

ABSTRACT

Title of Dissertation: A STUDY ON THE EFFECTS OF
CATALYST DISTRIBUTION AND
CHANGES TO THE PORE STRUCTURE IN
SILICA-SUPPORTED METALLOCENE
CATALYST FOR ETHYLENE
POLYMERIZATION

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The disintegration of the catalyst particle during the polymerization of ethylene into successively smaller fragments is necessary for high performance. However, rapid and extensive fragmentation without control may generate fine particles $< 100\text{ }\mu\text{m}$. These fine particles are of poor polymer quality and often lead to reactor fouling and impact process efficiencies and costs. Although methods such as pre-polymerization have been developed to mitigate the effects of fine particles, the root cause of their formation is poorly understood. In this dissertation, the effects of active site and pore size distributions after

the immobilization of catalytic compounds such as methylaluminoxane and metallocenes within silica supports on the fragmentation of the catalyst particle during polymerization are systematically investigated. The experimental results indicate a strong correlation between the intraparticle distributions of active sites and the contact time between silica particles and solutions containing catalytic compounds. Non-uniform distributions lead to evidence of extensive fragmentation and higher fractions of fine particles in gas phase polymerization. Next, catalysts with different distributions of active sites and pore diameters were utilized in both gas and slurry phase polymerization of ethylene. The polymer particle morphologies illustrate the effects of the presence and absence of a liquid diluent and the pore diameter on the fragmentation process. A diffusion-adsorption model was developed to generate dynamic radial concentration profiles and total concentrations of catalytic compounds within the particle. The model correlates with the experimental data which assists with the optimization of the preparation condition of the supported catalyst. The effect of pore diameter was further studied by preparing supported catalysts with three different commercially available silicas. The pore diameter was determined to have a significant effect on polymerization activity and polymer properties. Finally, a flat surface silica was developed to directly observe the formation of polymer chains at the active site. These results provide guidance to the preparation and synthesis of metallocene supported catalysts and optimize their performance in ethylene polymerization.

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THE PORE STRUCTURE IN SILICA-SUPPORTED METALLOCENE CATALYST
FOR ETHYLENE POLYMERIZATION

by

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Dedication

Dedicated to my family without whose support I would not have been able to finish this degree. First, my wife, Dr. Mei Wang. Without your financial and food support I would not have been able to finish this journey. Second, my parents, Thu and Quan. Without the support both of you have given me, I would not have been able to start this journey. Finally, our puppy Reid. Without you I may have been finished a few months earlier, but who's really counting?

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List of Abbreviations

Aluminum	Al
Brunauer–Emmett–Teller	BET
Barrett-Joyner-Halenda	BJH
Continuously Stirred Tank Reactor	CSTR
Fluidized Bed Reactor	FBR
Focused Ion Beam	FIB
Inert Condensing Agents	ICA
Inductively Coupled Plasma Mass Spectrometry	ICP-MS
Inductively Coupled Plasma Atomic Emission Spectroscopy	ICP-AES
Methylaluminoxane	MAO
Polyethylene	PE
Polypropylene	PP
Scanning Electron Microscopy	SEM
Scanning Electron Microscopy – Energy-Dispersive X-ray Spectroscopy	SEM-EDX
Scanning Electron Microscopy – Focused Ion Beam	SEM-FIB
Triethylaluminum	TEAL
Zirconium	Zr

Chapter 1. Introduction

1.1 Catalysts For α -Olefin Polymerizations

Polyolefins such as polyethylene and polypropylene are ubiquitous in modern society due to their advantageous physical and mechanical properties and ease in manufacturability and processability. Polyethylene (PE), polypropylene (PP), and their copolymers have excellent chemical resistance and high tensile and impact strength.¹⁻⁷ Moreover, their mechanical, thermal, and physical properties are extremely tunable and result in a variety of industrial applications such as in food packaging,⁸⁻¹¹ fibers for fabric,¹²⁻¹⁴ insulators for electrical cables and wires,¹⁵⁻¹⁷ implants in biomedical applications,¹⁸⁻²¹ and membranes in fuel cells.²²⁻²⁵ Melt processing increases their versatility by allowing the addition of other materials such as graphite to improve electrical conductivity²⁶⁻²⁸ or carbon nanotubes and metallic powder to form high strength composites.²⁹⁻³¹ High volume processes reduce their production cost while the raw materials used to manufacture PE and PP (ethylene and propylene) are readily available as a refined byproduct in crude oil and natural gas processing.³²⁻³⁴

1.1.1 Ziegler-Natta Catalysts

Earlier industrial processes utilized Ziegler-Natta catalysts which used mixtures of TiCl_4 and alkyl aluminum to form TiCl_3 and other TiCl_3 -based compounds as the active site to produce polyolefins.³⁵⁻³⁸ These catalysts were valued for their ability to, for the first time, form stereoregular polymer such as isotactic polypropylene (**Figure 1.1**).

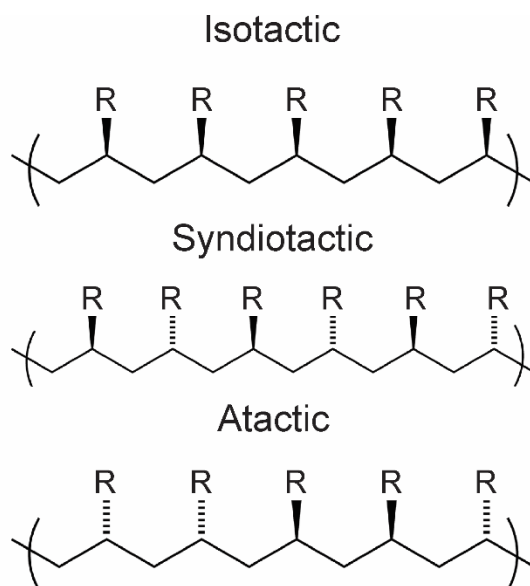


Figure 1.1. Typical representation of different types of stereoisomerism.

These compounds were further developed by immobilizing the Ziegler-Natta catalysts onto crystalline MgCl_2 supports which led to higher activity while retaining their stereoselectivity.³⁹⁻⁴² The immobilization of catalysts on these supports is highly complex due to the different lateral faces of MgCl_2 , the formation of different active sites, and the multiple insertion methods of monomer during polymerization.⁴³⁻⁴⁷ The multisited nature of supported Ziegler-Natta catalysts leads to catalyst particles containing active sites with different polymerization activities, the simultaneous production of polymer chains with varying levels of stereo- and regio- selectivity, and broad molecular weight distributions with the definitive role of each component unclear.⁴⁷⁻⁵⁰

1.1.2 Metallocene Catalysts and Their Advantages

Stereorigid ansa-bridged metallocene compounds synthesized by Brintzinger and coworkers were also found to be stereospecific in the production of isotactic polymer.⁵¹⁻⁵³ These metallocene compounds are characterized by a metal active site, usually Zr, which is sandwiched between two cyclopentadienyl-based groups that restrict monomer access to the metal center through steric and electronic factors (Figure 1.2).⁵⁴⁻⁵⁷

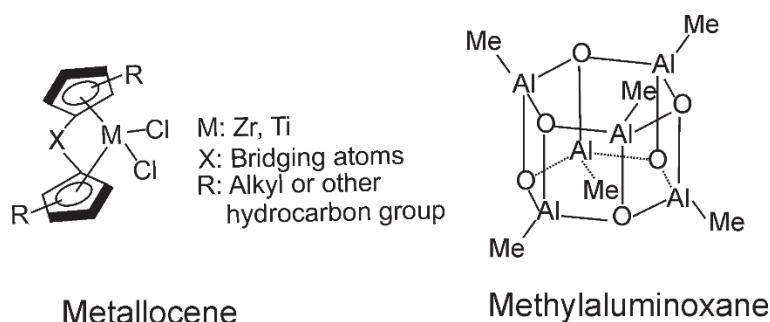


Figure 1.2. Typical structure of a metallocene compound and proposed methylaluminoxane structure.⁵⁸

Interest in these compounds significantly increased with the discovery of methylaluminoxane (MAO) by Sinn and Kaminsky.⁵⁹⁻⁶¹ When used as a cocatalyst with metallocene catalysts, MAO increased the catalyst activity by several orders of magnitude through alkylation of the metallocene center and formation of the cationic active site.⁶²⁻⁶⁶ Due to the restriction from the catalyst ligand groups, monomer compounds must coordinate with the catalyst compound with only one arrangement allowing access to the metal center to initiate polymerization and form a single polymer chain.

This “single-site” nature has many advantages over the multiple insertion modes seen for Ziegler-Natta catalysts.⁶⁷⁻⁶⁹ First, direct correlation between the polymerization kinetics and stereospecificity and the catalyst structure can be determined by methods such as X-ray diffraction.⁷⁰⁻⁷³ The polymer microstructure and tacticity can be easily controlled as only one orientation of polymer can be formed based on the catalyst’s ligand groups.^{53, 72, 73} Generally, C_2 -symmetric catalysts produce isotactic polymers while C_s -symmetric catalysts produce syndiotactic polymers (**Figure 1.3**).⁷⁴

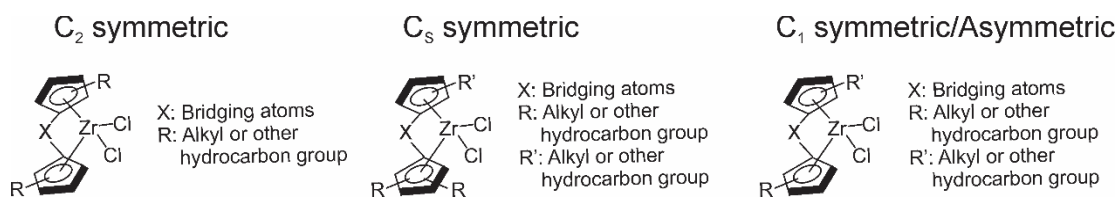


Figure 1.3 Symmetries seen in ansa-bridged metallocenes.

Second, the formation of the cationic active center of metallocene/MAO system is well-defined through NMR spectroscopy and guides the design of catalyst compounds to form polymer with desired properties.^{63-65, 75} Third, the single-site nature of the catalyst uniquely produces polymer with narrow molecular weight distributions that approaches the theoretical value of polydispersity ($M_w/M_n = 2.0$).⁷⁶⁻⁷⁸ The homogeneous nature of the polymer chains lengths formed leads to superior mechanical, thermal, and rheological properties and uniform solubility characteristics.⁷⁹⁻⁸² Finally, manipulation of the molecular weight distribution through clear mechanisms such as the introduction of hydrogen and other chain transfer agents allows alteration of the polymer property without affecting the polymer composition.⁸²⁻

When metallocenes are used to polymerize ethylene with comonomers such as propene, 1-hexene, or 1-octene, the comonomers are uniformly incorporated within the polymer chains and the product retains the narrow molecular weight distributions found in polyethylene.^{51, 86-88} Moreover, the rate and amount of incorporation and branching of polymer chains can easily be controlled via the ligand groups of the metallocene compound, catalyst concentration, and comonomer to monomer feed with well-defined incorporation models to obtain desired polymer properties.⁸⁹⁻⁹¹ This led to the creation of several commercially relevant polymers such as linear low density polyethylene and other copolymers with lower melting points and crystallinities, and better processability.

1.2 Supported Catalysts and Their Advantages

Despite these innate advantages, use of metallocenes in their homogeneous forms has several challenges that limit their applications. For instance, metallocenes are soluble in diluents used in slurry processes which leads to severe reactor fouling such as sheeting on the reactor walls and are also unable to be used in gas phase processes.⁹²⁻⁹⁵ Therefore, metallocene compounds are normally immobilized on inert supports to form supported catalysts which not only retain metallocenes' innate advantages, but also address the shortcomings of the homogeneous forms. For example, immobilizing the metallocenes on supports leads to better morphology of the polymer product with high bulk density and a well-defined shape as the support acts as a template for polymer growth.⁹⁵⁻⁹⁹ Also, the amount of MAO needed to activate the metallocene is significantly reduced from the 1000 – 10000 Al/Zr mol ratio in its

homogeneous form to a minimum 100 – 300 in its supported form due to the generation of weak Lewis acid sites from interactions between MAO and the silica surface that enhance activation of the metallocene.¹⁰⁰⁻¹⁰⁴ Lastly, immobilization onto supports allows metallocenes to be used in pre-existing processes designed for supported Ziegler-Natta catalysts including gas phase and slurry phase processes.¹⁰⁵

1.2.1 Advantages of Silica as Support Material for Metallocene Catalysts

Metallocene compounds have been effectively immobilized on several inert supports such as MgCl_2 , alumina, zeolites, and amorphous silica gel to form supported catalysts.¹⁰⁵⁻¹⁰⁷ Of these, amorphous silica offers several inherent advantages and is one of the most common support used to industrially immobilize metallocene compounds. For instance, the surface of silica possesses a natural abundance of silanol groups that can act as potential binding sites.¹⁰⁸ Three types of naturally occurring silanol groups are present: isolated (Type 1), geminal (Type 2), and siloxane groups (Type 3).¹⁰⁹⁻¹¹² Of these, isolated silanol groups readily react with MAO and metallocenes.^{102, 113} The type and total concentration of silanol group can be controlled through heat treatment by calcination in air at temperatures between 200 and 600°C (**Figure 1.4**).¹¹⁴⁻¹¹⁶ The desired calcination temperature and concentrations of silanol groups can vary and largely depend on the metallocene catalyst used.

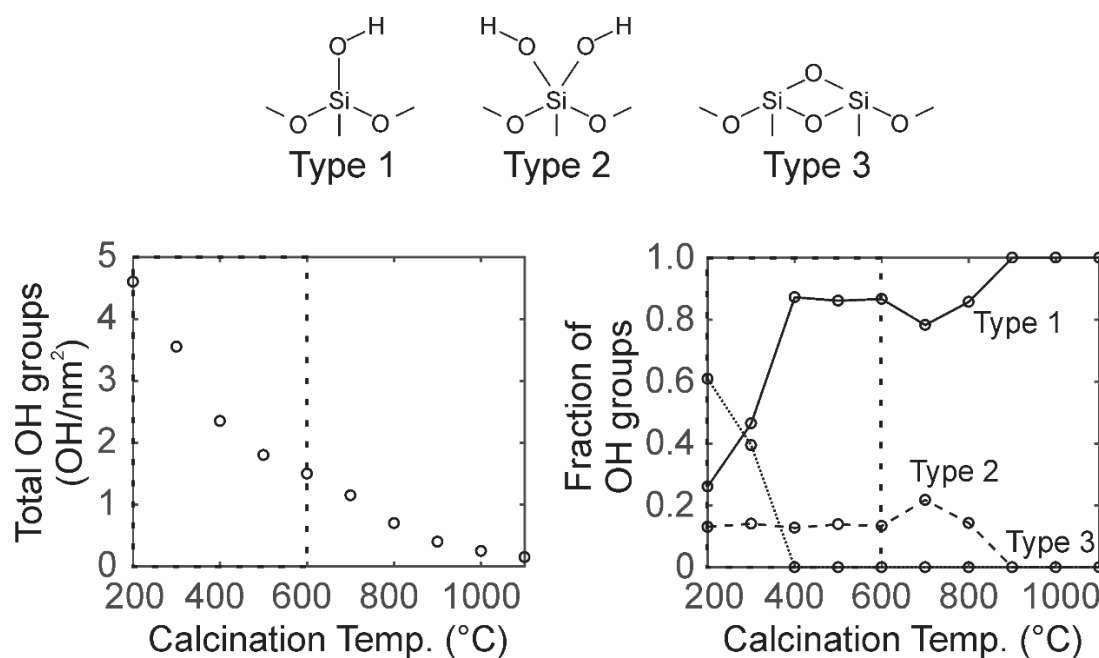


Figure 1.4. Effect of calcination temperature on silica silanol groups and type.¹¹⁰

1.2.2 Effects of Silica Particles Pore Structures on Active Site Distribution

Another advantage is how physical properties of silica particles are easily tuned during their synthesis process to optimize the amount of immobilized metallocene compounds and their activity. Most commercial silica used in supported catalysts are spherical with surface areas ranging from 50 – 800 m^2/g , pore volumes between 1.0 – 3.0 cm^3/g , and particle sizes between 20 – 80 μm . Traditionally, silica particles used in supported catalysts are produced using in a sol-gel method where a liquid slurry of sodium silicate and sulfuric acid forms silicic acid which polymerizes and forms gels and particles as it precipitates out of solution.¹¹⁷⁻¹¹⁹ The overall silica particle is composed of primary silica particles between 10 – 50 nm that form aggregates between 200 – 500 nm. The random arrangement of these large aggregates produces a silica matrix with complex internal pore space with mixtures of large void spaces, macropores (pores > 50 nm),

mesopores (pores between 2-50 nm), and micropores (pores ≤ 2 nm). We define pores larger than the upper limit of those measurable from N₂ physisorption (micron sized) as void spaces.¹²⁰ Interstices between the primary particle and their aggregates are primarily mesopores and can sterically control access of catalytic compounds dissolved in solution during the immobilization process and monomer and cocatalyst during the initial instants of polymerization. For instance, Sano et al., Kumkaew et al., and Silveira et al. observed minimal polymerization activities when mesoporous sieves and other supports with pore sizes smaller than 10 nm were used to support metallocenes in both slurry and gas phase polymerization of ethylene.¹²¹⁻¹²⁴ Recent studies using techniques such as Small Angle Neutron Scattering, computational experiments, and ¹H NMR, have shown that MAO has a cage structure with a size around 1.9 nm and a radius of gyration of 5 nm while metallocene compounds are usually around 1 nm depending on the ligand groups.^{58, 125-128} The size of the compounds may have inhibited access and prevented the formation of active sites within smaller pores. The effect of steric hinderance due to the pore size on mass transfer of monomer and comonomer also becomes apparent based on the amount of comonomer that is incorporated into the final polymer product. Kumkaew et al., Paredes et al. and Silveira et al. observed higher incorporation of 1-hexene using (n-BuCp₂)ZrCl₂/MAO in both gas and slurry phase when using supports with higher pore sizes.¹²⁹⁻¹³² These results show that the pore diameter and pore size distribution of the silica support have a significant effect on the performance of the supported catalyst.

1.2.3 Importance of Intraparticle Mass Transfer on Distribution of Active Sites

In addition to mesopores, large micron-sized interstitial voids between silica aggregates are frequently observed within silica particles produced through spray-drying methods.¹³³ **Figure 1.5** shows the cross-sections of two types of silica particles that we analyzed: one with interstitial voids produced by spray-drying (P-10, Fuji-Silysia) and one without produced by microemulsion methods (DM-L-303, AGC). During the synthesis process, interstitial void spaces are uniformly distributed throughout the silica particle which may facilitate the mass transfer of catalytic compounds during the immobilization process.

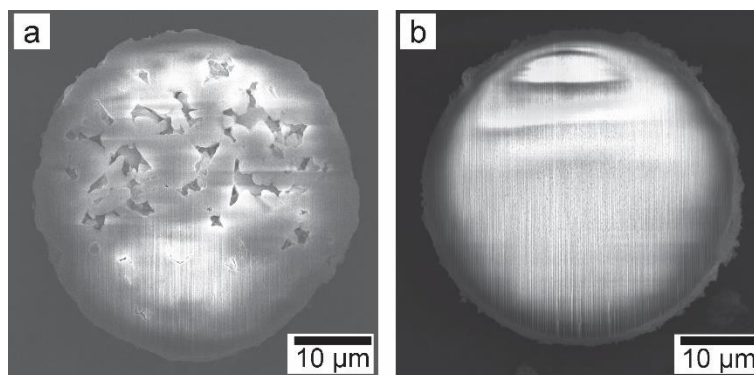


Figure 1.5. Cross-sectional SEM image of silica particles (a) with interstitial voids and (b) without interstitial voids.

During the immobilization process, mass transfer of catalytic compounds (MAO or metallocene) through the silica particle must occur to form active sites throughout the interior of the particle. The effect of mass transfer can be observed from elemental map analysis of the cross-sections of supported catalysts which shows the locations of Al and Zr, representing MAO and metallocene active sites, after the immobilization process. Active sites can either be uniformly distributed throughout the

particle or solely located near the edge of the cross-section in a core-shell distribution. Bashir et al.¹³⁴ observed that silica particles with interstitial voids (Grace 948) had uniform distribution of Al while silica particles without interstitial voids (PQ MS1732) had a core-shell distribution of Al despite similar pore volumes and identical preparation conditions. They proposed that interstitial voids provide a pathway for the compounds to bypass the tortuous pore space and access the interior of the particle. The dependence of the distribution of active site on the silica pore structure indicates that dynamic mass transfer of catalytic compounds during the immobilization process must be considered.

Further evidence of the importance of mass transfer during the immobilization process was seen based on the size of the silica particle. Tisse et al.^{135, 136} observed that supported catalysts that were 100 μm in size had lower polymerization activities compared to those that were 45 μm in size despite identical preparation procedures. The polymerization activity of the larger catalysts increased after longer contact times between the particles and the MAO solution. They proposed that larger particle sizes have higher mass transfer resistance during the immobilization process and fewer active sites are formed compared to smaller particles given the same length of contact time. While the silica particle influences the mass transfer and final location of catalytic compounds such as MAO or metallocenes during the immobilization process, the preparation method used to form supported catalysts affects the nature of the active site during polymerization.

1.3 Preparation Methods of Supported Catalysts

Various methods to prepare supported catalysts have been reported and can be classified as either adsorption methods or chemical tethering methods. For the former case, thermally treated silica particles are brought in contact with solutions containing dissolved catalytic compounds such as MAO or metallocene. During contact, the compounds diffuse through the pore structure of the silica and immobilize onto the internal surfaces of the pore through reaction with silanol functional groups. Three methods are used: (i) direct immobilization of metallocene to the silica particle, (ii) mixture of a MAO and metallocene solution first, followed by immobilization of both compounds to the silica simultaneously, and (iii) sequential immobilization of MAO to the silica particle to form MAO-modified silica followed by immobilization of metallocene to the MAO-modified silica. The method used to immobilize the metallocene affects the nature of the active site within the silica particle.^{98, 107, 137}

1.3.1 Direct Immobilization of Metallocene

Earlier methods to prepare supported catalysts directly immobilized metallocene compounds to the silica particle through covalent bonds with the silanol groups. Thermally treated silica particles were contacted with an organic solution of dissolved metallocene compounds for 1 to 24 hours, generally at room temperature.^{94, 115, 138-140} van Grieken et al.¹¹⁶ observed that the Zr content (corresponding to metallocenes) of the supported catalysts decreased with an increase in the silica calcination temperature which corresponded with a decrease in overall silanol groups. Sacchi et al.¹⁴¹ studied the immobilization of ZrCl_2 -based metallocenes and found that

the molar ratios of Zr/Cl of the supported catalysts were approximately 1.0. This result corresponded to the reaction of one metallocene compound to one silanol group through removal of the chloride ligand and generation of the cationic metallocene complex active site (**Figure 1.6**). However, Collins et al.¹³⁹ and dos Santos et al.¹⁴² both observed different polymerization rates of supported catalysts with similar Zr content. It was proposed that two types of active sites were formed where one was active and the other was inactive during the immobilization process. Panchenko et al.¹⁴² confirmed through IR spectroscopy that both mono- and bidentate surface species, corresponding to the active and inactive form, were present on the supported catalyst (**Figure 1.6**). Residual silanol groups were also found to adversely affect immobilized metallocenes either by decomposition or formation of groups that hindered activation.^{143, 144}

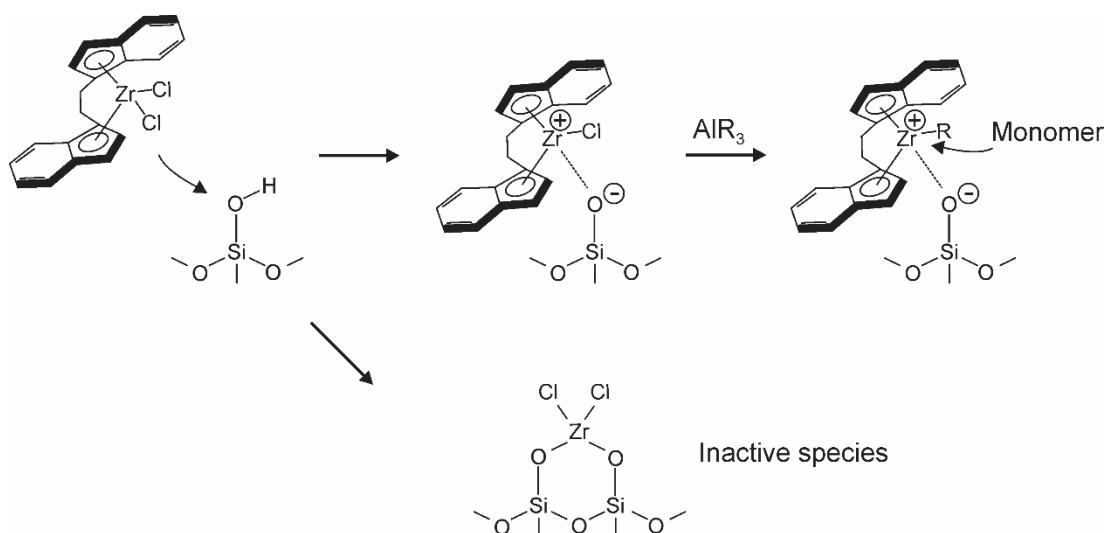


Figure 1.6. Immobilization of metallocene to the silica surface.¹⁴³

1.3.2 Mixture of Metallocene and MAO Prior to Immobilization

Mixing the MAO solution with the metallocene compounds prior to contact with the silica was proposed to address the formation of inactive metallocene species on the silica and reduce the number of steps during the immobilization process. Direct contact between the metallocene and MAO in solution is believed to improve activation and formation of the cationic active site prior to immobilization. However, both activated and unreacted compounds in solution may randomly immobilize onto the support and complicate characterization of the immobilized compounds on the silica.¹⁴⁵ Carrero et al.¹⁰⁴ prepared a series of supported catalysts with varying Al/Zr ratios in solution prior to immobilization and observed that supported catalysts with higher Zr content exhibited less activity. They proposed that inactive species formed while the metallocene catalyst was in solution with MAO were also immobilized. Additionally, the activated complex can be easily disturbed due to the steric and electronic factors of the silica surface and lead to an inactive form.^{105, 146}

1.3.3 Sequential Immobilization of MAO and Metallocene

The most common technique to prepare supported catalysts is the reaction of MAO with the silanol groups followed by immobilization of the metallocene compound. While the exact structure of MAO is still ambiguous, trimethylaluminum, a major reactant in the production of MAO, behaves similarly and readily reacts with isolated silanol groups on the silica surface.¹⁴⁷⁻¹⁵¹ The product of this reaction, hereby referred to as MAO-modified silica, is then used to immobilize the metallocene compound. The immobilization and activation mechanism of metallocenes to the

MAO-modified silica is similar to that found for metallocenes in solution. Metallocenes in solution encounter immobilized MAO during diffusion through the silica pore structure. The immobilized MAO alkylates the metallocene complex and forms the cationic metallocene active site (**Figure 1.7**).¹⁵²⁻¹⁵⁴

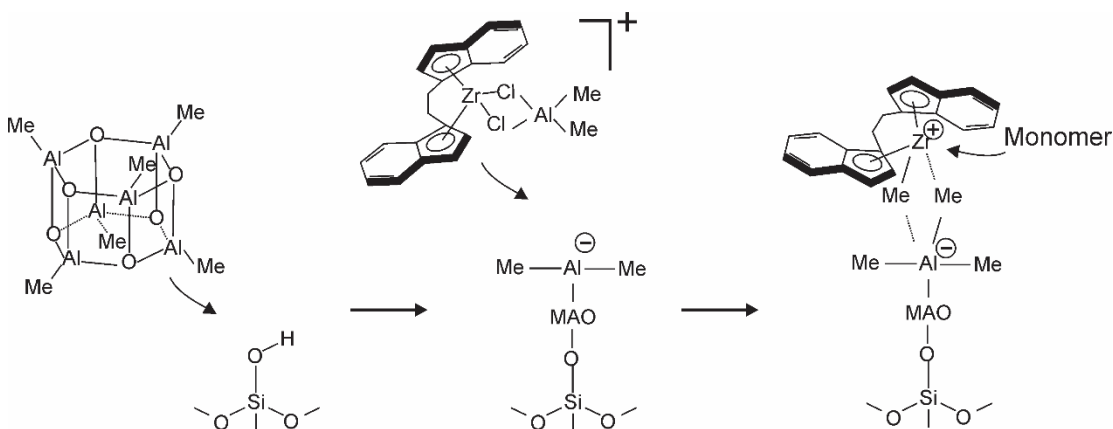


Figure 1.7. Immobilization of metallocene to the MAO-modified silica surface.⁹⁷

The presence of the MAO layer provides several advantages to the immobilized metallocene compounds. First, reaction between MAO compounds and silanol groups is believed to form moderate Lewis acid sites on the silica surface accompanied by the formation of AlMe₂⁺ cations.^{102, 147, 155} The presence of these ions is widely believed to activate and stabilize the cationic metallocene active site.¹⁵⁵⁻¹⁵⁸ Confinement within the pores leads to higher concentrations of these ions, enhancing their effects. Second, the activated metallocenes are effectively surrounded by Lewis acid sites on the surface of the pores, further stabilizing the cationic active site and prevent dissociation and leaching. In addition, less external cocatalyst during the reaction, such as triethylaluminum (TEAL), is required as the metallocene is already in an activated state. Third, saturation of the silica surface with MAO compounds prevents any

undesired reactions between the metallocene and the silanol groups that lead to the formation of inactive species. Lastly, immobilized MAO compounds effectively act as spacers, preventing bimolecular deactivation reactions between neighboring metallocene compounds.^{78, 159, 160} The nature and distribution of these active sites coupled with the silica pore structure affect the initial instants of polymerization and growth behavior of the polymer particle.

1.4 Fragmentation and Growth of the Supported Catalyst

The growth of the polymer particle starts with the formation of polymer chains at immobilized active sites within the pores of the supported catalyst. As polymer accumulates and expands at the active site, stress exerted onto the surrounding pore structure leads to fracturing of the pore wall, creating new pathways for monomer access to newly revealed active sites within the catalyst particle.¹⁶¹⁻¹⁶³ Two models developed from supported Ziegler-Natta catalysts that are frequently used to describe and calculate the growth of polymer particles from metallocene supported catalysts are the multigrain model (MGM) and the polymeric flow model (PFM). MGM is based on the experimental observation of the near-instantaneous breakup of the MgCl_2 support into small fragments at the start of the reaction, each of which contains a catalyst crystallite.¹⁶⁴⁻¹⁶⁷ These fragments are encapsulated by polymer that continuously expand over the course of the reaction and make up the overall polymer particle. PFM simplifies the transport of monomer through the polymer particle by assuming the diffusion through the pores of the particle and the polymer layer surrounding each active site is equal.^{168, 169} While both models have been shown to accurately predict

molecular weight distribution and polymer growth rates,^{170, 171} key assumptions such as instantaneous fragmentation or uniform porosity may not be valid in all metallocene supported catalyst systems. Nieglisch et al.¹⁷² observed the presence of large unreacted islands of silica approximately 10 μm in diameter within low activity polyethylene particles. Similarly, Zheng et al.¹⁷³ observed large silica fragments within polypropylene particles surrounded by a polymer shell. A comparable polymer shell on the exterior of the supported catalyst was also seen by Zechlin et al.¹⁷⁴ at early stages of the reaction during the polymerization of ethylene in slurry phase prior to extensive fragmentation. As aforementioned, the pore structure of silica is randomly arranged with the presence of large interstitial voids and macropores. These void spaces have a significant effect in the fragmentation behavior and may account for the discrepancy between models and experimental results.

Experimental observation of the fragmentation of metallocene supported catalysts generally follows two separate behaviors. The first is the layer-by-layer or shrinking core model where fragmentation of the silica support occurs successively from the surface region and proceeds toward the center (**Figure 1.8**).^{173, 175-177} Expansion of the polymer near the surface ruptures the continuous exterior, forming large void spaces for monomer to access active sites located in the interior of the particle.¹⁷⁸⁻¹⁸⁰ This process repeats at the surface of the unreacted core and proceeds until the entire particle has fragmented. If this rupture does not occur, monomer must diffuse through the polymer shell, which represents a significant diffusion limitation, limiting further growth and the presence of large unreacted silica fragments.¹⁸¹⁻¹⁸³

Another method of fragmentation that is frequently seen is referred to as the continual bisection model where the support will successively fragment from internal void spaces and form smaller fragments (**Figure 1.8**).¹⁸⁴⁻¹⁸⁶ Polymer will first form within macropores of the catalyst particle due to reduced mass transfer limitations. The accumulation of polymer within the macropores leads to stress between opposite polymer layers and the formation of large aggregates. Monomer will then diffuse through the macropores of these aggregates and the process continues until the particle is completely fragmented. Zheng et al.¹⁷³ proposed that the dominant method of fragmentation is dependent on the porosity of the silica where the continual bisection model occurred in particles with higher porosities while layer-by-layer model occurred in less porous silica.

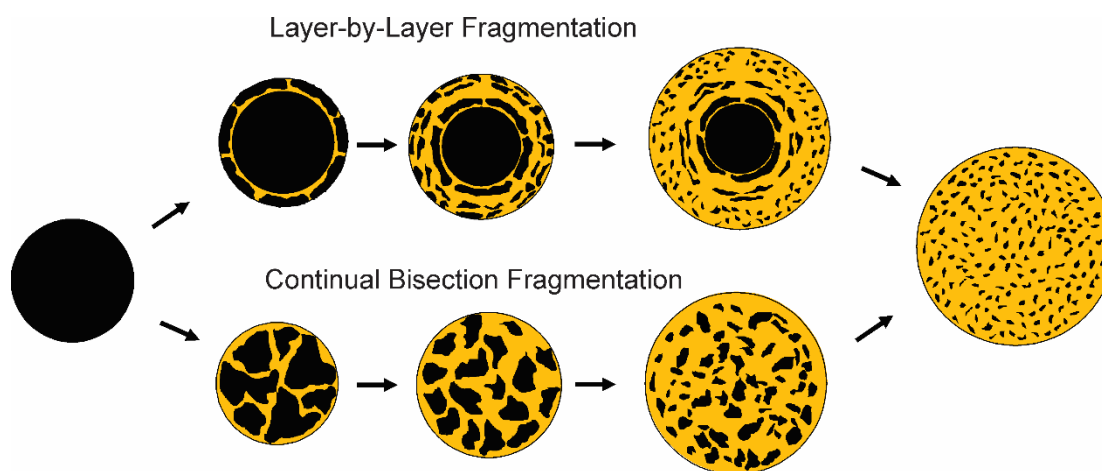


Figure 1.8. The layer-by-layer and continual bisection model of fragmentation of the silica support (black) from the formation of polymer (yellow) over the course of the reaction.

