalcitite, smectite, mica, and kaolin have all been employed as inorganic supports for single-site α-olefin polymerization catalysts. Yano and co-workers at Tosoh impregnated and ion-exchanged clays with aqueous solutions of Brønsted acids such as quaternary ammonium complexes ($[HNMe_2Ph]^+$ [465] or $[HNMe_2(n\text{-}C_{18}H_{37})]^+$ [466]). Drying the resultant solid afforded efficient support/activators for metallocene dichloride, precontacted with an alkylaluminum complex, which acts only as an alkylating agent and scavenger.[465] Subsequent studies showed that active systems could be formed by the addition of dimethylmetallocene to the ammonium-impregnated clay without the addition of an alkylating or scavenger reagent.[467]

Clay surfaces have also been ion exchanged or chemically modified with an inorganic complex to form support/activators for $^{Me}Cp_2ZrMe_2$ in the ab-

Table 10.

	modifier	activity (kg of PE/g of clay·h)
Na-mica	none	1.1
	H_2SO_4	0.5
	$ZnSO_4 \cdot 7H_2O$	1.5
	$Cr(NO_3)_3 \cdot 9H_2O$	0.9
Mont-1[a]	none	1.5
	$AlEt_3$	2.1
	$ZnEt_2$	1.3
	$BuNH_2$	0

[a] Mont-1 = montmorillonite pretreated with $MgSO_4 \cdot 7H_2O$.

sence of a scavenger agent. Takahashi et al. treated mica and montmorillonite with various inorganic complexes to form several active systems (Table 10) in which the acidity of the clay-based support played a major role in the activity of the supported catalyst.[468] For example, when the acidic surface of the modified montmorillonite is removed via treatment with a base ($BuNH_2$ or 2,6-$Me_2C_5H_3N$), the resultant catalyst activity is reduced or rendered completely inactive in the polymerization of ethylene. Sun and co-workers at Dow have also prepared modified clay-based supports.[469] The group utilized montmorillonite as a base support to produce agglomerated ammonium or anilinium ion-exchanged aluminum–magnesium or fluorinated magnesium silicate aerogels following modification. The supports proved to be effective activators for zirconocene or constrained geometry butadiene polymerization catalysts. Pretreating the clay surface with an alkylaluminum complex, prior to contact with a solution of metallocene dichloride and trialklyaluminum, has been extensively studied by workers at Mitsubishi[470] and Idemitsu[470] and by Weiss et al.[472]

Aluminoxane-activated zirconocenes have been immobilized on montmorillonite by Tang et al.[473,474] The zirconocene catalysts were immobilized inside an aminopropylsilane-modified montmorillonite pretreated by acidization and calcination. The solid catalyst was then activated by MAO and used to polymerize ethylene. The aminopropylsilane modification expanded the distance between the interlayers of the clay and was believed to allow better penetration of the catalyst and monomer with the internal structure of the clay support. The group has also reported the synthesis of silica–clay hybrid supports that were used to produce hybrid polymer nanocomposities.

The development of polymer nanocomposites composed of an organic polymer matrix with dispersed inorganic nanofillers has become an area of increased scientific interest, especially since the successful synthesis of nylon6/clay nanocomposites was reported.[475] Because polyolefins are apolar in nature, the standard procedures to exfoliate the clay, by intercalating into the lattices of the polar clay, are extremely difficult. This has provided a unique opportunity for supported single-site catalysts. Several groups have overcome the synthesis problem by developing the in situ polymerization of the olefin with single-site catalysts that are supported within the clay galleries, with the growing polymer mass gradually pushing apart the interlayers until the clay is exfoliated and dispersed within the growing polymer matrix.[476–479] Similarly, clay pretreated with poly(styrene-*co*-acrylonitrile) has been treated with MAO to form a supported cocatalyst that activated $Et(Ind)_2ZrCl_2$. The supported catalyst was then used to polymerize propylene to form a hybrid material.[480]

9. “Hybrid” Multicomponent Catalyst Systems

Hybrid multicomponent catalyst systems containing a supported single-site α-olefin polymerization catalyst have become an area of increased research activity and possibly represent one of the most important areas for supported single-site catalytic research in the future.

9.1. Supported Tandem Oligomerization/Copolymerization

Some of the most interesting polyethylene resins to be developed are the short-chain branched LLDPE resins. As mentioned earlier, these resins are produced on an industrial scale by the copolymerization of ethylene and a higher α-olefin such as 1-butene, 1-hexene, or 1-octene. These higher α-olefins are usually produced separately by the oligomerization of ethylene.[481] The prospect of catalytically converting one feedstock into a higher α-olefin, which could then be copolymerized to give short-chain branched PE in a single reactor, led to the development of the tandem catalyst systems. The classical example was reported by Beach et al. using $Ti(O^iPr)_4/AlEt_3$ and $TiCl_4/MgCl_2$, where the $Ti(O^iPr)_4/AlEt_3$ component oligomerizes ethylene to predominately 1-butene, while the $TiCl_4/MgCl_2$ component co-incorporates ethylene and the oligomers into short-chain branched polyethylene resins.[482] Examples of homogeneous tandem catalysts giving short- or long-chain branched polyethylene resins also include single-component chromium[483] or titanium[484] systems, in which a fraction of the active sites were over-reduced to form an oligomerization species while the remainder acted as a copolymerization catalyst, and more recently by two-component systems[485] such as those developed by Bazan et al.[486]

At present, relatively few examples of supported tandem oligomerization/copolymerization systems exist. Wang and co-workers at Du Pont reported the coimpregnation of a bis(imino)pyridine iron catalyst capable of oligomerizing ethylene with $Me_2C(Cp)(Flu)ZrCl_2$[487a] and a bis(imino)pyridine iron polymerization catalyst[487b] onto MAO-modified silica to produce branched polyethylenes. A similar example has also been reported by Killian and co-workers, who coimpregnated a nickel-based oligomerization and a metallocene-based copolymerization catalyst onto MAO-modified silica.[488]

Alternatively, Okuda et al. reported a tandem catalyst system in which the oligomerization catalyst, pyridyl-2,6-diisopropylphenylimine nickel dibromide, is left in the homogeneous phase, while a constrained geometry copolymerization catalyst is immobilized onto a heterogeneous support.[489] The nickel catalyst produced linear 1- and 2-olefins and while the latter were reported to be inert and were not incorporated into the polymer resins, their presence was believed to complicate the copolymerization process. Furthermore, analysis of the polymer resins unexpectedly indicated that only methyl-branched side chains were present, which led the group to propose an elaborate multicomponent mechanism to explain the formation of exclusively methyl-branched polymer resins. Bis(imino)pyridine iron oligomerization catalysts have also been utilized in the homogeneous phase with a heterogeneous *rac*-Et(Ind)$_2$ZrCl$_2$/MAO/montmorillonite copolymerization catalyst.[490] Increased Fe/Zr ratios led to a decrease in resin density and melting point, while chain branching and molecular weight increased.

Several considerations need to be taken into account before one chooses whether to immobilize the oligomerization catalyst, such as the cocatalyst used in the homogeneous phase and whether it could inhibit, leach, or be involved in chain transfer reactions. Additionally, producing the oligomeric comonomers on the surface and in close proximity to the copolymerization component may lead to a high local concentration of the comonomer. The flexibility to independently form the polymerization reaction, adjusting the α-olefin production to control the polymer density, is of major importance and hence would favor feeding in the oligomerization catalyst separately from the polymerization catalyst.

An additional possible pitfall for such tandem catalysis is that in commercial processes, it is common practice to use hydrogen to regulate the molar mass of the polyolefin. In the case where the oligomerization catalyst is also sensitive to hydrogenolysis, the quite expensive production of alkanes from olefin feedstock can be envisaged.

9.2. Mixed Supported Polymerization Catalysts

As mentioned earlier, single-site catalysts produce tailored polymer resins in terms of molecular weight, molecular weight distribution, stereoregularity, and comonomer incorporation, and while characteristics such as narrow molecular weight distributions and uniform comonomer incorporation have allowed single-site catalysts to produce polymers with improved physical properties, such as impact resistance, environmental crack resistance, and clarity, their processability has proved difficult. In processing, molecular weight distribution and molecular weight are important factors, broad molecular weight distributions affording higher flowability in the molten state at high shear rates, especially important in extrusion processes, while broadened molecular weight distributions possess higher zero-shear viscosities, which are advantageous for blow molding applications. Several methods have been developed to tailor the molecular weight and molecular weight distribution of the final polymer. The first involves blending polymers produced with individual catalysts, but here a problem may arise with respect to poor miscibility. The second is multireactor technology, which has been covered in a previous section. Finally, the use of tandem catalysts in a single reactor has been developed, using catalyst components with different comonomer incorporation abilities, stereoselectivities, hydrogen response, and ability to chain walk.

9.2.1. Mixed Ziegler–Natta and Single-Site Catalysts

Hybrid catalysts derived from a heterogeneous Ziegler–Natta catalyst and a single-site catalyst component represent some of the most interesting examples of tandem catalysis and have demonstrated that the interface of what some consider to be rival technologies can lead to considerable synergistic benefits with regard to the final polymer product.

Nowlin and Mink, along with their co-workers at Mobil[491] and Exxon-Mobil,[492] reported the use of mixed Ziegler–Natta/single-site systems in the tandem copolymerization of ethylene and 1-hexene. In general, the Ziegler–Natta catalyst component was synthesized by contacting MgBu$_2$/butanol-modified silica with TiCl$_4$. The solid catalyst was then impregnated with a solution of MAO/metallocene using the "incipient wetness" technique. The resultant catalysts proved to be highly active, producing resins with broad or bimodal molecular weight distribution and improved physical properties. In addition, the calcination temperature of the initial silica support was found to be of great importance in terms of catalyst activity, with a calcination temperature of 700–800 °C leading to the most active systems. Similar polyethylene-producing systems have also been reported by industrial[493] and academic laboratories,[494] and include immobilization of samarocene[495] and self-immobilizing metallocenes.[496] Additional hybrid ethylene polymerization systems have been formed by contacting a metallocene solution with Ti(O^{i}Pr)$_4$/TiCl$_4$[497] or polymer-supported TiCl$_4$-based heterogeneous catalysts.[498]

Tandem catalysis has also been utilized in propylene polymerization. Reddy and Shamshoum reported the synthesis of resins consisting of an intimate blend of iso- and syndiotactic polypropylene from an isospecific Ziegler–Natta catalyst that had been impregnated with a solution of Me$_2$C(Cp)(Flu)ZrCl$_2$/MAO.[499] Reactor blends of isotactic and elastomeric polypropylene have been reported from a system synthesized by the impregnation of a Et(Ind)$_2$ZrCl$_2$/MAO solution onto Zr(CH$_2{}^t$Bu)$_4$/Al$_2$O$_3$.[500]

9.2.2. Mixed Single-Site Catalysts

Several reports involving the immobilization of two single-site catalysts on the same support have been disclosed. Kim and Soares reported the synthesis of intimate blends of polyethylene resins in which the molecular weight distribution and chemical composition could be controlled by the combination of Et(Ind)$_2$ZrCl$_2$/Cp$_2$HfCl$_2$ or Et(Ind)$_2$ZrCl$_2$/Me$_2$SiCp*N(^{t}Bu)TiCl$_2$ supported on MAO-modified silica.[501a] In the latter system, the precatalysts' respective ability to co-incorporate comonomer led to resins with varying chemical compositions. Polyethylene resins produced with the supported Et(Ind)$_2$ZrCl$_2$/Cp$_2$HfCl$_2$ system possessed unimodal or bimodal molecular weight distributions, with high or low molecular weight shoulders, dependent on polymerization variables such as hydrogen concentration. The hafnocene component is more responsive to hydrogen than Et(Ind)$_2$ZrCl$_2$ and polymerization at high hydrogen concentrations therefore yielded a polymer resin possessing a low molecular weight, hafnocene-polymerized fraction and a higher molecular weight, Et-$(Ind)_2ZrCl_2$-polymerized fraction, while the reverse is observed in the absence of hydrogen.[501b] Polyethylene resins have also been produced with several other supported binary metallocene systems, such as $Me_2Si(Cp^*)(^{Me}Cp)ZrCl_2/Me_2Si(Ind)_2ZrCl_2$,[502] $Cp_2NbCl_2/(^{bu}Cp)_2ZrCl_2$,[503] $(^{bu}Cp)_2ZrCl_2/Cp_2ZrCl_2$,[504] or other mixtures.[505] Additionally, binary systems that consist of a combination of metallocenes supported on separate carriers[506] or with one component unsupported have been reported.[507]

The above examples[501−507] describing the use of binary metallocene systems to produce reactor blended polyethylene resins have all been activated by methylaluminoxane. Oshima and Takaoki have recently described the use of a novel support/activator to immobilize binary metallocene systems. The support/activator was initially synthesized by contacting $ZnEt_2$ with half an equivalent of C_6F_5OH, followed after time by an equivalent of H_2O in THF. The product from the reaction was then contacted with silica to form a support/activator that was capable of effectively activating a TIBA-contacted binary solution of *rac*-$Et(Ind)_2HfCl_2$ and $(^{bu}Cp)_2ZrCl_2$.[508] Examples of supported binary metallocene/post-metallocene systems are relatively rare at present. Researchers at Univation have reported the coimmobilization of $IndZr(O_2C^tBu)_3$ with various zirconium complexes containing nitrogen-functionalized chelates to form a supported binary system.[509]

Reactor blends of polypropylene have been achieved with binary metallocene systems. Reactor blends of syndiotactic[510] or isotactic[511] polypropylene with broadened molecular weight distribution have been formed by coimpregnation of $Ph_2C(Cp)(Flu)ZrCl_2$ and $Me_2C(Cp)(2,7\text{-}^tBu_2\text{−}Flu)ZrCl_2$[510] or by the consecutive impregnation of $Me_2Si(H_4\text{-}Ind)_2ZrCl_2$ and $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$[511] onto MAO-modified silica, respectively. In addition, mixed iso- and syndiotactic[512] and iso- and atactic blends[513] have also been reported with supported binary metallocene systems.

10. Modeling Supports and Supported Catalyst Systems

As we have illustrated throughout this review, supporting catalysts is a far from trivial endeavor. Catalyst leaching, resulting in poor polymer morphology, reactor fouling, and loss of activity are persistent problems. Improvement in immobilization techniques and an in depth understanding of the chemical processes occurring on the support surface remain therefore topics of great importance.

The molecular structure of the supported catalysts is a key step for the understanding of the rules governing the stability and reactivity of the system. However, detailed studies on inorganic materials such as magnesium chloride, silicas, zeolites, and clays, as well as the supported catalysts thereof, are considerably hampered by the heterogeneity of these systems. The molecular properties are best studied by a combination of physio-chemical methods, such as IR, Raman, and NMR spectroscopy, as well as XPS, EXAFS, and XANES. However, these techniques are generally bulk measurements and their sensitivity is often inadequate to obtain accurate data of the various sites that are present on the surface in low concentration.

To get more insight at a molecular level into the interaction of catalyst precursors with the surface and the structure and reactivity of the heterogeneous catalyst, suitable model systems are of great importance. Modeling studies can be divided into three main categories being (i) homogeneous complexes that mimic supports and supported catalysts, (ii) modeling studies (surface organometallic chemistry) on, for example, single-crystal surfaces, glass, or silica wafers, and (iii) theoretical studies. In this review, the focus will be on the use of homogeneous model systems in understanding and developing heterogeneous olefin polymerization catalysts. It will be shown that homogeneous models can contribute to improvement of immobilization strategies and provide useful suggestions about the stability and reactivity of supported catalysts. However, their homogeneous nature also forms a clear disadvantage because the mobility of these systems allows them to undergo consecutive reactions affording thermodynamically stable products, which is not possible for the surface-linked species for which they serve as a model.