However, the appearance of both highly and minimally porous regions within silica particles often leads to evidence of both shrinking core and continual bisection

fragmentation models even within the same particle. Using *ex situ* techniques such as X-ray ptychography with X-ray fluorescence to perform non-invasive characterization of prepolymer particles along with focused ion beam techniques to view the cross sections of polymer particles after short reaction times, Weckhuysen's group was able to view the initial areas of growth and fragmentation.¹⁸⁷⁻¹⁸⁹ They found that despite using the same grade of supported catalyst, weakly fragmented particles followed the shrinking core model while heavily fragmented particles followed the continual bisection model. Zaroni et al.¹⁸⁹ observed evidence of both layer-by-layer and continual bisection fragmentation in the cross-sections of polymer/catalyst particles after gas phase and slurry phase polymerization of ethylene. Polymer growth and expansion near the surface of the particle experienced layer-by-layer fragmentation while polymer growth within internal interstitial voids experienced continual bisection fragmentation. These results show that the manner and progression of fragmentation are heavily dependent on the pore structure of the silica.

1.5 Formation of Fine Particles

While fragmentation is a necessary and essential process in polymer particle growth, several scientific and technical issues remain. Ideally, the growth of polymer at the active site occurs at relatively equal rates throughout the polymer/silica particle and forms a polymer matrix that encompasses silica fragments dispersed within it. However, heterogeneous polymer growth rates in different areas of the particle and the rapid production of polymer too quickly for a continuous matrix to form prior to

expansion and separation of the polymer aggregates, and may lead to rapid fragmentation and the formation of fine particles ($< 100\ \mu\text{m}$).¹⁹⁰⁻¹⁹²

1.5.1 Adverse Effects of Fine Particles

The presence of fine particles is extremely detrimental toward industrial processes as they often lead to agglomeration within the reactor and fouling of the piping and heat exchangers. Agglomeration disproportionately impacts gas phase fluidized bed reactors and exacerbates poor thermal control. Due to the small margin between reaction temperatures (90°C) and the polymer melting temperature (110°C), fine particles will often melt and solidify on the reactor walls which adversely impact the reactor's thermal stability. Additionally, uncontrolled polymerization within the particle often leads to rough particle morphology and loss of the desired spherical shape. This is especially important in fluidized bed reactors as non-spherical particles have increased drag and affect the fluidization behavior and stability in addition to impacting their processability downstream of the reactor.^{193, 194} The formation of fine particles in slurry phase processes is reduced due to the presence of the liquid diluent. The presence of liquid diluent provides good thermal control and acts as a heat sink and remove excess heat generated.

1.5.2 Methods to Mitigate Effects of Fine Particles

One of the most common approach to mitigate the formation of fines is pre-polymerization. The supported catalysts first pass through a secondary reactor which operates at mild conditions (low temperature or low monomer concentration) prior to the main reaction vessel.¹⁹⁵⁻¹⁹⁷ Lower degrees of fragmentation and growth occur and

silica fragments can be contained within the polymer phase formed. These prepolymers are then transferred to the main reactor to undergo polymerization under designed reaction conditions. The control of polymer particle morphology obtained by the inclusion of the prepolymerization stage was shown to be improved and overall catalyst activity increased as the active sites were already exposed by early catalyst particle fragmentation.^{186, 198-200} However, this method requires an additional prepolymerization reactor unit and associated equipment. In addition, the reaction time within the pre-polymerization reactor needs to be optimized to control the particle morphology and avoid premature catalyst deactivation.

Another common industrial practice is operation of the fluidized bed reactor under condensed mode, where liquid hydrocarbons, or induced cooling agents, are added to the fluidized bed reactor.^{201, 202} In this method, the feed temperature is reduced below the dewpoint temperature and up to 18 wt.% of the liquid in the form of droplets is added to the reactor feed stream. As the droplets flow up the reactor, they will evaporate and assist in the removal of heat generated by the polymerization reaction, preventing catalyst overactivity. In addition, the presence of the liquid droplets softens the polymer particles making the polymer chains more deformable, reducing the stress exerted on their surroundings.²⁰²⁻²⁰⁴ However, their application is limited due to the possibility of being adsorbed by the polymer particle and their addition and evaporation must be carefully controlled to prevent liquid pooling and mud formation.

The use of liquid hydrocarbon or mineral oil within the pores of the supported catalyst has also been proposed to reduce the formation of fines, serving the same purpose of the diluent in slurry phase.²⁰⁵⁻²⁰⁸ Work by McKenna's group observed that

the presence of oil drastically reduced the number of fine particles after the reaction and the overall polymerization activity. While oil only coats the exterior and internal pores, these particles are prone to agglomeration during the feed and startup period of the reactor and might lead to other process issues.²⁰⁵ Additionally, removal of the oil must also be considered after the reaction is complete as its presence will affect polymer properties such as melting point and crystallinity.²⁰⁶⁻²⁰⁸

1.5.3 Possible Causes of Uncontrolled Fragmentation

While these methods can alleviate the formation of fine particles and their effects, they do not address their root cause. This is due to the multitudes of factors that can lead to rapid polymerization and fragmentation. These can generally be divided into two categories: those related to the choice of silica and those related to the supported catalyst activity. The former includes the porosity, pore dimension, and mechanical strength of the silica. Interstitial voids and areas of loosely bound silica aggregates within the particle could lead to heterogeneity in stress buildup necessary for fragmentation.¹⁶² However, it is unclear if this behavior is present in other classes of silica particles, including those without interstitial pores. As aforementioned, the choice of pore size distribution of silica will impact the mass transfer process and the subsequent locations of active sites. In addition, the arrangement of the meso- and macropores is an important factor in the fragmentation behavior. However, the pore structure of the particle after immobilization of catalytic compounds may be different from its initial state. Studies of the supported catalyst after immobilization revealed that the average pore diameter, surface area, and pore volume of commercial silica decreased with increasing Al content.^{101, 189, 209, 210} It is thus difficult to accurately

compare fragmentation behavior between studies as the immobilization of catalytic compounds will affect the pore structure differently based on the amount of immobilized compounds and the initial pore structure. **Table 1.1** shows reported pore diameters and aluminum content (amount of MAO immobilized) of the original silica and supported catalyst.

Table 1.1. Reported pore sizes and Al wt. % of supported catalysts

Silica support	Al wt.% in silica	Original pore diameter (nm)	Final pore diameter (nm)	MAO layer thickness (nm)	Ref.
ES767	17.0	42	22	20	101
PQ MS1732	18.8	10.1	5.5	4.6	209
PQ MS3040	15.8	28.5	11.8	16.7	209
PQ MS3040	10.7	27	22	5	210
PQ MS3040	9.8	24	19	6	210
Grace 948	15.6	23.2	10.8	12.4	209
Grace 948	8.8	24	14	10	210
Grace 948	7.6	23	15	8	210
ES70W	14.5	24	17	7	189

Despite similar Al content, the thickness of the MAO layer will vary due to inherent differences in the pore structures of the silicas used. Of the studies that used the same type of silica (Grace 948 and PQ MS3040), a general trend of thicker MAO layers with higher Al content is seen. Velthoen et al.¹⁰¹ observed with ES767 silica that MAO will first adsorb in larger pores until the MAO layer thickness reaches a limit, presumably due to inability to enter the smaller pores. The presence of the MAO layer may affect the mechanical strength of the particle. Through the reinforcement of silica particles with silicon oligomers, McDaniels et al.^{211, 212} found that the activity of silica particles and fragility decreased with smaller pore volumes/porosities after depositing the silicon layer. This was attributed to higher degrees of contact between the silica aggregates which strengthened the particle and inhibited fragmentation. However, it is unclear whether the MAO layer within the supported catalyst will have a similar effect.

The supported catalyst activity is mainly dependent on the local density of active sites within the supported catalyst. Ideally, active sites are located uniformly throughout the particle to ensure even growth during the reaction and the formation of a continuous polymer matrix. Supported catalysts with non-uniform distributions of MAO have been reported to cause uneven fragmentation of catalyst particles and low bulk density of the polymer formed.^{101, 134, 210, 213, 214} Metallocene compounds immobilized in areas with lower concentrations of MAO do not receive the aforementioned benefits associated with MAO compounds and are ultimately less active during reaction. Thus, the radial concentrations of both MAO and metallocene within the particle must be accounted for to ensure complete activation of the immobilized metallocene compounds. As aforementioned, solutions containing MAO or metallocene must diffuse through the pore structure and immobilize in a mass transfer process during the preparation procedure. Ample contact time between the particle and solution is needed to guarantee a uniform distribution of active sites. However, a wide range of contact time between the silica and catalytic solution has been used in reported studies to prepare supported catalysts. **Table 1.2** shows the range of contact time used along with their respective support and metallocene compound.

Table 1.2. Examples of contact times used in preparing MAO/metallocene supported catalysts

Support	Metallocene catalyst	Time in MAO solution (h)	Time in metallocene solution (h)	Ref.
Grace 948	nBuCp ₂ ZrCl ₂	4	1	¹¹³
Grace 948 and PQMS 3040	nBuCp ₂ ZrCl ₂	1	1	²¹⁵
Grace 948	nBuCp ₂ ZrCl ₂	1	0.5	²¹⁶
Grace 948	nBuCp ₂ ZrCl ₂	1	1	²¹⁷

Porous polymer support	nBuCp ₂ ZrCl ₂	2-3	2-3	218
Porous polymer support	nBuCp ₂ ZrCl ₂	10	2-3	182
Mesoporous molecular sieves	nBuCp ₂ ZrCl ₂	12	4	123
Variety of silica	nBuCp ₂ ZrCl ₂	0.5	0.5	219
Variety of silica	nBuCp ₂ ZrCl ₂	1	1	136
ES70	nBuCp ₂ ZrCl ₂	1	1	114
ES70W	Cp ₂ ZrMe ₂	4	2	189
Aldrich, grade 62	rac-Et(Ind) ₂ ZrCl ₂	1	24	220
Grace 948 and MS-3040	rac-Et(Ind) ₂ ZrCl ₂	2 or 4	2 or 4	210
Grace 532	Cp ₂ ZrCl ₂	2	2 to 4	221
Grace 948	Cp ₂ ZrCl ₂	4 or 8	4 or 8	222
Witco SMAO ^{a)}	Me ₂ Si(Ind) ₂ ZrCl ₂	N/A	0.5	223
Witco SMAO ^{a)}	Et(Ind) ₂ ZrCl ₂	N/A	0.25	224

^{a)}SMAO already has MAO immobilized

As can be seen, most studies utilized contact times between 1 and 4 hours for both MAO and metallocene solution with a variety of silica supports. Despite a dearth of literature regarding the distribution of active sites, uniform distribution of active sites in silica particles has been assumed or little attention has been paid to the active site distribution in silica particles. Most reports of active site distribution focused on the elemental mapping of Al because the Zr content is very low (<1.0 wt. %) for SEM-EDX mapping. While elemental mapping provides a qualitative view of where MAO is located, it does not provide quantitative values to ensure that the local density of active sites is the same throughout the particle. Overall metal content is obtained either by inductively coupled plasma mass spectrometry (ICP-MS) or inductively coupled plasma atomic emission spectrometry (ICP-AES) from dissolving the supported catalysts, or through beam methods such as Rutherford backscattering or SEM-EDX, which can only detect metal content up to a certain depth (~2 μm). While these methods

measure the total metal content, the data on their spatial distribution in silica particles are not obtainable. Thus, in order to obtain a comprehensive view of the local density and distribution of active sites within the supported catalyst, both qualitative and quantitative methods must be used complementarily.

1.6 Research Objectives

The aim of the dissertation is to investigate the effects of catalyst preparation procedure on the fragmentation of silica-supported metallocene catalysts and the resulting polymer particle morphology. Several factors such as the distribution of active sites, the silica pore structure, and the changes in the pore structure after immobilizing MAO have been identified and their effects have been examined. Specific research objectives are as follows:

1. To investigate the effects of contact time between the silica particles and the solutions of catalyst compounds (MAO and metallocenes) on the total immobilized amount and distribution of aluminum and zirconium;
2. To investigate the effects of active site distributions on the reaction kinetics and the fragmentation behavior of supported catalysts in slurry and gas phase polymerization of ethylene;
3. To develop a mathematical model for the immobilization of MAO and metallocene in porous silica particles to calculate radial distributions of active sites for various preparation conditions;

4. To investigate how the pore diameter of an initial type of silica is changed by the immobilization of catalytic compounds and if that affects the fragmentation behavior or polymer properties;
5. To compare the fragmentation and polymerization behavior of the supported catalysts with silica particles made by different processes with (spray-dried) and without (microemulsion) interstitial voids
6. To develop a flat surface silica model that mimics the conditions seen at the silica surface to observe the growth of polymer at the active site;

The first objective is examined in **Chapter 2** where supported catalysts with varying distributions of MAO and metallocenes were prepared. This was done by varying the contact times between the silica particle and the MAO solution and the MAO-modified silica and the metallocene solution. Analysis of the catalyst cross-section illustrates a marked dependence on the distribution of active sites and the contact time. When used in gas phase polymerization of ethylene, a significant fraction of fine polymer particles was produced with catalysts with non-uniform distributions. The second objective is addressed in **Chapter 3** where supported catalysts with varying distributions and pore diameters were used in both gas phase and slurry phase polymerization of ethylene. The kinetic, thermal, and fragmentation behaviors reveal the importance of the pore diameter in the final catalyst particle which differs from its initial size. The third objective is addressed in **Chapter 4** with supported catalysts prepared with a separate silica support and varying preparation conditions including contact time and metallocene solution concentration. The measured Al (for MAO) and Zr (for metallocene) concentrations were used to produce a mathematical diffusion-

adsorption model that predicts the total and radial distribution of Al and Zr within the particle that agrees with experimental results. The model is used to better understand other reported results such as the dependence on polymerization activity on particle size. The fourth and fifth objectives are addressed in **Chapter 5** where three different commercial silica with and without interstitial voids were used to immobilize varying amounts of MAO to obtain catalysts with varying pore diameters. Polymerization activity and thermal properties such as the crystallinity and melting temperature were shown to be influenced by the pore diameter of the catalyst. The last objective is addressed in **Chapter 6** where a flat surface silica catalyst model was developed with exposed active sites. The nascent growths of both polyethylene and polypropylene in gas and slurry phase reaction were observed and illustrate how the presence of the liquid diluent affects polymer morphology. **Chapter 7** summarizes the dissertation and provides possible future research into furthering the study of the impact certain catalyst properties have on the fragmentation behavior.

Chapter 2. Spatial Distribution of Active Sites in Porous Silica

Microparticles During Catalyst Preparation Process

2.1 Introduction

The industrial production of polyolefins is primarily performed using heterogeneous supported catalysts such as Ziegler-Natta catalysts, chromium oxide catalysts, and metallocene catalysts in conjunction with coactivators such as methylaluminoxane (MAO) and aluminum alkyls. When single-site metallocene catalysts are used in liquid-slurry or gas phase polymerization processes, they are immobilized onto porous amorphous silica microparticles of 30-50 μm in average diameter. The preparation of silica-supported metallocene catalysts is a critical step to obtain high catalyst activity, selectivity, and desired polymer particle morphology. Various techniques of preparing silica-supported metallocene catalysts have been reported in the literature.^{98, 105, 107, 137} The three most common heterogeneous metallocene catalyst preparation methods are:

- (i) To immobilize MAO on the silica first and then treat the MAO-modified silica with metallocene to form catalytically active complexes;
- (ii) To contact MAO and metallocene in solution to generate active sites and immobilize the catalyst on the silica support;
- (iii) To impregnate or graft metallocene directly onto the silica support by the reaction between surface silanol groups and metallocene.^{97, 225, 226}

In the first method, thermally treated amorphous silica microparticles are contacted with an organic solution of MAO to form MAO-modified silica which are

then immersed in a solution containing the metallocene catalyst. In the second method, a solution of MAO and metallocene compounds is used to contact the silica particles. Both MAO and metallocene will simultaneously diffuse through the pore structure and form active sites. In the third method, only a solution containing metallocene is used. In all these catalyst impregnation methods, the catalytic compounds (MAO or metallocenes) in solution diffuse through the tortuous micro- and macro-pores of silica. Through adsorption and complexation of the catalytic compounds, active sites are formed and anchored onto the silica pore surfaces. The distribution of these active sites within a porous silica micro-particle is a critical factor that impacts the overall polymerization activity, polymer properties, and particle fragmentation.

Fragmentation of the heterogeneous catalyst/polymer particles during α -olefin polymerization reaction is one of the most prominent and characteristic physico-chemical phenomena of the process and has been the subject of extensive theoretical and experimental research in the past years. The catalyst particle fragmentation is a critical process to achieve high catalytic activity and desired final polymer morphologies.^{179, 213, 227} In industrial polyolefin processes, catalyst particle shape replication is desirable; the final polymer particle shape is similar to that of the initial catalyst particle (usually spherical). However, uncontrolled or irregular fragmentation and the generation of very small diameter fine polymer particles less than 125 μm are frequently observed in olefin polymerization processes, notably in fluidized bed gas phase polymerization processes. Such fines often lead to increased agglomeration of the polymer particles, deposit in the recycle stream, and foul the piping and heat exchangers, making the reactor operations difficult. The fines with high catalytic

activity due to high concentrations of active catalyst components tend to segregate into certain poorly circulated regions of the fluidized bed reactor, especially in the upper disengagement zone.^{190, 228} However, the mechanisms of formation of fine particles in gas phase polymerization reactors are not fully understood. It is generally recognized that catalyst particle fragmentation and overall catalyst activity are dependent on several factors such as silica particle size and texture,^{124, 135, 229} polymerization conditions,^{145, 178, 189} and the overall catalyst activity itself that is further influenced by the amount of MAO and metallocene immobilized onto the silica support.^{102, 216, 230} The fragmentation of a silica catalyst particle occurs due to the buildup of hydraulic pressure within the pores as the amount of polymer in the catalyst pores increases during the polymerization.^{162, 163} Thus, it is highly likely that the local polymerization rate or catalyst activity will influence the rate of polymer formation in very narrow pore space, especially during the early stage of polymerization. The catalyst activity in turn is dependent on the density of active site which is directly affected by the preparation procedure.

In this chapter, we have investigated the effect of spatial distribution of catalyst components in silica support particles on the polymer particle morphology and particle fragmentation in gas phase polymerization of ethylene. To this purpose, we varied the catalyst preparation procedures by changing two major variables: the MAO impregnation time and the metallocene catalyst impregnation time. The distributions of aluminum and zirconium in the cross-sections of the silica-supported catalysts were analyzed using focused ion beam (FIB) and energy-dispersive X-ray spectroscopy

(SEM-EDX). The total aluminum and zirconium concentrations in silica particles were measured using Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

2.2 Experimental

2.2.1 Preparation of Supported Catalyst

The silica support used in this study is the commercially available P-10 (Fuji-Silysia Chemical) with an average surface area of 317 m²/g, a pore volume of 1.41 cm³/g, an average pore width of 30 nm, and an average particle size of 35.8 μm (Data provided by the manufacturer). The silica particles as received were first sieved to a narrow size cut (32 – 45 μm) to minimize the effect of particle size variation on the distribution of catalytic components. The sieved silica particles (0.5 g) were then placed in a 25 mL Pyrex glass bottle and calcined at 250°C in air for 19 h and then transferred to a glovebox in an argon environment to prepare the silica-supported catalysts.

The calcined silica particles were treated with a MMAO-12 solution (7 wt. % solution in toluene, Sigma Aldrich; $[(CH_3)_{0.95}(n-C_8)H_{17}]_{0.05}AlO)_n$) under gentle agitation. To obtain MAO-modified silica, 6 mL of MAO solution was slowly added to the Pyrex bottle with the calcined silica. The mixture of silica and MAO solution was heated to 110°C for either 1 or 19 h in order to obtain MAO-modified silica particles with varying amounts of adsorbed MAO and different intraparticle distributions. It is expected that a relatively non-uniform distribution of MAO with short contact time (1 h) and relatively uniform distribution of MAO with long contact time (19 h) may be obtained. After the contact time, agitation was stopped, and the particles were allowed to settle to the bottom of the bottle. The supernatant MAO

solution was removed, and 10 mL of fresh toluene was added. The toluene-silica mixture was gently stirred for 5 minutes at 90°C and again the supernatant toluene was removed. This rinsing step was performed three times to remove unbound MAO. The MAO-modified silica particles were then treated with a toluene solution of *rac*-dimethylsilylbis (2-methyl-4-phenylindenyl) – dimethyl zirconium (WR Grace) at 70°C under gentle agitation. To examine the effect of metallocene distribution within the silica-supported catalyst, the contact times between the MAO-modified silica and metallocene solutions were varied (1, 4, 8, 12, and 24 h). Details of the impregnation procedure used are shown in **Table 2.1**.

Table 2.1. Preparation conditions of supported catalysts

Supported catalyst ^{a)}	Time in metallocene solution (h) ^{b)}	Time in metallocene solution (h) ^{c)}
1-1	1	1
19-1	19	1
19-4	19	4
19-8	19	8
19-12	19	12
19-24	19	24

^{a)}Silica used: 0.5 g; ^{b)}Al content: 5.98 mmol; ^{c)} Zr content: 39.84 μ mol

Afterward, the supported catalyst particles were washed with the aforementioned rinsing procedure with toluene three times to remove unbound metallocene compounds. The final catalyst particles were dried *in vacuo* overnight at room temperature and the supported catalyst was recovered as free-flowing particles. **Figure 2.1** depicts the surface anchored MAO-metallocene complex in the silica pore.

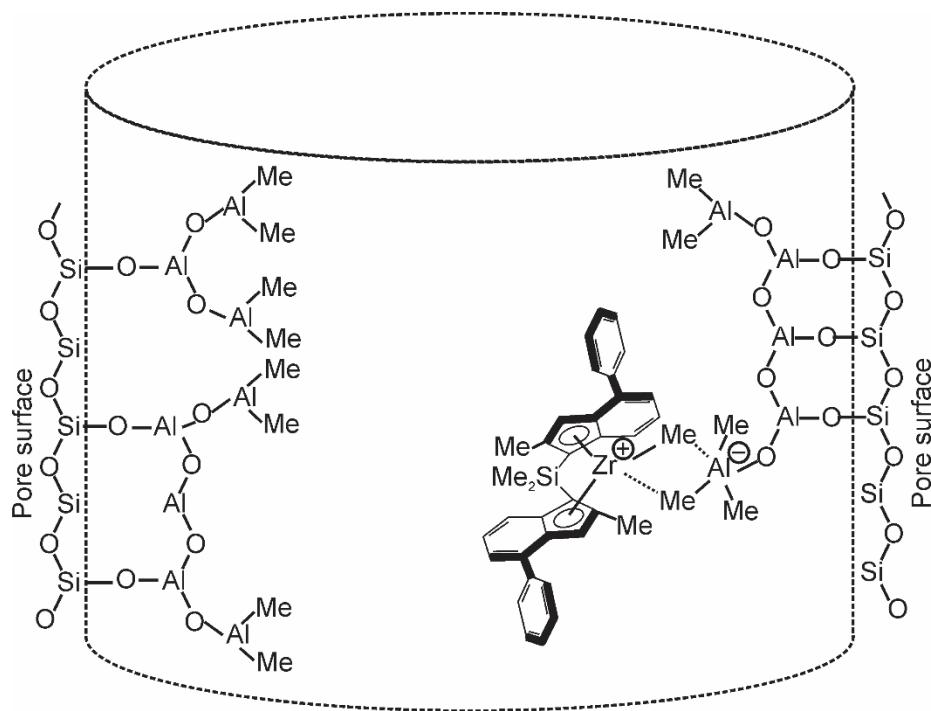


Figure 2.1. *rac*-dimethylsilylbis (2-methyl-4-phenylindenyl) – dimethyl zirconium complexed with MAO at the silica pore surface.

2.2.2 Gas Phase Polymerization of Ethylene

Gas phase ethylene polymerization experiments using the silica-supported catalysts prepared as described in Table 2.1 were performed using a sealed 350 mL high pressure glass reactor equipped with an ethylene injection port and a thermocouple. 50 g of sodium chloride particles (Sigma-Aldrich) were used as a seedbed. The salt particles were dehydrated in a vacuum oven at 250°C for at least 48 h before transferred to an argon glove box. The heterogenized metallocene catalyst was first pre-contacted with a triethylaluminium (TEAL) solution (1M in hexane, Sigma-Aldrich) for 30 minutes to activate the catalyst in the reactor. The volume of TEAL to catalyst was fixed to the $[Al]_{TEAL}/[Zr]_{solution}$ mole ratio of 1000. After the precontact time between the TEAL and the catalyst, the solvent in the mixture was removed and

the dehydrated salt particles were added to the reactor. The contents in the reactor were gently agitated to uniformly disperse the catalyst within the seedbed. The catalyst-loaded reactor assembly was removed from the glove box and then placed in a constant temperature water bath set to 60°C. The vapor pressure from any possible residual TEAL solution was negligible. After the reaction temperature in the reactor was reached, polymerization grade ethylene gas was supplied to the reactor to start the reaction. In these experiments, the salt bed was left unstirred in order to avoid the effect of attrition of catalyst particles due to collision by mechanical agitation. The gas phase ethylene polymerization rate during the polymerization was monitored by measuring the monomer consumption rate using a mass flow meter installed in the ethylene supply line to maintain the reactor pressure constant at 50 psi with a backpressure regulator. After 1 h of reaction, ethylene supply valve was closed, and the reactor was degassed. Then, 30 mL of 10 vol% HCl/methanol solution was injected into the reactor to deactivate the catalyst. The contents were stirred at room temperature in water to dissolve the salt particles. The polymer particles obtained were then vacuum filtered, dried in a vacuum oven overnight, and weighed for analysis. A schematic of the experimental setup for gas phase polymerization is shown in **Figure 2.2**.

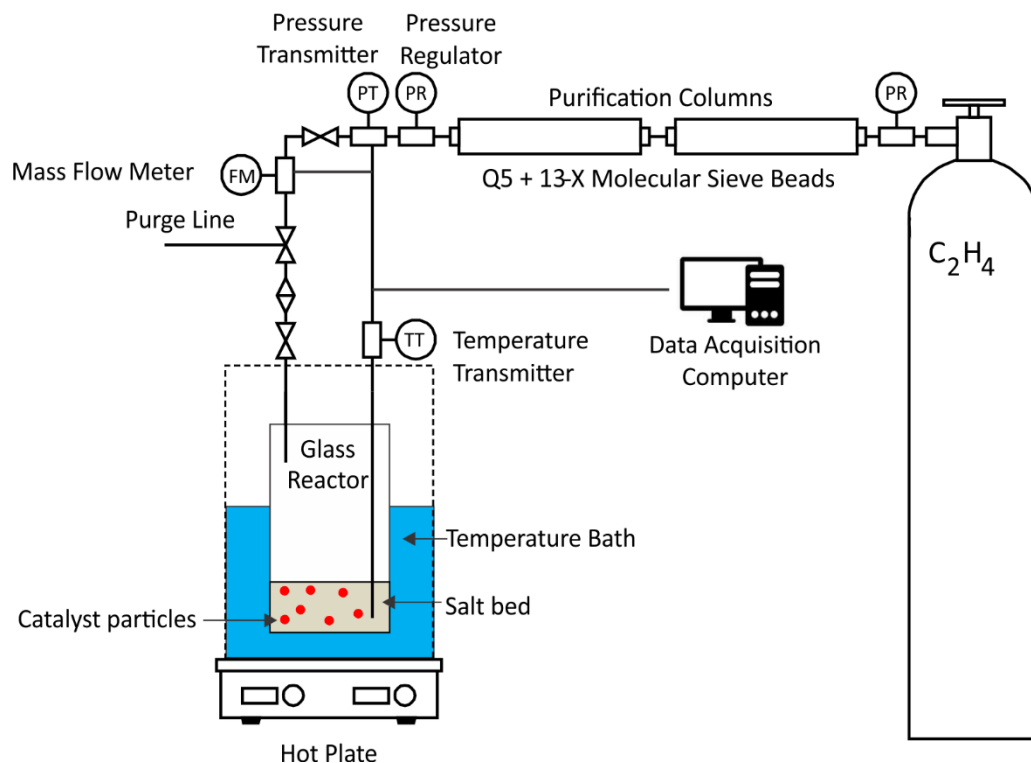


Figure 2.2. Schematic of gas phase polymerization experimental setup.

2.2.3 Characterization of Supported Catalyst and Polymer

The exterior morphologies of the prepared silica-supported catalyst particles and the polymer particles produced by gas phase polymerization were analyzed by scanning electron microscopy (SEM) (Tescan XEIA FEG SEM) with a 10 kV beam. Prior to SEM analysis, the samples were attached to the SEM sample holder with carbon tape and sputter-coated with gold (Hummer X Sputter Coater) for 1 minute to improve image quality. The cross-sections of the catalyst particles were analyzed using the focused ion beam (Tescan GAIA FEG SEM) technique with Ga^+ ions in order to preserve the fine pore structure of the impregnated silica catalyst particles and obtain a flat surface for analysis. Energy-Dispersive X-ray spectroscopy (SEM-EDX) (EDAX,

Octane Plus) with a 10 kV beam was used to analyze the composition of the surface layer and at several points within the cross-section of the catalyst particles.

The overall compositions (aluminum and zirconium) of the silica-supported catalyst particles were measured using Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Thermo Scientific Element 2). The catalyst sample (0.01 g) was dissolved in 15 mL of concentrated nitric acid (30 wt. %) to dissolve the aluminum and zirconium content for 10 days. Afterwards, the nitric acid-catalyst solution was diluted by mixing 1 mL of the solution with 9 mL of deionized water to obtain a solution with < 3 wt.% nitric acid to perform the analysis.

2.3. Results and Discussion

2.3.1 Overall Catalyst Composition

In this chapter, we hypothesize that the fragmentation of a silica/polymer particle in gas phase polymerization is influenced by the distribution of catalyst components (MAO and metallocene) within the silica support. More specifically, we hypothesize that the generation of fines or very small particle fragments in gas phase ethylene polymerization can be caused by the premature fragmentation of silica/polymer particles in the exterior surface region of the catalyst particles due to higher concentrations of active sites. To test this hypothesis, catalysts with different spatial distribution of active catalyst sites were prepared. To this purpose, we varied the impregnation time of the silica and MAO solution along with MAO-modified silica particles in metallocene solution to obtain the supported catalyst with different radial Al and Zr concentration profiles. The treatment of silica with MAO is very important

because MAO loading leads to the generation of weak Lewis acid sites in the supported activator which are responsible for metallocene activation.^{75, 102, 155, 157} These sites should be uniformly distributed throughout the particle to ensure local Al/Zr ratio is a minimum between 100 - 300 to fully activate the catalyst for ethylene polymerization.^{63, 102, 104} Uniform distribution of active catalytic sites (i.e., Zr sites) in silica particles has been assumed in most of the literature as the catalyst impregnation time is usually several hours or longer. However, changes to the Al and Zr contents based on the contact time might indicate that this not the case.

The overall Al and Zr concentrations in the supported catalysts obtained using different preparation conditions are shown in **Table 2.2**. An increased contact time with the MAO solution from 1 h to 19 h led to 38% increase in the amount of Al immobilized on the silica support. For long MAO-silica contact times (19 h), the immobilized Al content ranged from 24 to 31 wt. %, which is slightly higher than those reported in literature when other commercial silica particles were used as supports.^{101, 209}

Table 2.2. Aluminum and Zirconium content immobilized on the silica

Supported catalyst	Al wt.% in silica	Zr wt.% in silica	Activity (g/mmolZr.h) ^{c)}
1-1	18.73	0.34	289
19-1	25.93	0.42	307
19-4	31.02	0.54	295
19-8	25.48	0.57	364
19-12	23.55	0.55	296
19-24	25.30	0.37	278

^{c)} Ethylene pressure: 50 psig, at 60°C, 1 h

The amount of Zr immobilized in silica shows a strong dependence on the contact time between the MAO-modified silica and the metallocene solution. It is shown in Table 2.2 that the immobilized Zr amount is higher when the contact time

between the MAO-modified silica and the metallocene solution is increased. Although the amount of Zr immobilized in porous silica particles varies from catalyst to catalyst, the overall Zr content ranges between 0.1-0.5 wt. Zr/SiO₂ for many silica-supported catalysts.^{138, 139, 209} Quite high Zr content is established in very short contact times (e.g., 1 h), which is consistent with the literature.^{140, 217} Table 2.2 also shows that the Zr concentration reaches a maximum value after 8 h and then decreases as the contact time is further increased. Similar observations where the Zr content was lowered at long contact times were reported by dos Santos et al.¹⁴⁰ who directly supported (nBuCp)₂ZrCl₂ onto commercial silica (Grace 948). They proposed that the decrease in the amount of Zr was attributed to catalyst decomposition due to possible condensation reactions or poisoning that occurred at longer contact times.

The experimental results shown in Table 2.2 indicate that the amount of metallocene compounds immobilized within the silica particles depends on the contact time between the MAO-modified silica and the metallocene solution. At short contact times (e.g., 1 h), the total amount of Zr or catalytically active sites reaches a relatively large value and continues to increase with longer contact time. Then, it is possible that at short contact times, the catalyst sites may not be uniformly distributed in the silica particle but preferentially near the external surface region of the silica catalyst particle. Regions of high Zr concentration (near the particle surface) and low Zr concentration (in the interior of the particle) present in the catalyst particle may cause uneven growth during the polymerization due to a spatial nonuniformity of active catalyst sites. For instance, polymerization rates will be higher in regions with high concentrations of active sites and the differences in local polymerization rates can affect the progress of

pore filling, buildup of hydraulic pressure within the pores, and eventually particle fragmentation.

2.3.2 Spatial Distribution of Al and Zr in Catalyst Particles

Although we can measure the overall content of Al and Zr in the silica particles by ICP-MS analysis, the spatial distribution of these elements on a cross-sectional plane of the silica particle is needed to test the hypothesis that areas of high concentrations of active sites might occur due to intraparticle mass transfer resistance. One possible method to use scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX). Using this method, Al and Zr concentrations of the surface layer up to a depth of 2.2 μm as approximated from the expression provided by Andersen and Hasler can be obtained.²³¹ Differences between measured Al and Zr concentrations from SEM-EDX and from ICP-MS might be able to quantitatively detect the presence of higher concentrations of active sites near the surface. Approximately 200 particles were analyzed in this way for each preparation condition to obtain the Al and Zr concentrations. **Figure 2.3** shows SEM image of Catalyst 19-1 and the associated EDX area scan results which indicate that both Al and Zr are present on the surface. Similar analyses were performed for other supported catalysts. Due to the low sensitivity of EDX at lower concentrations, analysis of the particles prepared with shorter contact times had some margin of error in the Zr measurements. This error decreased for analysis of particles prepared with longer contact times with higher Zr concentrations. Errors in the measurements of Al concentrations were minimal.

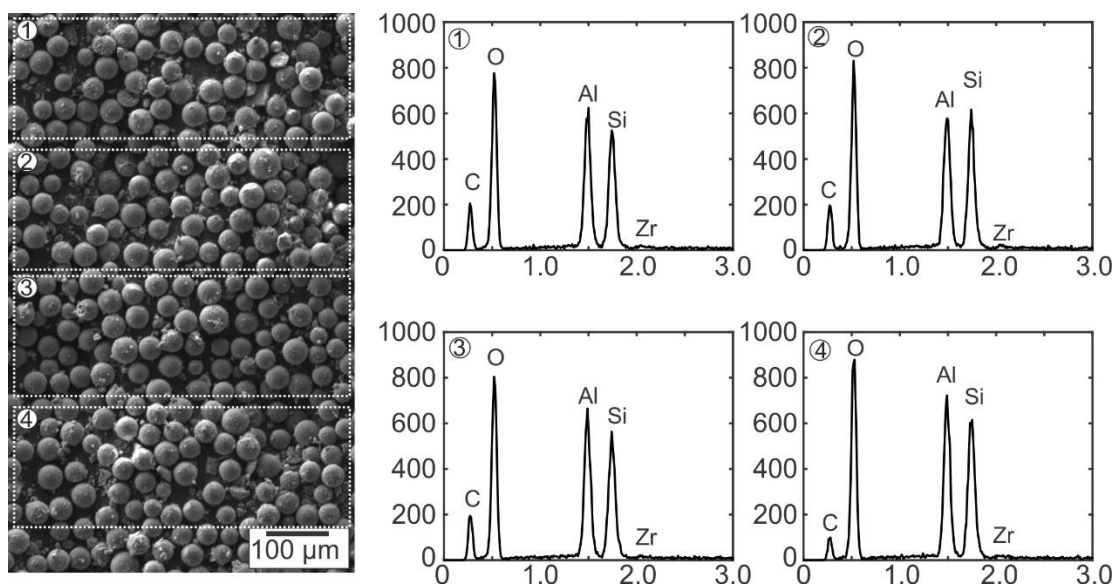


Figure 2.3. SEM image of Catalyst 19-1. Numbers represent location of EDX area scan with corresponding EDX spectra.

Figure 2.4 illustrates how the ratio of Zr wt.% (i.e., Zr wt. % in the surface region/Zr wt.% in the core region) changes over time. Here, the ratio of 1.0 indicates uniform distribution of Zr active sites within the particle. This ratio at short contact time (1 h) between the MAO-modified silica and metallocene solution is around 1.6 and almost double that at longer contact times (24 h) which is approximately 1.0. Despite the margin of error in the measurements, these results clearly show the qualitative difference in the Zr concentrations at the surface over time. These results indicate that the distribution of active sites is highly influenced by the contact time.

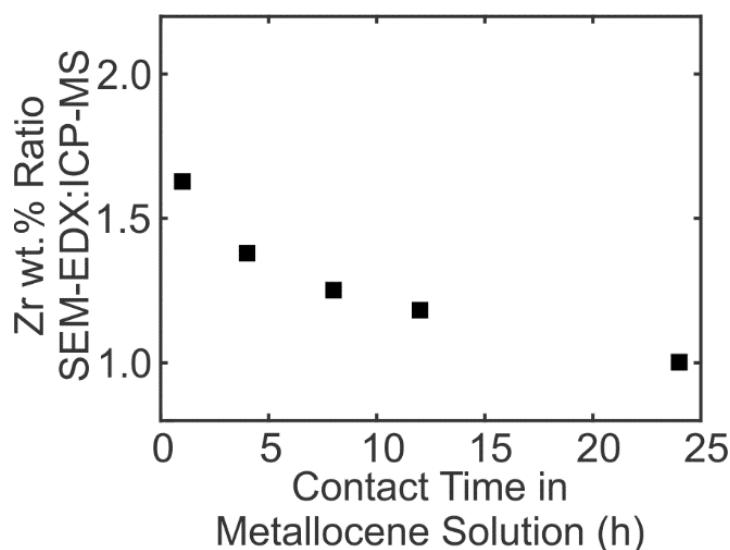


Figure 2.4. Ratio of Zr wt.% measured by SEM-EDX to ICP-MS.

While the comparison between the Al and Zr concentration at the surface and within the overall particle can be used to estimate the spatial distribution, cross-sectional analysis of the particle is needed to confirm whether this approximation is accurate. For the analysis of the particle cross-section, we used the FIB technique where Ga^+ ions (Beam energy: 30 keV, Current: 7.5 nA) were used to cut the top hemisphere of the catalyst particle. The beam current was decreased to 2.0 nA to polish the cross-section and reveal the internal structure of the porous silica particle as well as obtain a flat surface for analysis of aluminum and zirconium. **Figure 2.5** illustrates the EDX line scan results for the Catalyst 1-1, Catalyst 19-1, and Catalyst 19-8 at the center of the cross-section. The line scans of Catalyst 19-1 and Catalyst 19-8 show that the longer contact time between the silica and the MAO solution yields more uniform distribution of Al. It is to be noted that the line scans shown in Figure 2.5 do not necessarily represent the complete spatial distribution of Al and Zr in the particle cross-section.

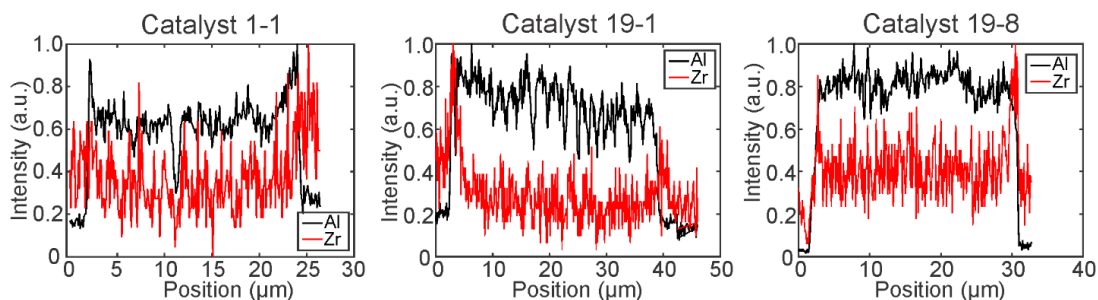


Figure 2.5. EDX line scan of the cross-sections of Catalysts 1-1, 19-1, and 19-8.

To obtain complete elemental Al and Zr distribution maps in a particle cross-section, numerous point scans throughout the cross section (~ 50) were measured using SEM-EDX. Scan times were set to 1 minute for each point scan to maximize the signal and obtain accurate measurements. The results were integrated using the interpolation function *griddata* in MATLAB. In this method, each spatial point (defined by an X and Y coordinate within the particle cross-section) with the measured Al or Zr concentration was used to approximate the values in the nearby areas using the triangulation-based natural neighbor interpolation method. **Figure 2.6** shows the analysis results.

The first three images in the top row (Fig. 2.6 a-c) show the cross section and elemental maps of Catalyst 1-1 which was prepared by impregnating silica particles in the MAO solution for 1 h followed by contact with the metallocene solution for 1 h. Since the contact time between the MAO-modified silica and the metallocene solution was relatively short (1 h), this preparation condition was expected to yield non-uniform intraparticle distribution of Al and Zr. Indeed, Figures 2.6b and 2.6c clearly show that the interior region of the silica has not been fully accessed by Al or Zr.

The second row of Figure 2.6 shows similar analysis for Catalyst 19-1 which was prepared with a longer contact time in the MAO solution (19 h) followed by contact

with the metallocene solution for 1 h. Figure 2.6e shows that Al is more uniformly distributed than the previous case (Catalyst 1-1) with high Al content at the center of the particle. This corresponds to the higher overall Al content per silica particle after 19 h contact time compared to the previous case with shorter MAO contact time (25 vs 18.73 wt.% Al, Table 2.2). Figure 2.6f shows that the Zr concentration is high near the external surface region of the particle but very low near the center of the particle, similar to that of Catalyst 1-1. Both Catalyst 1-1 and 19-1 have similar overall Zr concentrations (0.34 and 0.42 wt.% Zr) after being prepared in the metallocene solution for the same amount of time.

The third row of Figure 2.6 shows the images of the Catalyst 19-8 particle with 19 h contact time in the MAO solution and longer contact time between the MAO-modified silica and metallocene solution (8 h). Figures 2.6h and 2.6i show that Al and Zr distributions are quite uniform across the particle cross-section. The mass concentration of Zr is far smaller than the concentration of Al in line with the preparation conditions. While the overall Zr content for this catalyst is around 0.6 wt.%, the individual particle analyzed has the Zr content ranging from 0.3 to 0.45 wt.%. This indicates that catalysts with a range of Zr concentrations may have been produced.

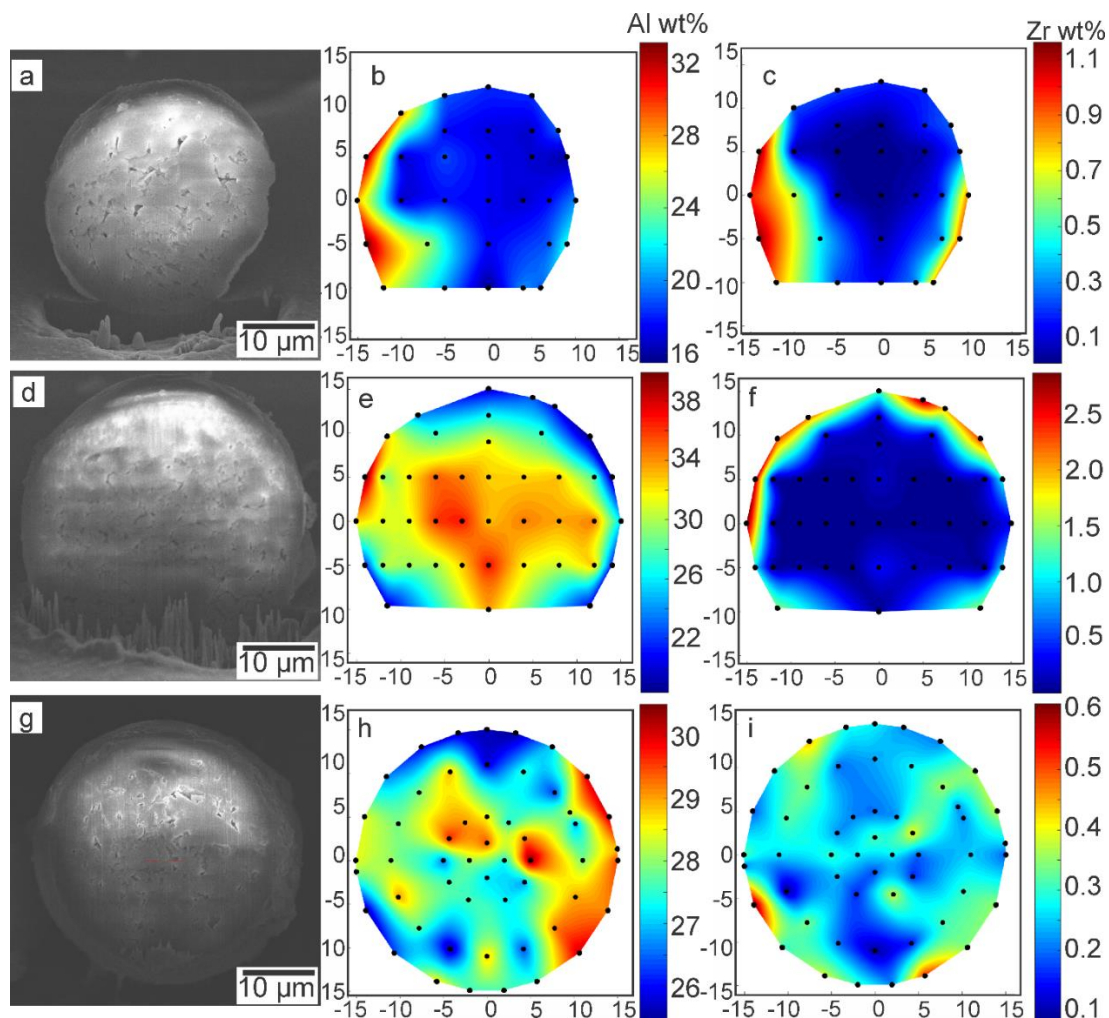


Figure 2.6. Top row: (a) Cross-section of Catalyst 1-1 prepared in MAO solution for 1 h and metallocene solution for 1 h. Interpolated elemental distribution of (b) aluminum and (c) zirconium. Black dots denote SEM-EDS analysis at the corresponding point of cross-section Second row: Same analysis, but for Catalyst 19-1 prepared in MAO solution for 19 h and metallocene solution for 1 h. Third row: Same analysis, but for Catalyst 19-8 prepared in MAO solution for 19 h and metallocene solution for 8 h.

The results shown in Figure 2.6 illustrate the strong dependence of the Al and Zr distribution on the contact time during the preparation process, suggesting that catalyst preparation procedure needs to be carefully established to warrant the uniform distributions of both Al and Zr in the catalyst particles. Figure 2.6 also indicates that the kinetic aspects of diffusion and adsorption/complexation of the metallocene

molecules may have to be taken into account in designing the preparation procedure for high-performance supported catalysts.

2.3.3 Polymer Morphology

The varying distributions of MAO (Al) and Zr within a silica particle are expected to lead to different polymer particle morphologies in ethylene polymerization. **Figure 2.7** shows SEM images of the polyethylene particles obtained from the gas phase polymerization at 60°C and 50 psig ethylene partial pressure after 1 h of reaction using the different sets of catalysts with different spatial Al and Zr distributions. Figure 2.7a and Figure 2.7b show large fractions of very small particle fragments whereas Figure 2.7c show minimal particle fragments. It is to be noted that before the catalyst immobilization, the original silica particles were sieved to sizes above 32 μm . After catalyst immobilization, the particles remained spherical and free of fine silica particles (Figure 2.3). Thus, the particle fragments observed in Figure 2.7a and Figure 2.7b are entirely the result of fragmentation during the polymerization reaction.

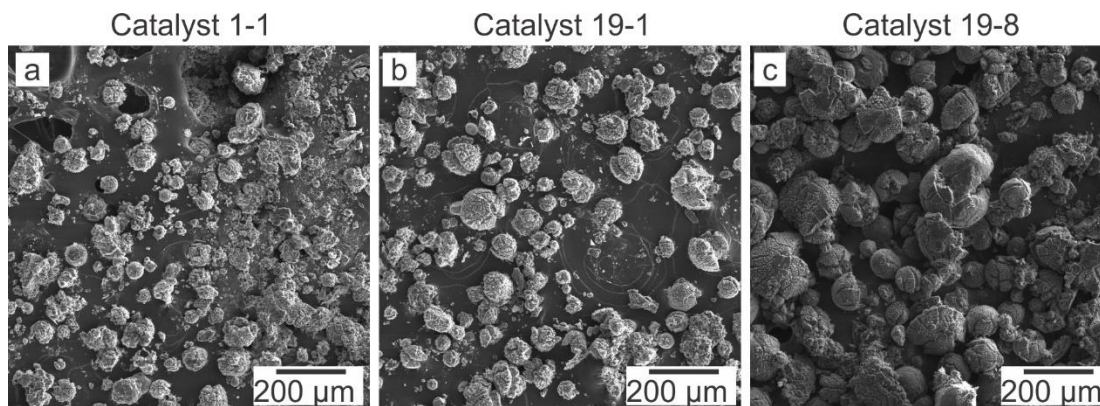


Figure 2.7. Polyethylene particles produced after 1 h gas phase reaction at 60°C from (a) Catalyst 1-1, (b) Catalyst 19-1, and (c) Catalyst 19-8.

The morphologies of individual polymer particles provide insight into how fragmentation was impacted by the distribution of active sites (**Figure 2.8**). Figure 2.8a shows a representative polymer particle formed from Catalyst 1-1 which had non-uniform distributions of both Al (MAO) and Zr (metallocene). The particle is no longer spherical and has an uneven exterior comprised of polymer aggregates. Figure 2.8b shows a representative polymer particle formed from Catalyst 19-1 which had uniform distribution of Al and non-uniform distribution of Zr. The particle has been split into two hemispheres containing large cracks and separated into several rectangular polymer aggregates on the surface. Figure 2.8c shows a polymer particle produced from Catalyst 19-8 that had uniform distribution of both Al and Zr. It is mostly intact and spherical although the edges of the surface aggregates similar to those seen in Catalyst 19-1 along with large cracks on the surface are seen.

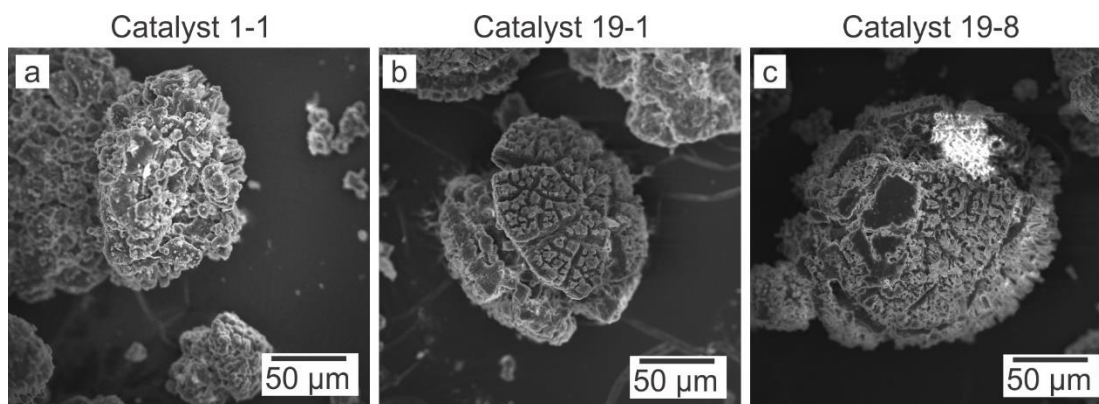


Figure 2.8. SEM image of representative particle from (a) Catalyst 1-1, (b) Catalyst 19-1, and (c) Catalyst 19-8.

Polymer chains formed at active sites will cause the expansion of the silica/polymer aggregates where they are located as they continually grow. The relatively porous exterior of the polymer particle formed from Catalyst 1-1 suggests that polymerization did not extensively occur. A possible explanation can be found

from the elemental map of Al and Zr. Low concentrations of both Al and Zr, corresponding to MAO and metallocene, were seen at the center of the particle. Thus, the remaining core region experiences lower levels of polymerization after it is exposed after fragmentation. The expansion from the compact spherical catalyst particle to the two hemispheres shape seen from Catalyst 19-1 demonstrates areas of uneven growth rates where high polymer growth near the exterior of the catalyst leads to expansion while little growth is seen in the center. Due to the presence of MAO in the core region of Catalyst 19-1, polymer growth is sufficient to form a polymer matrix with the exterior region. Uniform distribution of Al and Zr in Catalyst 19-8 leads to even polymer growth throughout the catalyst and intact polymer particles.

In addition to intact polymer particles, large numbers of fine particles were produced from Catalysts 1-1 and 19-1. **Figure 2.9** shows representative fine particles seen after reaction. Fragments seen from Catalyst 1-1 are usually smooth and irregularly shaped (Figure 2.9a). However, some fragments from Catalyst 19-1 have small fibrils approximately 1 μm in length growing from them (Figure 2.9b). These fibrils are shorter than those found on the surface of the large polymer particles obtained from Catalyst 19-8 (Figure 2.9c) and is evidence of continued polymer growth. These SEM images of polymer particles clearly suggest that the formation of very small particle fragments in gas phase ethylene polymerization is strongly correlated with nonuniform distribution of active catalyst (Zr) in the catalyst particles.

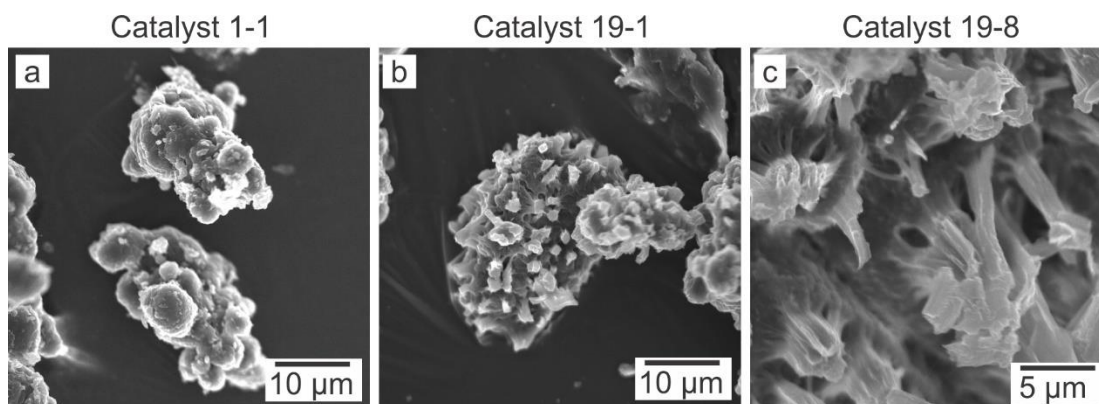


Figure 2.9. SEM image of fragment from (a) Catalyst 1-1 and (b) Catalyst 19-1. (c) SEM image of surface of particle from Catalyst 19-8.

While evidence of extensive fragmentation is seen after 1 h of reaction, the progression of the fragmentation over the course of the reaction time and how it is affected by the distribution of active sites is also examined. **Figure 2.10** shows the SEM images of polymer particles at different reaction times with silica supported catalysts with relatively non-uniform Zr distribution (Catalyst 19-1). The overall particle image of Figure 2.10a shows that at 10 min of reaction, polymer has already been formed on the surface of the catalyst particle and the fracture of the surface has started due to the particle expansion. The observed morphology is similar to that of Ziegler-Natta catalyst reported in the literature for early stages of gas phase propylene polymerization.²³² In the magnified surface shown in Figure 2.10b, we can observe the protrusion of fibrillar polymer bundles and stress fibrils between the fragmented surface layers and fragments. After 30 minutes of reaction, the polymer particle became larger and the particle surface consists of a mosaic of smaller fragments as surface rupture continued with the particle expansion (Figure 2.10c). Thick polymer-silica blocks that were seen earlier can be found at the surface of the particle with polymer fibrils now around 5 μm in length (Figure 2.10d). After 60 minutes of reaction, the

morphology of the polymer particle established at 30 min is still maintained with polymer fibrils around 10 μm in length (Figure 2.10e, f). Particle sizes after 60 minutes remain relatively similar to those seen after reaction for 30 minutes.

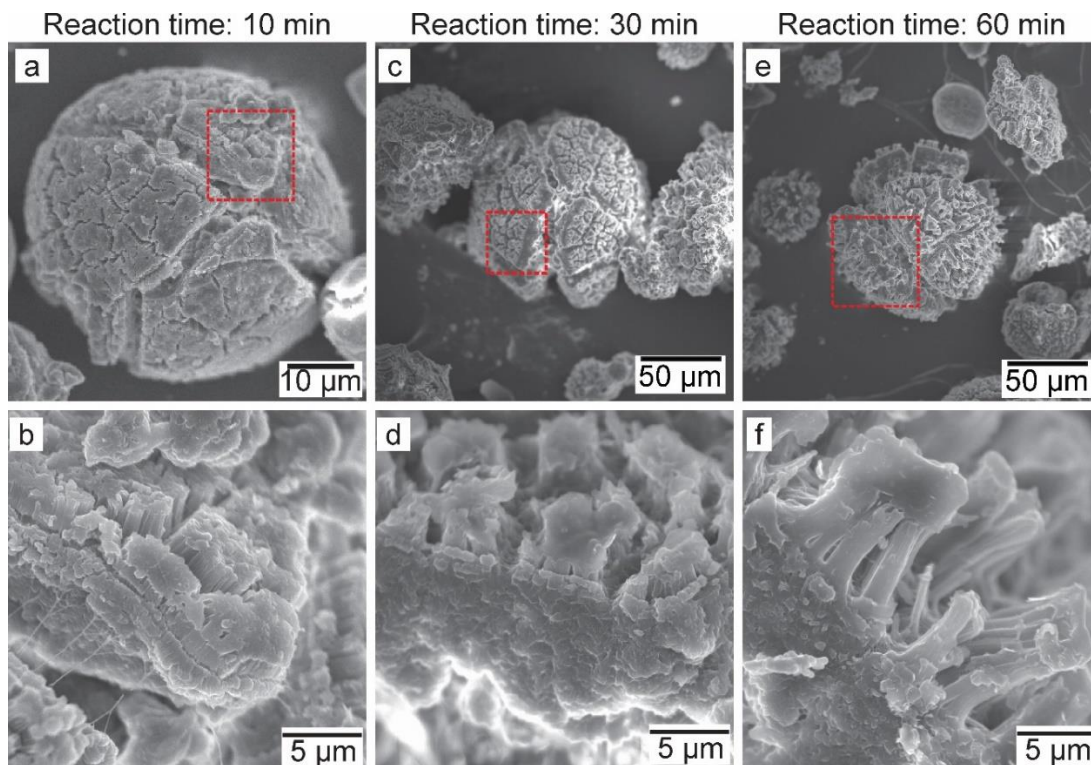


Figure 2.10. SEM images of polyethylene particles after (a-b) 10 minutes, (c-d) 30 minutes, and (e-f) 60 minutes in gas phase polymerization with Catalyst 19-1; Red squares represent the enlarged zones.

Figure 2.11 shows polymer particles from supported catalysts with relatively uniform Zr distribution (Catalyst 19-8). The growth and morphology of polymer particles are similar to the previous case, but there are some key differences. Compared to Catalyst 19-1, few thick polymer fibrils are observed at the particle surface and less cracks are seen on the surface (Figure 2.11a). After 30 minutes, the texture of the polymer particle appears denser and more spherical with less open spaces between the polymer aggregates (Figure 2.11c). This observation might be due to the presence of

more active sites in the interior of the particle where polymerization of ethylene occurs. After 60 minutes, we observe that the polymer particle morphology is maintained and the particle has grown larger to approximately 100 – 130 μm (Figure 2.11e). It should be noted that there are many polymer particles in the reaction mixture and the images shown in Figures 2.10 and 2.11 illustrate some samples of these particles of different sizes and morphologies.

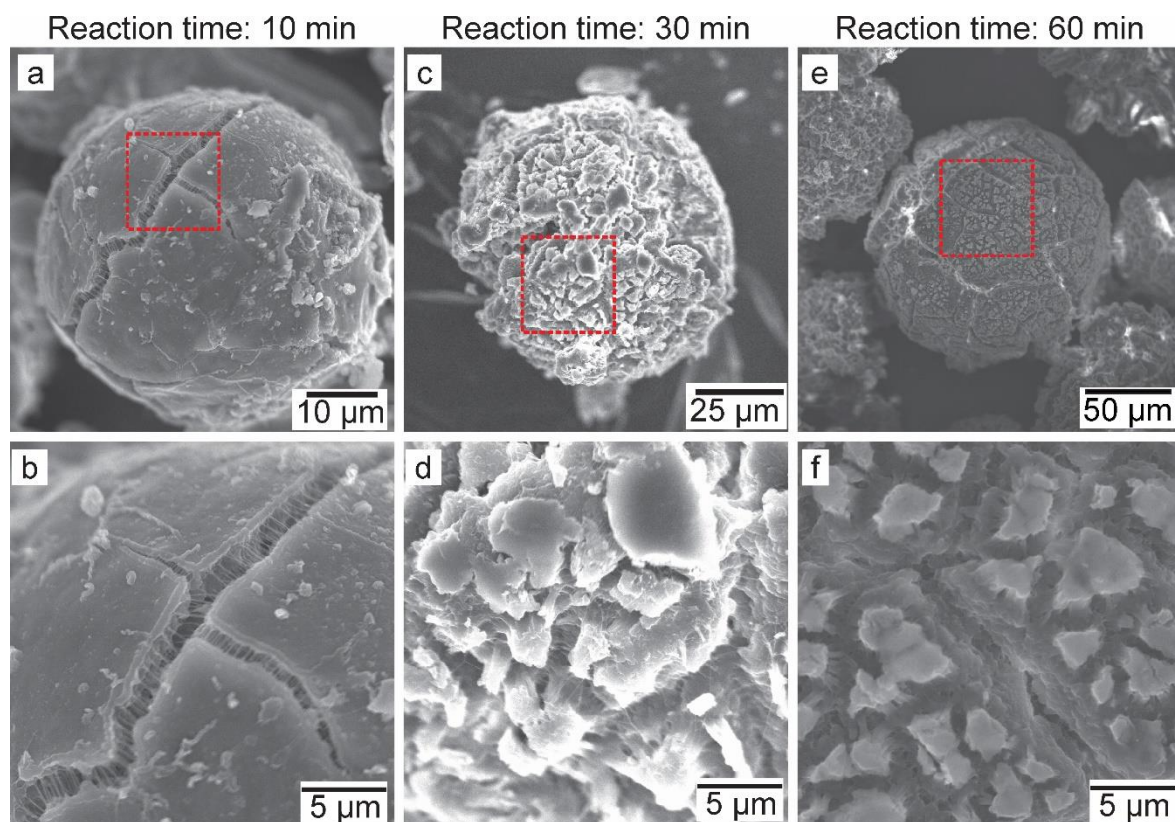


Figure 2.11. SEM images of polyethylene particles after (a-b) 10 minutes, (c-d) 30 minutes, and (e-f) 60 minutes in gas phase polymerization with Catalyst 19-8; Red squares represent the enlarged zones.

2.3.4 Analysis of Fine Particle Fragments

Since a large fraction of fine particles was generated with nonuniformly distributed catalyst particles in gas phase polymerization, the compositions of these

fine particle fragments were analyzed and the results are shown in **Figure 2.12**. Figure 2.12a shows the particle fragments smaller than 10 μm chosen for our analysis with points further analyzed by SEM-EDX marked by numbers. Figure 2.12b shows the elemental scan of Point 6 marked in Figure 2.12a. The elemental spectrum indicates that this very small particle fragment contains negligible amount of Zr and mainly consists of silica and polymer. But another small particle fragment (marked as 9 in Figure 2.12a) shows the presence of both Al and Zr (Figure 2.12c). The small particle fragments in Figure 2.12a might be ones generated just before the reaction was terminated (1 h) with not enough time to grow or if they were generated earlier, the active sites might have been deactivated and unable to polymerize ethylene and thus remain as small fragments. Such fine particle fragments are likely to be entrained in the high flow rate exit gas stream if the gas phase polymerization is carried out in a fluidized bed reactor. Also, they can easily deposit on the surfaces of pipes and heat exchangers in the recycle stream. If they stick to the reactor walls, the layer of such small particles may eventually cause the formation of polymer sheeting.

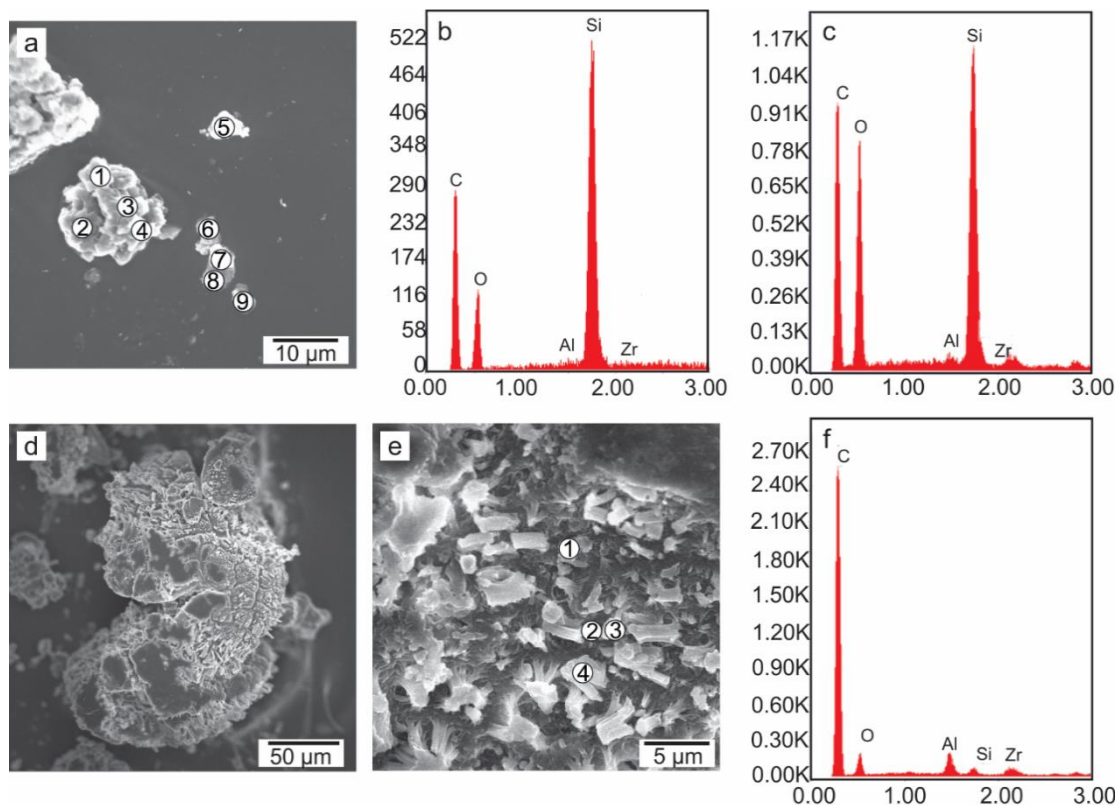


Figure 2.12. (a) SEM image of fragments after 1 hour of reaction using Catalyst 19-1. Numbers represent locations of EDX spot analysis. (b) EDX Spectra from Spot 6 and (c) Spot 9. (d) SEM image of large polymer particle after 1 hour of reaction using Catalyst 19-1 and (e) surface morphology. (f) EDX Spectra from Spot 1 in (e).

An example of a larger polymer particle and a magnified view of the particle surface obtained from the Catalyst 19-1 is shown in Figure 2.12d and Figure 2.12e. The polymer particle surface contains cracks and reveals the fragments with short polymer fibrils, clearly indicating that polymer particle expansion and fracture occurred at the particle surface. These cracks are the evidence of the growth of polymer particle due to polymerization. The diameters of the polymer fibrils are about 3 μm and form bundles of short length (c.a. 5 μm) attached to small fragments of silica. Figure 2.12f shows the elemental scanning spectrum at Point 1 marked in Figure 2.12e. Notice that although the fragment itself is small, it contains both Al and Zr along with higher

amounts of carbon (polymer). Although not shown, other points in Figure 2.12e showed similar results.

Based on the foregoing experimental study, we propose the mechanism of the particle fragmentation near the young catalyst particle exterior as illustrated in **Figure 2.13**. It shows that when the catalyst site concentration is high near the outer regions of a silica particle, polymer is rapidly formed, filling the pores, and disintegrating thin polymer layers into very small particle fragments. Some fragments may contain catalyst sites (Zr) and some fragments may consist of polymers with negligible amount of catalyst sites. Once such initial fragmentation or disintegration of surface layers is complete, the polymer particles will expand with internal fragmentation of remaining silica and subsequent polymer production without generating very fine particle fragments. According to this mechanism, the silica-supported catalyst with low active site concentrations near the outer surface region may reduce the formation of catalyst fines or very small particle fragments.

Several methods have been proposed in the literature to alleviate the formation of catalyst fines in gas phase polymerization including the use of anti-static agents,²³³⁻²³⁵ catalyst poison in the form of a liquid or gas,²³⁶⁻²³⁸ or small amounts of liquid hydrocarbon or mineral oil.^{205, 207, 208} In all these methods, a small amount is used to coat and deactivate the active sites at the surface of the catalyst particle prior to the main reaction while leaving the interior active sites intact. A reduction in the number of active sites at the surface of the particle by increasing the contact time and allowing them to access the interior may remove the need of using such additives.