10.1. Homogeneous Model Supports

Various ligand systems have been used as homogeneous models for inorganic supports. Although clays and surface sites of magnesium chloride have been modeled,[514] silica is by far the most commonly modeled support. Silica surfaces have mainly been mimicked by silanols, silsesquioxanes, and calix[4]arenes.[515−517] Of all, silsesquioxanes are probably the most realistic structural models for silica surface silanol sites. With functionalities ranging from vicinal and geminal silanols to isolated silanols, (strained) siloxane rings, and (partially) silylated silanols, silsesquioxanes represent various silica surface sites present depending on the calcination temperature and surface treatment. However, good structural models for the support are no guarantee for good models for the corresponding supported catalysts. Heterogeneous olefin polymerization catalysts derive their high activity from their isolated and highly unsaturated nature. Due to their mobility in solution, the catalytic activity of most homogeneous model systems suffers from their tendency to form electronically saturated aggregates. Nevertheless, several homogeneous models for traditional heterogeneous olefin polymerization catalysts and immobilized (co)catalysts have been reported that show moderate to good activity.

10.2. Modeling of Traditional Heterogeneous Catalysts

The first metallocene to be used in olefin polymerization, Cp_2TiCl_2,[14,15] was actually a homogeneous model for the titanium sites in Ziegler−Natta catalysts. Based on their results on titanocene dichloride in combination with triethylaluminum, Natta and coworkers suggested that the active titanium species in Ziegler−Natta catalysts consisted of bimetallic sites containing organometallic bonds. Likewise, group 4 metal *ansa*-bis(indenyl) systems were initially developed as homogeneous model systems for the isospecific sites in Ziegler−Natta propylene polymerization catalysts.[518] Recently, the groups of Kol and Busico have reported on octahedral group 4 metal species that show a more structural resemblance with these isospecific sites in Ziegler−Natta catalysts.[519] The zirconium catalyst is quasi-living for the polymerization of α-olefins and highly active. The corresponding titanium species turned out to be somewhat less isospecific and less active than the zirconium one.

Besides modeling only the local geometry of the metal sites, several studies have appeared on mimicking metal sites on a support. For example, Sobota et al. modeled third generation (magnesium chloride-based) Ziegler−Natta systems ($MX_{(3)4}/MgCl_2/AlEt_3$).[514] Reacting $MgCl_2$ with hydroxyl-ethers to mimic magnesium chloride surface sites gave interesting octahedral magnesium chloride alkoxide species that on subsequent treatment with transition metal precursors and aluminum alkyls gave bimetallic complexes. In addition an interesting example of a silsesquioxane-based catalyst system has also been reported as a homogeneous model for a Ziegler−Natta type of catalyst.[520] The precatalysts $[Mg_4(\mu_3\text{-}\eta^2\text{-thffo})_2(\mu\text{-}\eta^2\text{-thffo})_4Cl_2]/TiCl_4$ (thffo = tetrahydrofurfuryl alcohol)[514] and $[(c\text{-}C_6H_{11})_7Si_7O_{12}MgTiCl_3]_n$ (n = 1, 2)[520] could be activated with $AlEt_3$ to afford active ethylene polymerization catalysts.

Various homogeneous chromium olefin polymerization catalysts have also been developed, several of which were denoted as model systems for the Phillips catalyst[10] or Union Carbide catalyst[444] The Phillips catalyst has been modeled by several groups using siloxanes, silsesquioxanes, and even nitrogen-based ancillary ligands.[521−524] Simple chromate esters, $(Ph_3SiO)_2CrO_2$ and $\{[O(OSiPh_2)_2]_2Cr({=}O)_2\}_2$, and Feher's silsesquioxane chromate, $[(c\text{-}C_6H_{11})_7Si_7O_{11}OSiMe_3]CrO_2$, have all been employed as homogeneous models for the Phillips precatalyst; however, unlike the real Phillips catalyst, these complexes could not be activated with ethylene alone and $AlMe_3$ was needed to obtain an active catalyst. The activities of the thus-formed catalysts are moderate and sensitive to the amount of $AlMe_3$ used to generate the active species. The silsesquioxane chromate species, for example, achevied its highest activity when 2 equiv of $AlMe_3$ per silsesquioxane chromate is employed.

The Union Carbide catalyst consists of silica-grafted chromocene.[444] For the reaction of chromocene with silica surface silanols, various products have been proposed ranging from isolated or dimeric $\equiv SiO-CrCp$ and $[CpCr(\mu\text{-}OSi\equiv)(OSi\equiv)]_2$ sites to the oxidation product $(\equiv SiO)_2Cr(H)Cp$.[444,525] However, exclusive proof for the existence of such species is not available to date. The first homogeneous model systems for the Union Carbide catalyst were neutral Cp^*CrR_2 and cationic $[Cp^*(L)CrR]^+$ (L = Lewis base) half-sandwich complexes.[526] Interestingly, both the neutral and cationic species are active in ethylene polymerization. Corresponding neutral divalent chromium compounds, $Cp^*CrMe\cdot L$, only gave small amounts of oligomers.[527d] Other examples are the constrained geometry catalyst $[Me_2Si(NR)C_5Me_4]CrR\cdot L$ and chromium cyclopentadienyl systems containing a pendant neutral functionality.[527] Homogeneous cyclopentadienyl chromium alkoxides, siloxides, calix[4]arenes, and silsesquioxanes are also known, but these complexes either are completely inactive or form very poor ethylene polymerization catalysts.[517c,528]

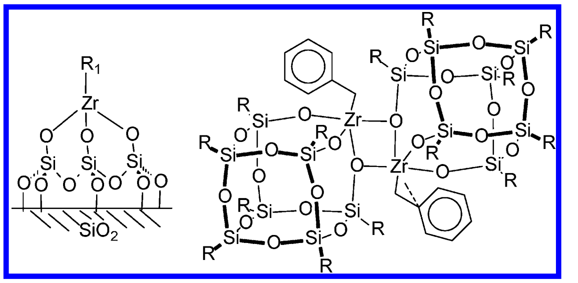


Figure 12. Silica supported zirconium alkyl species and its silsesquioxane based model system.

Using silsesquioxanes as models for silica surface silanol sites, Feher et al.[529] mimicked silica-supported vanadyl species.[530] The vanadyl silsesquioxane $\{[(c\text{-}C_6H_{11})_7Si_7O_{12}]V{=}O\}_n$ (n = 1, 2) exists in both monomeric and dimeric form.[530] After activation with $AlMe_3$ (1−5 equiv), ethylene (1 atm) is polymerized (M_w = 48 000, M_w/M_n = 2.3). The narrow molecular weight distribution indicates the presence of a single-sited catalyst system.[529] Similar to the silsesquioxane chromate, the activity of the vanadium catalyst is sensitive to the amount of $AlMe_3$ used, and the highest activity was observed when 3 equiv of $AlMe_3$ was used as cocatalyst. Floriani et al. prepared several vanadium calix[4]arene complexes as model systems for oxide-supported vanadium species.[517d] However, their ability to polymerize α-olefin has never been reported.

Alumina- and silica-supported zirconium alkyl and hydride species have proved to be interesting olefin polymerization catalysts.[438−443] Thorough studies on the molecular structure of the silica-supported zirconium system revealed that the active site consists of a zirconium hydride bonded to three siloxy functionalities. Attempts to mimic this surface species by reacting the cyclopentyl-substituted trisilanol $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ with an equimolar amount of $Zr(CH_2Ph)_4$ resulted in a dimeric zirconium benzyl complex, $\{[(c\text{-}C_5H_9)_7Si_7O_{12}]ZrCH_2Ph\}_2$ (Figure 12).[531]

The formation of such a dimeric structure is a typical example of consecutive aggregation that homogeneous systems can undergo to form a thermodynamically stable structure. Consequently, comparing these dimeric models with silica-grafted zirconium hydride species should be met with great care. Nevertheless, like the silica-grafted zirconium hydride system, this dimeric zirconium complex is a single component olefin polymerization catalyst. The activity of this neutral complex was explained by the peculiar dimeric structure of this zirconium silsesquioxane complex, in which one of the zirconium atoms acts as an adjacent Lewis acid activating the other zirconium. This compares well with the fact that zirconium hydride supported on silica doped with Lewis acidic aluminum sites showed enhanced activity compared to the all-silica system.[441b] The proposed synergistic effect of the two zirconium centers in the dimeric structure is intensified when one of the benzyl groups of the dimer is abstracted by a strongly Lewis acidic borane, $B(C_6F_5)_3$. For the thus-formed cationic mono(benzyl) dimer, an increase in ethylene polymerization activity of over 2 orders of magnitude was observed (2400 g of PE/(mmol·h)) compared to the neutral dimer (10 g of PE/(mmol·h)). With such activity, this complex is not only a model for oxide-supported zirconium species; it is also an interesting catalyst itself. The M_w/M_n of 2.3 indicates that the catalyst is truly single-sited. The molecular weight ($M_w = 6600$) is, however, very low. The analogous hafnium complex $\{[(c\text{-}C_5H_9)_7Si_7O_{12}]HfCH_2Ph\}_2$ showed a very similar behavior. Whereas the complex itself is a poorly active ethylene polymerization catalyst (<10 g of PE/(mmol·h)), addition of $B(C_6F_5)_3$ as cocatalyst resulted in an impressive increase in catalyst activity (4800 g of PE/(mmol·h)). The corresponding titanium silsesquioxane compound, $[(c\text{-}C_5H_9)_7Si_7O_{12}]TiCH_2Ph$, proved to be monomeric in solution, and its structure resembles more the above-mentioned silica-supported zirconium hydride system; however, it showed no ethylene polymerization activity.

Interestingly, the zirconium calix[4]arene benzyl system resembles its silsesquioxane analogue, $\{[(c\text{-}C_5H_9)_7Si_7O_{12}]ZrCH_2Ph\}_2$, in that it is also dimeric.[517e,f] Whether the zirconium calix[4]arenes are active olefin polymerization catalysts has never been reported. The tripodal tris(amido)methane zirconium benzyl,[532] also used as a homogeneous model system for Basset's silica-supported zirconium species, is monomeric but contains an η^2-bonded benzyl group. Hydrogenolysis readily forms the corresponding zirconium hydride, which is dimeric in the solid state but monomeric in solution. Like the silica-supported zirconium hydride, this species isomerizes α-olefins and polymerizes ethylene.

10.3. Modeling of Silica-Grafted Homogeneous Catalysts

Model studies on supported homogeneous catalysts have been carried out not only to mimic the actual supported metal site but also to optimize supportation strategies. One of the earliest immobilization methods consisted of grafting metallocenes and half-sandwich complexes onto partly dehydroxylated silica. Recently Basset et al. used surface organometallic chemistry to study the synthesis, characterization, and olefin polymerization activity of (half) metallocenes grafted onto oxidic supports.[453] Studies on the synthesis, characteristics, and reactivity of the corresponding homogeneous model complexes have also been carried out to contribute to the better understanding of such heterogeneous catalysts. These systems have been modeled mainly using silsesquioxanes[533] and to a lesser extend by using simple siloxanes (Figure 13).[534] In several studies, their reactivity and stability toward leaching was tested. All metallasilsesquioxanes formed active catalysts after MAO-induced cleavage of the metal−siloxy bond. Even the terdentate ligand in $[(c\text{-}C_5H_9)_7Si_7O_{12}]MCp'$ (M = Ti, Zr, Hf; Cp′ = C_5H_5, 1,3-$C_5H_3(SiMe_3)_2$, Cp*) was readily displaced by MAO to yield active catalysts. Do and co-workers[533h] demonstrated that MMAO-induced metal−siloxy bond breaking in $[(c\text{-}C_5H_9)_7Si_7O_{12}]MCp^*$ is temperature-dependent. At low to ambient temperature, M−O bond breaking leads to a bimodal system. At elevated temperatures, M−O bond breaking is facile and affords a single-site, silsesquioxane-free catalyst.

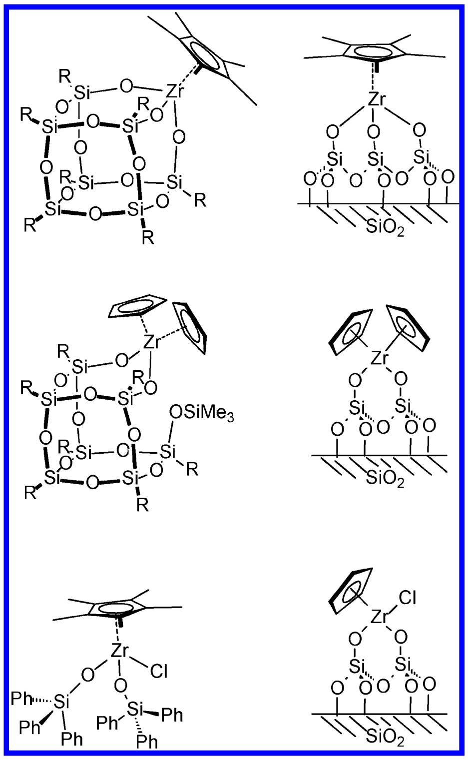


Figure 13. Silica-grafted (half-)sandwich complexes and some examples of homogeneous model systems thereof.

Protonolysis reaction of the monosilanol $(c\text{-}C_5H_9)_7Si_8O_{12}(OH)$ with $Cp''TiR_3$ yielded the mono(cyclopentadienyl)titanium silsesquioxane dialkyl species $Cp''[(c\text{-}C_5H_9)_7Si_8O_{13}]TiR_2$ (Cp″ = 1,3-$C_5H_3(SiMe_3)_2$, R = Me, CH_2Ph),[533d,e] which are realistic models for silica-grafted half-metallocenes and are very similar to the silica-grafted $Cp''ZrR_3$ species reported by Basset et al.[453] Like the corresponding $SiO_2(500)$-supported ($\equiv$Si−O)Cp^*ZrMe_2 system, the $Cp''[(c\text{-}C_5H_9)_7Si_8O_{13}]TiR_2$ complexes are themselves inactive but can be activated with "non-aluminum" cocatalysts such as $X^+[B(C_6F_5)_4]^-$ ($X^+ = Ph_3C^+$, $PhN(H)Me_2^+$) or $B(C_6F_5)_3$. The thus-obtained cationic titanasilsesquioxane species, $\{Cp''[(c\text{-}C_5H_9)_7Si_8O_{13}]TiR\}^+\{RB(C_6F_5)_3\}^-$, proved to be active in the polymerization of ethylene (M_w = 260 000, $M_w/M_n = 3.3$) and 1-hexene (atactic, $M_w = 3000$, $M_w/M_n = 2.0$).[533e] Silsesquioxanes containing one silanol and a neighboring siloxide ring of variable size have been used to study the effect of adjacent siloxides on the stability and catalytic activity of grafted titanium alkyl species (Figure 14).[533j] Compared to the cationic titanasilsesquioxane species, $\{Cp''[(c\text{-}C_5H_9)_7Si_8O_{13}]TiR\}^+\{RB(C_6F_5)_3\}^-$, the presence of a neighboring siloxide ring resulted in a lower activity but had a positive effect on the stability and lifetime of the catalyst.