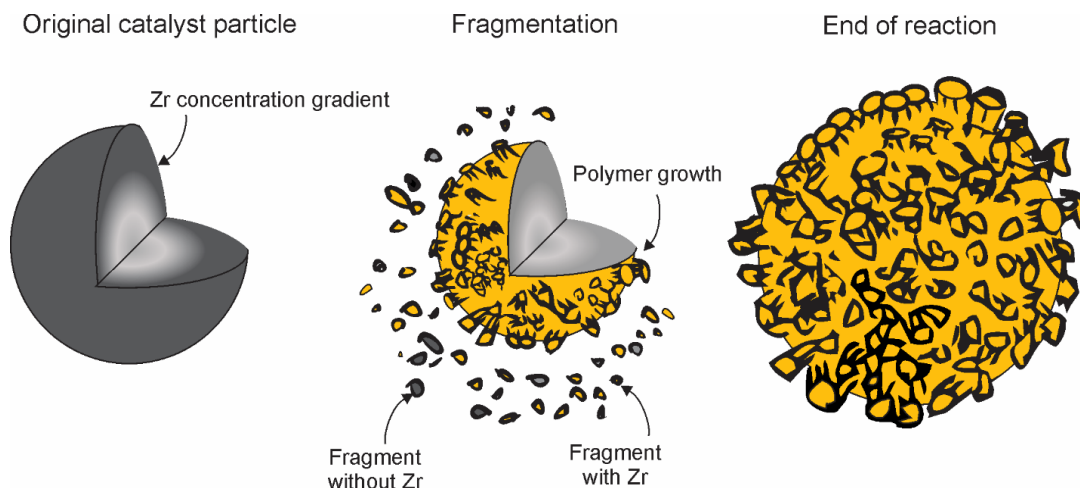


Figure 2.13. Proposed scheme of surface fragmentation due to nonuniform distribution of active sites: high concentration of Zr near the silica particle surface causes the premature fracture of silica/polymer and generates fine particle fragments.

2.4. Concluding Remarks

In this Chapter, we have shown that the distribution of MAO and metallocene compounds in silica-supported metallocene catalysts has significant effects on the fragmentation behavior of catalyst and polymer particles during the gas phase polymerization of ethylene. While the metallocene catalyst employed in the current study is a relatively low activity catalyst, the correlation between the contact time and overall immobilized metallocene can be applied to other silica-supported metallocene catalysts of higher activities. The two types of catalysts with different Zr distributions were prepared by changing the contact time between MAO-modified silica and a metallocene solution. The SEM-EDX analysis of the cross-section clearly shows that short impregnation times result in uneven Zr concentrations in the particle. The high concentration of Zr in catalyst particle surface region caused the formation of very small particle fragments of sizes less than 10 μm . Some of these fragments contained Al and Zr (catalyst sites) but some were free of catalyst. The gas phase polymerization

also resulted in the polyethylene morphology characterized by short and thick fibrils grown from silica fragments in an expanding polymer particle.

Chapter 3. Comparison of Catalyst Distributions and Performances between Gas and Slurry Phase Polymerization of Ethylene

3.1 Introduction

Industrially, polyolefins such as polyethylene or polypropylene are produced in processes that are either gas phase, slurry phase, solution phase, or a combination of the three.^{105, 107, 239} Inherent differences between the gas and slurry phase processes offer distinct challenges in catalyst and process design. One distinct difference is the presence of the diluent liquid phase in slurry processes that is absent in gas processes. The inclusion of the liquid phase significantly affects the polymerization process. Firstly, the liquid phase allows for effective heat removal away from the catalyst/polymer particles. Overheating of catalyst particles adversely causes the deactivation of active sites as well as high rates of polymerization, leading to rapid polymer accumulation within the pores of the catalyst and extensive silica particle fragmentation.^{184, 240-243} Secondly, there is a sequence of mass transfer resistances: gaseous monomer must dissolve in the bulk liquid phase following the thermodynamic solubility limitations, then diffuse to catalyst/polymer particles. If the reaction is sufficiently fast, such mass transfer resistances can lead to lower monomer concentrations at the active sites, effectively reducing the reaction rate and causing the polymerization process to be diffusion-controlled.^{244, 245} Finally, the solvent present in the solid particle phase increases mobility of the growing polymer chains, allowing them to move within and eventually out of the pores.²⁴⁶ This mobility reduces the

amount of pressure exerted by the polymer onto their surroundings, reducing the rate of fragmentation.^{162, 163, 247}

The lack of liquid causes numerous issues for gas phase processes, primarily in dealing with the heat dissipation from the solid phase. The limitations in the heat removal capacity of the fluidizing gas can lead to catalyst overactivity and the disintegration of the catalyst into fine particles which are likely to be entrained in the gas flow stream. In Chapter 2, we reported that some of these fine particles have active sites present and continue polymerization. These fine catalyst/polymer particles can easily agglomerate due to static electricity and attach to the reactor walls, causing the formation of local hot spots, sheeting, and fouling of the reactor wall surfaces.^{207, 208, 228} While several methods detailed in Chapter 1 are used to mitigate the effects of fine particles, they do address the root cause of the formation of fine particles which inherently begins with the preparation of the supported catalyst.

Despite the innate differences and challenges between slurry and gas phase reactions, silica-supported metallocene catalysts designed for either processes are often prepared using identical conditions. The preparation of these catalysts and their active site distributions determine their catalytic performance and morphology of the polymer. For instance, in Chapter 2, we have reported that the preparation conditions, contact time in particular, significantly impacted the distribution of active sites within the catalyst. Catalysts with higher concentrations of active sites near the surface of the particle led to higher fractions of fine particles formed in gas phase polymerization of ethylene.

Another important factor that is affected by the preparation condition is the pore diameter. The amount of MAO adsorbed in silica particles during their immobilization process has been reported to change the pore diameter of the silica.^{101, 134, 210} The pore diameter of supported catalysts can affect the accumulation of polymer prior to fragmentation of the pore wall as well as the activity of the catalyst. For instance, Sano et al. and Kumkaew et al. reported that supports with narrower pore diameters increased the activity of MAO/(n-BuCp)₂ZrCl₂ in ethylene polymerization in gas and slurry phase.^{122, 123, 129} They proposed that the narrower pore diameter shifted configuration of the MAO to a more active form that enhanced catalyst activity. While previous studies have focused on the effects of these factors on the catalyst activity and polymer properties, not much has been known about such effects on the overall morphology of the polymer.

In the present study, we investigate the effects of active site distribution and changes to the pore diameter after immobilization of MAO and metallocene on the polymer morphology in both gas and slurry phase reactions. Silica-supported metallocene catalysts were prepared with varying distributions of active sites and amounts of immobilized MAO with the overall Zr (metallocene) and Al (MAO) concentrations measured with Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). Changes to the pore diameters after the preparation process were measured using N₂ physisorption. These effects on the polymer morphology after liquid slurry and gas phase polymerization of ethylene were observed.

3.2 Experimental

3.2.1 Preparation of Supported Catalyst

The details of the preparation process of supported catalysts with the P-10 silica supports have been described in Chapter 2.2.1. In short, sieved silica particles were first calcined in air at 250°C and then contacted with a MAO solution to form MAO-modified silica. The MAO-modified silica was then contacted with a metallocene solution to form the final supported catalyst. It is expected that relatively non-uniform distributions of metallocene will be obtained at short contact times (1 h) and uniform distributions of metallocene will be obtained at long contact times (> 8 h) as seen in Chapter 2.

In this chapter, the procedure was slightly modified. First, the silica was contacted with varying volumes of MAO solution (4, 5, 6, and 7 mL) for 19 h. It is expected that this will yield MAO-modified silica with uniform distribution of MAO. In addition, the different volumes are expected to lead to different overall Al (from MAO) concentrations and different pore diameters due to the thickness of the MAO layer. Second, the concentrations of the metallocene solution were varied based on the volume of MAO used to obtain a 150 mol_{Al}:mol_{Zr} between the total Al concentration in the MAO solution and total Zr concentration in the metallocene solution. This was done in order to minimize the effect of Al/Zr mol ratio on the activation of the active site. Details of the preparation procedure used are seen in **Table 3.1**.

Table 3.1. Preparation conditions of supported catalysts

Supported catalyst ^{a)}	Volume of MAO solution (mL) ^{b)}	Total Al in solution (mmol)	Concentration of metallocene solution (mmol-Zr/L) ^{c)}	Total Zr in solution (μmol)	Time in metallocene solution (h)
4-1	4	3.98	4.43	26.56	1
4-4	4	3.98	4.43	26.56	4
4-8	4	3.98	4.43	26.56	8
4-12	4	3.98	4.43	26.56	12
4-24	4	3.98	4.43	26.56	24
5-1	5	4.98	5.53	33.20	1
5-4	5	4.98	5.53	33.20	4
5-8	5	4.98	5.53	33.20	8
5-12	5	4.98	5.53	33.20	12
5-24	5	4.98	5.53	33.20	24
6-1	6	5.98	6.64	39.84	1
6-4	6	5.98	6.64	39.84	4
6-8	6	5.98	6.64	39.84	8
6-12	6	5.98	6.64	39.84	12
6-24	6	5.98	6.64	39.84	24
7-1	7	6.98	7.75	46.48	1
7-4	7	6.98	7.75	46.48	4
7-8	7	6.98	7.75	46.48	8
7-12	7	6.98	7.75	46.48	12
7-24	7	6.98	7.75	46.48	24

^{a)}Silica used: 0.5 g; ^{b)} Time in MAO solution: 19 h; ^{c)}Volume of metallocene solution used: 6 mL

3.2.2 Characterization of Supported Catalyst and Polymer

The Al and Zr concentrations of the supported catalyst particles were measured with Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES, Shimadzu ICPE-9000). The samples were prepared with the procedure detailed in Section 2.2.3.

The gas adsorption isotherms of the original silica and the supported catalyst were measured using N₂ physisorption at 77K (Micromeritics ASAP 2020). Particles

were first dried overnight in a vacuum oven at 80°C overnight. For the analysis, 0.20 g of the particles were placed in the sample tube, sealed, and degassed at 120°C under vacuum for 12 h. Then, the dried particles and sample tube were weighed to obtain the weight after the first degas. Using this weight, the free space was measured to calibrate the analysis. Afterwards, the particles and sample tube were degassed again at 120°C for 4 h prior to analysis and measurement of the nitrogen adsorption-desorption isotherm. The BET method was used to calculate the specific surface areas while the pore volume and pore size distribution were measured using the Barrett-Joyner-Halenda (BJH) method with the adsorption branch of the isotherm.

The exterior morphologies of the prepared silica-supported catalyst particles and subsequent polymer particles produced were investigated by scanning electron microscopy (SEM) (Tescan XEIA FEG SEM) with a 10 kV beam. The samples were analyzed with the procedure detailed in Section 2.2.3.

3.2.3 Gas Phase Polymerization of Ethylene

The prepared catalysts detailed in Table 3.1 were used in gas phase polymerization of ethylene. Further details of the polymerization procedure are given in Section 2.2.2.

3.2.4 Slurry Phase Polymerization of Ethylene

Slurry phase polymerization of ethylene with the prepared silica-supported catalyst were performed by first mixing the catalysts with 180 mL of hexane solvent and triethylaluminium (TEAL) solution as cocatalyst (1M, Sigma-Aldrich) in a sealed

500 mL high pressure glass reactor inside a glove box. The catalyst-loaded reactor assembly was removed from the glove box and then placed in a constant temperature water bath set to 60°C. After the reaction temperature in the reactor was reached, polymerization grade ethylene gas was supplied to the reactor to start the reaction with constant stirring. The slurry phase ethylene polymerization rate during the polymerization was monitored by measuring the monomer consumption rate using a mass flow meter installed in the ethylene supply line to maintain the reactor pressure constant at 50 psi with a backpressure regulator. After 1 h of reaction, the reaction was stopped by purging the reactor and deactivating the catalyst with 10 vol.% HCl/methanol. The polymer particles were then vacuum filtered and dried in a vacuum oven overnight. Schematic of the experimental setup for slurry phase polymerization is shown in **Figure 3.1**.

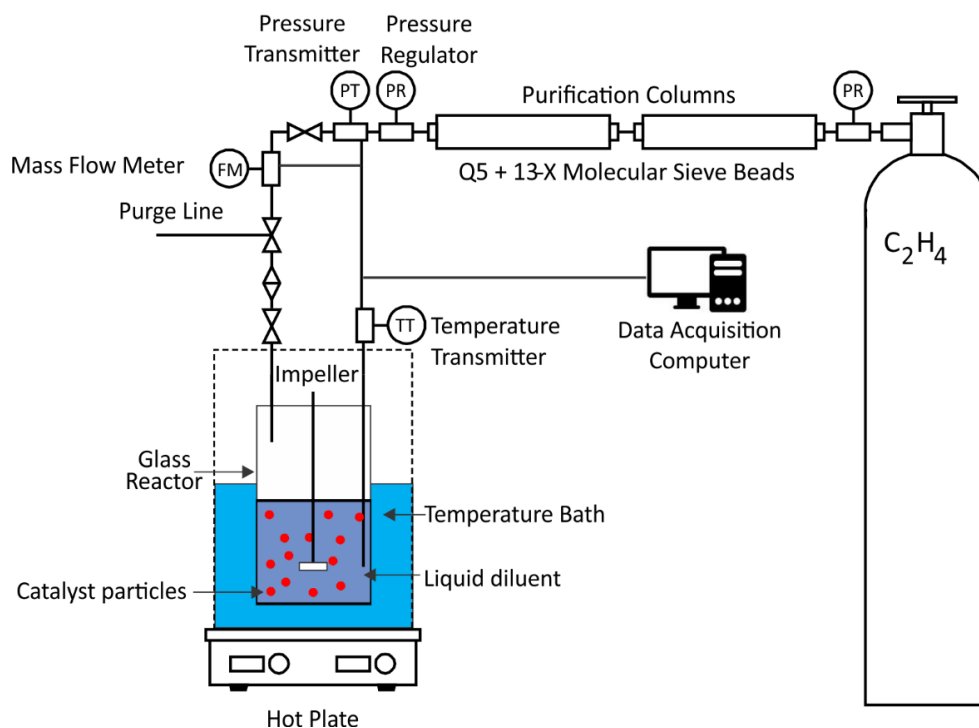


Figure 3.1. Schematic of slurry phase polymerization experimental setup.

3.3 Results and Discussion

3.3.1 Overall Catalyst Composition

The overall Al and Zr concentrations of the supported catalysts prepared under various conditions are shown in **Figure 3.2**. Two variables were examined: the volume of MAO solution and the concentration of metallocene solution, and the contact time between the MAO-modified silica and the metallocene solution.

Figure 3.2a shows the Al concentration in the supported catalyst after 0.5 g of silica was treated with different amounts of MAO solution for 19 h. While high Al concentrations (17 wt.%) are obtained with 4 mL of MAO solution, this linearly increases as larger volumes are used until a limiting value around 26 Al wt.% is reached at 6 mL. An incremental increase in the Al concentration is seen when the volume increases to 7 mL. The maximum Al wt.% on the silica supported used in this study is slightly higher compared to other commercial silica-supported metallocene catalysts previously reported.^{101, 113} Figure 3.2b shows the Zr concentrations of the supported catalysts after 8 h contact time which represents the highest measured Zr concentration value for the particular solution concentration. A qualitatively similar trend to the Al concentration is seen. The Zr concentration linearly increases up to around 0.6 Zr wt.% which was consistent with the maximum values reported for other silica-supported metallocene catalysts.^{102, 140}

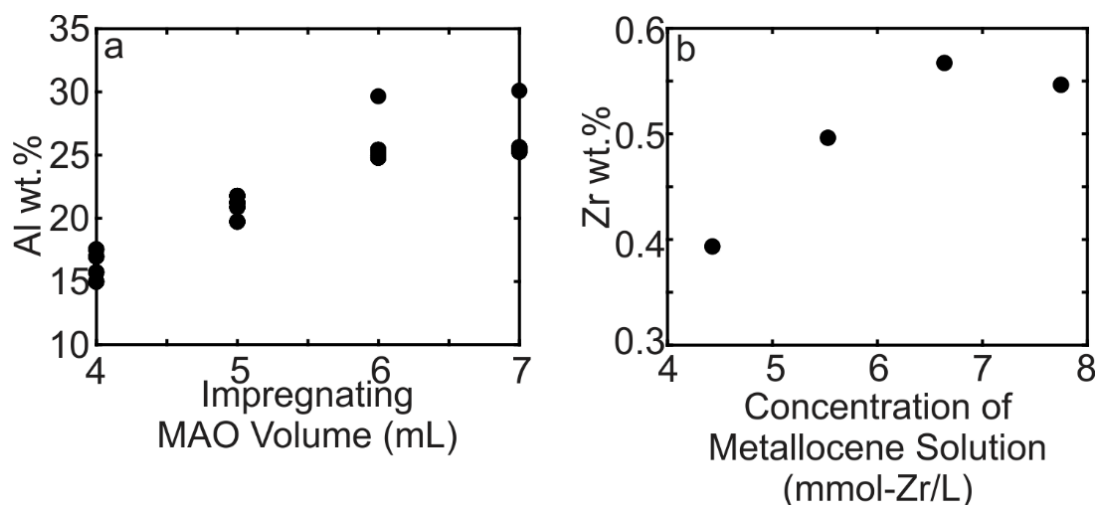


Figure 3.2. (a) Aluminum concentrations of supported catalysts prepared in varying volumes of MAO solution for 19 h. (b) Zirconium concentrations of supported catalysts prepared with varying solution concentrations after 8 h contact time.

Figure 3.3 shows the Zr concentration of the supported catalysts after different contact times between the MAO-modified silica and the metallocene solution. The Zr concentration increases from 1 h up to approximately 8 h to its maximum value after which a decrease is seen. This is seen regardless of the metallocene solution concentration. A similar dependence of Zr concentration on contact time was observed in Chapter 2. The decrease in Zr concentration at long contact times (> 12 h) was attributed to catalyst decomposition due to possible condensation reactions or poisoning.¹⁴⁰

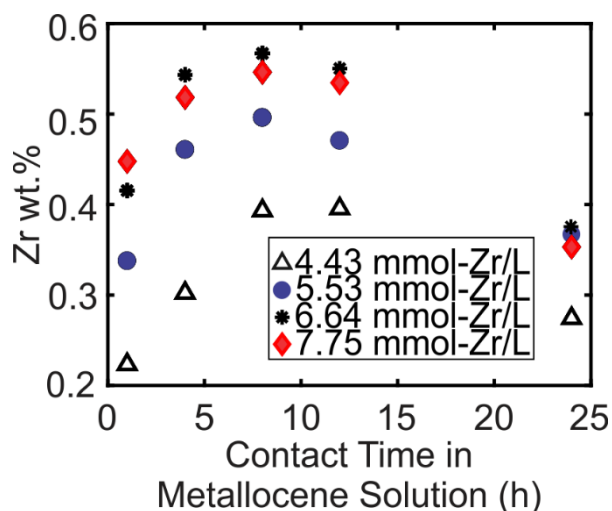


Figure 3.3. (a) Zirconium concentrations of supported catalysts prepared with varying solution concentrations.

The experimental results shown in Figures 3.2 and 3.3 demonstrate the importance of preparation conditions on the final composition of the supported catalysts. Both Al and Zr concentrations corresponding to immobilized MAO and metallocene reach a maximum value where further increase to either the MAO solution volume or metallocene solution concentration yields minimal changes. The dependence of active site distribution and contact time was previously demonstrated in Chapter 2. As the contact time between the silica and MAO solution is sufficiently high (19 h), it can be assumed that MAO is uniformly distributed. However, short contact times (1 h) lead to non-uniform distributions of metallocenes with higher concentrations near the surface of the particle.

3.3.2 Distribution of Active Sites

Intraparticle mass transfer resistance may lead to the immobilization of metallocene compounds in the area near the surface of the particle at short contact

times. We have previously shown in Chapter 2.3.2 that the distribution of active sites within the supported catalysts can be approximated with concentration ratios of Al and Zr (in wt.%) at the surface region and at the core region of a particle which was confirmed by elemental maps of the cross-section. The ratio of 1.0 indicates uniform distribution of the compound (MAO or metallocene) within the particle. The Al and Zr concentrations at the surface of the particle were measured using SEM-EDX which can only measure up to 1 micron depth. **Figure 3.4** shows the SEM image of Catalyst 6-1 and 5-1 and the associated EDX area scan results which indicate that both Al and Zr are present on the surface. It can be seen that the signals for Al and Zr are higher for Catalyst 6-1 and comprise a larger fraction of the overall spectra, indicating higher proportions of these elements are present.

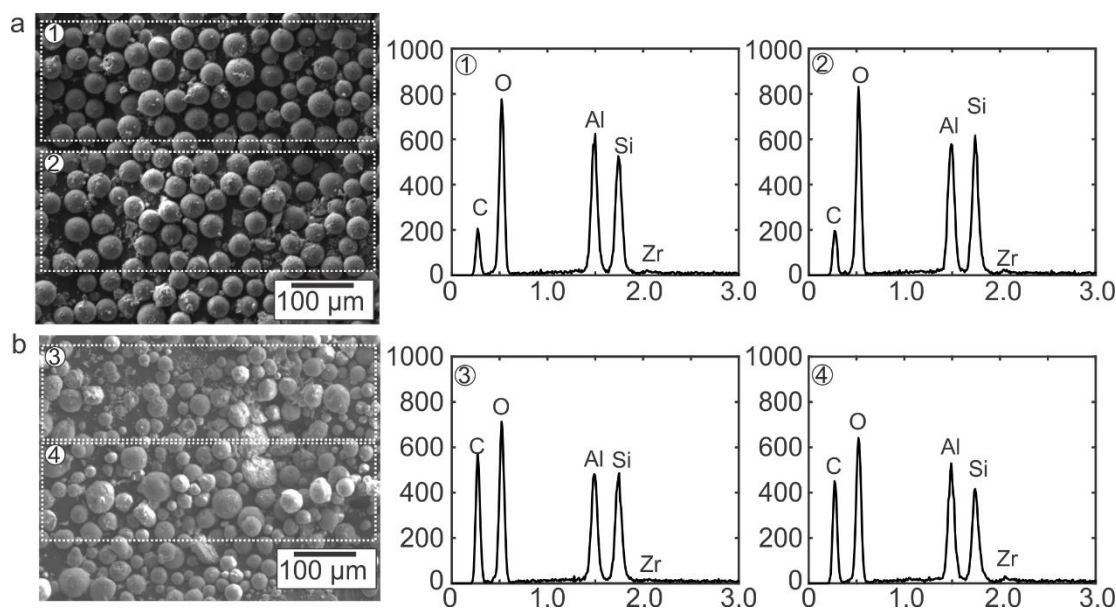


Figure 3.4. (a) SEM image of Catalyst 6-1. (b) SEM image of Catalyst 5-1. Numbers represent location of EDX area scan with corresponding EDX spectra.

Figure 3.5 shows the ratio of Al wt.% calculated from the Al concentrations measured from SEM-EDX to ICP-MS. These points represent the average of all catalysts prepared with the same MAO volume. It is seen that values around 1.10 are obtained, indicating a uniform distribution of MAO after 19 h of contact time.

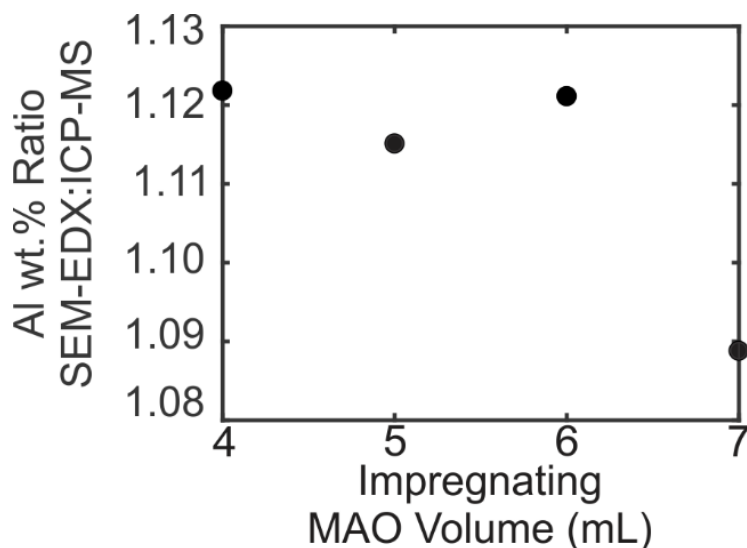


Figure 3.5. Ratio of Al wt.% measured by SEM-EDX to ICP-MS.

Figure 3.6 shows the concentration of Zr (from metallocene) of the prepared supported catalysts measured from SEM-EDX. Similar Zr concentrations are seen for the first 8 h of contact followed by a decrease after 24 h, similar to the removal of Zr observed by ICP-MS. Figure 3.6b illustrates how the ratio of Zr wt.% (i.e., Zr wt. % in the surface region/Zr wt.% in the core region) changes over time. This ratio at short contact time (1 h) between the MAO-modified silica and metallocene solution is 1.6~2.0 and almost double that at longer contact times (24 h) which is 1.0~1.2. These results indicate that the distribution of active sites is highly influenced by the contact time.

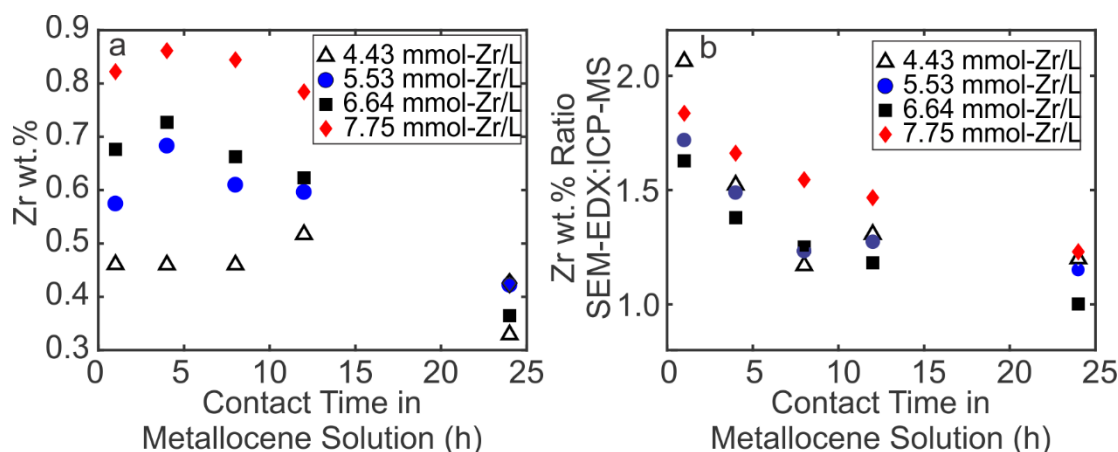


Figure 3.6. (a) Zirconium concentrations of supported catalysts prepared with varying solution concentrations measured by SEM-EDX. (b) Ratio of Zr wt.% measured by SEM-EDX to ICP-MS.

3.3.3 Pore Structures of Silica and Supported Catalysts

The pore structure of the silica particle is expected to change as the immobilization of MAO, which is used in excess amount, forms a layer that narrows the pores. Immobilized metallocenes are assumed to not significantly alter the pore structure since they are present in small amounts. **Figure 3.7** shows the nitrogen adsorption/desorption isotherms of the original P-10 silica and supported catalysts with the lowest Al concentration (Catalyst 4-8, 17 Al wt.%) and highest Al concentration (Catalyst 7-8, 25 Al wt.%). All are Type IV isotherms which is typical for silica structures.^{131, 248} It can be seen that the original silica has a steep H1 type hysteresis loop which indicates high pore uniformity and pore connectivity as well as agglomerates of uniform spheres.²⁴⁹ At higher MAO loading (e.g., 25 wt.%), the hysteresis loop becomes flatter and wider indicating the blocking of pores and a more disorganized pore space.²⁵⁰⁻²⁵² Similar observation was reported in the literature by

Alonso-Moreno et al.²⁵³ where the hierarchal MCM-41 structure became less ordered after the immobilization of MAO.

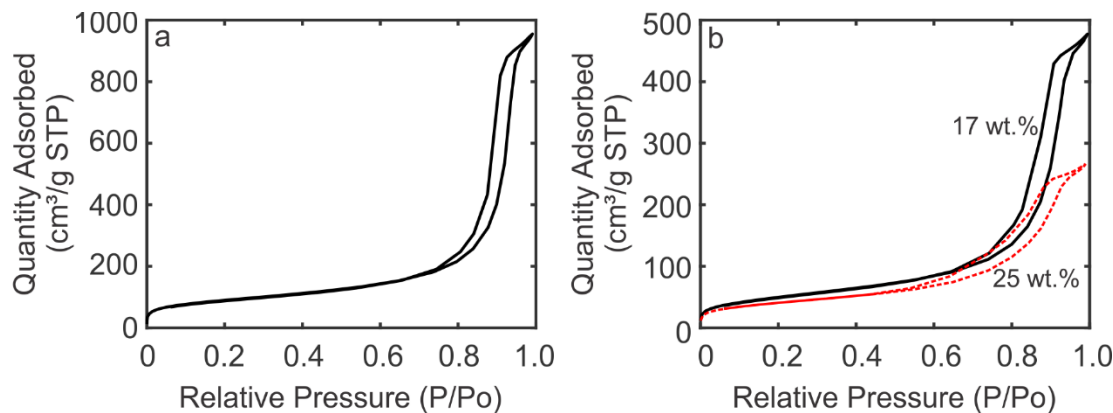


Figure 3.7. Adsorption-desorption isotherm of (a) original P-10 silica and (b) Catalyst 4-8 (17 wt.% Al) and 6-8 (25 wt.% Al).

Figure 3.8 shows the pore size distributions, average pore widths, surface areas, and pore volumes of the original silica and the prepared supported catalysts. Increased Al concentration within the catalyst (immobilized MAO) from 17 to 25 wt.%, corresponding to Catalysts 4-8, 5-8, 6-8, and 7-8, led to a successive reduction in the original pore size distribution. The average pore width decreased from 18 nm to approximately 11 nm. Likewise, the original pore volume and surface area of the silica (317 m²/g and 1.41 cm³/g respectively) significantly decreased to minimum values of 148 m²/g and 0.4 cm³/g.

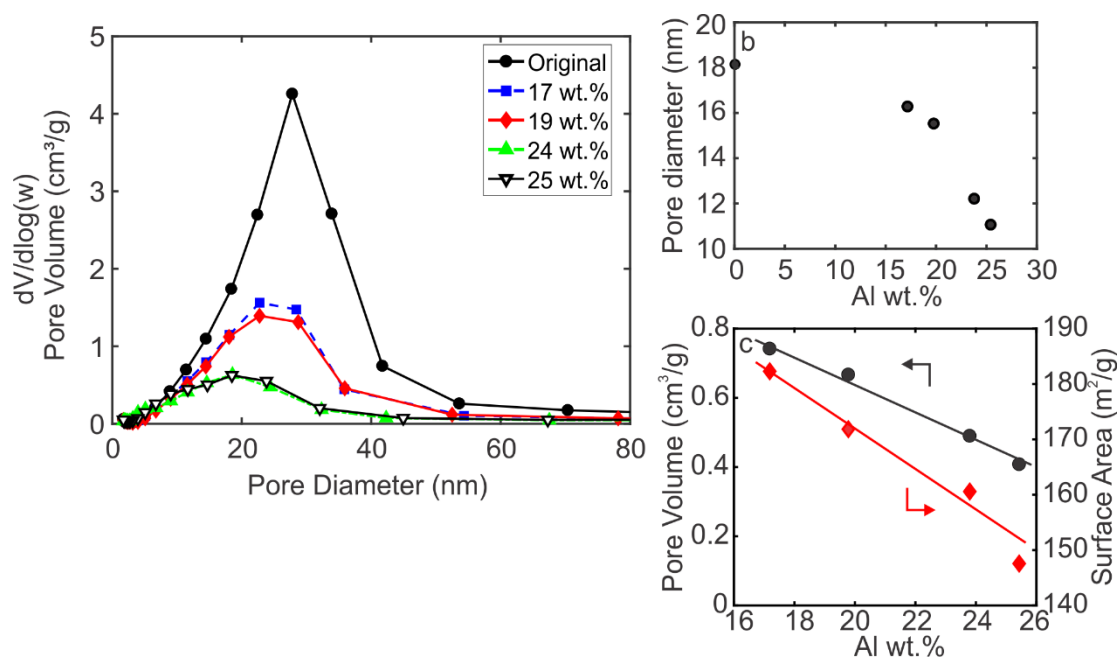


Figure 3.8. (a) Pore size distributions, (b) average pore widths, and (c) pore volumes and surface areas of the original silica and supported catalysts with various Al concentrations.

The results shown illustrates that the immobilization of MAO can significantly alter various properties of the original silica such as pore volume, pore size distribution, and surface area. It is seen that the initial pore size distribution is centered at approximately 30 nm, but it decreases to approximately 18 nm at the highest Al concentration (25 Al wt.%). MAO preferentially immobilizes in larger pores due to decreased mass transfer resistance until the compounds are unable to access smaller pores. The change in pore diameter represents the addition of a MAO layer with a maximum thickness of roughly 3.5 nm. These results are qualitatively similar to those obtained by Velthoen et al.¹⁰¹ where a different silica support (ES767) was used to prepare catalysts with up to 17 Al wt.%. McDaniel et al.²⁵⁴ prepared Cr/silica-titania catalysts with various pore volumes by coalescence of the silica aggregates and observed lower activities from catalysts with low pore volumes. However, this method

of decreasing pore volumes strengthened the particle and reduced fragmentation and is unknown whether the formation of MAO layer will have a similar effect.

3.3.4 Polymerization Activity

The supported catalysts prepared in our experimental study were used to perform both liquid slurry phase and gas phase polymerization of ethylene at 60°C for 1 hour. **Table 3.2** shows the measured time averaged catalyst activities in slurry phase polymerization. The first variables examined are the volume of MAO and metallocene solution concentration used during the preparation process. Catalysts prepared with higher MAO volumes/metallocene concentrations (order from lowest to highest: Catalysts 4-X, Catalysts 5-X, Catalysts 6-X, Catalysts 7-X, X being contact time with metallocene solution) have higher Al and Zr concentrations (Figure 3.2), leading to higher activity in terms of g-PE/g-cat.h during slurry phase polymerization. The second variable examined is the contact time between the MAO-modified silica and the metallocene solution. Catalysts prepared with longer contact times have higher Zr concentrations (Figure 3.3) and likewise higher activity (order from lowest to highest: Catalysts X-1, Catalysts X-4, Catalysts X-8, Catalysts X-12, Catalysts X-24, X being volume of MAO). Normalizing the time averaged polymerization rate to the amount of Zr adsorbed in the supported catalyst (g-PE/mmol-Zr.h) reveals that the catalyst activity in slurry phase ethylene polymerization is between 600 – 700 g-PE/mmol-Zr h. When accounting for the concentration of ethylene in the liquid phase ($[C_2H_4]_{slurry} = 0.291 \text{ mol L}^{-1}$), the catalyst activity is approximately $2.20 \times 10^3 \text{ g-PE/mmol-Zr} \cdot [C_2H_4]_{slurry} \cdot \text{h}$. Minimal difference is seen between the groups of catalysts with the same Al concentration (i.e., those prepared with the same volume of MAO).