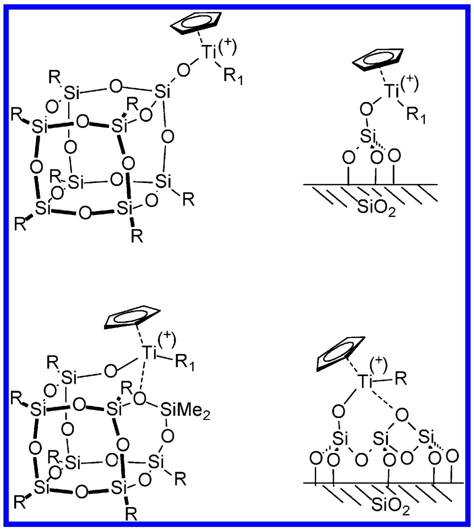


Figure 14. Different silica-grafted cationic titanium sites and their silsesquioxane-based models.

10.4. Modeling of Silica-Grafted Cocatalysts

The most common route to immobilize metallocenes consists of physisorbing the catalyst precursor onto a support that is pretreated with the cocatalyst (e.g., MAO, $Al(Cl)_nR_{3-n}$, or $B(C_6F_5)_3$). Alternatively, the untreated support is treated with a metallocene/MAO mixture. In both cases, the cocatalyst is chemically linked to the support, and the activated metallocene cation will in turn be bonded to the supported cocatalyst by means of electrostatic interactions. The interaction of the cocatalyst with the support is of great importance since this will strongly determine the possibility of leaching. The most commonly used cocatalyst is MAO. However, there are no model studies on supported MAO, which is not surprising since both amorphous silica and MAO are poorly defined. Silsesquioxane and silanol model supports have been used to mimic the interaction of partly dehydroxylated silica surfaces with trimethylaluminum (Figure 15).[535,536]

Several dimethyl aluminum siloxanes and methyl aluminosilsesquioxanes were obtained and structurally characterized. These aluminum species are probably not very suitable models for Lewis acidic aluminum sites on pacified silica surfaces, because the aluminosiloxanes and aluminosilsesquioxanes invariably dimerize to give electronically saturated aluminum centers. For the preparation of supported MAO, partly dehydroxylated silicas are used that contain large amounts of silanol groups. Reacting such silicas with aluminum alkyls might result in Brønsted acidic aluminosilicate structures, which in turn can react further with additional aluminum alkyls. As expected, the Brønsted acidic $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2Al^-\}\{H^+\}$[537] is readily deprotonated by trimethylaluminum affording the novel C_2-symmetric $[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2Al_2Me_2$ (**XI**, Figure 15).[535] The structure of this complex is also very robust and isomerizes to the thermodynamically most stable mixture of $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]AlMe\}_2$ only after prolonged heating (1000 h, 76 °C).

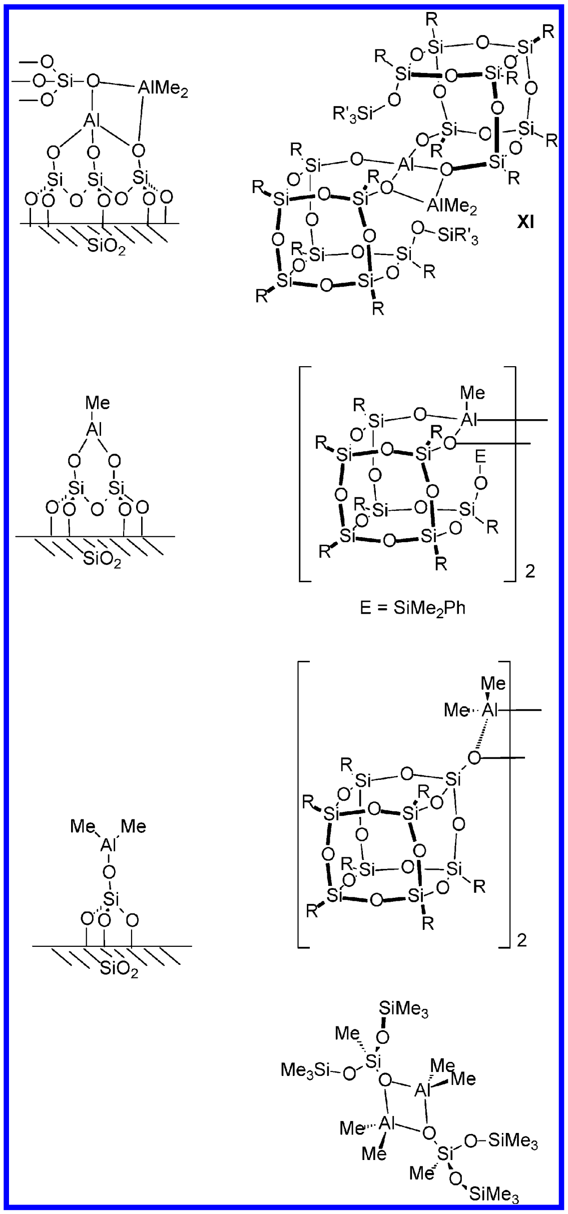


Figure 15. Schematic presentation of silica-grafted aluminum sites and corresponding methylaluminosilsesquioxane and dimethylaluminosiloxane structures.

None of the methyl aluminosilsesquioxanes are Lewis acidic enough to abstract a methyl from Cp_2ZrMe_2. Deprotonation of the Brønsted acids $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiR_3)]_2Al^-\}\{H^+\}$ (SiR_3 = $SiMe_3$, $SiMePh_2$)[537] did not afford weakly coordinating anions $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiR_3)]_2Al^-\}$ supporting cationic metallocene species in a similar fashion as, for example, to strongly acidic sulfonated metal oxides.[454-458] Instead, a clean redistribution reaction resulted, yielding $[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]ZrCp_2$, methane, and various methyl aluminosilsesquioxane species.[533h,535]

In an interesting study, Brintzinger et al.[536c] reported on the reaction of $[Me_2Al(\mu_2\text{-}OSiR_3)]_2$ with *N,N*-dimethyl anilinium tetrakis(pentafluorophenyl)borate and the subsequent reaction with Cp_2ZrX_2 (X = Cl, Me). It was found that $[Me_2Al(\mu_2\text{-}OSiR_3)]_2$ reacts with $\{PhN(H)Me_2\}^+\{B(C_6F_5)_4\}^-$ to afford $\{Me_2Al(\mu_2\text{-}OSiR_3)AlMe\cdot N(Ph)Me_2\}^+\{B(C_6F_5)_4\}^-$, which abstracts a chloride or methyl from Cp_2ZrCl_2 or Cp_2ZrMe_2, respectively (Figure 16). When the same reaction was

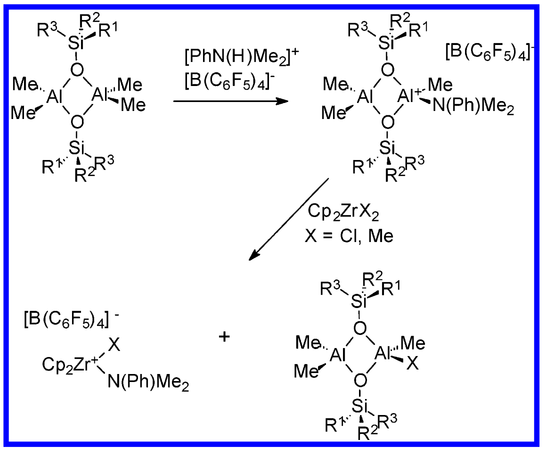


Figure 16. Reaction of $[Me_2Al(\mu_2\text{-}OSiR_3)]_2$ with $[PhN(H)Me_2]^+[B(C_6F_5)_4]^-$ and Cp_2ZrX_2 (X = Cl, Me).

performed with $Me_2Si(Ind)_2ZrMe_2$, an active ethylene polymerization catalyst was obtained.

Boranes and borates have also been immobilized and used as cocatalysts.[249−262] Whereas physisorbed, tethered, and grafted boron species have been reported, so far only silica-grafted boranes[258c,538] and borates[539] have been modeled. Representative examples are the neutral silsesquioxane tris(borane), $R_7Si_7O_{12}[B(C_6F_5)_2]_3$, and the silsesquioxane−borato ammonium salt, $\{[(c\text{-}C_5H_9)_7Si_7O_{13}]B(C_6F_5)_3\}^-\{PhN(H)Me_2\}^+$ (Figure 17). Recently Basset reported a comparative study on silica-grafted ammonium borates and hydroxy-, siloxy-, and silsesquioxane ammonium borates.[258c] With the help of homogeneous models, they found experimental conditions in which surface silanols are efficiently transformed into well-defined ammonium borate functionalities.

While stable in the absence of Cp_2ZrMe_2, already at low temperature, the silsesquioxane−borane complex $R_7Si_7O_9[OB(C_6F_5)_2]_3$ reacts with Cp_2ZrMe_2 to form the inactive $R_7Si_7O_{11}ZrCp_2[OB(C_6F_5)_2]$ and $(C_6F_5)_2BMe$, indicating that the B−O bond is readily split (Figure 17).[252,538] When zirconocene dibenzyl $Cp_2Zr(CH_2Ph)_2$ is reacted with the silsesquioxane−borato ammonium salt $\{[(c\text{-}C_5H_9)_7Si_7O_{13}]B(C_6F_5)_3\}^-\{PhN(H)Me_2\}^+$ in the presence of ethylene or 1-hexene, an active polymerization catalyst is obtained.[539] However, mechanistic studies showed that the expected $\{Cp_2ZrCH_2Ph\}^+\{[(c\text{-}C_5H_9)_7Si_7O_{13}]B(C_6F_5)_3\}^-$ was not formed. Instead, as a result of the relative labile B−O bond, the cationic zirconocene silsesquioxane $\{[(c\text{-}C_5H_9)_7Si_7O_{13}]ZrCp_2\}^+\{PhCH_2B(C_6F_5)_3\}^-$ was formed (Figure 17). This complex is in equilibrium with the neutral $[(c\text{-}C_5H_9)_7Si_7O_{13}]Zr(CH_2Ph)Cp_2$ and free borane $B(C_6F_5)_3$. It was demonstrated that exclusively in the presence of an excess of $Cp_2Zr(CH_2Ph)_2$ an active catalyst is formed. The free borane that, together with $[(c\text{-}C_5H_9)_7Si_7O_{13}]Zr(CH_2Ph)Cp_2$, is in the equilibrium with $\{[(c\text{-}C_5H_9)_7Si_7O_{13}]ZrCp_2\}^+\{PhCH_2B(C_6F_5)_3\}^-$ reacts with $Cp_2Zr(CH_2Ph)_2$ to yield $\{Cp_2ZrCH_2Ph\}^+\{PhCH_2B(C_6F_5)_3\}^-$, which was found to be the actual active catalyst of this system.[539] Further proof for the lability of the B−O bond in silsesquioxane borates was given by the reaction of the triethylammonium salt of the silsesquioxane borate, $\{[(c\text{-}C_5H_9)_7Si_7O_{13}]B(C_6F_5)_3\}^-\{Et_3NH\}^+$. The low acidity of the ammonium ion prevented protonation of the zirconium alkyl. However, the reaction with $Cp_2Zr(CH_2Ph)_2$ resulted in selective ligand exchange and the formation of $[(c\text{-}C_5H_9)_7Si_7O_{13}]Zr(CH_2Ph)Cp_2$ and $\{PhCH_2B(C_6F_5)_3\}^-\{Et_3NH\}^+$. Due to the lability of the B−O bond, the silsesquioxane-based boranes and borates are unsuitable cocatalysts. Whether these systems are reliable models for silica-grafted boranes and borates is not completely sure. Recent reports proved that polyethylene with good particle morphology (spherical, high bulk density) and no reactor fouling can be obtained using silica-grafted borates, irrespective of any possible leaching of the borane cocatalyst as observed in the silsesquioxane systems.[249−262]

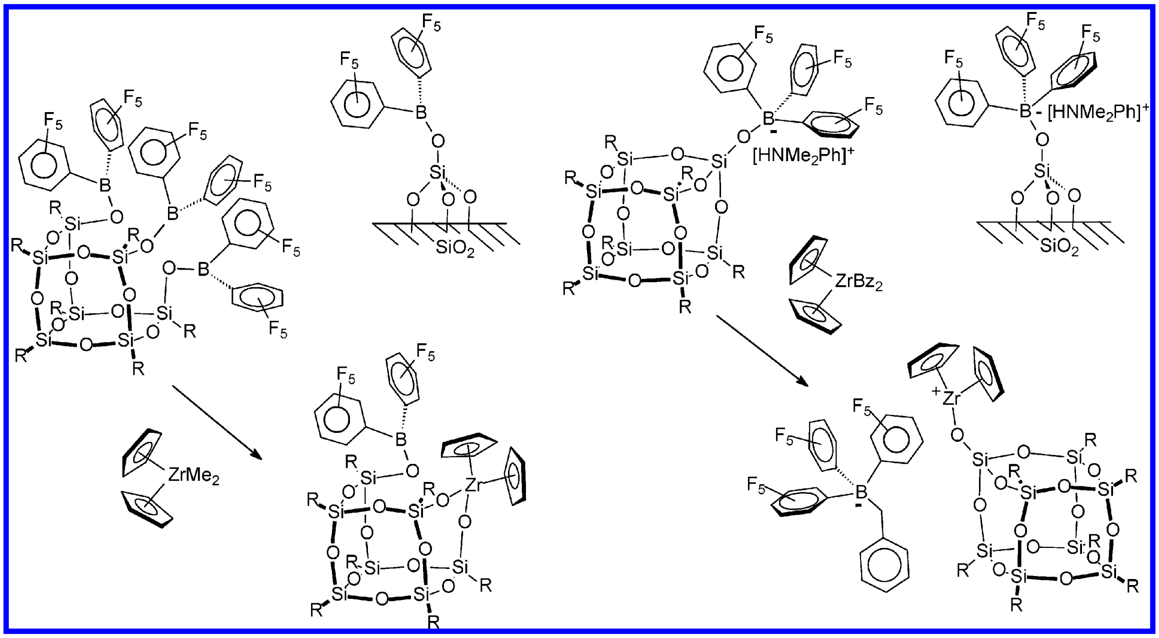
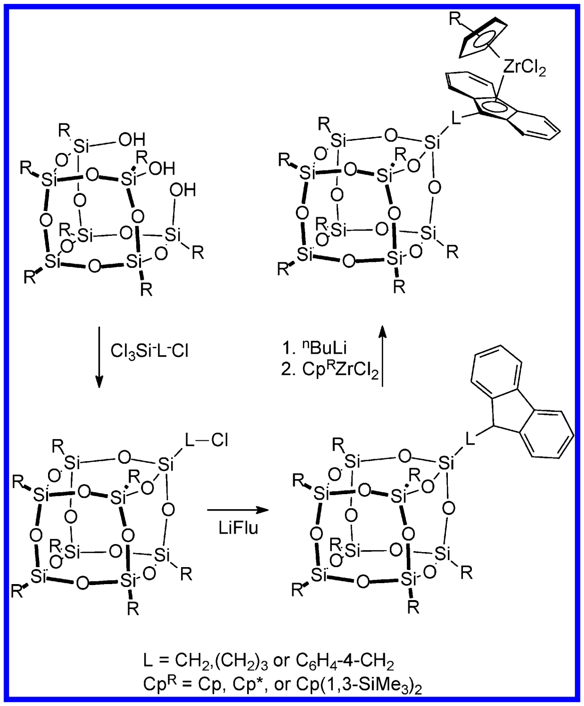


Figure 17. Schematic representation of silica-grafted boranes and borates, their silsesquioxane-ligated model systems, and their reactivity toward dialkyl zirconocenes.

Scheme 48



L = CH$_2$,(CH$_2$)$_3$ or C$_6$H$_4$-4-CH$_2$
Cp^R = Cp, Cp*, or Cp(1,3-SiMe$_3$)$_2$

10.5. Modeling of Silica-Tethered Catalysts

The tethering of organometallic compounds to a silica support is one of the most challenging routes to immobilize a catalyst system. While several studies on tethering of olefin polymerization catalysts to silicas are reported, curiously enough hardly any information is available on the effectiveness of the applied immobilization method, the stability of the catalysts, and the effect of the support on these immobilized catalysts. There are two general routes that are applied, (i) building-up the ligand and subsequently the metal complex at the surface and (ii) tethering a presynthesized catalyst precursor containing an anchorable functionality. Both routes clearly have their limitations and advantages. Studies using silsesquioxanes to mimic catalyst tethering have shown that these model supports are also very suitable for optimizing synthetic strategies.[540]

Scheme 48 shows an example of how first a ligand and subsequently the corresponding metal complex can be built up at the surface, together with an example of a silsesquioxane-based model system. The second strategy, consisting of treating the support with a catalyst precursor containing an anchorable functionality, has the highest chance of forming a uniform surface metal complex. However, synthesis of such metal complexes containing a pendant anchorable, reactive functionality is often not trivial. Reacting $\mathrm{Cp''[EtOSi(Me)_2CH_2Flu]ZrCl_2}$ with $(c\text{-}\mathrm{C_5H_9})_7\mathrm{Si_7O_9(OH)_3}$ resulted in loss of the fluorenyl ligand and formation of the corner-capped zirconium silsesquioxane, $[(c\text{-}\mathrm{C_5H_9})_7\mathrm{Si_7O_{12}}]\mathrm{ZrCp''}$. The same reaction of $(c\text{-}\mathrm{C_5H_9})_7\mathrm{Si_7O_9(OH)_3}$ with the more hydrolysis-stable $\mathrm{Cp''[EtOSi(Me)_2C_5Me_4]ZrCl_2}$ initially resulted in $(c\text{-}\mathrm{C_5H_9})_7\mathrm{Si_7O_9(OH)(O_2Zr(Cp'')(C_5Me_4SiMe_2OEt)}$, which slowly reacted further under formation of ethanol to the silsesquioxane-tethered $[(c\text{-}\mathrm{C_5H_9})_7\mathrm{Si_7O_9(O_2Zr(Cp'')(C_5Me_4SiMe_2O\text{-})}]_n$ (Figure 17). Clearly, reaction of the zirconium chloride substituents is faster than grafting of the pendant silyl ether. As long as the cyclopentadienyl ligands remain attached to the zirconium, this route can still lead to a uniform silica-tethered metallocene catalyst. As we have seen earlier, silsesquioxane-grafted zirconocenes form active olefin polymerization catalysts after activation with MAO, because the latter effectively splits Zr–OSi bonds. Hence, complexes of the type $[(c\text{-}\mathrm{C_5H_9})_7\mathrm{Si_7O_9(O_2Zr(Cp'')(C_5Me_4SiMe_2O\text{-})}]_n$ can be activated in the same way albeit that now the metallocene remains attached to the surface by the tethered cyclopentadienyl group (Figure 18). It should be noted that at present there has been no study performed on the effects of MAO on the silsesquioxane structure at the large excess commonly used to activate the zirconium species.

Homogeneous models systems have not only been used to optimize synthetic strategies. Lee and coworkers have performed studies on the effect of

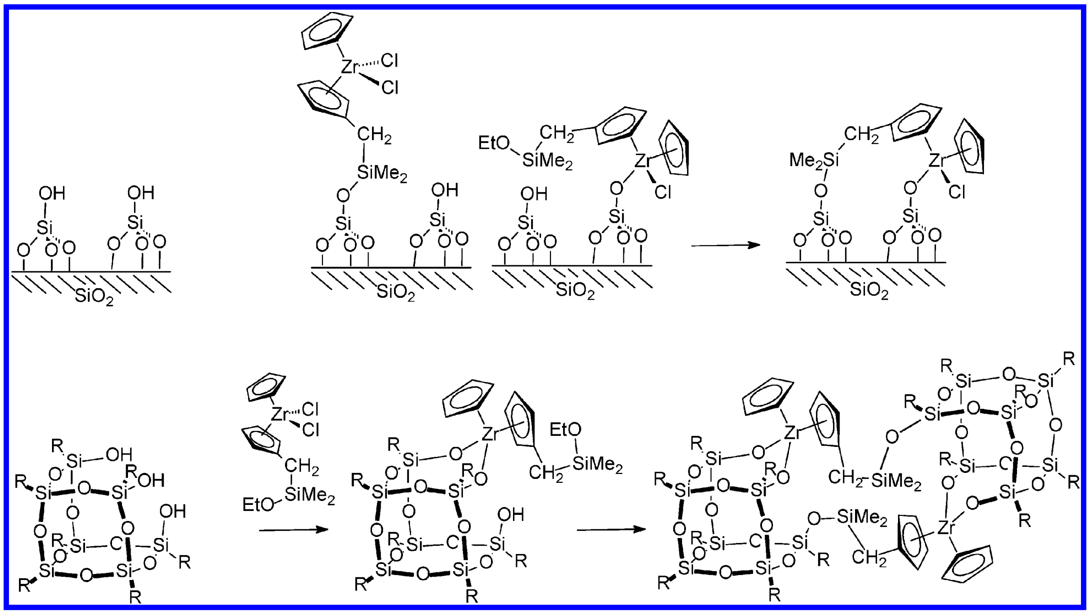


Figure 18. Immobilization of a metallocene containing a graftable functionality.

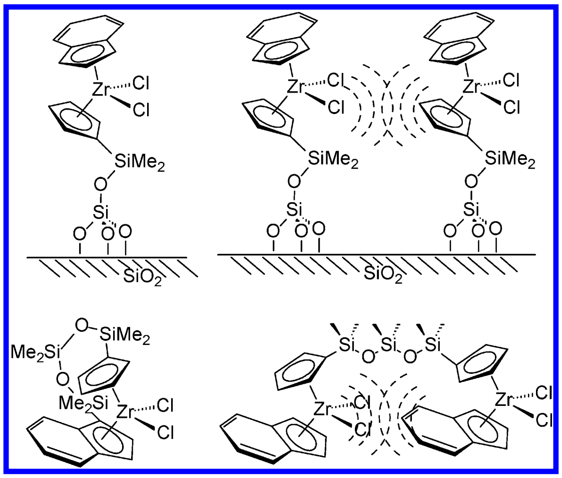


Figure 19. Siloxane-bridged zirconocenes as models for silica-tethered zirconocenes and the effect of catalyst loading.

catalyst loading on the catalyst activity.[541] As a model for silica-tethered metallocenes, they used metallocenes linked together by siloxane bridges of variable length (Figure 19). The prime feature was that the activity increased with longer linkages, whereas the molecular weight and polydispersity increased.

Several homogeneous systems have been developed that structurally resemble several features of the inorganic supports for which they serve as a model. The rigid three-dimensional structure of, for example, silsesquioxanes and di- and tripodal nitrogen donor ligands are some of them. With these model supports, features such as the stability and reactivity of the corresponding metal complexes can be studied, which affords detailed insight that would be difficult to obtain with heterogeneous catalyst systems. However, since their mobility in solution allows aggregation reactions to thermodynamically stable complexes, many of the homogeneous metal complexes do not structurally resemble the silica-supported systems.

11. Polymeric Supports

11.1. Polysiloxanes

Tethered polysiloxane-supported catalysts have been prepared by the hydrolysis or cohydrolysis of a silyl chloride- or silyl ethoxide-containing ancillary ligand. The ancillary ligands, bridged by a dichlorosilyl moiety, Cl_2SiCp' ($Cp' = C_5Me_4$, Ind and Flu), were hydrolyzed or cohydrolyzed with a dihydroxy-functionalized linker by Soga et al. to produce a series of tethered ligands, which could be deprotonated and reacted with $ZrCl_4$ to produce heterogeneous precatalysts, Scheme 49.[542]

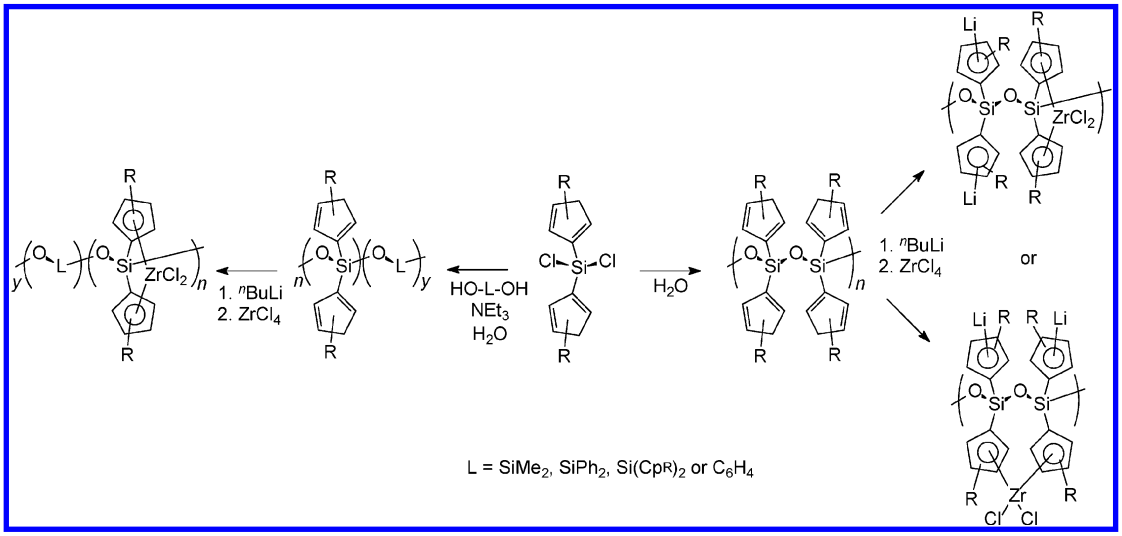
The quantity of reagents ($Cp'/^{n}BuLi/Zr = 2:2:1$) used to synthesize the supported precatalyst should have led to quantitative conversion, but the extent of zirconium incorporation varied greatly between the supports (1−75%, based on one Zr to two Cp′), indicating that a considerable amount of the inner portion of these supports is inaccessible to at least one or all of the reagents and may seriously hinder the fragmentation of the support. It was also established that the supported precatalysts constructed from the homogeneous hydrolysis of $Cl_2SiCp'_2$ outperformed those obtained when $Cl_2SiCp'_2$ is reacted with a dihydroxy-containing complex. Additionally, relatively good activities were observed for the MAO-activated indenyl- and fluorenyl-containing precatalyst, while the tetramethylcyclopentadienyl-containing precatalyst showed surprisingly poor activity in ethylene polymerization. This series of polysiloxane-supported zirconocene precatalysts was also applied to ethylene-*co*-1-octene and propylene polymerization, using MAO as cocatalyst. Coupling reactions between $Cl_2Si(Ind)_2$ and *p*-dilithiophenyl or *p*-dilithiodiphenyl have also been used to form supported metallocenes. The *p*-(silylene)phenylene-supported precatalysts were used to homopolymerize ethylene and propylene. In the case of propylene polymerization, an enhancement in catalyst stability, stereoselectivity, and regioselectivity was observed, when compared to the corresponding mononuclear and dinuclear catalysts, $Ph_2Si(Ind)_2ZrCl_2$ and $C_6H_4(SiPh(Ind)_2ZrCl_2)_2$, respectively. However, broad molecular weight distributions were observed for polypropylene ($M_w/M_n = 2.9-4.5$) and especially polyethylene ($M_w/M_n = 4.4-8.5$).[543]

Dos Santos et al. have cohydrolyzed bisindenyldiethoxysilane ($Ind_2Si(OEt)_2$) with TEOS (ratio of indene to TEOS 1:3−5) to form indene-containing xerogels that can be converted to a supported metallocene, following lithiation and metathesis with $ZrCl_4{\cdot}2THF$.[544] More recently, Deffieux and co-workers have produced an indene-modified silica support via reaction of bisindenyldichlorosilane, Me_2SiCl_2, $(ClMe_2Si)_2O$, and TEOS under a non-hydrolytic sol−gel process. The supports, once metalated, were found to be active in the polymerization of ethylene, producing resin with high polydispersities (M_w/M_n 3.1−127).[545]

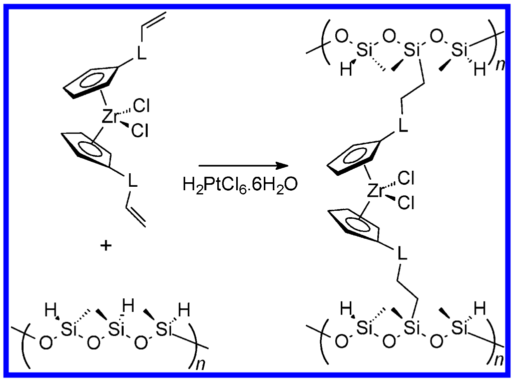
Metallocenes tethered to a polysiloxane through the cyclopentadienyl ligand have been assembled by hydrosilylating $(CH_2{=}CH\text{-}L\text{-}Cp')_2ZrCl_2$ ($L = (CH_2)_2$ or CH_2SiMe_2, $Cp' = Cp$ or Ind) with polymethylhydrogensiloxane in the presence of chloroplatinic acid, forming a cross-linked polysiloxane, Scheme 50.[546] Polymethylhydrogensiloxane-*co*-dimethylsiloxane has also been used by Nagy and Tyrell to construct a tethered metallocene. In this case, the silane functions of the polymer were brominated and reacted with LiCp to form a tethered cyclopentadiene, which could be converted into a zirconocene complex (Scheme 51).[547] The groups have also used other polysiloxane copolymers to form immobilized precatalysts. The reaction of 1,5-diamino-2-methyl-pentane with 1,5-dichlorohexamethyltrisiloxane formed a copolymer material whose amine functions could be lithiated and reacted with $CpZrCl_3$, Scheme 52. The resultant tethered precatalyst, when used in combination with MAO, effectively polymerized ethylene.[548]

Polysiloxanes derived from the hydrolysis of chloro- or alkoxy-silanes leave polymeric materials with hydroxyl groups that require capping, usually with a silane complex (HMDS or $ClSiR_3$).[542,543,545] Alt and co-workers took advantage of these functional groups to tether an ansa-bridged difluorene ligand.[549] The hydroxyl groups of polymethylsiloxane microgels