Table 3.2. Polymerization activity of supported catalysts in slurry phase ^{a)}

Supported catalyst	Slurry phase polymerization activity (g-PE/g-cat.h)	Slurry phase polymerization activity (g-PE/mmol-Zr.h)	Slurry phase polymerization activity (g-PE/mmol-Zr. [C ₂ H ₄] _{slurry} .h)
4-1	18.26	744	2.56 x10 ³
4-4	22.07	665	2.28 x10 ³
4-8	24.61	569	1.96 x10 ³
4-12	22.31	513	1.76 x10 ³
4-24	20.69	687	2.36 x10 ³
5-1	22.20	598	2.06 x10 ³
5-4	31.22	617	2.12 x10 ³
5-8	37.16	682	2.34 x10 ³
5-12	31.91	617	2.12 x10 ³
5-24	26.97	669	2.30 x10 ³
6-1	28.26	619	2.13 x10 ³
6-4	33.17	555	1.91 x10 ³
6-8	38.82	623	2.14 x10 ³
6-12	34.52	571	1.96 x10 ³
6-24	25.66	636	2.19 x10 ³
7-1	40.98	833	2.86 x10 ³
7-4	36.28	637	2.19 x10 ³
7-8	40.89	681	2.34 x10 ³
7-12	34.90	594	2.04 x10 ³
7-24	27.88	718	2.47 x10 ³

^{a)} Reaction temperature: 60°C, Ethylene partial pressure: 39 psig.

Table 3.3 shows similar trends when the same supported catalysts are used in gas phase polymerization although overall activities are generally 50% lower compared to slurry phase reactions. The polymerization activity in terms of g-PE/mmol-Zr h is between 200 – 300 g-PE/mmol-Zr h. Based on the concentration in the gas phase ([C₂H₄]_{gas} = 0.097 mol L⁻¹), the polymerization activity is approximately 2.62 x 10³ g-PE/mmol-Zr.[C₂H₄]_{gas}.h. Interestingly, it is seen that Catalysts 7-X have on average lower activity in gas phase compared to Catalysts 6-X despite similar Al and Zr concentrations (Catalysts 6-X: Al wt.% 24.29, minimum Zr wt.% 0.42, Catalysts 7-X: Al wt.% 25.45, minimum Zr wt.% 0.45). Thus, the discrepancy in activity may be due

to the difference in the pore structure (Figure 3.8) where Catalysts 7-X have lower values of pore diameter (12 vs 11 nm), pore volume (0.49 vs 0.41 cm³/g), and surface area (160 vs 148 m²/g) compared to Catalysts 6-X. The difference in pore structure may lead to variation in the kinetic and thermal behavior of the catalysts during the reaction.

Table 3.3. Polymerization activity of supported catalysts in slurry phase ^{a)}

Supported catalyst	Gas phase polymerization activity (g-PE/g-cat.h) ^{c)}	Gas phase polymerization activity (g-PE/mmol-Zr.h)	Gas phase polymerization activity (g-PE/mmol-Zr. [C ₂ H ₄] _{slurry} .h)
4-1	5.60	228	2.35 x10 ³
4-4	9.09	274	2.82 x10 ³
4-8	9.76	226	2.33 x10 ³
4-12	9.22	212	2.19 x10 ³
4-24	5.03	167	1.72 x10 ³
5-1	9.38	253	2.61 x10 ³
5-4	11.40	225	2.32 x10 ³
5-8	11.35	208	2.15 x10 ³
5-12	10.33	200	2.06 x10 ³
5-24	8.13	202	2.08 x10 ³
6-1	14.15	310	3.20 x10 ³
6-4	17.48	293	3.02 x10 ³
6-8	22.80	366	3.77 x10 ³
6-12	17.88	296	3.05 x10 ³
6-24	11.30	280	2.89 x10 ³
7-1	18.62	378	3.90 x10 ³
7-4	15.15	266	2.74 x10 ³
7-8	14.53	242	2.50 x10 ³
7-12	12.06	205	2.12 x10 ³
7-24	9.45	244	2.51 x10 ³

^{a)} Reaction temperature: 60°C, Ethylene partial pressure: 50 psig.

3.3.5 Polymerization Kinetics of the Supported Catalysts

The instantaneous activity over the course of the reaction provides insight on the fragmentation behavior of the catalysts during polymerization. During slurry phase polymerization, ethylene in the gas phase will dissolve into the liquid diluent phase in a gas-liquid equilibrium. From Appendix I, it is shown that the mass transfer of

monomer from the gas to liquid phase occurs relatively quickly (~ 2 minutes) from the initial state ($[\text{C}_2\text{H}_4]_{\text{slurry}} = 0 \text{ mol L}^{-1}$) to the equilibrium state ($[\text{C}_2\text{H}_4]_{\text{slurry}} = 0.291 \text{ mol L}^{-1}$) at constant pressure (50 psig). As the polymerization progresses, the concentration of ethylene dissolved in liquid will decrease, leading to a drop in the reactor pressure. Thus, the flow of ethylene gas to the reactor in order to maintain the pressure of 50 psig as explained in Chapter 2.3.4 can be used to measure the polymerization kinetics.

Figure 3.9 shows the kinetic profiles in slurry phase polymerization using Catalysts 6-X and Catalysts 7-X. It is seen that when normalized to the Zr content and the concentration of ethylene in liquid, Catalysts 7-X have higher overall activities. For both sets of catalysts, the time between the ethylene gas dissolving into the liquid at the start of the reaction (2 minutes) and when maximum activity is reached, hereby referred to as induction time, is approximately 20 minutes. Interestingly, Figure 3.9b shows that there is a subtle dependence between the induction time and the contact time between the MAO-modified silica and the metallocene solution. Catalyst 7-8 with 8 h contact time with the metallocene solution has a ~ 20 minutes induction time compared to Catalyst 7-1 with 1 h contact time with the metallocene solution which has an induction time ~ 30 minutes.

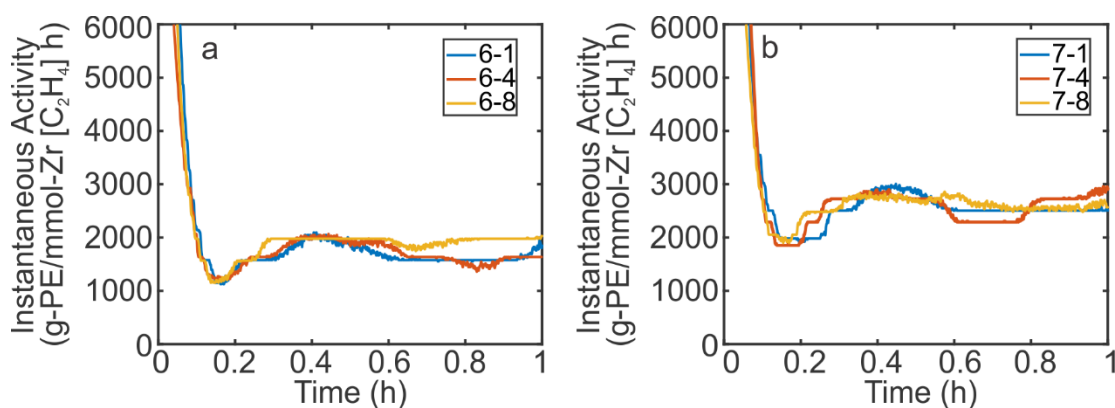


Figure 3.9. Kinetic profiles of (a) Catalysts 6-X and (b) Catalysts 7-X during slurry phase polymerization. X represents the contact time between MAO-modified silica and metallocene solution.

Figure 3.10 shows the kinetic profiles of the same catalysts when used in gas phase polymerization. Similar to slurry phase polymerization, higher overall activities are obtained with Catalysts 7-X. However, the activities of Catalysts 7-X continually decrease after 30 minutes of reaction while those of Catalysts 6-X remain relatively constant. Interestingly, a dependence on the induction time on the contact time is also seen. However, this influence is opposite of that observed for slurry phase reactions where shorter contact times between the MAO-modified silica and the metallocene solution led to a shorter induction time during the reaction.

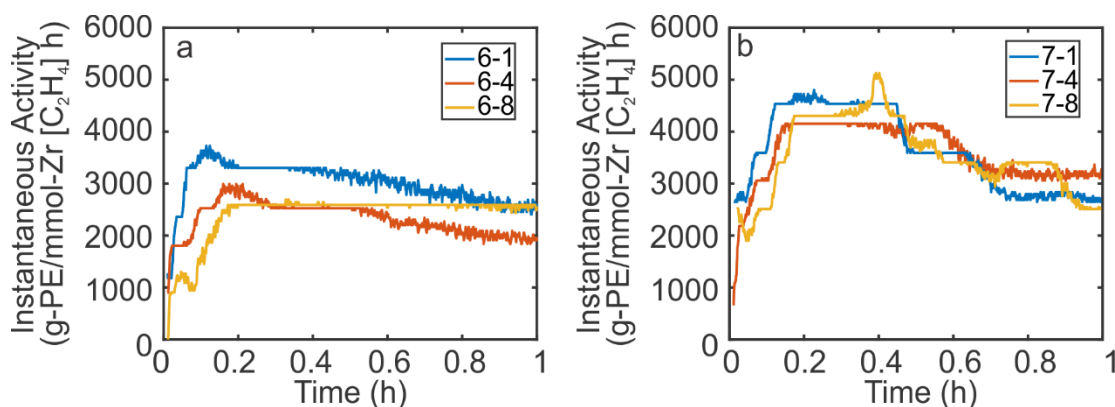


Figure 3.10. Kinetic profiles of (a) Catalysts 6-X and (b) Catalysts 7-X during gas phase polymerization. X represents the contact time between MAO-modified silica and metallocene solution.

Differences between slurry and gas phase polymerization are apparent from the polymerization kinetics. When normalized to the Zr content and the concentration of ethylene in the bulk phase, it is shown that the gas phase activity is $\sim 30\%$ higher compared to the slurry phase. A possible explanation can be found from the sorption

effect where the concentration of monomer in the semicrystalline polymer surrounding the active site can be higher than that in the bulk gas phase.^{242, 255, 256}

Induction time is affected by a variety of factors including mass transfer resistance based on larger particle sizes,^{209, 257, 258} lower concentration of active sites at the surface and more gradual fragmentation,¹⁷⁴ and the presence of a thick polymer layer at the surface caused by non-uniform distribution of catalytic compounds.^{214, 259, 260} In slurry phase polymerization, Catalyst 7-1 has a longer induction time compared to Catalyst 7-8 while the difference between Catalyst 6-1 and 6-8 is negligible. Due to the shorter contact time with the metallocene solution, Catalyst 7-1 has lower Zr contents with higher concentrations near the surface. The comparatively low number of active sites may lead to slower fragmentation of the catalyst and a longer reaction time to totally expose the active sites for polymerization. However, in gas phase polymerization both Catalyst 6-1 and Catalyst 7-1 had shorter induction times compared to Catalyst 6-8 and Catalyst 7-8. The higher concentrations of Zr near the surface of Catalyst 6-1 and Catalyst 7-1 may allow gaseous monomer to more easily access the active sites quickly reach the maximum activity.

It is also seen that despite similar Al and Zr content within Catalysts 6-X and Catalysts 7-X, polymerization activities with Catalysts 7-X were higher. As aforementioned, Catalysts 7-X have more narrow pore diameters and smaller surface areas and pore diameters compared to Catalysts 6-X. The surface area impacts the active site density which has been reported to affect polymerization activity. For instance, Silveira et al.²¹⁹ proposed that a high concentration of Zr active sites per area increased activity in polymerization of ethylene and reduced the effect of poisoned

active sites. In addition, the thicker MAO layer present in Catalysts 7-X may enhance the activity of the immobilized metallocenes.

3.3.6 Temperature Profiles During Polymerization Reaction

The temperature profile during the reaction can also give insight into the progression of fragmentation and exposure of active sites. Again, both sets of Catalysts 6-X and Catalysts 7-X are examined. **Figure 3.11** shows the temperature for both cases within the reactor during slurry phase polymerizations remains relatively constant throughout the reaction.

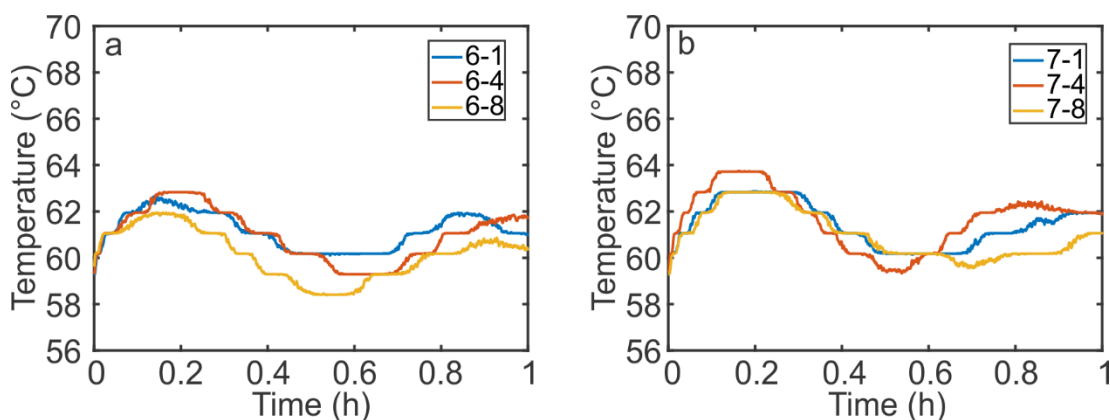


Figure 3.11. Reactor temperature of (a) Catalysts 6-X and (b) Catalysts 7-X during slurry phase polymerization. X represents the contact time between MAO-modified silica and metallocene solution.

Figure 3.12 shows the reactor temperature in gas phase polymerization for Catalysts 6-X and Catalysts 7-X. While the temperatures for Catalysts 6-X rise approximately 2~4°C within the initial 10 minutes of reaction, a 5~10°C increase is seen for Catalysts 7-X within 20 minutes into the reaction which roughly corresponds to the induction time needed to reach the maximum instantaneous activity. It is also

seen that the temperature rise in Catalysts 7-X is in the order of Catalyst 7-1, Catalyst 7-4, and Catalyst 7-8 from least to highest. This order also corresponds to the shift from non-uniform distribution to uniform distribution of active sites as well as total Zr content within the catalyst.

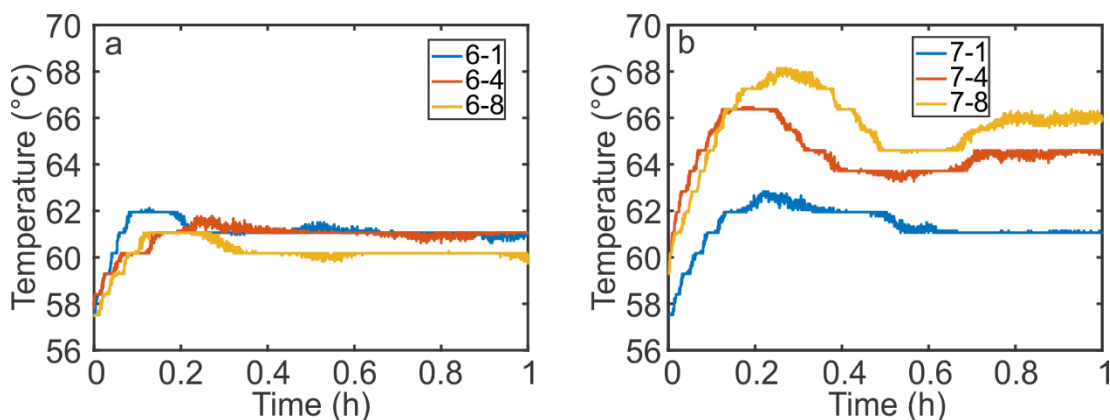


Figure 3.12. Reactor temperature of (a) Catalysts 6-X and (b) Catalysts 7-X during gas phase polymerization. X represents the contact time between MAO-modified silica and metallocene solution.

The ability to regulate temperature and remove heat with the presence of the liquid diluent is one of the main differences between slurry and gas phase reactions. A subtle relation between the kinetic induction time and time to reach the maximum temperature is seen with both being similar. As the amount of catalyst within the reactor is small (0.1 g), it was expected that any thermal deviation from the reaction temperature would be minimal. However, it is seen that the temperatures for Catalysts 7-X during gas phase polymerization were significantly higher. This temperature rise can be detrimental and cause overheating of the particle. Tioni et al.²⁶¹ showed that a change in the reactor gas temperature from 80°C to 100°C during gas phase ethylene polymerization resulted in the calculated particle surface temperature of almost 135°C.

Meanwhile, Roos et al.²⁴¹ and Wu et al.²⁶² found that deactivation of the supported catalyst increased at higher gas phase reaction temperature. As the temperatures remain at elevated levels for the entirety of the reaction, they may be the cause of the decrease in instantaneous activity seen for Catalysts 7-X in gas phase (Figure 3.10).

3.3.7 Polymer Morphology from the Supported Catalysts

The kinetic and temperature profiles of the two cases illustrate different polymerization rate behaviors based on the contact time between the MAO-modified silica and the metallocene solution. It is expected that this difference would result in variations in polymer morphology. **Figure 3.13** shows the SEM images of polyethylene particles after 1 hour in slurry phase at 60°C produced from Catalysts 6-X. Figure 3.13a shows that the polymer particles from Catalyst 6-1 have grown to between 75 – 125 μm . Large macropores and small silica fragments approximately 2 μm in size are seen throughout the surface of the particle. Polymer particles produced from Catalyst 6-4 are between 100 – 150 μm . While similar silica fragments to those seen from Catalyst 6-1 are seen on the surface of the particle, more polymer are seen within the macropores. Catalyst 6-8 with the highest Zr concentration produced polymer particles around 125 – 200 μm .

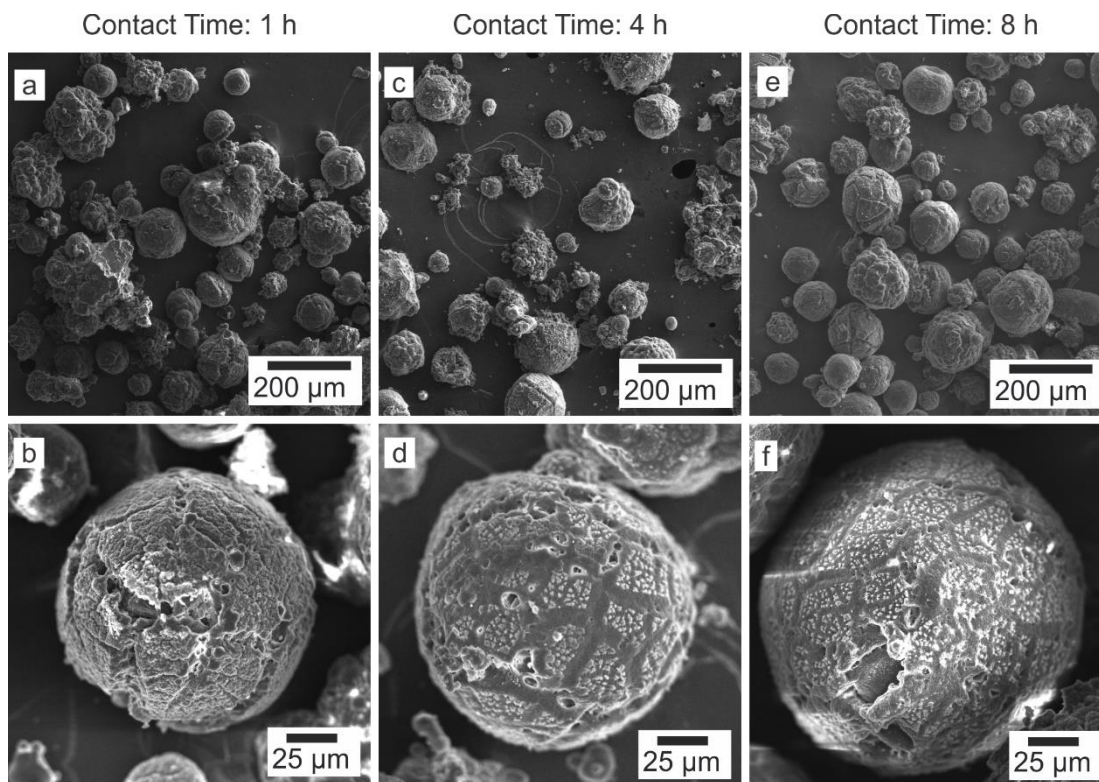


Figure 3.13. SEM images of polyethylene particles after 1 hour of slurry phase reaction with supported catalysts: (a,b), Catalyst 6-1; (c,d), 6-4; (e,f), Catalyst 6-8.

Figure 3.14 illustrates SEM images of the polyethylene particles obtained with Catalysts 7-1, 7-4, and 7-8 with varying distributions of active sites. While the polymer particles from Catalyst 7-1 are similar sized to those produced from 6-1, the surface morphology is more rough with irregularly shaped globules. No silica fragments are seen on the surface of the particle. Fine particles approximately 50 μm are seen in addition to larger particles ($\sim 175 \mu\text{m}$) for polymer produced from Catalyst 7-4. Although most of the large particles are intact, large fractures are seen on the surfaces, indicating the expansion of the polymer particle. Increasing fractions of smaller fine particles and larger fractures within the polymer particles are seen for Catalyst 7-8.

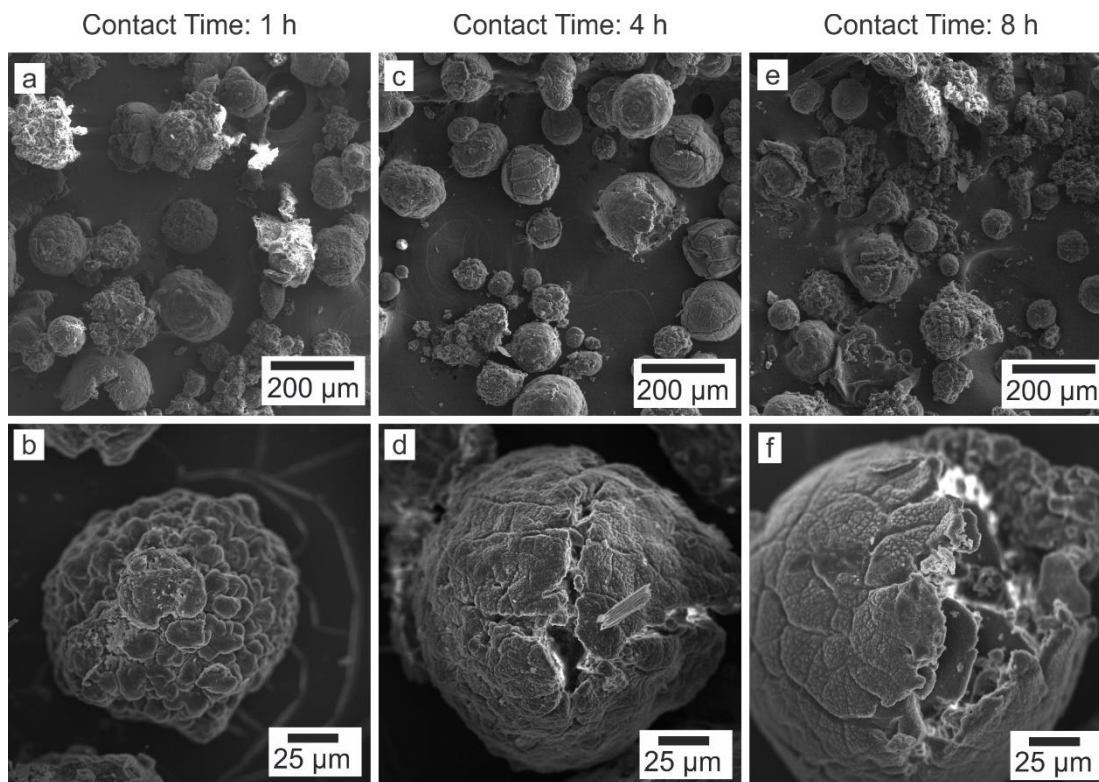


Figure 3.14. SEM images of polyethylene particles after 1 hour of slurry phase reaction with supported catalysts: (a,b), Catalyst 7-1; (c,d), 7-4; (e,f), Catalyst 7-8.

Inherent differences between gas and slurry phase reactions lead to variations in polymer morphology that are more directly dependent on the supported catalyst used. **Figure 3.15** shows SEM images of polyethylene particles produced in gas phase polymerization from Catalysts 6-X. Polymer particles from Catalyst 6-1 are a mix of small fragments and particles that experienced expansion near the surface and minimal growth in the center. The surfaces of these open particles are made up of fibrillar polymer bundles directly from active sites on silica fragments. For catalysts prepared with longer contact times (Catalyst 6-4 and 6-8), lower fractions of small fragments are seen, and larger particle sizes with a more spherical shape are observed.

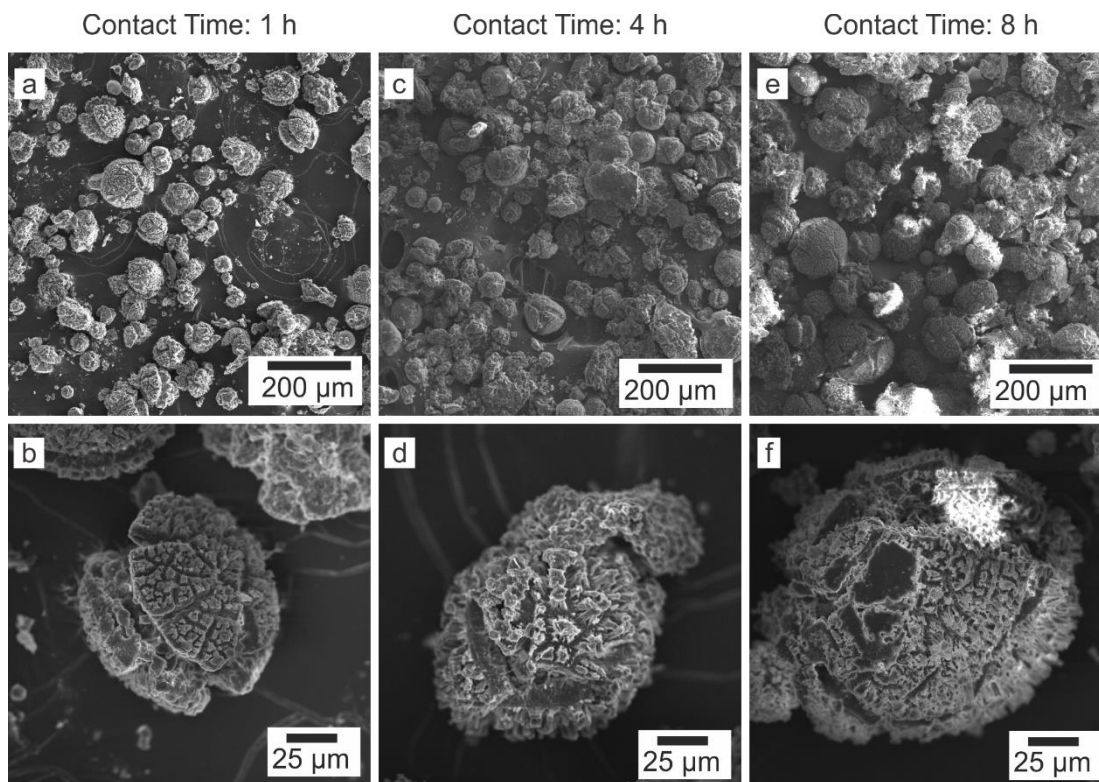


Figure 3.15. SEM images of polyethylene particles after 1 hour of gas phase reaction with supported catalysts: (a,b), Catalyst 6-1; (c,d), 6-4; (e,f), Catalyst 6-8.

Figure 3.16 shows that Catalysts 7-X show subtle differences in the final polymer morphologies compared to those seen in Figure 3.15. A much higher fraction of fine particles is seen after Catalyst 7-1 was used in gas phase polymerization with larger fragments approximately 30 – 75 μm in diameter and fine particles between 5 – 10 μm . Longer contact times and more uniform distribution of active sites lead to successively smaller fragments (10 – 20 μm for Catalyst 7-4 and 8 μm for Catalyst 7-8) and higher fractions of these fragments.

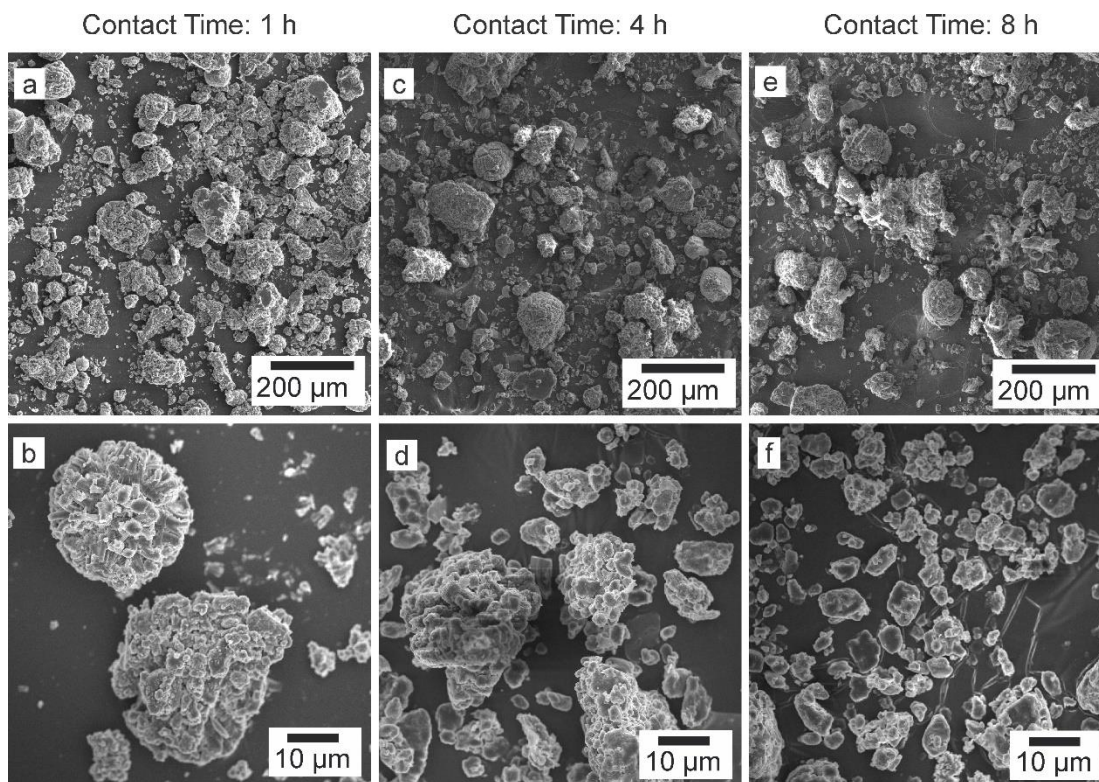


Figure 3.16. SEM images of polyethylene particles after 1 hour of gas phase reaction with supported catalysts: (a,b), Catalyst 7-1; (c,d), 7-4; (e,f), Catalyst 7-8.

The particle morphologies reflect the trends observed in overall activity, kinetic data profiles, and temperature change during the reaction. For both slurry and gas phase reactions, polymer formed at the active sites builds up within the pores and exerts pressure on the surrounding pore walls and leads to stress until the particle fragments.^{163, 178, 247, 263} It is shown that in slurry phase reactions, the shift from non-uniform distribution of active sites to uniform distribution of active sites increased the amount of polymer formed within the macropores, leading to larger overall particles for from Catalysts 6-X. While larger polymer particles obtained with catalysts prepared with longer contact times are also seen for Catalysts 7-X, large fractures are seen at the surface along with smaller catalyst fragments. It is also shown that Catalysts 7-X

experienced significant fragmentation in gas phase polymerization with large fractions of fine particles. Higher extents of fragmentation compared to Catalysts 6-X are seen with progressively smaller polymer particles as the location of active sites shifts to a more uniform distribution. Thermal deactivation of the active sites on these fine particles might have occurred due to the high temperature deviation and halted their growth. This would explain the decrease in activity seen from Catalyst 7-4 and 7-8 compared to 7-1 as the fraction of fine particles formed increased. A more gradual fragmentation and exposure of the interior active sites to start polymerization leads to a lower temperature deviation for Catalysts 6-X particles. This corresponds to the conclusion reached by Kosek et al.²⁴³ via dynamic simulation where overheating of catalyst particles can be reduced by slowly exposing the active sites. However, the reason for why Catalysts 6-X particles experienced a slower fragmentation while Catalysts 7-X particles experienced a more rapid fragmentation is not clear. As the Zr concentration of both cases are similar, we propose that this difference in fragmentation behavior is based on the pore diameters which in turn is based on the Al concentration. With a decreased pore diameter, it is possible that the catalyst particle became more susceptible to fragmentation during the reaction and led to uncontrolled fragmentation. Not only are the MAO compounds in closer vicinity to the active site and promote activity, but less void space is available for the polymer chains to grow before contacting with neighboring chains or the opposite pore wall (**Figure 3.17**).

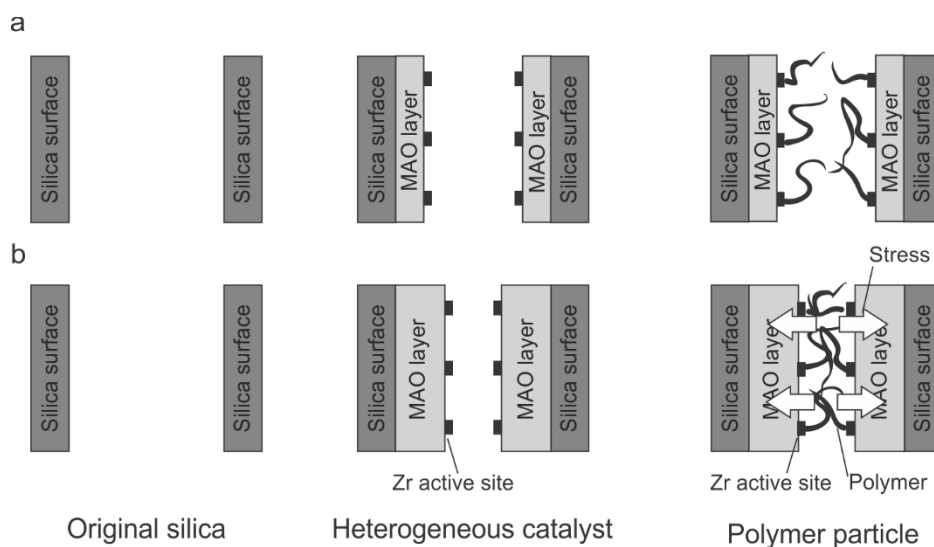


Figure 3.17. Schematic of how (a) less MAO adsorbed (b) more MAO adsorbed affects the pore structure of the silica and lead to fragmentation.