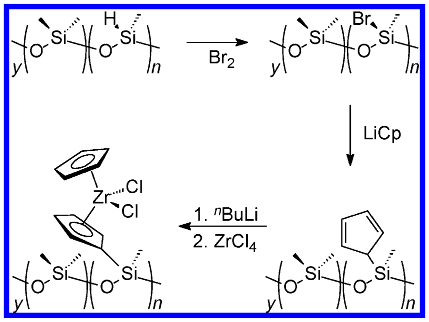
Scheme 49



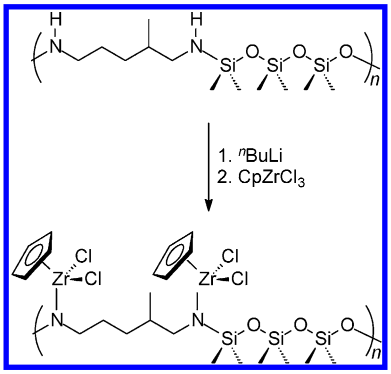
Scheme 50



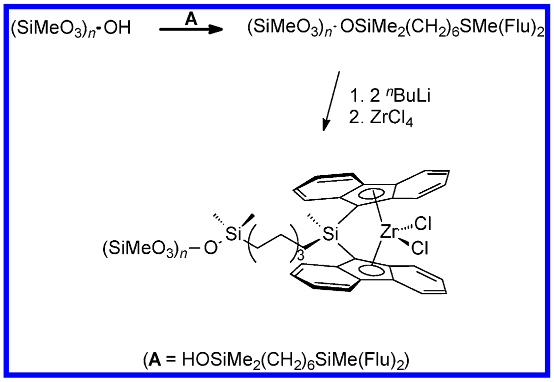
Scheme 51



Scheme 52



Scheme 53



were end-capped with $\mathrm{HOSiMe_2(CH_2)_6SiMe(Flu)_2}$, Scheme 53. Deprotonation and subsequent metathesis with $\mathrm{ZrCl_4}$ afforded a supported metallocene capable of producing a moderately active catalyst species (up to 1.44 kg/(g of Zr·h)) in conjunction with MAO. The polymethylsiloxane microgels were also modified to facilitate the in situ generation and immobilization of MAO. The surface of the microgels was partially pacified with $\mathrm{Me_2(Oct)Si(OEt)}$, $\mathrm{Me_2SiH(OEt)}$, or $\mathrm{Me_2SiH(OEt)}$, the latter being subsequently used to hydrosilylate octene to form the finished support. The remaining hydroxyl groups on the supports were pacified with HMDS. The modified polymethylsiloxane was then treated with TMA, followed by an appropriate amount of water, to form MAO-like structures on the surface of the support. The support pacified via hydrosilylation with octene proved to be the most effective substrate in comparative polymerization experiments with a metallocene precatalyst.[550] The supported cocatalysts could also be employed to activate late transition metal catalysts.[551] The efficiency of the supported cocatalysts, in combination with different precatalysts, was found to strongly depend on the TMA/$\mathrm{H_2O}$ ratio used in the in situ generation of MAO. No one ratio of TMA/$\mathrm{H_2O}$ was found to be ideal for all precatalysts.[551a] As a result, each precatalyst needed a specific supported MAO microgel, whose TMA/$\mathrm{H_2O}$ ratio had been optimized to achieve maximum activity. The optimized systems did, however, prove to be comparable to some commercially available silica-supported MAOs.[552]

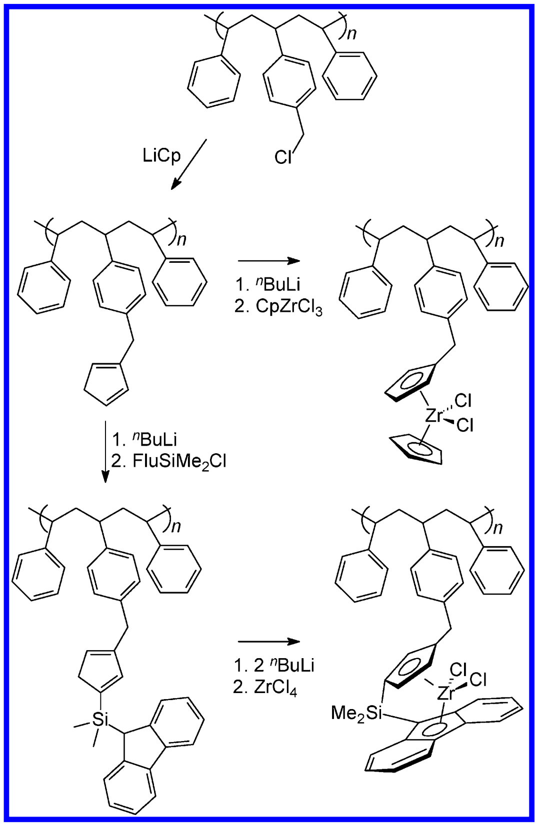
It is worth considering at this point the presence of reactive groups within a supported system and their effect on a catalyst performance. Obviously, the deactivation of the active species by such groups is of utmost importance, but additional consideration should be given to their ability to undergo chain transfer reactions with the active species before and especially during polymerization. If such reactions were to take place, then the effect on the molecular weight capabilities of a system may need to be assessed. Hydrosilane-containing complexes are one such example and have been extensively reported by Marks and co-workers to be efficient chain transfer agents for homogeneous and heterogeneous single-site α-olefin polymerization catalysts.[553] In fact, polysiloxanes such as polymethylhydrosiloxane have themselves been used as chain transfer agents for single-site catalysts, immobilized on porous polyethylene particles.[554] The addition of a polysiloxane modifier to the system was also reported to increase catalyst activity in ethylene-*co*-α-olefin polymerization.

11.2. Polystyrene

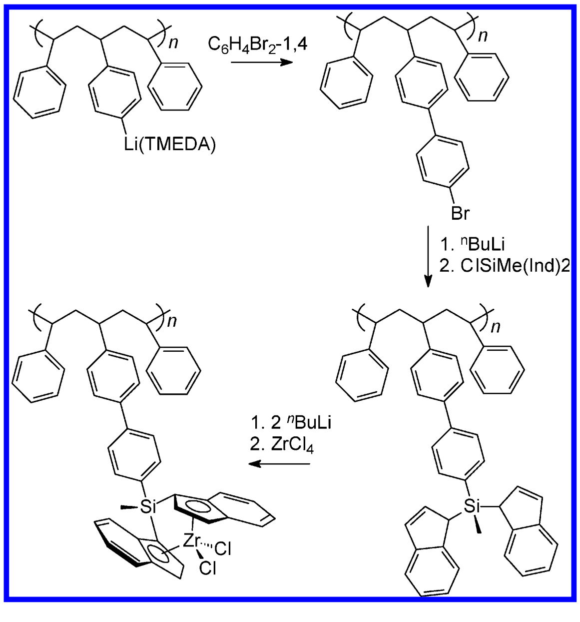
There has been considerable interest in polystyrene-bound α-olefin polymerization precatalysts, and this has led to the development of numerous and often elaborate routes to supported pre- and cocatalysts. It is believed by some that polystyrene supports possess properties ideally suited to the immobilization of single-site α-olefin polymerization catalysts. This derives from the belief that polystyrene is a more chemically compatible support relative to silica and other inorganic supports. Additionally, the catalytic species reside within a mobile hydrocarbon-rich matrix, providing a polymerization microenvironment that more closely resembles a homogeneous solution polymerization. Polystyrene supports are also very versatile materials in terms of the incorporation of functional groups, either by copolymerization of styrene with functionalized vinylbenzenes or by post-modification of preformed polystyrene beads, which are commercially available in different sizes and cross-link densities. Lightly cross-linked polystyrene can also swell, allowing access to the inner core of the particle during functionalization. A fine line has to be trod, however, when considering cross-link density, because too low a level may lead to formation of a partially soluble or dimensionally unstable carrier particle and too high a level may hinder the carrier particle “fragmentation”.

Polymeric supports derived from the copolymerization of styrene, divinylbenzene, and 4-chloromethyl-vinylbenzene have proved to be flexible starting materials for supporting single-site catalysts. Such chlorinated polymers have been treated with a cyclopentadienyl anion to form a polystyrene-bound cyclopentadiene that could be converted in additional steps to a supported unbridged[555] or bridged[556] metallocene (Scheme 54). Polystyrene-bound cyclopentadienes have also been used to construct late transition metal polymerization catalysts.[557] Supported pseudo-C_2-symmetric metallocenes were synthesized when lithiated cross-linked polystyrene was reacted with $Cl_2Si(Ind)_2$ or $PhClSi(Ind)_2$ to form the supported ancillary ligand, which could be converted into the corresponding metallocene.[558] Alternatively, the lithiated polystyrene was reacted with 1,4-dibromobenzene before lithiation, reaction with $MeClSi(Ind)_2$, and conversion to the zirconocene (Scheme 55). Analysis of this supported catalyst indicated that the zirconocene sites are solely present on the surface of the support with no zirconium being detected inside the support. As a result, polymerization will only occur on the surface of the support.

Scheme 54

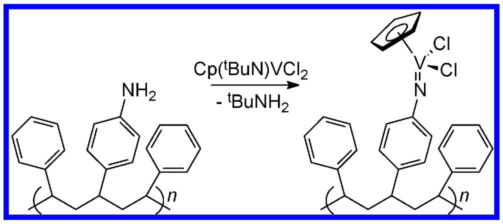


Scheme 55

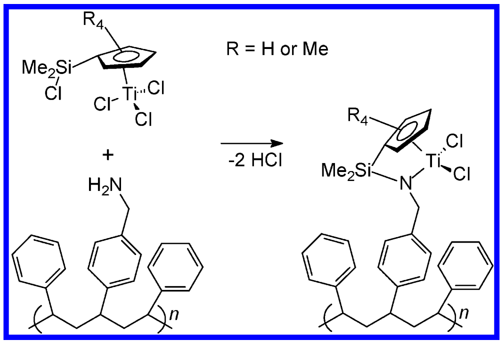


Gibson et al. utilized polystyrenes that contained amine functionalities to support the imidovanadium precatalyst complexes, $L(^tBuN)VCl_2$ (L = Cp or Cl), Scheme 56.[559] The polystyrene-supported cyclopen-

Scheme 56



Scheme 57

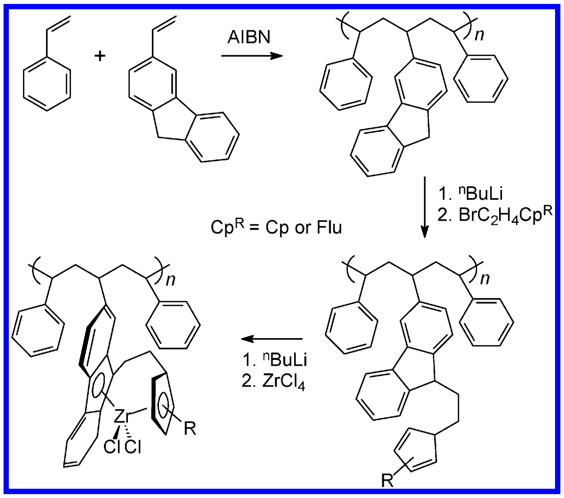


tadienyl-imidovanadium precatalyst was found to be 10−50 times more productive than the unsupported analogue, (Cp)(^{t}BuN)VCl$_2$, when activated with DEAC. However, the productivity of the supported catalyst is still relatively poor, 77.2 g/(mmol of V·h). Rapid catalyst deactivation, a widely observed phenomenon in olefin polymerization using vanadium-based catalysts and generally ascribed to the reduction of V(III) species to inactive V(II),[560] was not the cause of the poor productivity, because Gibson's supported vanadium system showed a steady rate of ethylene uptake throughout the duration of the polymerization, indicating that the vanadium system is atypically stable toward catalyst deactivation. Additionally, the polyethylene resins produced were high in molecular weight ($M_w \approx 2 \times 10^6$) and relatively broad in molecular weight distribution ($M_n/M_w = 4.9$).

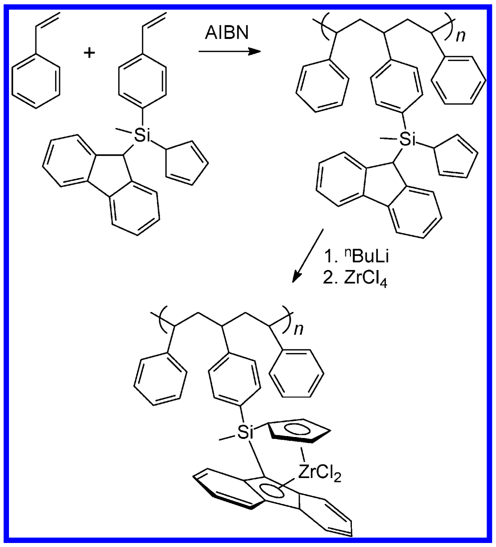
Primary amine-functionalized polystyrenes have also been used to immobilize CGC catalysts. In an adaptation of a Royo procedure,[561] aminomethyl-functionalized polystyrene is reacted with (C$_5$Me$_4$-SiMe$_2$Cl)TiCl$_3$ at a N/Ti mole ratio of 3:1 (Scheme 57).[562] The first equivalent of primary amine reacts with the titanium and silyl chloride, while the remaining two equivalents scavenge the HCl. The supported catalysts were tested for ethylene and ethylene-*co*-1-octene polymerization with MAO. Feeble productivities were observed in all cases (1.4−18 g of PE/(g of catalyst·h)), and analysis of the copolymer resins indicated the presence of LLDPE and HDPE, the latter being attributed to a leached active titanium species that poorly incorporated comonomer.

The above polystyrene-bound metallocenes have all been constructed by post-modification of a preformed polystyrene support. Resin-bound metallocenes have also been produced by the copolymerization of styrene with a vinyl-functionalized ancillary ligand. Alt and co-workers copolymerized 2-vinylfluorene with styrene using a free radical initiator (AIBN or BF$_3$·OEt$_2$).[563] The fluorine-containing copolymers could then be modified to form resin-bound metallocene, Scheme 58. Fully formed ligand sets have also been copolymerized with styrene, using AIBN as an initiator, Scheme 59. The zirconocene complexes derived from the copolymers were used to produce syndiotactic polypropylene with relatively high stereospecificity.[564] The synthesis of bis-indene and tetrahydroindene ligand sets that are capable of being copolymerized with styrene has recently been reported, although no attempt was made to support or metalate the ligand sets.[565]

Scheme 58

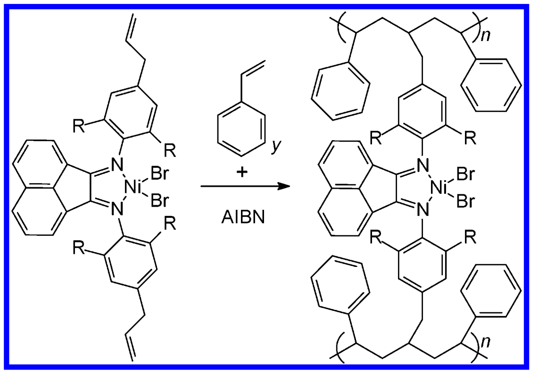


Scheme 59

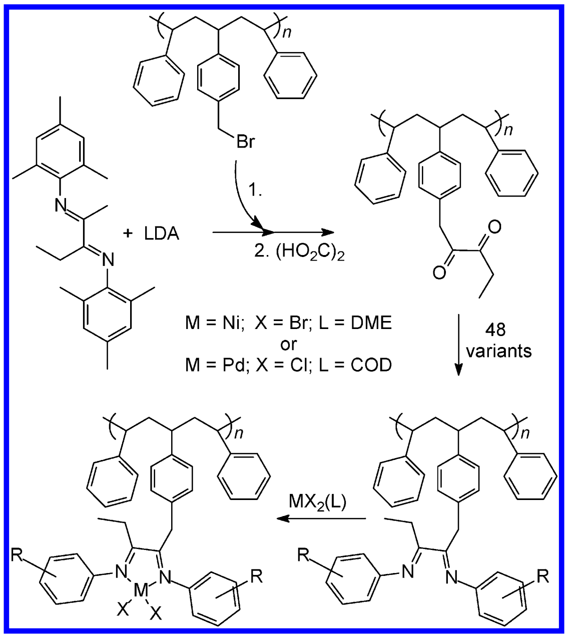


Metallocenes containing polymerizable functions on either the cyclopentadienyl[566] or silicon bridging atom[567] have been copolymerized with styrene. Jin et al. copolymerized (CH$_2$=CHCH$_2$)(Me)Si(Cp)$_2$ZrCl$_2$ with styrene to form a resin-bound metallocene. The supported precatalyst/MAO system was then used to polymerize ethylene and was found to be more active than (CH$_2$=CHCH$_2$)(Me)Si(Cp)$_2$ZrCl$_2$.[567] However, because the supported catalyst was not cross-linked, for instance, with divinylbenzene, it was found to be particularly soluble in the polymerization medium, toluene. The same group also copolymerized styrene with bis(imino)pyridine iron[568a] or nickel α-diimine complexes[568b] containing a polymerizable allyl function, which formed a cross-linked support (Scheme 60). Ethylene polymerization with the supported precatalyst was found to be of comparable activity

Scheme 60



Scheme 61

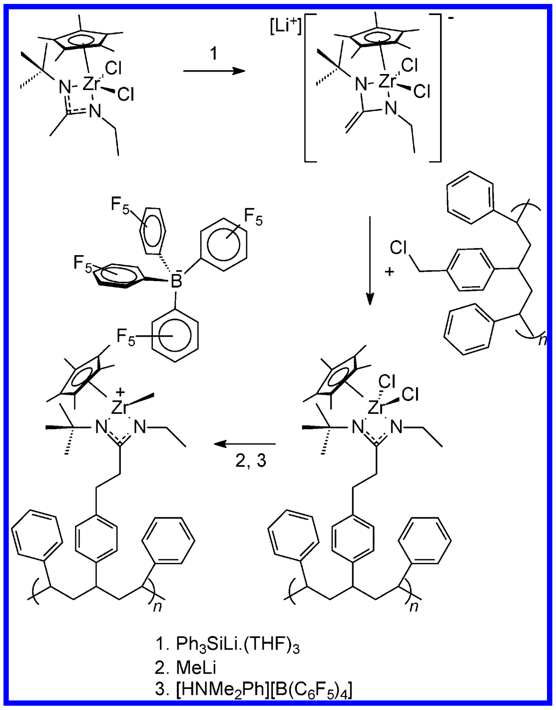


to the unsupported functionalized nickel α-diimine and produced resins with narrow molecular weight distribution and good morphology.[568b]

Advances in combinatorial chemistry and solid-phase synthetic methodologies have resulted in the ability to rapidly screen large libraries of catalysts. Murphy and co-workers at Symyx presented the first implementation of such methodologies in the polymerization of α-olefins.[569] Parallel synthesis generated a library of α-diimines via a condensation reaction of an unsymmetric polymer-bound α-diketone and over 48 commercially available anilines. The library could then be converted to the corresponding nickel and palladium complexes, Scheme 61. The polymer-bound precatalyst library was then used in a primary screening experiment involving the activation of each variant with MAO or a borate cocatalyst, polymerization being performed in a custom built 48 chamber parallel polymerization reactor. Furthermore, chemical-encoding techniques were used to distinguish catalyst performance trends. The use of similar polymer-bound α-diimine catalyst libraries has since been reported by others.[570]

The advances in solid-phase synthetic methodologies have also been utilized by Barrett and co-workers to developed spherical cross-linked polystyrene beads containing a *p*-nitrosulfonate function at

Scheme 62



1. $Ph_3SiLi.(THF)_3$
2. MeLi
3. $[HNMe_2Ph][B(C_6F_5)_4]$

the end of a tetraethylene glycol spacer.[571] The *p*-nitrosulfonate function was then converted to a cyclopentadiene, which in turn was reacted with $CpTiCl_3$ to form a resin-bound metallocene. However, the methylaluminoxane-activated resin-bound precatalyst synthesized in such a way showed low activity and poor morphology in ethylene polymerization, the spherical supports producing resin with "noodle-like" morphology.

Sita and co-workers have recently constructed a polymer-supported version of their remarkable amidinate-based precatalyst, $(Cp^*)(^tBuNC(Me)NEt)ZrMe_2$. Such catalysts have been utilized to produce poly-α-olefins (1-hexene and higher) in a living and highly stereoselective fashion.[572] The amidinate-containing precatalyst was immobilized onto commercially available chloromethylated polystyrene beads, and subsequent alkylation and activation led to a supported catalyst capable of polymerizing 1-hexene, Scheme 62.[573] The supported catalyst retained the stereospecific and living characteristics of the homogeneous system, albeit with a marked reduction in efficiency. At first glance, one might ask why one would wish to support a catalyst for such a soluble polyolefin. In this case, however, the immobilization of the zirconium complex was not driven by particle morphology or process-related considerations. Instead, suppression of bimolecular deactivation processes, ability to produce multiblock copolymers in a combinatorial manner, and separation of living from dead polymer chains were the main driving forces. The latter stems from the fact that living polymer chains are bound to the zirconium centers, which in turn are bound to the polystyrene support. As a result the "living" chains are rendered insoluble and can be separated from the dead chains in solution via simple filtration, assuming the concentration of dead chains is such that gel formation does not occur. As stated by the authors, such a supported system that reduces bimolecular deactivation and can easily be separated from the dead polymer fraction should lead to polyolefin products with even narrower molecular weight distribution. Furthermore, if a suitable chain-transfer agent could be found, such systems may even become recyclable.

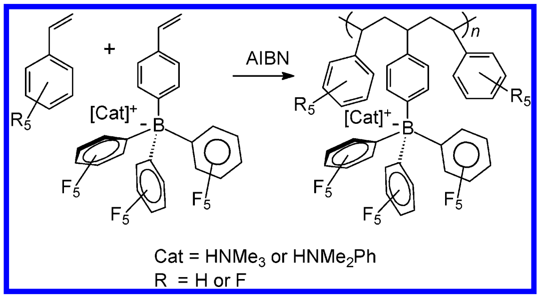
The immobilization of MAO-activated zirconocene has been achieved with several functionalized polystyrene supports. The ter-polymerization of styrene, divinylbenzene, and either acetoxy-styrene,[574] acrylamide,[575] or ethyl acrylate[576] has produced porous polystyrene supports that contain polar functionalities capable of encapsulating a zirconocene/MAO catalyst. The supported zirconocene/MAO catalyst derived from the acetoxy-functionalized support was shown to possess activities in ethylene-*co*-1-hexene polymerization comparable or superior to those derived from silica or commercially available unfunctionalized polystyrene, respectively.[574]

Wanke and co-workers reported the use of styrene copolymers containing 2-hydroxylethyl methacrylate as supports for MAO.[577] The supported cocatalyst could then be used to activate $^{bu}Cp_2ZrCl_2$ for gas-phase ethylene-*co*-1-hexene polymerization and produced resin particles that consisted of concentric spherical shells, which occurred for both low and high activity. Supported catalytic systems generated when a zirconocene/MAO or zirconocene/borate catalyst is treated with poly(vinylpyridine-*co*-divinylbenzene)[578] or poly(acetonitrile-*co*-divinylbenzene)[579] have also been reported to compare favorably to their silica-supported counterparts.

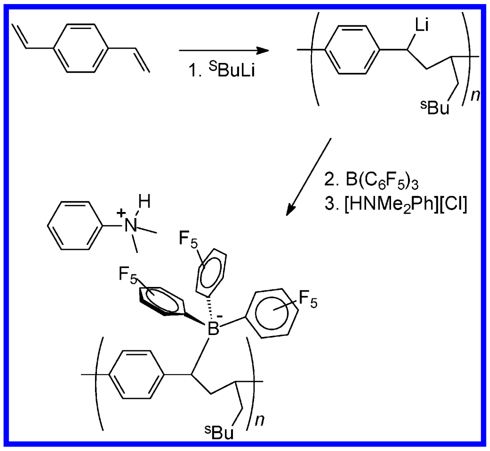
The synthesis of functionalized polystyrene capable of immobilizing a metallocene/MAO system can also be achieved by the postmodification of polystyrene resin. Resconi et al. reported the introduction of three different polar functionalities to cross-linked polystyrene.[580] Chemical modification of the polystyrene support was performed by either chloromethylation, lithiation and then treatment with CO_2, or acylation with $CH_3COCl-AlCl_3$ followed by reduction with $NaBH_4$ to afford polystyrene supports containing either an acetoxyl-, a carboxyl, or a hydroxyl functional group, respectively. The supports were then used to encapsulate a preactivated $Et(Ind)_2ZrCl_2$/MAO catalyst. Polymerization experiments with these supported systems demonstrated that sufficient cross-linking of the initial support is required to prevent reactor fouling.

Solid ionic cocatalysts have been prepared by covalently binding the anion or cation to a support resin. Covalently bound anions have been prepared by the AIBN-inititated copolymerization of [A]-$[B(C_6F_5)_3(C_6H_4CH{=}CH_2)]$ (A = $HNMe_3$ or $HNMe_2Ph$) with styrene or pentafluorostyrene, Scheme 63.[581] The polymer-bound ionic cocatalyst could then be used to activate and immobilize various zirconocene dichloride/TIBA systems. These activated catalysts were subsequently used to produce HDPE, LLDPE, or *i*PP resins in a slurry phase with an absence of reactor fouling. Ionic cocatalysts have also been formed by capping the lithiated end groups of an anionically polymerized polystyrene or polydivinylbenzene with $B(C_6F_5)_3$, followed by treatment with $[HNMe_2Ph][Cl]$.[386] In this case the borate anion is situated on the aliphatic backbone of the polymer support, Scheme 64.

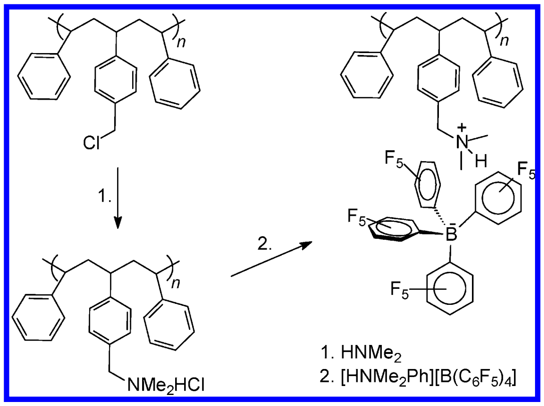
Scheme 63



Scheme 64



Scheme 65



The use of tertiary amine-functionalized polystyrene as polyionic counterions to $[B(C_6F_5)_4]^-$ has been reported to form immobilized ionic catalyst systems for a range of dimethyl-metallocenes.[582,583] Roscoe and Fréchet developed a polystyrene-supported trialkylammonium-borate bound to the polystyrene via a benzyl-amine group.[582] Treatment of the functionalized support with a solution of a dimethylmetallocene led to an immobilized catalyst system in which the active species is not chemically bound to the support, Scheme 65. The polymer support, however, has a higher dielectric constant than the surrounding polymerization medium, discouraging catalyst leaching. High activity was observed for ethylene-*co*-1-hexene and propylene polymerization. However, good morphology was shown to be polymerization temperature- or metallocene precatalyst-dependent, or both. Vizzini used virtually the same supported cocatalysts to activate $Me_2Si(2\text{-}Me\text{-}4\text{-}PhInd)_2ZrMe_2$ for the homopolymerization of propylene.[583] Comparative polymerization experiments were made between the polystyrene-supported borate and a silica-immobilized $[HNMe_2Ph][B(C_6F_5)_4]$. The polystyrene-supported systems were found to be less active than the corresponding silica-supported system. Additionally, the *i*PP produced had a molecular weight an order of magnitude lower, with a broader molecular weight distribution, but a higher melting temperature.

Simple swelling and shrinking of a polystyrene support has been applied to encapsulate a metallocene system. The active species is entrapped inside the shrunken pores of the support, like a ship in a bottle. The resultant system exhibited high activity and no reactor fouling and yielded resins with good spherical morphology.[584]

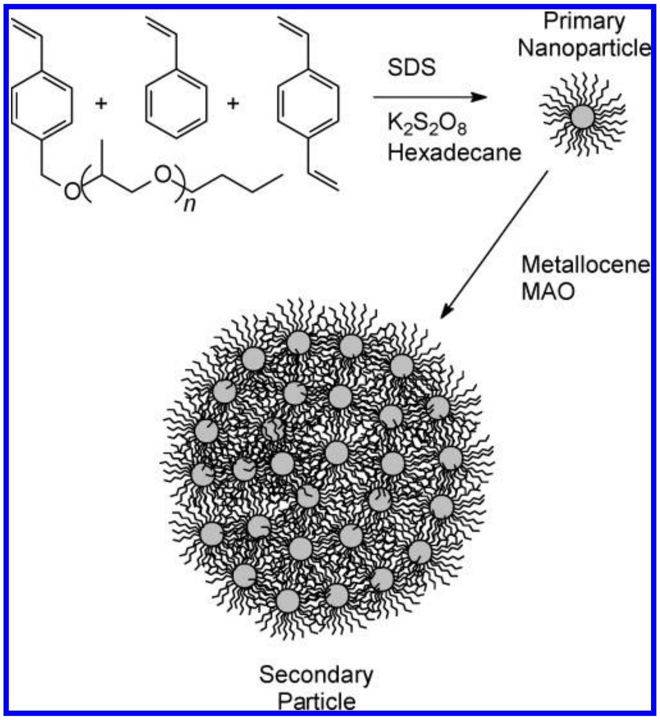
As mentioned previously, the majority of polystyrene supports are cross-linked with a rigid linker, such as divinylbenzene. Finding the optimal level of cross-link density is therefore important in terms of particle stability and fragmentation. Recently, Klapper and co-workers have proposed the novel solution of reversible cross-links to combat this problem.[585,586] The first strategy developed involved the use of cyclopentadiene-functionalized polystyrene resin in which the cyclopentadiene moieties undergo a Diels−Alder reaction with each other to form a cross-linked support.[585] The supports were additionally functionalized with methoxy[585a] or PEO[585b] groups to noncovalently encapsulate the metallocene/MAO complex. The supported catalysts showed good activity and produced polymer products with improved morphology in ethylene and propylene homopolymerization, as well as ethylene-*co*-α-olefin polymerization. The improvement in morphology was attributed to an enhanced particle fragmentation, brought on by the retro-Diels−Alder cleavage of the dicyclopentadiene cross-links under polymerization conditions. The protic polymer-bound cyclopentadiene moiety generated during the retro-Diels−Alder reaction has seemingly little effect on the catalytic performance. Further development by the group has led to the synthesis of polystyrene latex nanoparticles containing functionalized PEO or PPO chains on the surface. These uniform and well-defined primary nanoparticles (80−300 nm) were then reversibly aggregated by the interaction of a metallocene/MAO complex to form a secondary catalyst particle, Scheme 66.[586] The catalyst particles evenly fragmented during polymerization via the production of polyolefins in the boundary between the primary particles. The concept could be extended to borate-activated metallocenes with the incorporation of 4-vinylpyridine groups into the latex particles and pacification and reversible cross-linking of the PEO or PPO chains by AlR_3.[586a] Additionally, the group developed an original means of studying particle fragmentation by tagging the nanoparticles with a UV active dye. The chromophore and its distribution within the polyolefin particle could then be visualized with the aid of fluorescence microscopy.