3.4. Concluding Remarks

In this study, supported catalysts prepared with different distributions of active sites and pore diameters through different Al concentrations or amount of immobilized MAO. It is shown that Zr concentration increased with the contact time between the MAO-modified silica and the metallocene solution. In addition, longer contact times led to a more uniform distribution of active sites throughout the particle. As the amount of immobilized MAO increased, the pore diameter progressively constricts. When these catalysts were used in both slurry and gas phase polymerization of ethylene, similar activity in terms of g-PE/mmol-Zr.[C₂H₄].h were obtained. However, contrary trends were observed in the kinetic profiles despite the use of identical catalysts. The induction time between the start of the reaction and the maximum activity increased as the distribution of active sites transitioned to be more uniform in slurry phase while it decreased in gas phase. Observed polymer particle morphologies were qualitatively

consistent with the trends seen from the kinetic profiles of both phases. Despite similar Zr concentrations, larger fractions of fine particles were observed in both slurry and gas phase polymerization from prepared catalysts with a narrower pore diameter. The results demonstrate the need to prepare the supported catalysts for the intended reaction phase. Immobilizing the maximum amount of MAO may adversely contribute to the formation of fine particles and further study is needed to clarify their effects on the fragmentation process.

Chapter 4. Mathematical Modelling of the Catalyst Preparation Process

4.1 Introduction

In industrial α -olefin polymerization processes, heterogenization of metallocene compounds and the coactivator methylaluminoxane (MAO) on porous silica microparticles leads to several important benefits such as greater control of polymer particle morphology and reduction of reactor fouling,⁹⁵⁻⁹⁹ decrease in the amount of external cocatalysts,¹⁰⁰⁻¹⁰⁴ and the ability to be used in both liquid slurry and gas-phase processes.^{105, 228} Although some loss of catalyst activity by the heterogenization of metallocene on inert carrier materials is inevitable, sufficiently high catalyst activity is readily obtainable with heterogeneous or solid-supported metallocene catalysts for commercial manufacturing of polyolefins. Thus, the preparation of highly efficient solid-supported metallocene catalysts is one of the key elements in the successful operation of an olefin polymerization process.

In Chapter 2 and Chapter 3, we demonstrated that the preparation of supported catalysts will significantly impact the total concentrations and distributions of MAO and metallocene compounds within the P-10 silica particle. These two factors were shown to influence the ultimate catalyst performance during polymerization. However, polymerization activity have been reported to be affected by several physical attributes of the silica support including particle size,^{135, 136, 209} porosity,^{173, 211, 213, 254} and average pore size and pore size distribution.^{121, 123, 129, 264} Inconsistencies in the catalyst performances are frequently observed and even for the same metallocene catalyst, the direct comparison of catalyst performances between different studies is often difficult.

This is due to the variance in the choice of silica support, catalyst solution concentrations, and contact time between the support and catalytic solutions which contributes to differences.

In this chapter, we present the experimental and theoretical modeling studies on the catalyst impregnation process by focusing on the effects of intraparticle mass transfer of MAO and metallocene using a separate silica support (2408HT, WR Grace). Silica-supported catalysts were prepared by varying the volumes of the MAO solution, the contact times between the calcined silica and the MAO solution, the concentrations of the metallocene solution, and the contact times between the MAO-modified silica and the metallocene solution to observe if similar behavior seen in Chapter 2 and 3 are replicated. The overall Al and Zr concentrations, corresponding to the amount of immobilized MAO and metallocene, in the silica-supported catalysts were analyzed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The Al and Zr concentrations of exterior surface region of the catalysts were also analyzed with energy-dispersive X-ray spectroscopy (SEM-EDX). A mathematical model for the intraparticle catalyst impregnation process has been developed and the model simulation results are compared with the experimental data.

4.2 Experimental

4.2.1 Preparation of Supported Catalysts

Details of the preparation of the supported catalysts have been described in Chapter 2.2.1 and Chapter 3.2.1. In this chapter, the silica support used is the commercially available 2408HT[®] silica (WR Grace) with an average surface area of

313.4 m²/g, a pore volume of 1.53 cm³/g, an average pore width of 30 nm, and an average particle size of 32 μm (Data provided by WR Grace). To study the dynamic adsorption behavior, the silica and MAO solution was mixed at 110°C for various amounts of contact time (1, 4, 8, 12 and 19 h) to obtain MAO-modified silicas. The MAO-modified silica with the contact times of 1 and 19 h in MAO solution were chosen to contact with metallocene solutions at different durations in order to study the metallocene adsorption/complexation behavior on MAO-modified silica. According to the literature, the contact time of 1 h with MAO solution has been commonly employed but the exact spatial (or radial) distribution of MAO in silica particles was not always analyzed in detail.¹³⁴⁻¹³⁶ The volumes of MAO solution used were also varied between 2.7 to 8 mL, corresponding to 2.69 to 7.97 mmol of Al in solution, to observe their effect. The catalyst preparation conditions are listed in **Table 4.1**.

Table 4.1. Preparation conditions of supported catalysts

Supported catalyst ^{a)}	Volume of MAO solution (mL) ^{b)}	Total Al in solution (mmol)	Concentration of metallocene solution (mmol/L) ^{c)}	Total Zr in solution (μmol)	Time in MAO solution (h)	Time in metallocene solution (h)
2.7-1-1	2.7	2.69	3.00	17.93	1	1
2.7-1-8	2.7	2.69	3.00	17.93	1	8
2.7-19-1	2.7	2.69	3.00	17.93	19	1
2.7-19-4	2.7	2.69	3.00	17.93	19	4
2.7-19-8	2.7	2.69	3.00	17.93	19	8
2.7-19-12	2.7	2.69	3.00	17.93	19	12
2.7-19-24	2.7	2.69	3.00	17.93	19	24
4-1-1	4	3.98	4.43	26.56	1	1
4-1-4	4	3.98	4.43	26.56	1	4
4-1-8	4	3.98	4.43	26.56	1	8
4-1-12	4	3.98	4.43	26.56	1	12
4-1-24	4	3.98	4.43	26.56	1	24
4-19-1	4	3.98	4.43	26.56	19	1
4-19-4	4	3.98	4.43	26.56	19	4
4-19-8	4	3.98	4.43	26.56	19	8

4-19-12	4	3.98	4.43	26.56	19	12
4-19-24	4	3.98	4.43	26.56	19	24
4-4-0	4	3.98	0	0	4	0
4-8-0	4	3.98	0	0	8	0
4-12-0	4	3.98	0	0	12	0
5-1-1	5	4.98	5.53	33.20	1	1
5-1-4	5	4.98	5.53	33.20	1	4
5-1-8	5	4.98	5.53	33.20	1	8
5-1-12	5	4.98	5.53	33.20	1	12
5-1-24	5	4.98	5.53	33.20	1	24
5-19-1	5	4.98	5.53	33.20	19	1
5-19-4	5	4.98	5.53	33.20	19	4
5-19-8	5	4.98	5.53	33.20	19	8
5-19-12	5	4.98	5.53	33.20	19	12
5-19-24	5	4.98	5.53	33.20	19	24
5-4-0	5	4.98	0	0	4	0
5-8-0	5	4.98	0	0	8	0
5-12-0	5	4.98	0	0	12	0
8-1-1	8	7.97	8.85	53.12	1	1
8-1-8	8	7.97	8.85	53.12	1	8
8-19-1	8	7.97	8.85	53.12	19	1
8-19-4	8	7.97	8.85	53.12	19	4
8-19-8	8	7.97	8.85	53.12	19	8
8-19-12	8	7.97	8.85	53.12	19	12
8-19-24	8	7.97	8.85	53.12	19	24

^{a)}Silica used: 0.5 g; ^{b)}Concentration of MAO solution: 7 wt.% ^{c)}Volume of metallocene solution used: 6 mL

4.2.2 Characterization of Supported Catalyst and Polymer

The overall composition (Al and Zr concentrations) of the silica-supported catalyst particles was measured with Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Thermo Scientific Element 2). The samples were prepared with the procedure detailed in Section 2.2.3.

The exterior morphologies of the prepared silica-supported catalyst particles and subsequent polymer particles produced were investigated by scanning electron microscopy (SEM) with the procedure detailed in Section 2.2.3.

4.2.3 Slurry Phase Polymerization of Ethylene

The prepared catalysts detailed in Table 4.1 were used in slurry phase polymerization of ethylene. Further details of the polymerization procedure are detailed in Section 3.2.4.

4.3 Results and Discussion

4.3.1 Overall Catalyst Composition

The four variables of catalyst preparation conditions varied in our experiments were: volume of MAO solution, concentration of metallocene solution, contact time between the MAO solution and silica particles, and contact time between the metallocene solution and MAO-modified silica particles. Overall concentrations of Al and Zr in the silica particles prepared by different impregnation conditions were measured.

The Al concentration in MAO-modified silica (wt. % in silica) prepared with the conditions listed in Table 4.1 are shown in **Figure 4.1** which shows that high Al concentrations (12-13 wt.%) was obtained after a short contact time of 1 h. Similar observations with 1 h contact time were reported in the literature.^{114, 216, 265} Further increase in the Al concentration to 16-18 wt.% is observed as the contact time is lengthened and the limiting value of Al wt.% is reached after 12 h. Figure 4.1b shows

that the Al concentration in silica increases with the volume of MAO solution but the increase is not significant, suggesting that the saturation condition has already been established for the MAO solution volume used. However, similar rise in the Al concentration is seen for longer contact times for all cases.

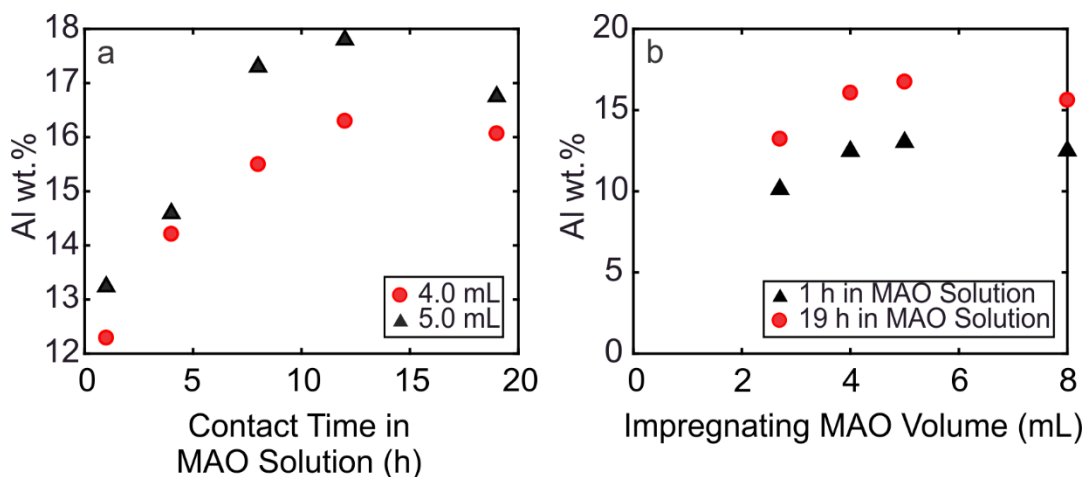


Figure 4.1. (a) Aluminum wt.% in MAO-modified silica based on silica-MAO solution contact time; (b) Aluminum wt.% in MAO-modified silica based on the volume of MAO solution used for impregnation.

Figure 4.2 shows the Zr concentration of supported catalysts prepared with the MAO-modified silica under the conditions listed in Table 4.1. While high Zr concentrations are obtained after a short contact time (1 h), they reach a maximum value after 8 h of contact time after which a decrease is seen. The similar trend was reported in the literature and the decrease in Zr content was attributed to catalyst decomposition and the leaching of the degenerated product.¹⁴⁰ This behavior is seen regardless of the Al (MAO) concentration within the MAO-modified silica. Figure 4.2c shows the increasing Zr concentrations with higher concentration of metallocene solution in contact with the MAO-modified silica.

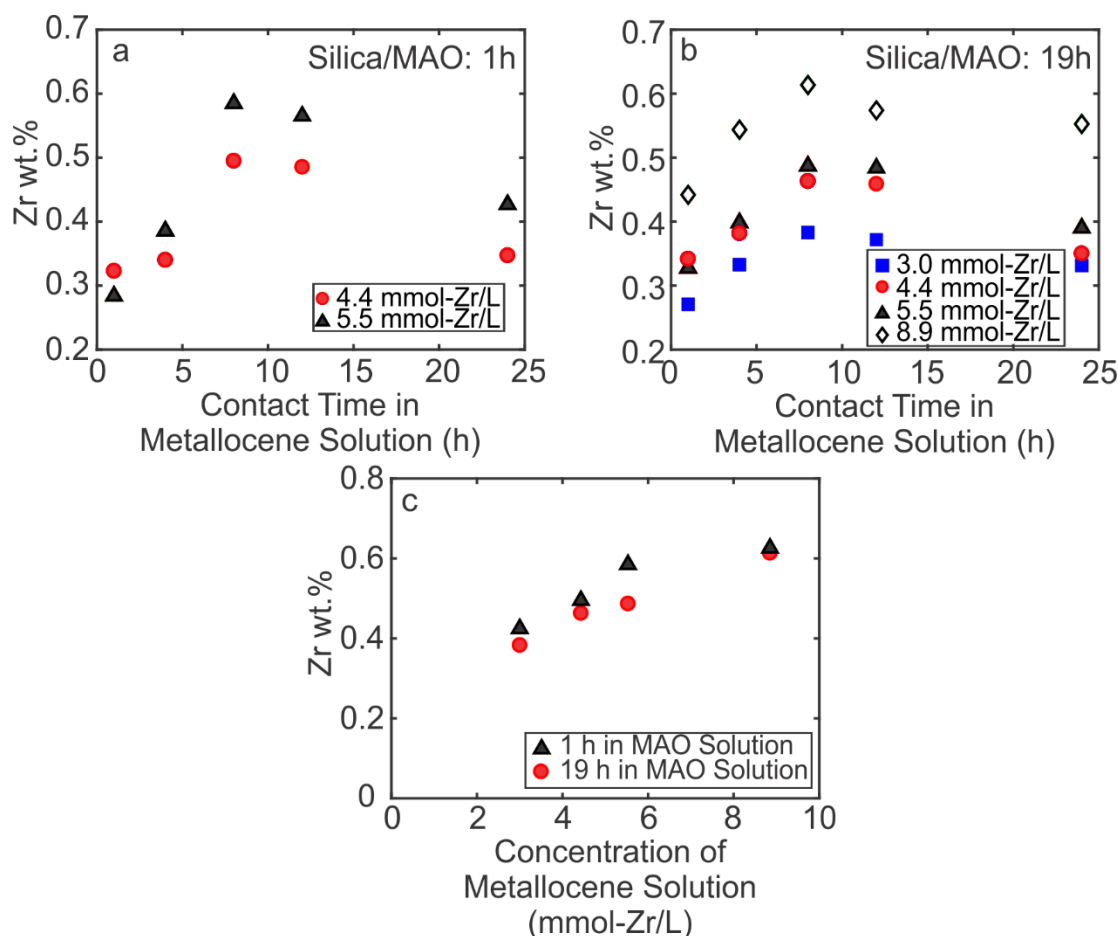


Figure 4.2. Zr wt. % vs. contact time of MAO modified silica for (a) contact time, 1 h and (b) contact time, 19 h with metallocene solution with different metallocene solution concentrations; (c) Zr wt. % vs. the concentration of metallocene solution for 1 h and 19 h contact time between MAO and silica.

The experimental results shown in Figure 4.1 and Figure 4.2 indicate that the Al concentration (corresponding to MAO) and Zr concentration (corresponding to metallocene) of the supported catalysts are dependent on two major factors: contact time between particles and solute solution and the amount of solutes in the solution (i.e. volume or concentration). Although high Al and Zr concentrations were obtained at short contact times (1 h), longer contact times led to increased immobilization of Al and Zr. The data shown in Figures 4.1 and 4.2 suggests that the catalyst impregnation

conditions need to be well designed to ensure consistent performance of the silica-supported catalysts. It is also to be noted that the Al and Zr concentrations in silica supports represent the overall amount, but it is quite possible that their intraparticle distributions may not be uniform and dependent on the preparation conditions.

4.3.2 Catalyst Distribution in the Particle Surface Region

We hypothesize that the spatial or radial (if particles are assumed to be spherical) distribution of the solute (MAO or metallocene) is dependent on the contact time between the silica support and their respective solutions. If there were a strong intraparticle mass transfer resistance for the catalytic compounds, solutes within the solution may diffuse and immobilize in the areas closer to the interface between the bulk solution and the external silica surface at short contact times. If such non-uniform distribution of catalyst components occurs, it can affect the overall catalytic activity as well as the resulting polymer particle morphology. Higher concentration of MAO in the external surface region of the silica has been reported to cause uneven fragmentation of catalyst particles and low bulk density of the polymer formed.^{101, 134, 210, 213, 214} With longer contact times between the silica particles and catalyst solutions (MAO solutions and metallocene solutions), more effective penetration and immobilization of Al and Zr are expected and higher catalyst activity can be obtained.

To determine the Al and Zr concentrations at the particle surface, we used scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX). As the penetration depth of the X-ray is around one micron, the results represent the composition at the outer edges of the silica-supported catalyst particle. Approximately

200 particles were analyzed in this way for each preparation condition to obtain the Al and Zr content. **Figure 4.3** shows an SEM image of supported catalyst particles and the EDX area scan results for the four particle groups marked in the SEM image. The elemental spectrums indicate that both Al and Zr are present on the supported catalysts and they are consistent for all particles.

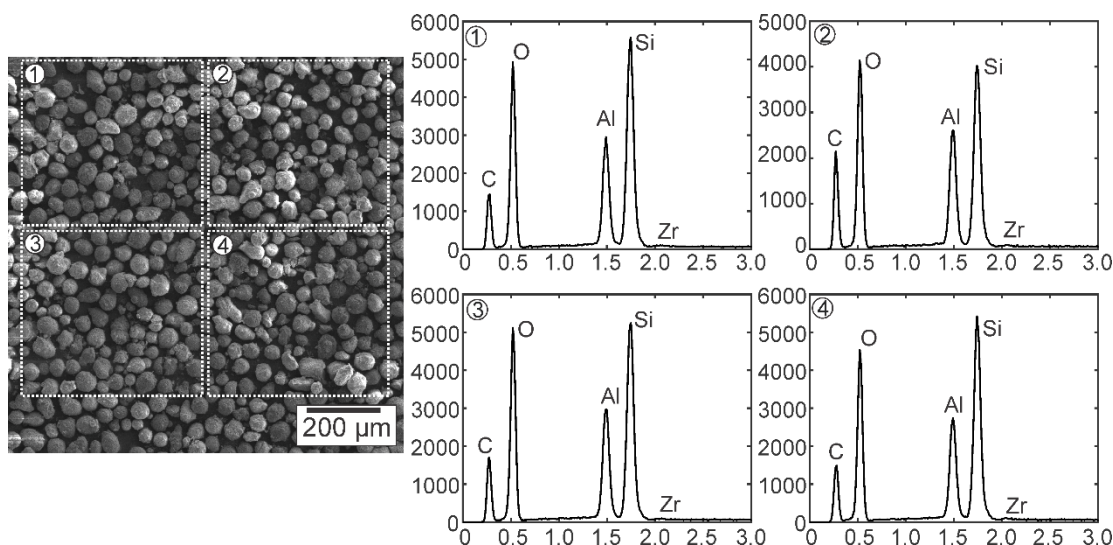


Figure 4.3. SEM image of supported catalyst 4-19-8. Numbers represent location of EDX area scan with corresponding EDX spectra.

To quantify the distributions of Al (in MAO) and Zr (in metallocene) in supported catalysts, the concentration ratios of Al and Zr (in wt.%) measured by SEM-EDX and ICP-MS at the surface region and at the core region of a particle have been calculated. **Figure 4.4** shows the ratio of Al wt.% (i.e., Al wt. % in the surface region/Al wt.% in the core region). Here, the ratio of 1.0 indicates uniform distribution of MAO within the particle. We observe that the ratio is much higher for the short contact time (1 h) between silica and MAO solution than for the longer contact time (19 h). The

ratio of 1.1 for 19 h contact time indicates that the MAO distribution within a silica particle is homogeneous or uniform.

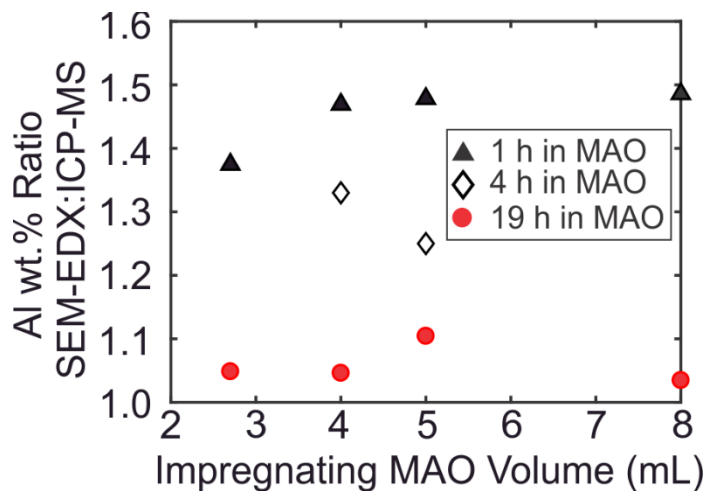


Figure 4.4. Ratio of Al wt.% measured by SEM-EDX to ICP-MS.

Figure 4.5 shows the Zr wt.% ratio plots for two cases: (a) silica treated with MAO for 1 h, (b) silica treated with MAO for 19 h. Both cases show that the Zr wt.% ratio is very high at short contact time, but it decreases gradually with longer contact time. It is to be noted that when the silica treated with MAO for 1 h was used, the initial ratio is 2.0~2.5 (Figure 4.5a) but the initial ratio is 1.2~1.5 for 19 h silica-MAO contact time (Figure 4.5b). Both Figure 4.5a and Figure 4.5b also show that the concentration of metallocene solution has a strong effect on the Zr wt.% ratio values. It is also clear that to obtain uniform distribution of metallocene within a particle, longer silica-MAO contact time, longer contact time for MAO-treated silica and metallocene, and higher metallocene solution concentration will be necessary.

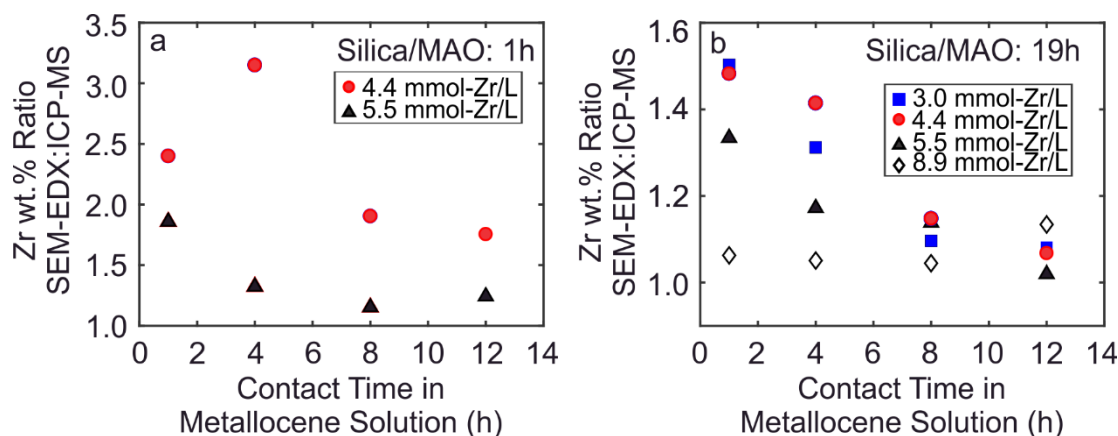


Figure 4.5. Ratio of Zr wt.% determined from SEM-EDX to ICP-MS for supported catalysts prepared with a contact time with the MAO solution for (a) 1 h and (b) 19 h.

The results shown in Figures 4.4 and 4.5 indicate that the catalyst compounds may initially accumulate at the outer edges of a particle and diffuse toward the particle center over time. This behavior is seen regardless of the MAO volume or metalocene solution concentration and suggests that a non-uniform distribution of the solute is possible at short contact times.

4.3.3 Mathematical Model

To obtain uniformly distributed catalyst sites in silica-supported catalysts, a large amount of experimental data is required to design ideal catalyst preparation conditions. Based on the experimental observations and data presented in the previous section, we develop a mathematical model for the catalyst impregnation process that can aid the catalyst preparation process. In other areas of chemical catalysis, several mathematical models have been reported to calculate the catalyst site distribution in catalyst particles,²⁶⁶⁻²⁷⁰ but none has been reported for silica-supported metallocene catalysts for ethylene or propylene polymerization.

To derive a catalyst impregnation model, the following assumptions are made:

- (1) The silica particles are spherical;
- (2) Initially, the particle is fully wet with the solvent (liquid);
- (3) An external film resistance exists at the interface between the catalyst solution and the silica external surface;
- (4) Mass transfer inside the particle follows the Fickian diffusion model;
- (5) Porosity of the particle is uniform throughout the particle;
- (6) MAO is chemisorbed to the silica surface;^{142, 147, 271}
- (7) Metallocene complexed with surface immobilized MAO may degenerate and leach away from the surface to the liquid phase in the silica pores;^{102, 215, 272}

4.3.3.1 Mathematical model for the immobilization of MAO

The MAO immobilization process is first modeled by the following equation (Model 1):

$$\varepsilon \frac{\partial C_{p-MAO}(r, t)}{\partial t} = \varepsilon D_{e-MAO} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_{p-MAO}(r, t)}{\partial r} \right) - (1 - \varepsilon) \frac{\partial n_{MAO}}{\partial t} \quad (4.1)$$

where ε is the porosity of the silica particle, $C_{p-MAO}(r, t)$ is the concentration of MAO in the pore space of the particle of radial position r at time t , D_{e-MAO} is the effective diffusivity of MAO, and n_{MAO} is the concentration of adsorbed (immobilized) MAO on the solid surface (i.e., pore surface). The last term in Eq. (4.1) represents the rate of

disappearance of the solute component from the bulk phase (i.e., pore space) due to adsorption. The initial and boundary conditions are given as follows:

$$C_{p-MAO}(0 \leq r \leq R; t = 0) = 0 \quad (4.1a)$$

$$\frac{\partial C_{p-MAO}(0, t)}{\partial t} = 0 \quad (4.1b)$$

If the interfacial mass transfer resistance is present at the spherical particle surface, the following boundary condition holds:

$$\varepsilon D_{e-MAO} \frac{\partial C_{p-MAO}(R, t)}{\partial r} = k_{L,MAO} (C_{b-MAO} - C_{p-MAO}(R, t)) \quad (4.1c)$$

Here, R is the particle radius, $k_{L,MAO}$ is the interfacial mass transfer coefficient and C_{b-MAO} is the concentration of MAO in the bulk liquid phase.

The rate equation for the adsorbed MAO is represented by the following equation:

$$\frac{\partial n_{MAO}}{\partial t} = k_a C_{p-MAO} (n_s - n_{MAO}) - k_d n_{MAO} \quad (4.2)$$

where k_a and k_d are the adsorption and desorption rate constants and n_s is the saturation concentration of MAO. At equilibrium, Eq. (4.2) corresponds to the Langmuir adsorption isotherm represented by:

$$\frac{n_{MAO}}{n_s} = \frac{KC_{p-MAO}}{1 + KC_{p-MAO}}, \quad K = \frac{k_a}{k_d} \quad (4.2a)$$

The initial condition for Eq. (4.2) is given as $n_{MAO}(0) = 0$.

While direct measurement of the adsorption and desorption process of MAO compounds from the silica surface is impractical, it is assumed that the Langmuir adsorption model is valid of the MAO-silica system. Desorbed MAO compounds may be able to react with the silanol group again with the other Al compounds present within their structures. It is also possible that due to the excess amount of MAO compounds in solution, another chemically identical MAO compound will react with the newly vacant silanol group.

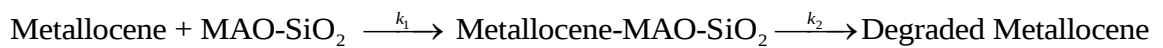
To account for the change in the concentration of MAO in the bulk liquid phase, the following equation is included:

$$\frac{\partial C_{b-MAO}}{\partial t} = -\frac{WSk_{L,MAO}}{V_{MAO}}(C_{b-MAO} - C_{p-MAO})_{r=R} \quad (4.3)$$

where V is the volume of the liquid phase (cm^3), W is the total mass of silica particles (g-silica), S is the specific interfacial surface area ($\text{cm}^2/\text{g-silica}$). The initial concentration of the MAO is given by C_{b0-MAO} (mol/cm^3).

4.3.3.2 Mathematical model for the immobilization of metallocene

The experimental data shown in Figure 4.2 suggests that some of the surface immobilized metallocene may degrade or decompose and leach away from the silica pore surfaces into the liquid phase in the pores, especially for long impregnation time.^{102, 215, 272} We propose the following scheme to account for this observed experimental data:



(Reaction scheme 1)

Then, the following equation is (Model 2):

$$\varepsilon \frac{\partial C_{p-Cat}(r,t)}{\partial t} = \varepsilon D_{e-Cat} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_{p-Cat}(r,t)}{\partial r} \right) - (1-\varepsilon) k_1 C_{p-Cat}(r,t) \quad (4.4)$$

where ε is the porosity of the silica particle, $C_{p-Cat}(r,t)$ is the concentration of metallocene compounds in the void pore space in the particle of radius r at time t , D_{e-Cat} is the effective diffusivity of the metallocene. The second term in Eq.(4.4) represents the rate of disappearance of the metallocene compounds from the bulk phase due to adsorption. The initial and boundary conditions are given as follows:

$$C_{p-Cat}(0 \leq r \leq R; t = 0) = 0 \quad (4.4a)$$

$$\frac{\partial C_{p-Cat}(0,t)}{\partial r} = 0 \quad (4.4b)$$

In presence of interfacial mass transfer resistance, the boundary condition added as:

$$\varepsilon D_{e-Cat} \frac{\partial C_{p-Cat}(R,t)}{\partial r} = k_{L,Cat} (C_{b-Cat} - C_{p-Cat}(R,t)) \quad (4.4c)$$

R is the particle radius, $k_{L,Cat}$ is the interfacial mass transfer coefficient for metallocene across the bulk-silica surface interface, and C_{b-Cat} is the concentration of Zr (in metallocene) in the bulk liquid phase.

For the surface-immobilized metallocene, the following rate equation is used:

$$\frac{\partial n_{Cat}}{\partial t} = k_1 C_{p-Cat} - k_2 n_{Cat} \quad (4.5)$$

The second term in Eq. (4.5) represents the loss of Zr through the detachment (leaching) of degraded or decomposed metallocene compound. The initial condition for Eq. (4.5) is given as $n_{Cat}(0)=0$.

For the bulk phase Zr (metallocene) concentration, an equation analogous to Eq.(4.3) was used.

The total Al and Zr concentration in a silica particle is calculated using Eq.(4.6):

$$n_{total}(t) = \frac{\int_0^R 4\pi r^2 n(r,t) dr}{\frac{4}{3}\pi R^3} = \frac{3}{R^3} \int_0^R r^2 n(r,t) dr \quad (4.6)$$

Where $n_{total}(t)$ is the total Al or Zr concentration in the silica particle and $n(r,t)$ is the concentration at a particular radial point within the particle (n_{MAO} or n_{cat}).

The above model equations were solved numerically in MATLAB using the finite difference discretization to approximate the spatial derivatives using the method of lines.^{273, 274} In this method, the spatial partial derivative is replaced by the finite difference approximation and is approximated by a system of ordinary differential equations with time as the independent variable. This system is integrated to obtain the solution which closely approximates the solution to the original partial differential equation. The physical parameter values of silica and catalyst components are listed in **Table 4.2**.

Table 4.2. Parameter values for the model

Variable	Value	Unit
Silica weight (W)	0.5	g
Silica particle radius (R)	1.75×10^{-3}	cm
Density of pure silica (ρ_{SiO_2})	2.65	g/cm ³
Density of silica particle (ρ_{Cat}) ^{a)}	0.3	g/cm ³
Porosity ($1 - \frac{\rho_{Cat}}{\rho_{SiO_2}}$)(ϵ)	0.89	-
Specific external surface area (S)	5.71×10^3	cm ² /g
Volume of MAO solution (V_{MAO})	4.0~5.0	cm ³
Volume of Metallocene solution (V_{Cat})	6.0	cm ³
Saturation concentration of MAO (n_{s-MAO}) ^{b)}	6.67×10^{-3}	mol/g
Bulk concentration of MAO (C_{b0-MAO})	1.0×10^{-3}	mol/cm ³
Bulk concentration of metallocene (C_{b0-Zr})	(3.0 – 8.8) $\times 10^{-6}$	mol/cm ³
Interfacial mass transfer coefficient for MAO (k_{L-MAO}) ^{c)}	1.38×10^{-6}	cm/s
Interfacial mass transfer coefficient for metallocene (k_{L-Cat}) ^{c)}	2.63×10^{-6}	cm/s

^{a)}Manufacturer provided ^{b)}Value of highest measured Al concentration in Figure 4.1

^{c)}Sherwood Number = 2 is assumed

4.3.3.4 Estimation of model parameters

After discretization of the model equations, the optimization protocol *fmincon* in MATLAB was used to estimate the model parameters (e.g., effective diffusivity values and rate constants) in the mass transfer of Al and Zr by fitting the experimental data shown in Figures 4.2-4.5 to Eq.(4.6). Initial estimates of the diffusivity constants of MAO and metallocenes were from the work of Hansen et al.²⁷⁵ where the bulk diffusivity of a MAO solution was measured to be 3.6×10^{-6} cm²/s. The diffusivities of MAO and metallocene were also estimated based on the Stokes-Einstein equation which is based on the size of the compound (radius of MAO: 46.2 Å, radius of metallocene: ~ 41 Å).^{125, 128, 276, 277} For MAO, the estimated diffusivity is 1.05×10^{-6} cm²/s while for metallocene the value is 1.19×10^{-6} cm²/s. Using those initial estimates, we calculated the immobilized solute concentration profile as well as the total

immobilized solute within the particle over time given by Eq. (4.6). The protocol then calculates the sum squared error between the total immobilized solute and the measured Al and Zr content. The optimization calculations were performed iteratively to estimate the diffusivity (D_{e-MAO} and D_{e-Cat}) and rate constants (k_a , k_d , k_1 , k_2) with minimum sum of squared errors. These solutions were successively used as initial estimates until the best fit was obtained. These values are listed in **Table 4.3**.

Table 4.3. Optimized parameter values

Parameter	Calculated Value	Units
Diffusivity (D_{e-MAO})	1.21×10^{-9}	cm^2/s
k_a	0.79	$\text{cm}^3/\text{mol-MAO.s}$
k_d	3.93×10^{-4}	1/s
Diffusivity (D_{e-Cat})	2.3×10^{-9}	cm^2/s
k_1	9.7×10^{-4}	1/s
k_2	3.1×10^{-5}	1/s

Using the simulation model and the optimized parameter values, we calculated the concentration profiles of Al (MAO) and Zr (metallocene compound) in the silica particle over time. **Figure 4.6** shows the model simulations and the experimental data for Al and Zr wt.% in silica as a function of contact times, respectively.

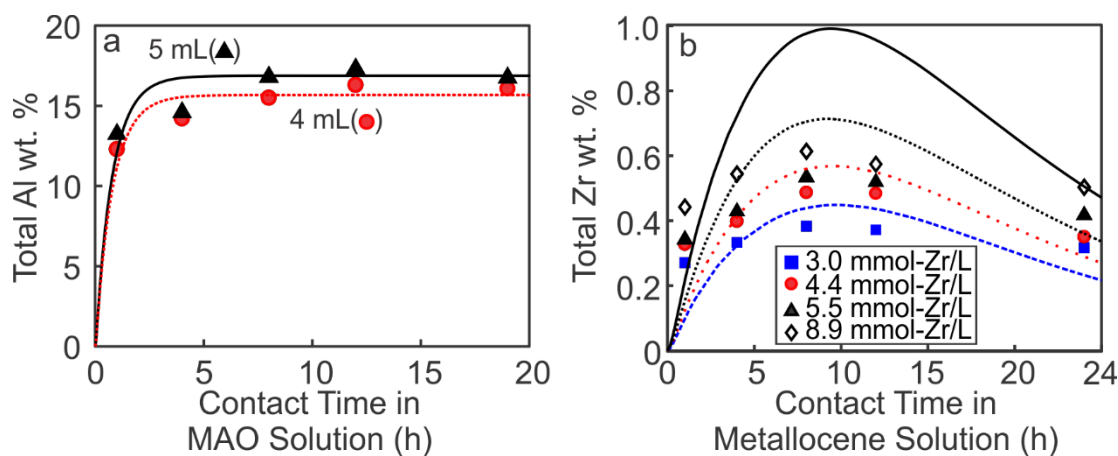


Figure 4.6. Model simulation results (lines) (a) Al wt.% in silica for two different MAO solution volumes, (b) Zr wt.% in silica for different metallocene solution concentrations.

Figure 4.6a shows that the model-calculated values of Al wt.% in silica agree quite well with the experimental data. Figure 4.6b shows good qualitative fits between the model and the measured Zr concentration data but it is seen that the model-calculated values are higher, especially at larger concentrations of metallocene solution. There are several possible reasons for this discrepancy. Firstly, high concentrations of metallocene compounds may lead to bimolecular deactivation reactions between neighboring metallocene compounds and removal of Zr from the supported catalyst.^{78, 159, 160} These reactions might occur at a higher rate at higher Zr concentrations. Secondly, we assume identical diffusivity constants (D_{e-Cat}) for all four different concentrations of metallocene. However, the diffusion coefficient has been observed to change with diffusion time,²⁷⁸ metal loading,^{279, 280} and silica particle tortuosity.²⁸¹ Both MAO and metallocene are expected to interact considerably with the pore wall leading to a lower diffusivity value compared to the bulk phase.²⁷⁵

Ideally, the supported catalysts would have a uniform distribution of Al and Zr throughout the particle. The radial profiles of immobilized Al (MAO) and Zr (metallocene) calculated by the model are shown in **Figure 4.7**. The amount of immobilized Al at the edge of the particle ($R = 1$) is almost double the amount of immobilized Al in the center ($R = 0$) while this ratio is around 1.3 for Zr regardless of solution concentration. These values are similar to those calculated by comparing the Al and Zr contents measured by SEM-EDX to ICP-MS after 1 h of contact time (Figure 4.4 and 4.5).

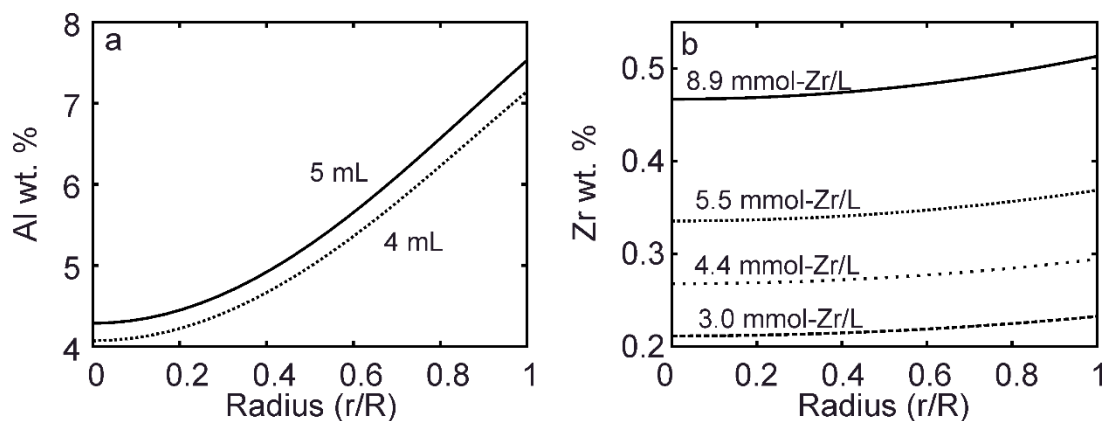


Figure 4.7. Concentration profiles of immobilized (a) Al for two different MAO solution volumes, and (b) Zr for different MAO solution concentrations. Contact time between silica and MAO solution and MAO-modified silica and metallocene solution is 1 h.

Ideally, the immobilized MAO would be radially uniform throughout the particle due to their importance in immobilizing and activating the metallocene compounds. A minimum molar ratio Al/Zr of about 100-200 is needed to generate the Lewis acid site to bind the metallocene active site.⁶³ Immobilized MAO will also form AlMe_2^+ that will alkylate the metallocene to form the cationic active site.^{102, 155, 157}

Figure 4.8 shows that supported catalysts prepared in MAO and metallocene solutions for 1 hour will have a radial gradient in the Al/Zr mol/mol ratio. Areas of high and low concentrations of immobilized Al would lead to metallocene compounds with varying levels of activation, polymerization activity, and polymer growth throughout the particle.

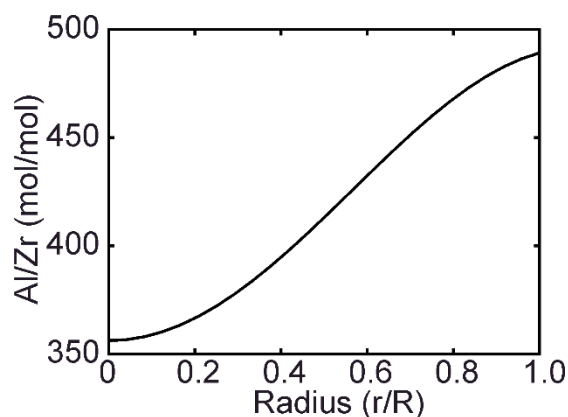


Figure 4.8. Al/Zr mol ratio profile for supported catalyst. Contact time between silica and MAO solution and MAO-modified silica and metallocene solution is 1 h.

4.3.3.5 Effect of Silica Particle Size on Active Site Distribution

The simulation model can be used to obtain the concentration profiles of immobilized Al (MAO) and Zr (metallocene) within the silica particle with different physical properties. The size of the silica particle is an important parameter that needs to be considered when preparing the supported catalyst. While the silica particles in this study were sieved to a narrow size cut, typical silica particles used as catalyst supports have a certain particle size distribution. In large silica-supported catalyst particles, intraparticle mass transfer limitations may be present for monomer transfer, affecting the polymerization rate.^{135, 136, 209, 258} Thus, it is useful to use the simulation model to understand the effect of silica particle size on the immobilization of catalyst compounds.

Figure 4.9 show the model-calculated radial concentration profiles of Al and the total Al wt.% per catalyst particle for three different particle sizes. Here, 1 h of contact time between silica and MAO has been used. It is seen that large silica particle size (e.g., 70 μm) exhibits a significant concentration nonuniformity in the particle and

requires almost three times longer contact times in MAO solution than medium sized particles (e.g., 35 μm) to reach concentration uniformity at the surface and center of the particle. These large particles will also have small total amount of Al (MAO) content per particle due to the depletion of MAO in the bulk solution. As such, large particle is expected to have low overall polymerization activity.

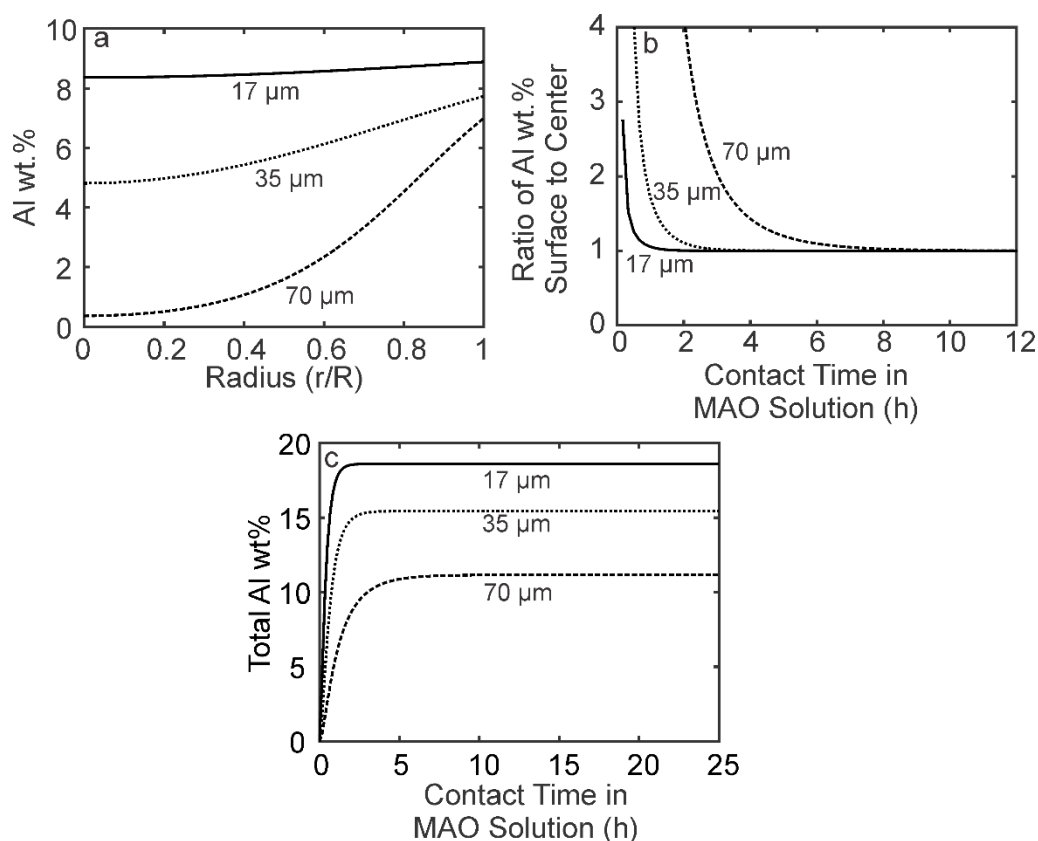


Figure 4.9. (a) Concentration profiles of immobilized Al for three different silica sizes after 1 h of contact time, (b) ratio of Al content at the surface ($R=1$) to center ($R = 0$), and (c) total Al content in supported catalyst over time in 4 mL MAO solution.

Figure 4.10 shows the similar plots for Zr (metallocene). For large particles, the radial Zr concentration nonuniformity is less pronounced than Al (MAO) (Figure 4.9a) as the diffusivity of metallocene is larger than that of MAO (Table 4.3). Figure 4.10b shows that large particles will still require longer contact times with the

metallocene solution compared to smaller particles to reach a uniform distribution. The detachment of metallocene compounds and inability to replace the vacant active site location with available compounds in solution leads to a higher non-uniformity for larger particles given the same concentration and volume of metallocene solution. In addition, the total wt.% of metallocene (active Zr) is as much as 3 times larger for 17 μm particle than for 70 μm . Also, to obtain maximum active Zr loading in the support, for this case studied, about 10 h of impregnation time will be needed.

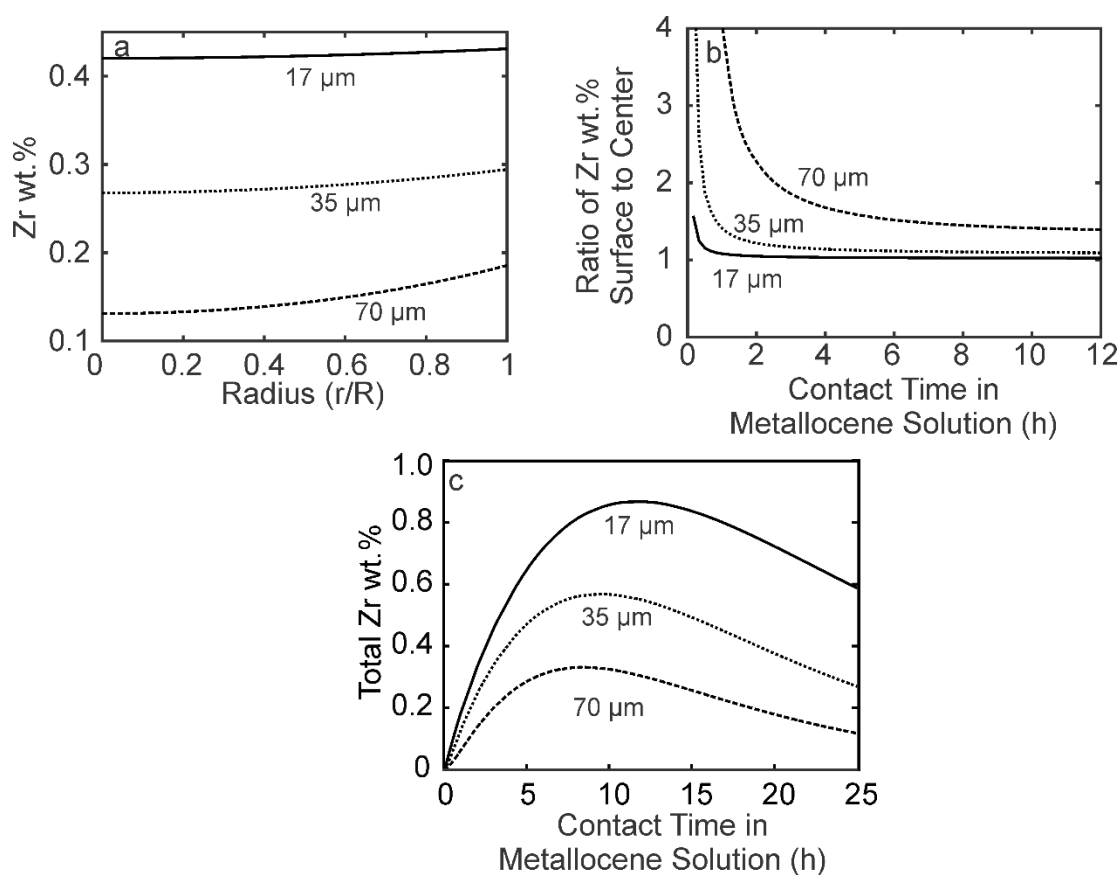


Figure 4.10. (a) Al and (b) Zr concentration profile within the supported catalysts based on particle sizes after 1 hour in each solution. (c) Total Al (d) and Zr content in supported catalysts over time.

The difference in the amount of immobilized Zr between particles of different sizes could explain the observation by Tisse et al.¹³⁶ that polymerization behavior is higher for smaller particles and lower for larger particles. Given the same contact time, smaller particles not only have a more uniform distribution of active sites compared to larger particles, they also contain more active sites due to decreased mass transfer resistance during the immobilization process.

4.3.4 Polymerization Activity

Liquid slurry polymerization of ethylene has been carried out at 60°C for 1 hour. After each experiment, the time average catalyst activity (g-PE/mmol-Zr.hr) was calculated from the polymer yield data. In the following, we shall discuss two cases: Case (i) the supported catalysts were prepared in the MAO solution for 19 h, Case (ii) the supported catalysts were prepared in the MAO solution for 1 h. These two cases represent the catalyst particles with different MAO distributions within the silica supports.

Figure 4.11 shows the experimental catalyst activity data for Case (i). It is seen that there is a clear trend of increasing activity for the catalysts prepared by contacting MAO-treated silica particles with metallocene solutions of different concentrations for longer contact times. The polymerization rate is seen to increase for contact times up to 8 h, but longer than 8-10 h contact time yields only marginal increase. It is also seen that for very low metallocene solution concentrations, the overall catalyst activity is quite low, indicating that the amount of active catalytic sites is not sufficiently large. However, the overall catalyst activity is also lowered for very high metallocene solution

concentrations (8.9 mmol-Zr/L). This possibly corresponds to the bimolecular deactivation reactions proposed earlier where high concentrations of active sites possibly leads to the formation of inactive species.

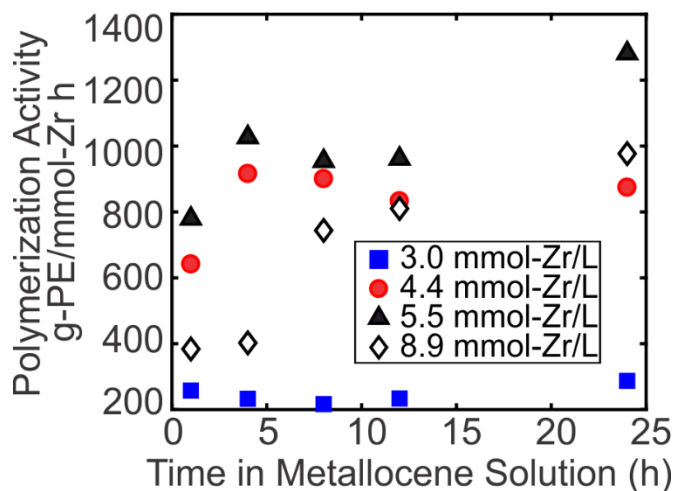


Figure 4.11. The effect of the contact time between MAO-modified silica and metallocene solutions on the time averaged polymerization rate (silica-MAO solution contact time: 19 h).

Figure 4.12 shows the results for Case (ii) where shorter contact time between the MAO-treated silica and metallocene solution was employed. Compared with the polymerization rates in Figure 4.11, Figure 4.12 shows that the overall catalyst activity is lower. It is thought that due to the short impregnation time of MAO, there is insufficient amounts of immobilized MAO compounds to activate and stabilize the active Zr sites.

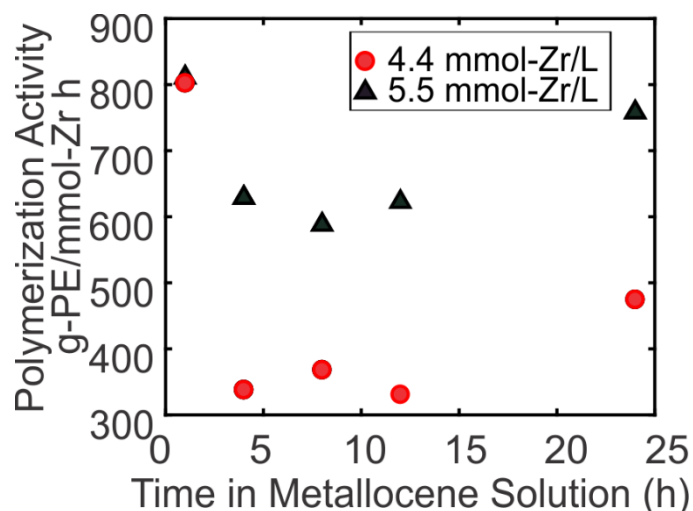


Figure 4.12. The effect of the contact time between MAO-modified silica and metallocene solutions on the time averaged polymerization rate (silica-MAO solution contact time: 1 h).

MAO has been known to passivate the silanol groups present on silica that can form bonds with metallocenes and form inactive species or deactivate the active sites.^{78, 102, 142, 220, 282} For short contact times between the silica particles and the MAO solution (e.g., 1 h), overall MAO content per particle is low and the immobilized MAO concentration primarily located near the surface of the particle is higher than that in the silica core region. Thus, when such MAO-treated silica particles are initially contacted with a metallocene solution (e.g. 1 h contact time), it is very likely that active metallocene sites will be preferably formed near the surface of the particle. For these supported catalysts, the Zr active sites are stabilized by the nearby MAO compounds. As the contact time between the MAO-modified silica and the metallocene solution is increased, metallocene compounds can immobilize directly to silanol groups within the silica core region. Although the Zr concentration of Case (ii) supported catalysts are high (Figure 4.2), the insufficient concentration of MAO in the core region may lead

to the reduced overall activity seen which qualitatively agrees with the model results shown in Figure 4.8.

4.3.5 Polymer Morphology

The effects of catalyst concentrations on the internal morphology of polyethylene particles have been examined for two cases: (i) nonuniform concentration of Zr (high Zr concentration at the surface, Catalyst 4-19-1), (ii) uniform concentration of Zr throughout the particle (Catalyst 4-19-8).

Figure 4.13 illustrates the SEM images of the polyethylene particles obtained with Catalyst 4-19-1 that has a uniform distribution of MAO and non-uniform distribution of metallocene (short contact time between MAO-treated silica and metallocene solution). Figure 4.13a shows that the polymer particle has grown to around 150 μm after 1 h of reaction. The particle has a spherical appearance with a bit of rough external surface. Figure 4.13b shows that the polymer particle surface contains fragmented silica/polymer micro-particles of about $\sim 3 \mu\text{m}$. The presence of stress fibrils between these micro-particle fragments indicate that the polymerization was quite active at the particle surface region. Figure 4.13c shows the magnified view of the particle fragments and stress fibrils. It is observed that the particle fragments are covered with polymers. Figures 4.13d-f show the cross-sectional views of a polymer particle. It is seen that the interior of the polymer particle has large void volumes which extend to the edge of the cross section created by the formation of polymers and catalyst fragmentation. Figures 4.13e shows that stress fibrils are hardly seen inside the particle, but they are clearly seen at the particle surface as shown in Figure 4.13f,

illustrating that the fragmentation is quite active near the particle surface as the particle expands due to polymerization.

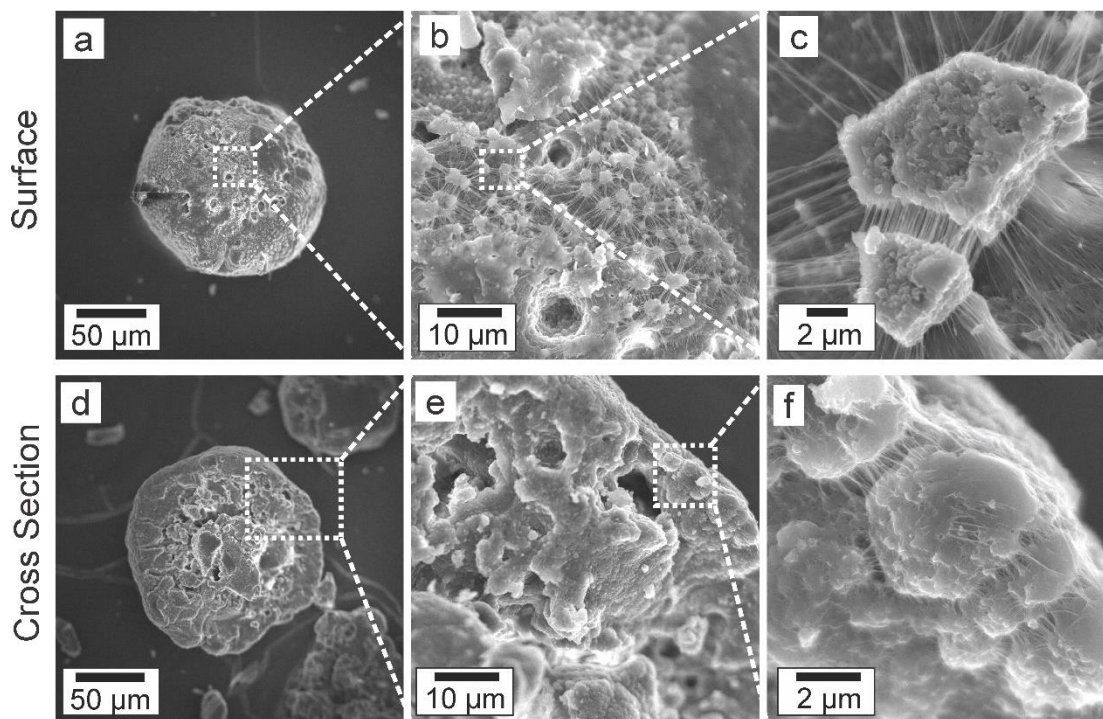


Figure 4.13. SEM images of polyethylene particles: (a)-(c) particle surface, (d)-(f) particle interior after 1 h of polymerization with (Catalyst 4-19-1; Squares represent enlarged zones that are shown on the right.

Large particle fragments at the surface of the polymer were also reported in the literature for the particles with low catalyst productivity and it was attributed to a core-shell distribution of MAO.^{210, 213} However, Catalyst 4-19-1 was prepared by contacting silica with MAO for 19 h that provides quite uniform distribution of MAO in the silica particles. It is possible that the number of metallocene active sites are primarily located near the surface region of the particle due to the short contact time between the MAO-modified silica and the metallocene solution. During the reaction, the catalyst particle exhibits non-uniform polymerization rate across the radius, leading to irregular catalyst

fragmentation. The lower activity can lead to slow polymer growth and some cavities inside the particle. Thus, it is more likely that these fragments and the polymer particle morphologies observed in Figure 4.13 are the result of low overall catalyst concentrations.

Figure 4.14 shows the SEM images of the particle surfaces and cross-sections of the polyethylene obtained with Catalyst 4-19-8 in which the distributions of both MAO and metallocenes are quite uniform due to long impregnation times for each component. Compared with Figure 4.13, Figure 4.14a shows that the polymer particle is larger (approximately 250 μm in diameter) with a more globular surface appearance. The surface globules show rather irregular shapes. The enlarged surface globules (Figure 4.14b) show the presence of a large number of very small particle fragments of approximately 500 nm in size that seem to be buried in the polymer matrix. Figure 4.14c shows that each of these small particle fragments are connected by stress fibrils, indicating that the silica particle fragmentation was very extensive and that each fragment has undergone repeated fragmentation or disintegration process until they have reached the size of about 500 nm. The cross-sectional view of the particle shown in Figure 4.14d-f shows voids as observed in lower activity catalyst (Figure 4.13) but to less extent. Figures 4.14d-f also show that the particle surface region is denser than the interior region and such dense region is about 50 μm thick with little voids.

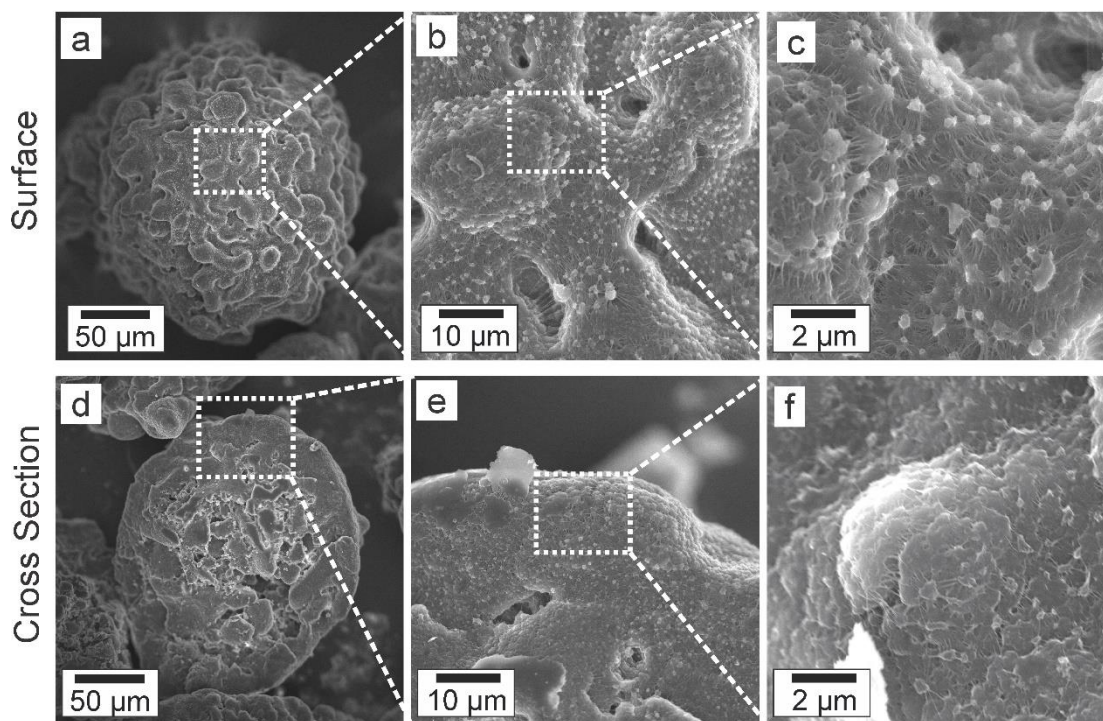


Figure 4.14. SEM images of polyethylene particles: (a)-(c) particle surface, (d)-(f) particle interior after 1 h of polymerization with Catalyst 4-19-8; Squares represent enlarged zones that are shown on the right.

The longer contact time between the MAO-supported silica and the metallocene solution led to higher and more uniformly distributed Zr content within the supported catalyst. The presence of active sites in the center of the particle led to growth throughout the particle and less void space is seen. Complete fragmentation of the surface has occurred due to the higher concentration of active sites leading to the smaller silica fragment size seen.

4.4 Concluding Remarks

In this study, the impregnation of silica with MAO and metallocene has been investigated through experimentation and mathematical modeling. A series of supported

catalysts were prepared by varying two main impregnation variables: the amount of solute (MAO or metallocene) in solution (via the solution volume and concentration) and the contact time between the silica and the solution. Characterization of the overall compositions of the supported catalysts shows that the Al and Zr amounts of the silica-supported catalyst depend upon the contact time and the catalyst solution concentrations. While the Al content increased over the course of 12 h and reached a limit value, the Zr content increased with time but decreased at extended contact times suggesting the loss of some immobilized metallocene, probably due to the decomposition and subsequent leaching into the pore liquid phase. This observation was incorporated into a mathematical model.

The proposed model predicts the total and radial distribution of MAO and metallocene within the particle and qualitatively matches the experimental results. Short contact times between the silica and the MAO solution and the MAO-modified silica and the metallocene solution lead to higher concentrations of Al and Zr near the surface region of the particle and lower overall metal concentration. Lower activity and levels of fragmentation were observed with supported catalysts prepared with shorter contact times. Importantly, these results indicate that preparation conditions such as contact time or solution concentration largely influence the performance of the catalyst and explain the range of polymer morphology seen despite the use of chemically identical metallocene catalysts and support. While the proposed model qualitatively agrees with the experimental results, it is important to note that the results presented are for one particular combination of catalytic compounds and silica. Although some parameters in the model are generalized such as the particle size and the overall

porosity, differences between the pore structures of different types of silica can be more nuanced. These differences in the pore structure will ultimately affect the effective diffusivities of MAO and the metallocene catalyst during the mass transfer process. As part of the optimization routine, the model is able to estimate the effective diffusivities based on the measured Al and Zr concentrations. However, this requires a large number of samples to obtain accurate results for each particular case. This is due to the lack of more detailed characterization methods of the silica pore structure. Current methods are limited to measuring the overall physical properties such as pore volume and surface area using certain estimations such as cylindrical pores for the complex and random arrangement of the silica primary particles. However, the proposed model provides a framework for which future advances in pore structure characterization can be incorporated as independent variables.

Previous research found that particle size influences the activity. Our model results illustrate that particle size will impact the Al and Zr concentration which further determine the performance of the catalyst. Overall, the proposed model introduces a new method to analyze the mass transfer of MAO and metallocene during the immobilization process of silica-supported metallocene catalysts. Further development of the proposed model should lead to better design and optimize the preparation of supported catalysts.

Chapter 5. Effects of Silica Pore Structure on the Immobilization and Activity of Supported Catalysts

5.1 Introduction

In this dissertation, porous amorphous silica particles were used to immobilize MAO and metallocenes. In Chapter 2, 3, and 4 it is shown that the preparation conditions such as volume of MAO used, metallocene solution concentration, and contact time between the particle and the catalytic solution directly impact the overall composition of the supported catalyst as well as the distribution of active sites. Similar adsorption behaviors of MAO and metallocene were seen when P-10 and 2408HT silica were used as supports. However, different adsorption limits (i.e., maximum Al or Zr wt.%) and distributions of active sites approximated by the ratio composition at the surface and the core of the particles were seen. An explanation can be found from the variation in pore structure within both silicas.

The pore structure of the particle, a complex internal pore space with mixtures of large interstitial void spaces, macropores, mesopores, and micropores, will have a direct effect on the mass transfer of the catalytic compounds during the immobilization procedure. During the preparation process of supported catalysts, MAO and metallocene sequentially diffuse through the tortuous pore structure and adsorb to the surfaces of the silica matrix. Based on the pore size distribution, the pore structure may facilitate or hinder the mass transfer of the catalytic compounds to form active sites.

The pore structure of the silica support used will also affect polymer growth and fragmentation during polymerization. Generally, fragmentation behavior of the supported catalyst can be categorized as either layer-by-layer where fragmentation of the silica support occurs successively from the surface region and proceeds toward the center,^{173, 175-177} or continual bisection model where the support will successively fragment from internal void spaces and form smaller fragments.¹⁸⁴⁻¹⁸⁶ Zheng et al.¹⁷³ observed different fragmentation behavior based on the silica porosity with extensive fragmentation occurring for particles with higher porosities. Similarly, Zaroni et al.¹⁸⁹ observed evidence of both layer-by-layer and continual bisection fragmentation in the cross-sections of polymer/catalyst particles after gas phase and slurry phase polymerization of ethylene. Polymer growth and expansion near the surface of the particle, where aggregates were tightly packed, experienced layer-by-layer fragmentation while polymer growth within internal interstitial voids experienced continual bisection fragmentation. Based on the desired performance, the initial pore structure and properties such as pore size distribution or pore volume are often used as selection criteria for the silica particles used to prepared supported catalysts.

However, the pore structure of the supported catalyst is often significantly altered from the initial silica. In Chapter 3, we illustrate that the immobilization of MAO will form a MAO layer within the pores and change the silica's pore diameter, pore volume, and surface area. The change to the pore structure of affected polymer growth and fragmentation during polymerization. A narrower pore diameter led to extensive fragmentation for catalysts prepared with P-10 silica.

Recent developments into porous silica particle synthesis have produced particles with narrower particle size distributions and uniform porosities using microemulsion methods. These particles are also characterized by a lack of large internal interstitial voids. Bashir et al.¹³⁴ observed that silica particles with interstitial voids (Grace 948) had uniform distribution of Al (corresponding to MAO) while silica particles without interstitial voids (PQ MS1732) had a core-shell distribution of Al despite similar pore volumes and identical preparation conditions. However, more rigorous immobilization methods such as longer contact time may lead to uniform distributions of active sites and explore the use of these silica type in polymerization.

In this work, we have investigated the effect of the immobilization of MAO on the pore structure of three commercially available microporous silica particles. Supported catalysts with varying pore dimensions were prepared by immobilizing different amounts of MAO through the use of various concentrations of MAO solution during the preparation process. The overall Al concentrations in silica were analyzed using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The pore size distribution of the original silica and their derivative supported catalysts were analyzed using N₂ physisorption. Cross-sections of the silica were analyzed using focused ion beam (FIB) to observe the internal pore structure. The supported catalysts were used in slurry phase and gas phase polymerization of ethylene.