11.3. Polyolefins

Porous polyolefins have proved themselves to be suitable support materials for the immobilization of single-site α-olefin polymerization catalysts. Like polystyrene, porous unfunctionalized polyolefins are swellable in some hydrocarbon solvents, such as toluene, at elevated temperatures. Therefore the encapsulation of a single-site system via swelling and shrinking of porous polyolefin support can be achieved in much the same way as the previously mentioned polystyrene systems.[584] It is worth noting that the loading mechanism for this procedure is one of physisorption of the metallocene to the support. As a result, the amount of catalyst loading for a specific system may vary greatly depending on the steric and electronic nature of the species. These systems have, however, been reported to produce heterogeneous PE-,[587,588] PP-,[589−591] or 1,2-polybutadiene-supported[592] catalysts suitable for use in gas- or slurry-phase polymerization processes, despite concerns that leaching of the catalyst species in a liquid medium or monomer may prevent the application of these supported catalysts in slurry-phase processes. Fait et al. immobilized a C_2-symmetric metallocene system onto porous polyethylene and polypropylene supports.[588] Higher catalyst loadings were achieved for the polyethylene systems, and while this led to a higher catalyst productivity in terms of kg of PP/g of catalyst, the polypropylene encapsulated catalyst demonstrated greater activity in terms of kg of PP/g of Zr.

Expanding the application of polyolefin materials via incorporation of polar functionalities has become an area of intense research activity and has led to the development of various functional polyolefin resins with graft or block structures.[593,594] As a result, porous functionalized polyolefin support materials, capable of fixating a high loading of metallocene/MAO catalysts have become accessible. One such support material is maleic anhydride-grafted polypropylene, which has been utilized by Sunaga and coworkers to immobilize MAO.[595] Several PP-supported

Scheme 66



MAO systems with differing MAO loadings, dependent on the extent of maleic anhydride grafting, were prepared and used as supported activators for various metallocene precatalysts in the polymerization of propylene. Recently, polar functionalized polypropylene-supported catalysts with higher catalyst loading capabilities than the corresponding unfunctionalized support have also been reported.[596] In this disclosure, porous polypropylene containing hydroxyl functionalities was synthesized by copolymerizing propylene with 5-hexenyl-9-BBN, using a fourth generation $MgCl_2$-supported Ziegler−Natta catalyst.[597] Treatment of the resulting polymer with H_2O_2/NaOH afforded a spherical hydroxyl-containing *i*PP resin, which when slurried in toluene and contacted consecutively with MAO and zirconocene dichloride formed an immobilized catalyst with a high catalyst loading. The supported catalyst was used to polymerize ethylene in toluene at 50 °C and was claimed to possess "relatively high productivities" (32 g of PE/(g of catalyst·h·b)) and produce PE resin with better morphology than those supported on unfunctionalized PP. The scanning electron micrographs, however, clearly show ruptured and hollow particle morphology. Once again, the use of toluene as polymerization diluent may have been the root of such poor morphology for the unfunctionalized support. As mentioned previously, the encapsulation of a metallocene/MAO system with a porous unfunctionalized polypropylene support is achieved by swelling and shrinking the polymer.[588−591] It would therefore be an exercise in futility to polymerize under conditions where the polymer support is reswollen, allowing the catalyst to leach out. HDPE has also been treated with CO_2 plasma to create a surface carboxylic acid function that can be used to support a metallocene/MAO catalyst.[598]

11.4. Dendrimers

Dendrimers are well-defined hyper-branched macromolecules, which can be functionalized with transition metals either in the core, globularly distributed, or on the surface. These dendritic-supported catalysts have provided mimics for enzymes and have been proposed to fill the gap bridged between homo- and heterogeneous catalysis.[599] At present, however, only few examples of supported α-olefin polymerization catalysts have been reported, the majority focusing on the synthesis of dendritic metallocene,[600] α-diimine nickel,[601] and bis(imino)pyridine iron[602] precatalysts. In the latter case, the dendritic bis(imino)pyridine iron complex was peripherally bound to a dendritic core and was found to display higher activity for ethylene polymerization and produce much higher molecular weight polymers than the corresponding single-nuclear complex in the case of low Al/Fe molar ratios.[602] Mager[603] and Rieger,[604] along with their respective co-workers, focused on modifying the dendrimers with borate and borane functionalities, respectively, to provide dendrimer-supported cocatalysts capable of activating dimethylmetallocene complexes. Mager et al. prepared a system where the boron functional groups are situated on the surface of the dendrimer, while Rieger et al. were able to functionalize the globule structure of the support. In the latter case, the supported boranes were found to be excellent activators for the asymmetric "dual-side" metallocene catalysts that form UHMWPP elastomers.[605] The system had previously suffered when immobilized on solid inorganic supports due to the support influence on the specific stereo-error formation mechanism. No information is presented on the morphology of the polyolefins produced by the dendrimer-supported systems, and it is difficult to imagine how such particles would fragment or rapidly dissipate the heat generated by so many active sites in such close proximity. However, systems may be developed in the future that lead to controlled particle morphology, possibly by using a dendrimer generated by a thermally reversible reaction such as Diels−Alder.

11.5. Polymer-Supported Inorganics

One alternative to forming spherical magnesium chloride supports, other than the previously mentioned alcohol adducts or modified silica, is to use spherical functionalized porous polymers as a carrier for magnesium chloride, which in turn is used to support MAO-activated metallocenes. Chlorobenzyl-functionalized polystyrene[606] and poly(vinyl chloride)[607] supports have both been used to encapsulate magnesium chloride and have acted as suitable supports for the immobilization of single-site polymerization catalysts. Porous polyethylene has also been impregnated with $Al(OEt)_3$.[608]

11.6. Self-Immobilization

One of the most unique concepts developed to support single-site α-olefin polymerization catalysis has been the "self-immobilization" approach. The core of this concept is a catalyst that has the ability to be co-incorporated into the growing polymer chain and thus provides its own support.

Self-immobilization was pioneered by Alt and co-workers, who synthesized a multitude of metallocene complexes that contained a metallacycle or a pendant functional group (vinyl, ω-alkenyl, or alkyne) that was capable of being copolymerized along with ethylene or propylene, Figure 1.[609−613] The group found that an activated solution of the functionalized metallocene could be subjected to a prepolymerization step with either ethylene or propylene. This prepolymerization step precipitated the precatalyst from solution, affording a heterogeneous polyolefin particle that co-incorporated the active catalyst. The catalytic polyolefin particles could then be isolated and reintroduced into a particle-forming polymerization process.

The metallacyclic complexes[610] possess several interesting features in that they have a higher activity than the parent dichloride complexes and form polyolefins that do not contain any halides. It is believed that the metallacycle remains intact following activation with MAO and that the olefin inserts into the metal−carbon σ bond, forming an ever larger metallacycle. Termination via β-hydrogen elimination results in a terminal olefin function that

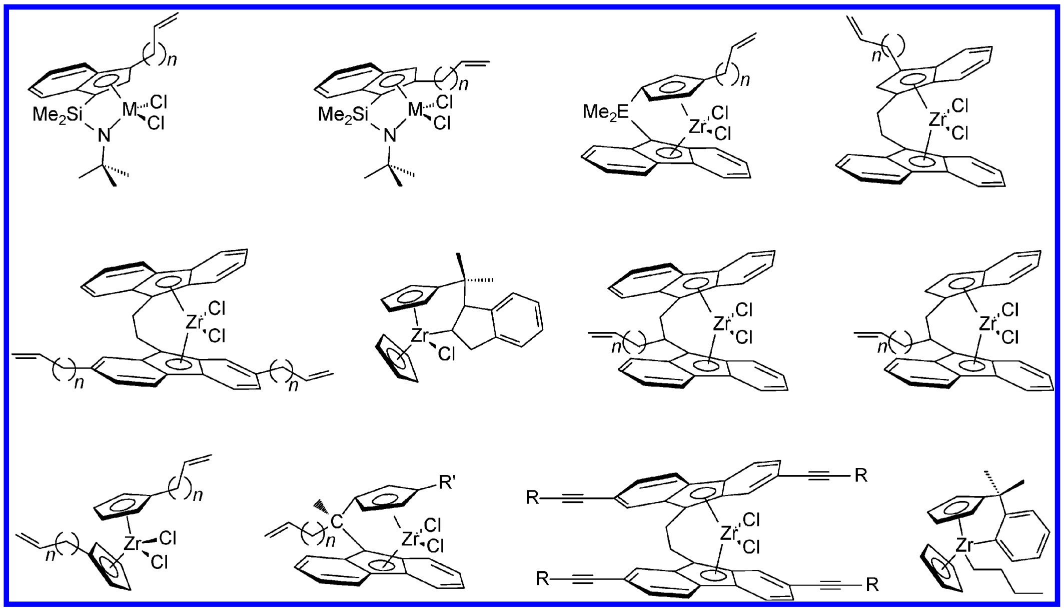


Figure 20.

can be copolymerized with the monomer at a different active site. For precatalysts containing a pendant functionality, the exact mechanism for the self-immobilization process is unclear and may involve one or more intra- or intermolecular processes. There is, however, limited spectroscopic (^{1}H NMR) evidence for a mechanism involving the intramolecular formation of a metallacycle, with the olefinic protons of the ω-alkenyl disappearing as soon as only 1 equiv of ethylene is added.[42e] It should be noted that if propagation involves a metallacycle then prepolymerization should be conducted in the absence of hydrogen as a chain transfer reagent.

Because the self-immobilization procedure removes the need for, and effects of, an inorganic carrier, it is perceived to possess clear advantages in terms of productivity and stereoselectivity. Self-immobilizing systems also have the advantage that the polymer products that they produce contain extremely low catalyst residue levels. As a result, the process can be used to produce films with exceptional clarity. With MAO as a cocatalyst, the protocol possesses an additional benefit resulting from the heterogenization of the active cationic complex, including the elusive [Me-MAO]$^-$ counteranion. Consequently, the excess of MAO required to effectively activate the precatalyst can be removed and reused by simple filtration, once precatalyst activation and precipitation has occurred. The ability to isolate and analyze the ionic catalyst using atomic absorption techniques also allowed the authors to speculate as to the nature of the [Me-MAO]$^-$ anion.

Alt and co-workers also studied the effect that placement and length of the pendant copolymerizable function had on activity and molecular weight for unbridged[610] and bridged[611,612] metallocene and constraint geometry precatalysts,[613] Figure 20. The results indicated that the polymer-incorporated precatalyst needs a certain degree of freedom to become available for the monomer, which they described as a “dog on a leash” phenomenon. A similar explanation is used to explain the variation in molecular weights with the steric environment influencing the rate of chain termination by β-hydride elimination. An example of the effect on activity can be seen when a series of constrained geometry precatalysts, Me$_2$Si(3-R-Ind)(^{t}BuN)MCl$_2$ (R = C$_3^=$ to C$_7^=$; M = Ti or Zr), was tested in ethylene polymerization, in conjunction with MAO.[613d] The results indicate that for the titanium precatalysts the optimal length of pendant ω-alkenyl in terms of activity is ω-butenyl, while for the zirconium analogue an ω-hexenyl chain gave the best results. Similarly, the length of the ω-alkenyl substituent in Ph$_2$Si(Flu)(3-R-Ind)ZrCl$_2$ (R = C$_3^=$ to C$_6^=$) was found to influence the activity and molecular weight of the polymer resin.[611c] In this case, however, the ω-pentenyl substituent gave the highest activity, while an increase in ω-alkenyl length led to a gradual increase in molecular weight.

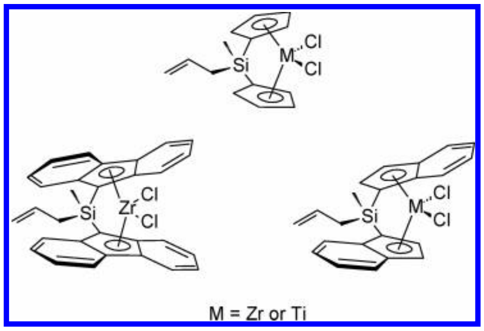
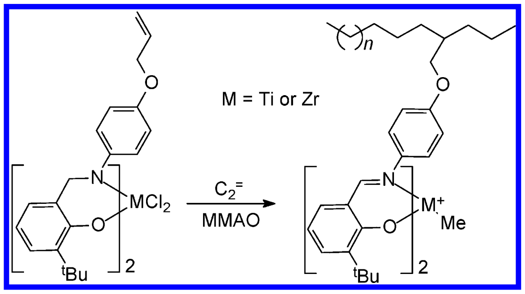


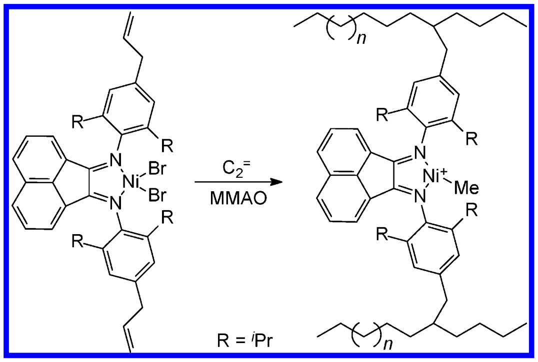
Figure 21.

A series of self-immobilizing *ansa*-metallocene precatalysts containing allyl-substituted silane bridges as the copolymerizable function has also been synthesized and tested in the presence of MMAO for ethylene polymerization by Jin et al., Figure 21.[614] The results of the polymerization experiments using MeSi(2-CH$_2$=CHCH$_2$)(Me)(Ind)$_2$ZrCl$_2$ showed that an incremental increase in temperature (0−40 °C) led to an increase in activity, but a further increase in temperature resulted in decreased activity (55 °C). The group proposed that deactivation of the metal center, along with decreased solubility of ethylene in toluene at higher temperatures, resulted in the

Scheme 67



Scheme 68



reduction in activity. A similar effect was found on varying the cocatalyst-to-precatalyst ratio, increased ratios leading to an optimal level, after which point a reduction in activity was observed. The authors attributed this to a deactivating effect of MMAO at high concentration. A comparison across the series of precatalysts was also made, and as one would expect, the zirconium complexes containing ansa-bridged bis(indenyl) and bis(fluorenyl) ligands outperformed the titanium bis(cyclopentadienyl) and bis(indenyl) analogues. What was a surprise, however, was that the catalytic performance for ethylene polymerization was attributed by the authors to the ability of the catalysts to co-incorporate catalytic amounts of themselves, rather than to the obvious metal and ligand structural property relationships.

Controlled particle growth of a self-immobilizing precatalyst has been reported by Diefenbach and coworkers at Albemarle.[615] The group gradually introduced ethylene (ca. 34 g) over a period of 2−3 h to a cooled (15 °C) toluene solution of MeC(3-CH$_2$=CH-{CH$_2$}$_2$)(Flu)(Cp)ZrCl$_2$ (ca. 0.75 g), activated by MAO (ca. 70 g of 30 wt % solution in toluene). The prepolymer, when isolated and analyzed, was found to have an average particle size of 30 μm. The self-immobilized prepolymer was then introduced into a slurry process operating under more rigorous conditions (30 bar, 90 °C) to afford a polymer resin with an average size of 1 mm and a relatively narrow particle size distribution. Self-supporting metallocenes have also been immobilized onto a supported activator, in what might be considered a “belt and braces” approach to supportation.[616]

Quasi-spherical polymer particles have been observed by Jin and co-workers, using self-immobilizing group 4 phenoxy-imine[617] or nickel α-diimine[618] precatalysts in conjunction with MMAO, Schemes 66 and 67. The mechanism for the polymer particle morphology is explained in terms of “seed particle” formation with further polymerization leading to polymer particles that replicate the morphological characteristics of the seed particles with the relative size of the polymer particle being determined by the catalyst productivity. The size of the final polymer particles produced was on the order of tens of micrometers, which would be considered as fines, albeit well-defined fines, if this was the final product size. However, larger particle sizes could possibly be achieved, if a stable catalyst system could be found that was capable of transitioning to a heterogeneous polymerization process. For the reported phenoxy-imine systems in Scheme 67,[617] such stability may be difficult to achieve at present, because catalytic activity decreases rapidly at temperatures above 40 °C. An additional drawback of this system is the broad molecular weight distribution (M_w/M_n = 3.5−19.2) of the polymer resins. This is in stark contrast to the nickel α-diimine system, Scheme 68, which produced polymer resin with narrow molecular weight distribution (1.8−2.3).

The ethylene polymerization activity of the allyl-containing nickel α-diimine (3318 kg of PE/(mol of Ni·h)) was claimed to be comparable to the non-allyl-containing complex (824 kg of PE/(mol of Ni·h)). However, caution should be taken when comparing a system that has an Al/Ni ratio of 2500:1 to one of 10:1. The self-immobilizing catalyst produced PE with a melting temperature of 117 °C (1 atm, 0 °C) indicative of SCB-PE. ^{13}C NMR was used to analyze the nature of these short chain branches and revealed a linear structure containing almost exclusively methyl branches. The group has also successfully self-immobilized allyl-functionalized derivatives of Grubbs’[35d] neutral, single-component salicylaldiminato nickel precatalyst complexes, Figure 22.[619] The self-immobilizing precatalysts were tested in ethylene polymerization and were found to be much more active than the unfunctionalized analogues and showed similar sensitivities to changes in polymerization conditions and ligand structure.

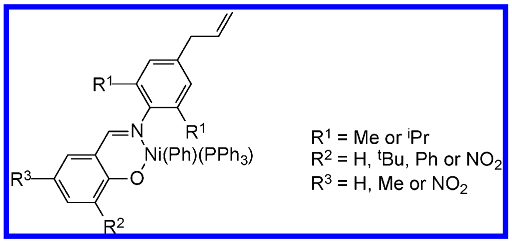


Figure 22.

The self-immobilization of bis(imino)pyridyl iron precatalysts that contain ω-alkenyl functions has been claimed by two separate groups. Herrmann et al. prepared precatalysts containing ω-butenyl, -pentenyl, or -hexenyl functions on the acetyl position,[383] while Jin et al. synthesized ω-propenyl functionalized anilines, Figure 23.[618] The precatalysts were then used in conjunction with MMAO to polymerize ethylene under relatively mild conditions (1−4 bar, 0−80 °C). In all cases, rapid catalyst deactivation was observed with an increase in polymerization temperature, and the resultant polymer resins possessed

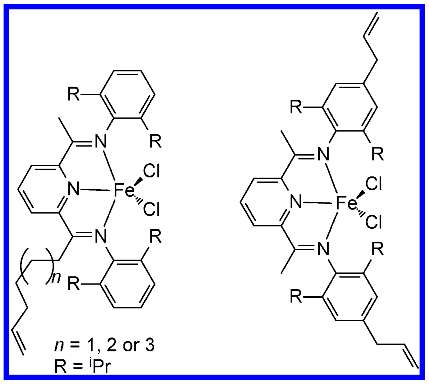
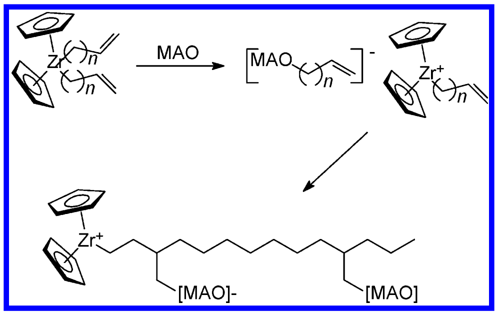


Figure 23.

Scheme 69

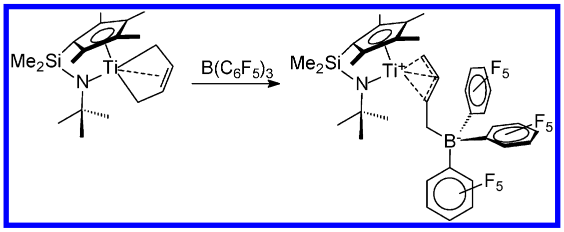


exceptionally broad or bimodal molecular weight distributions.

Spectroscopic and qualitative evidence was reported for the incorporation of the precatalyst within the backbone of the growing polyethylene chain, and at first glance this may appear to be a trivial result. However, it is both surprising and interesting when one considers factors such as the exceptionally poor results that have been reported for propylene homopolymerization, the sterically hindered metal center ($R = {}^{i}Pr$, Figure 22), the relatively bulky nature of comonomer function on the precatalyst, and the poor ability to co-incorporate higher α-olefins even when present at high concentrations within the polymerization medium, let alone at catalytic levels.

A similar process to the self-immobilization of a precatalyst has been used to immobilize cocatalyst complexes. Alt and co-workers synthesized zirconocene precatalyst containing ω-alkenyl ligands. The group proposed that the precatalysts, when activated by MAO, transfer the ω-alkenyl ligand to MAO, resulting in an ω-alkenyl-functionalized MAO capable of being copolymerized with ethylene, Scheme 69.[620] The activities of the isolated prepolymerized catalyst systems were found to be lower than those for the homogeneous or silica-supported systems. The authors attributed this to an insufficient amount of available MAO, leading to only partial activation of the precatalyst. No reactor fouling was observed in all cases, including the homogeneous polymerization of the ω-alkenyl-zirconocenes. The activation of a single-site butadiene-containing precatalyst by tris(pentafluorophenyl)borane, Scheme 70, may also be considered to be a self-immobilizing system in the sense that the borate is co-incorporated into the initial polymer chain.[621]

Scheme 70



12. Everything and the Kitchen Sink

The quest for effective immobilization of single-site α-olefin polymerization catalysts, allied with the search for hybrid biosynthetic or inorganic–organic polymer materials, has resulted in a variety of unconventional materials being considered as supports. Everyday bio-based materials, such as cellulose,[622] starch,[622,623] cyclodextrins,[624] chistosan,[622] and flour,[625] have all been used to form supported aluminoxane-activated systems, as have unconventional inorganic support materials such as talc,[626] hollow $MgCO_3$, and $CaCO_3$,[627] fillers such as dyes, glass,[628,629] ceramics,[629] or metals,[630] and others.[631]

Carbon-based supports such as graphite,[628,632] fluorinated-graphite,[628] carbon black,[633] and nanotubes[634] have been used to support MAO activated metallocene precatalysts. In the latter system, the supportation is used to exfoliate and homogeneously distribute the nanotubes within a polymer matrix, rather than for process consideration. Even ultradispersed diamond black powder has been reported to be an effective support material for aluminoxane-activated systems, due to the presence of surface carbonyl groups. However, large scale production of a support that is synthesized by “detonation transformation of carbon-containing explosives with negative oxygen balance” may not be easy or wise.[635]

13. Outlook and Summary

When considering the future of α-olefin polymerization catalysis as a whole, one should consider single-site catalysts in relation to existing Ziegler–Natta or chromium-based systems. Single-site catalysts have made significant inroads into certain market segments, but replacement of “traditional” heterogeneous catalysts has been slower than was anticipated a decade ago. Nevertheless, single-site catalysis has enormous potential for the further development of value-added polyolefin materials and the targeting of new applications.

To become commercially viable, the majority of single-site polymerization catalyst systems must be adapted to operate in existing polyolefin production processes. As a result, a considerable amount of research has been undertaken in this field. This review has attempted to survey the many recent advances made, focusing in particular on the requirements, challenges, pitfalls, and ingenious solutions that have ensued. We have also made an effort to relate these developments to the manufacturing technologies in use today, in the hope of bringing greater understanding to the “technology” part of the often misused term “drop-in technology”.

The sheer amount of research published in either the patent or the open literature on the subject of immobilized single-site α-olefin polymerization catalysts may lead one to ask "what is there left to do?" However, there are still numerous areas and opportunities left to explore, such as alternative supports or activators, and several questions still remain unclear or unanswered, for example, the exact interactions and mechanisms at work on the support surface during the immobilization, activation, and polymerization steps, the effects of local environments (pore size, etc.), and how one effectively characterizes the catalytically active species on a support, especially at low loading. All of these problems are exemplified when one considers the ubiquitous MAO/SiO_2, which on the face of it is one of the "simplest" and most extensively used systems employed in the immobilization of a precatalyst. MAO/SiO_2 is, however, an extremely complicated system when one considers all the possible structures and the reactivities of various surface species. Therefore, what has gone before may well turn out to be the tip of the iceberg and will undoubtedly lead to the study of single-site catalyst immobilization continuing to be a fascinating field of polyolefins research.

14. Abbreviations

acac	acetylacetone
BET	Brunauer−Emmett−Teller
$C_2^=$	ethylene
$C_3^=$	propylene
CGC	constrained geometry catalyst
CP-MAS	cross polarization-magic angle spinning
Cp	cyclopentadienyl moiety
Cp*	pentamethylcyclopentadenyl moiety
CSTR	continuously stirred tank reactor
DEAC	diethylaluminum chloride
DRIFTS	diffuse reflectance Fourier transform spectroscopy
DSC	differential scanning calorimetry
EDX	energy-dispersive X-ray
EPDM	ethylene−propylene diene monomer
EXAFS	extended X-ray absorption fine structure spectroscopy
FI	phenoxy-imine based catalyst
Flu	fluorenyl moiety
FTIR	Fourier transformed infrared spectroscopy
GPC	gel permeation chromotography
HDPE	high-density polyethylene
HMDS	hexamethyldisilazane
IBAO	isobutylaluminoxane
Ind	indenyl moiety
Ind-H_4	tetrahydroindenyl moeity
LDPE	low-density polyethylene
LLDPE	linear low-density polyethylene
IR	infrared
MAO	methylaluminoxane
MCM	mobile crystalline material
MDPE	medium-density polyethylene
MMAO	modified methylaluminoxane
NMR	nuclear magnetic resonance
*a*PP	atactic polypropylene
*i*PP	isotactic polypropylene
*s*PP	syndiotactic polypropylene
SEM	scanning electron microscopy
SOMC	surface organometallic complex
TEA	triethylaluminum
TEOS	tetraethoxylsilane
TIBA	triisobutylaluminum
TMA	trimethylaluminum
UHMWPE	ultrahigh molecular weight polyethylene
UHMWPP	ultrahigh molecular weight polypropylene
ULDPE	ultralow-density polyethylene
UV−vis	ultraviolet−visible spectroscopy
XANES	X-ray absorption near edge structure spectroscopy
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy

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16. Appendix: Additional Publications up to the End of August 2005

We are aware of 25 open literature reports in the above category. They have contributed to the following areas (using the numbering system of the table of contents). Section 2.3. Kiparissides et al. describe the development of the "Random-Pore Polymeric Flow Model" for describing single particle growth, accounting for both internal and external mass and heat resistances,[636] Pinto et al. describe a "Two Phase Model" for particle fragmentation,[637] and Loos et al. describe cross-sectional SEM and EDX investigations of single particles in the early-stages of polymer growth.[638] Section 2.7. Wang and Jin report on spherical polymer morphology resulting from the homogeneous polymerization of ethylene by MAO-activated half-sandwich picolyl-functionalized carborane iridium, ruthenium, and rhodium precatalysts.[639]

Section 3.1. Pruski et al. disclose that strong hydrogen-bonded silanol groups are still present on MCM-41 even after calcinations to 350 °C in vacuo.[640] Sections 3.2. and 3.3. Dos Santos and co-workers use X-ray emission and absorption spectroscopy to study silica-grafted zirconocenes.[641] Section 3.3. Bergstra and Weickert describe a comparative kinetic study of the gas- and slurry-phase polymerization of ethylene over a heterogeneous metallocene catalyst,[642] Chadwick et al. investigate the characterization and performance of various MAO/SiO_2 support procedures,[643] Carlini et al. report ethylene polymerization over a silica-supported MAO-activated bis(salicylaldiminate)nickel catalyst,[644] and Entezami et al. report a supported MAO/zirconocene.[645] Section 3.4. Resconi et al. report on the preparation of oxygen-bridged borate anions derived from $B(C_6F_5)_3$, H_2O, and a base.[646]

Section 5.1. Otero et al. synthesized indenylzirconium complexes containing an $-OSiR_2R'$ (R = Me; R′ = Me or ^{t}Bu) functionality capable of acting as a reactive tether to silica,[647] Burkett, Coughlin et al. studied tethered constrained geometry catalysts in mesoporous silica,[648] and Li and co-workers constructed silica-tethered bis(imino)pyridine iron based catalysts.[649]

Section 6. Ochędzan-Siodlak and Nowakowska report heterogenization of a zirconocene on $AlEt_2Cl$-modified $MgCl_2(THF)_2$,[650] and Mao et al. report preparation of spherical $MgCl_2$-supported activator for bis(imino)pyridine iron based precatalysts.[651]

Section 8. Hwu et al.[652] and Sivaram et al.[653] work on clay-supported zirconcene and bis(imino)pyridine iron based catalysts, respectively.

Section 10. Thüne et al [654] and Chabal et al.[655] developed a flat silicone wafer capable of mimicking silica and the constructed surface borane species, tethered bis(imino) pyridine Fe catalyst,[654] and tethered bis-indene ligands.[655]

Section 11.2. Wang and co-workers used Diels−Alder cross-linked polystyrene to encapsulate a metallocene/MAO catalyst system,[656] and Coughlin et al. developed supported half-metallocene "piano stool" catalysts, covalently bound to poly(styrene-*co*-4-hydroxystyrene).[657] Section 11.6. Alt reviews self-immobilization[658] and related metallacyclic complexes.[659]

Section 12. Zhang et al. report surface modifcation of silica with 3-(trimethoxysilyl)propyl methacrylate and subsequent copolymerization of the surface species with 4-vinylpyridine to an organic−inorganic hybrid support for zirconocene catalyst.[660]

17. Supporting Information

Basic definitions of the differing grades of polyethylene and polypropylene. This material is available free of charge via the Internet at http://pubs.acs.org.

18. References

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(44) This section was constructed with the help of (a) correspondence and presentations by Prof. G. Weickert (University of Twente) and G. Mei (Basell) given at the biennial NIOK/COP (Catalytic Olefin Polymerization Centre, Rijksuniversitait Groningen) 'Olefin Polymerization Courses' and (b) Borealis, Univation, Basell, and Chevron Phillips corporate websites.

(45) Companies with commercial high-pressure autoclave or tubular reactor technologies are Basell (*Lupotech T*), Sabic-Europe (*CTR Technology*), ExxonMobil, EniChem, and Equistar.

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