5.2 Experimental

5.2.1 Preparation of Supported Catalyst

The physical characteristics of the three commercial silica used in this study are shown in **Table 5.1**. Details of the preparation of the supported catalysts have been described in Chapter 2.2.1 and Chapter 3.2.1.

Table 5.1. Physical properties of pristine commercial silica used in this work

Silica trade name	Manufacturer	Surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (nm)	Average particle size (μm)
P-10	Fuji-Silysia	288.7	1.46	20.23	35.8
2408HT	WR Grace	313.4	1.36	20.31	32.0
DM-L-303	AGC	296.2	2.21	45.86	35.2

MAO solutions with varying concentrations were prepared by mixing 3.0 mL of a MAO stock solution (30 wt.% solution in toluene, WR Grace) and varying amounts of toluene (Sigma-Aldrich) at room temperature for 15 minutes. The prepared MAO solutions were slowly added to the calcined silica particles (0.5 g) and stirred with gentle agitation at 110°C to produce MAO-modified silica. It is expected that immobilized MAO will be present throughout the entire particle due to the long contact time of 19 h. Metallocene solutions with concentrations of 4.6 and 6.7 mmol-Zr/L were prepared by mixing 0.012 g and 0.017 g of *rac*-Et(Ind)₂ZrCl₂ (Sigma-Aldrich) with 6 mL of toluene for 30 minutes. The two targeted zirconium concentrations of the supported catalysts were 0.5 and 0.7 wt.% Zr/SiO₂ and are hereby referred to as Catalysts X-Y-1 and Catalysts X-Y-2 respectively where X is the silica and Y is the MAO solution concentration in wt.%. The metallocene solution was added to the

MAO-modified silica particles and gently mixed for 8 h for 70°C to produce supported catalyst particles. After each step, the silica was washed with toluene three times to remove unbound MAO or metallocene compounds. Free-flowing supported catalyst particles were obtained after drying *in vacuo* overnight at room temperature. Concentrations of the solutions used to prepare the supported catalysts are shown in **Table 5.2**.

Table 5.2. Concentrations of solutions used to prepare supported catalysts

Supported catalyst ^{a)}	Total volume of MAO solution (mL) ^{b)}	Concentration of MAO solution (mol-MAO/L)	Concentration of metallocene solution (mmol-Zr/L) ^{c)}
X-5-1	18	0.75	4.6
X-5-2	18	0.75	6.7
X-10-1	9	1.51	4.6
X-10-2	9	1.51	6.7
X-15-1	6	2.26	4.6
X-15-2	6	2.26	6.7
X-20-1	4.5	3.02	4.6
X-20-2	4.5	3.02	6.7
X-30-1	3	4.53	4.6
X-30-2	3	4.53	6.7

^{a)} X represents silica trade name, ^{b)} Stock MAO solution: 3 mL, Toluene: remaining volume ^{c)} Volume: 6 mL

5.2.2 Characterization of Supported Catalyst and Polymer

The overall composition (Al and Zr concentrations) of the silica-supported catalyst particles was measured with Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES, Shimadzu ICPE-9000). The samples were prepared with the procedure detailed in Section 2.2.3.

The exterior morphologies of the prepared silica-supported catalyst particles and subsequent polymer particles produced were investigated by scanning electron microscopy (SEM) with the procedure detailed in Section 2.2.3.

The crystallinity and the melting point of the polymer particles were analyzed with differential scanning calorimetry (DSC, TA Instruments DSC2500). All samples were accurately weighed (10 mg) and sealed in hermetic aluminum pans. Samples were heated to 200°C and kept for 10 minutes to erase thermal history and then cooled to 50°C at a rate of -10°C/min. The sample was then reheated to 200°C at a rate of 10°C/min to obtain the peak melting temperature (T_m) and the curve was integrated to measure the heat of fusion ΔH_f . The crystallinity was calculated using the heat of fusion obtained and the heat of fusion for a perfectly crystalline polyethylene ($\Delta H_{f0} = 290$ J/g) in terms of $\Delta H_f/\Delta H_{f0}$.

5.2.3 Gas Phase Polymerization of Ethylene

The prepared catalysts detailed in Table 5.2 were used in gas phase polymerization of ethylene. Further details of the polymerization procedure are detailed in Section 2.2.2.

5.2.4 Slurry Phase Polymerization of Ethylene

The prepared catalysts detailed in Table 5.2 were used in slurry phase polymerization of ethylene. Further details of the polymerization procedure are detailed in Section 3.2.4.

5.3 Results and Discussion

In this study, we hypothesize that the internal pore structure of silica may be altered by the use of excess amount of MAO and such changes in the silica pore dimensions can affect the polymerization performance of the catalyst. It is expected that the absence of interstitial voids within the silica particles will lead to different degrees of fragmentation and growth compared to silica particles with interstitial voids.

5.3.1 Silica Exterior and Interior Morphology

We have first analyzed the morphology of silica particles before the immobilization of MAO and catalyst. SEM images detailing the exterior and interior morphology of three different commercial silicas with a range of physical characteristics are shown in **Figure 5.1** and **Figure 5.2**. All three silica samples are spherical with similar values of specific surface area (Table 5.1). Two silica supports (P-10 and 2408HT) have similar pore volumes ($\sim 1.4 \text{ cm}^3/\text{g}$) and pore diameters ($\sim 20 \text{ nm}$). Both P-10 (Figure 5.1a) and DM-L-303 (Figure 5.1c) silica have smooth exterior surfaces while 2408HT has a rough exterior surface that resembles the agglomerated matrix texture (Figure 5.1b). The smooth surface of DM-L-303 is due to the production process which is based on the microemulsion synthesis method of using a microchannel reactor to produce the silica particles.²⁸³⁻²⁸⁵ In contrast, the 2408HT silica is produced using the spray-drying method where silicon oxide particles are first dry milled, then wet milled, and finally spray dried to obtain particles with a rough spherical shape.¹³³ The manufacturing process of the P-10 silica was only disclosed as a sol-gel process

which is granulated into a spherical shape. The varying manufacturing process is expected to lead to different internal pore structures and morphologies.

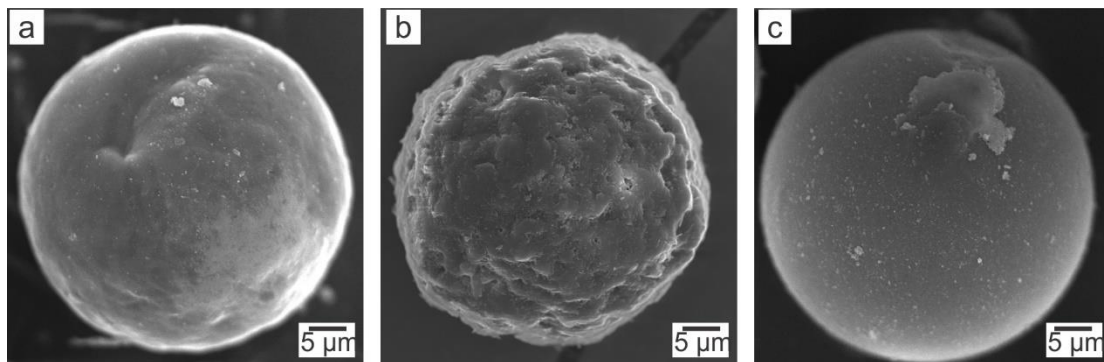


Figure 5.1. Exterior morphology of silica particles (a) P-10, (b) 2408HT, and (c) DM-L-303.

To observe the interior morphology of the particle, the top hemisphere of the silica particle was cut using Ga⁺ ions in the FIB technique (Beam energy: 30 keV, Current: 7.5 nA). The beam current was decreased to 2.0 nA to polish the cross-section and preserve the internal structure of the porous silica particle. Figure 5.2a shows that internal structure of P-10 has several interstitial voids around 2 μm in diameter. These void spaces are evenly located throughout the silica and are present near the edge of the particle (Figure 5.2b) and the center (Figure 5.2c). The inside views of the voids reveal silica aggregates of around 200 – 500 nm in diameter. Figure 5.2d shows that the cross-section of the 2408HT silica contains larger interstitial voids ranging between 5 and 10 μm which are uniformly located throughout the particle (Figures 5.2e and 5.2f). Silica aggregates of the 2408HT silica are approximately 1 – 2 μm in diameter. Figure 5.2g illustrates that no macropores are seen in the cross section of the DM-L-303 particle. Instead, the pore structure is completely made up of mesopores around 50

nm uniformly dispersed throughout the particle (Figures 1k and l). Silica aggregates are approximately 50 – 100 nm in diameter.

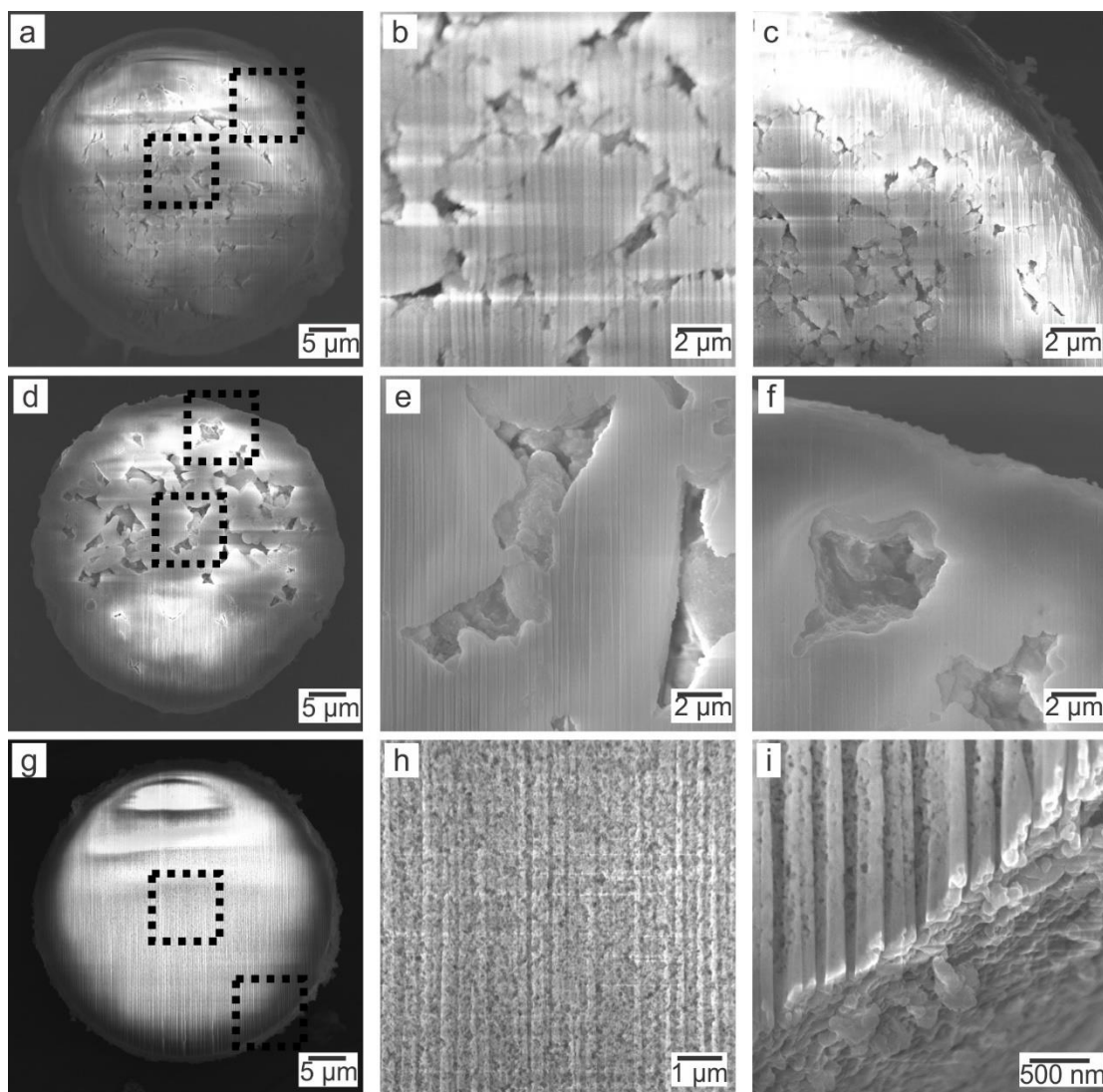


Figure 5.2. Cross section of silica particles and internal morphology of (a-c) P-10, (d-f) 2408HT, and (g-i) DM-L-303

The internal structures of the silica structure are a direct result of their synthesis method. Interstitial voids within the silica are commonly associated with silica produced with spray-dried synthesis methods as the silica aggregates are randomly arranged when sprayed. These silicas such as Grace 948 are frequently used in studies

in metallocene supported catalysts.^{133, 146} Microemulsion synthesis methods that use a microchannel reactor lead to a more controlled synthesis process and reduce the size and number of interstitial voids due to the constricted growth and Ostwald ripening of the overall particle. These methods not only affect the internal structure, but also the pore structure of the silica.

5.3.2 Pore Structures of Silica Particles

The pore structure of the silica particle is expected to differ based on the synthesis process. **Figure 5.3** shows the nitrogen adsorption/desorption isotherms of the original P-10, 2408HT, and DM-L-303 silica. All are Type IV isotherms with H1 type hysteresis loops which are typical for silica structures and indicate high pore uniformity and pore connectivity as well as agglomerates of uniform spheres.^{131, 248, 249} While P-10 and 2408HT silica have similar hysteresis loops, it is seen that the one for DM-L-303 is considerably more steeper and narrow. This qualitatively correlates to the pore structure of DM-L-303 seen in Figure 5.2 where pores are uniformly distributed with no large interstitial voids.

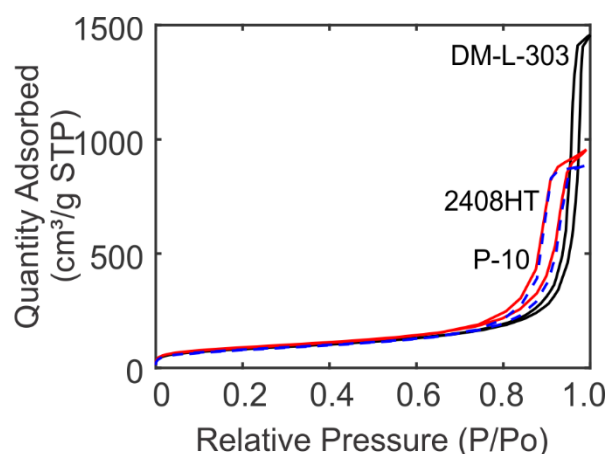


Figure 5.3. Adsorption-desorption isotherm of the original P-10 silica (red solid line), 2408HT silica (blue dashed line), and DM-L-303 silica (black solid line).

Figure 5.4 shows the pore size distributions, cumulative surface areas, and cumulative pore volumes of three grades of silica. The measured pore size distributions of P-10 and 2408HT silicas are similar and are both centered at around 25 nm with the range between 5 and 60 nm. The measured pore size distribution of DM-L-303 is slightly broader than the other two silicas with mesopores between 20 and 80 nm and centered at 45 nm. It is important to note that N_2 physisorption cannot accurately measure macropores and does not account for the interstitial voids seen within the silica. However, these large pores are not believed to have a large impact on the overall pore volume.²⁸⁶

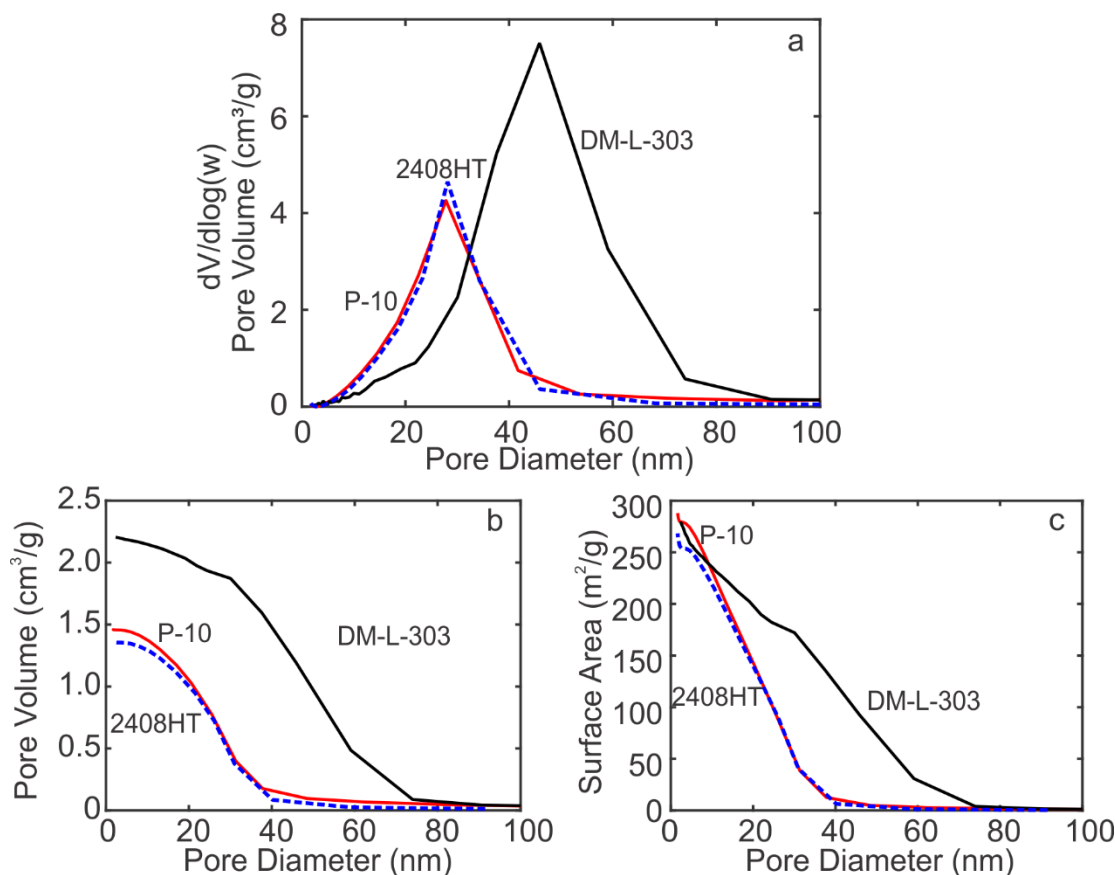


Figure 5.4. (a) Initial pore size distribution curves, (b) cumulative pore volumes, and (c) cumulative surface areas of three silica samples: P-10 (red solid line), 2408HT (blue dashed line), and DM-L-303 (black solid line).

During the catalyst immobilization process, the MAO and metallocene compounds diffuse through the tortuous pore network to access the interior of the particle to form active sites. Due to the sizes of the MAO and metallocene compounds, it is expected that they will experience a steric hinderance from entering pores smaller than 10 nm. Thus, to maximize the number of active sites present within the supported catalysts, a large fraction of pores within the silica should be larger than 10 nm. It is seen that approximately 5 - 7% of pores of the P-10 and 2408HT silica and 3% of the DM-L-303 silica are less than 10 nm. Figure 5.4c shows that these pores account for approximately 20% and 16% of the total surface area. The difference in the fraction of pores smaller than 10 nm might lead to variations in the maximum amount of MAO that is able to be immobilized onto the silica during the preparation process.

5.3.3 Overall Catalyst Composition

The Al concentration of each supported catalyst prepared from the three types of silica has been analyzed as shown in **Table 5.3**. It is seen that an increase in the MAO solution concentration leads to an increase in the total Al content within the supported catalyst. However, supported catalysts prepared with 2408HT reach a limiting Al concentration of approximately 20 wt.% Al with minimal increase when the MAO solution concentration increased to 4.53 mol-MAO/L.

Table 5.3. Aluminum compositions of supported catalysts

Supported catalyst ^{a)}	P-10 Al wt.% in silica	2408HT Al wt.% in silica	DM-L-303 Al wt.% in silica
X-5-1	17.4	14.3	17.6
X-5-2	17.4	14.6	17.3
X-10-1	19.1	17.1	18.2
X-10-2	18.7	17.7	18.9
X-15-1	19.4	19.5	19.5
X-15-2	21.2	18.5	19.9
X-20-1	21.9	21.6	19.8
X-20-2	21.4	20.7	20.5
X-30-1	22.0	20.5	22.3
X-30-2	23.2	19.1	21.5

^{a)} X represents silica trade name

Table 5.4 shows the Zr concentration of the supported catalysts. The targeted zirconium contents of the supported silica were 0.5 (for supported catalysts labeled -1) and 0.7 wt.% (for supported catalysts labeled -2). The supported catalysts prepared at the lower metallocene solution concentration have completely immobilized the dissolved metallocene catalysts while not all compounds in solution were immobilized at the higher solution concentration. It is seen that supported catalysts prepared with DM-L-303 have higher Zr contents.

Table 5.4. Zirconium compositions of supported catalysts

Supported Catalyst ^{a)}	P-10 Zr wt.% in silica	2408HT Zr wt.% in silica	DM-L-303 Zr wt.% in silica
X-5-1	0.49	0.46	0.45
X-10-1	0.47	0.50	0.44
X-15-1	0.49	0.49	0.51
X-20-1	0.50	0.48	0.49
X-30-1	0.48	0.44	0.46
X-5-2	0.55	0.54	0.63
X-10-2	0.56	0.58	0.60
X-15-2	0.56	0.53	0.63
X-20-2	0.54	0.55	0.63
X-30-2	0.56	0.55	0.63

^{a)} X represents silica trade name

5.3.4 Langmuir Adsorption of MAO

It is shown in Chapter 4 that the immobilization of MAO can be modeled as a Langmuir adsorption process and we assume that the model remains valid for the MAO-silica system for the three types of silica. It is assumed that the Al concentration within the MAO-modified silica has reached equilibrium as the silica particles were contacted with the MAO solution for 19 h. In addition, the MAO compounds in solution is assumed to be in excess such that the desorption of MAO compounds from the silica surface and the adsorption of MAO compounds mimic adsorption equilibrium. As such, the immobilized Al concentration can be calculated using the Langmuir adsorption model represented by Eq. (5.1) and its linearized form by Eq. (5.2).

$$\frac{q_e}{q_m} = \frac{KC_e}{1 + KC_e} \quad (5.1)$$

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{Kq_m} \quad (5.2)$$

Here, q_e is the measured Al concentration at equilibrium for each MAO solution concentration (g-Al/g-SiO₂), q_m is the calculated maximum Al concentration (g-Al/g-SiO₂), K is the adsorption equilibrium constant (cm³/mol), and C_e is the concentration of Al in the bulk phase MAO solution (mol/cm³).

Figure 5.5 shows the linearized equation Eq. (5.2) with the measured Al concentrations of the supported catalysts prepared with different MAO solution concentrations as well as the fit with the Langmuir adsorption model. Figure 5.5b shows that the model agrees quite well with the experimental data.

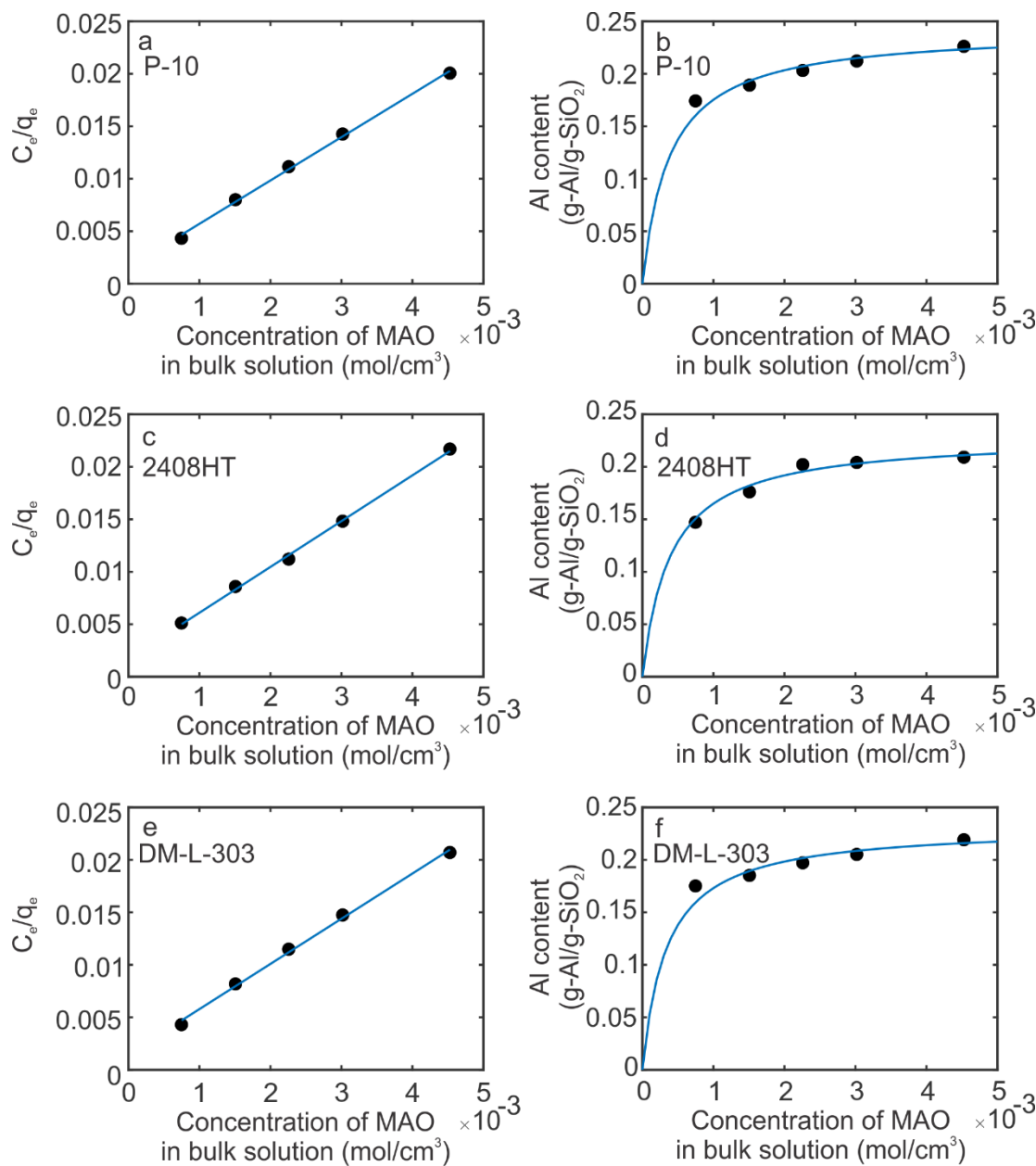


Figure 5.5. Linearized Langmuir isotherm model (Eq. 5.2) and predicted immobilized Al concentration (line) with data points for (a-b) P-10, (c-d) 2408HT, and (e-f) DM-L-303.

The parameters K and q_m calculated by Eq. (5.2) are shown in **Table 5.5**. It is seen that the three types of silica have similar limits of Al concentrations around 23 Al wt.%. The values for the equilibrium constant, are highest for DM-L-303 followed by

P-10 and then 2408HT. It is assumed that the MAO-silica system follows the Langmuir adsorption model

Table 5.5. Adsorption variables for MAO for three silica types

	P-10	2408HT	DM-L-303
q_m (Al wt.% in silica)	24.2	22.9	23.2
K (L/mol-MAO)	2.62×10^3	2.57×10^3	2.93×10^3

5.3.5 Changes in Physical Structure of Silica After Immobilization

5.3.5.1 Changes in Pore Diameter and Pore Size Distribution

The pore size, pore volume, and surface area of the silica are expected to change with the immobilization of MAO and metallocene compounds. We hypothesize that the local pore environment in the vicinity of the active sites sterically impacts the growth of the polymer chain at the active site and affect the progress of pore filling and fragmentation. N₂ physisorption was used to measure the pore structure of the silica before and after the immobilization process of catalytic compounds. **Figure 5.6** shows how the pore diameter of each grade of silica changed with the measured Al content (immobilized MAO). The pore diameter decreased linearly with the Al wt.% until minimal changes in the pore diameter is seen. However, the smallest measured pore diameter is different for each silica.

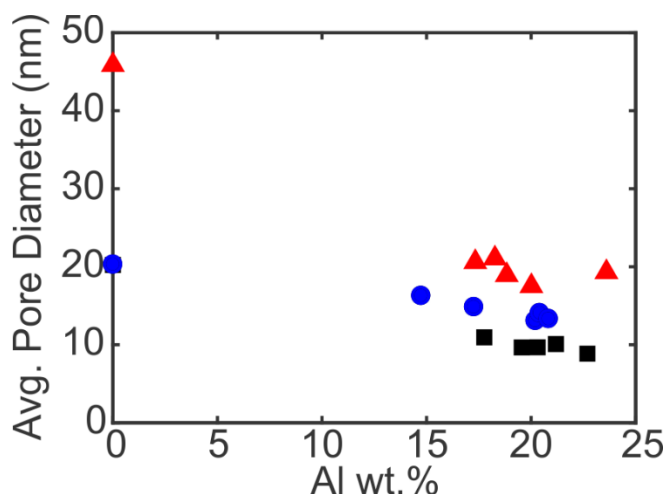


Figure 5.6. Pore diameter of the supported catalysts prepared from three silicas based on immobilized Al wt. %. P-10 (black squares), 2408HT (blue circles) and DM-L-303 (red triangles).

Figure 5.7 shows the pore size distributions of each supported catalyst and how they changed based on the measured Al wt.%. Figure 5.7a shows that the pore volume of supported catalysts produced using P-10 silica decreases significantly from their initial value of $1.4 \text{ cm}^3/\text{g}$ with increasing amounts of immobilized MAO (Al wt.%). As the immobilized Al wt.% increases, the pore size distribution shifts toward smaller pores as the MAO preferentially immobilizes within larger pores due to easier mass transfer. At 20 Al wt.%, a bimodal peak distribution is seen centered at ~ 9 and 18 nm (Figure 5.7b). This indicates that MAO is unable to access the pores smaller than 10 nm which is consistent with reported studies on the effect of pore size on polymerization activity.^{122, 129, 287}

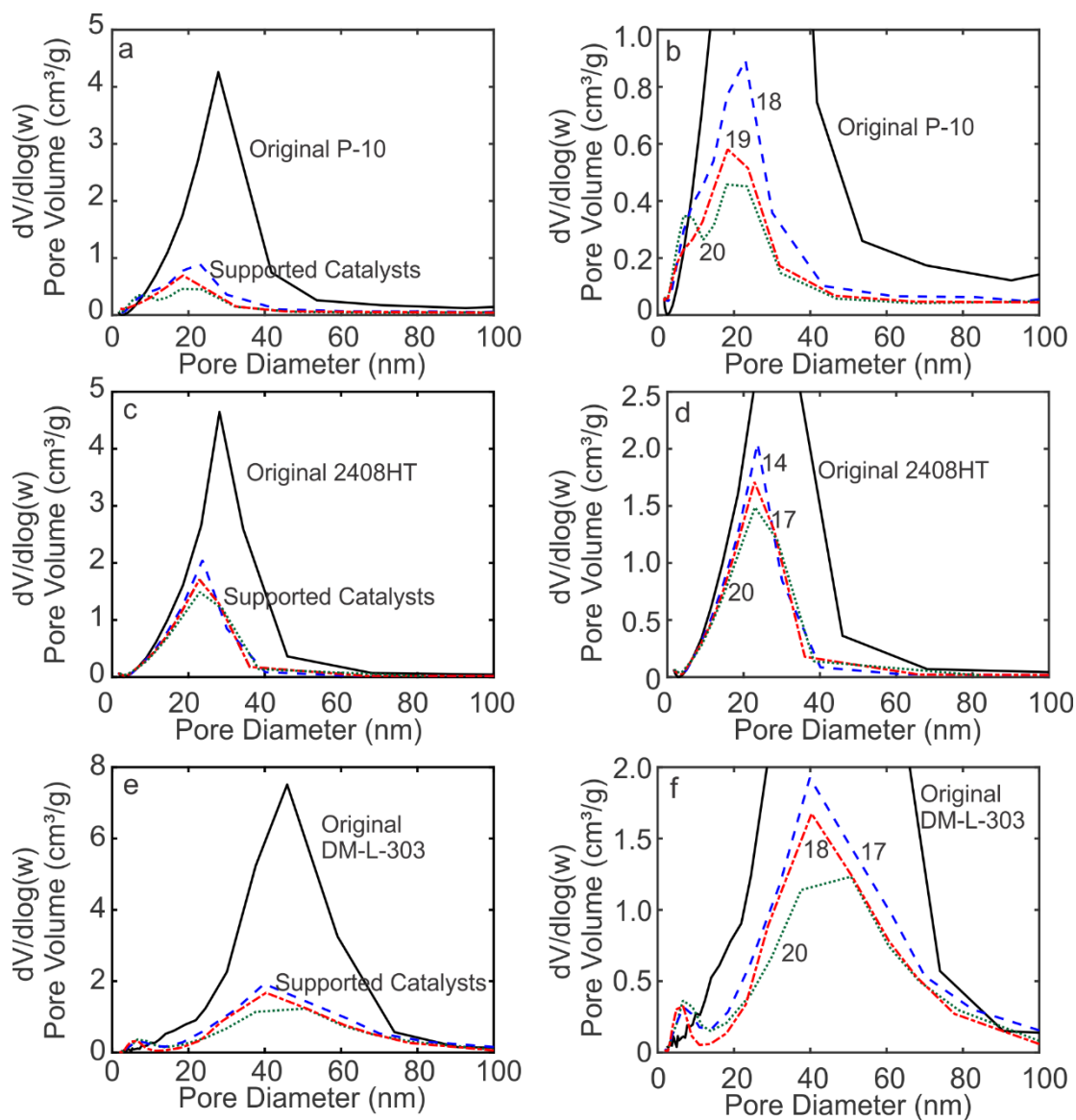


Figure 5.7. Pore size distribution of (a-b) P-10 and associated supported catalysts, (c-d) 2408HT and associated supported catalysts, and (e-f) DM-L-303 and associated supported catalysts. Numbers represent immobilized Al wt.%.

Supported catalysts produced with the 2408HT silica show a similar decrease from the original median pore diameter of 30 nm to approximately 21 nm after the immobilization of MAO (Figure 5.7c). However, the peak is unimodal with all pores decreasing in volume (Figure 5.7d). A possible explanation can be found from the physical structure of the silica shown in Figure 5.2. The internal structure of the 2408HT silica has several large interstitial voids and the silica is made up of larger-sized aggregates. During the immobilization of MAO and the formation of the MAO layer on the exterior of these aggregates, further access to smaller pores may be blocked and hence no reduction of pore diameter is seen.

Unlike the other silicas, supported catalysts prepared with DM-L-303 show a smaller decrease from the original median pore diameter of 45 nm to 40 nm (Figure 5.7e). A similar bimodal pore size distribution at high MAO loading is seen although the pores centered at about 40 nm comprises a much larger fraction compared to those centered at 5 nm (Figure 5.7f). The lack of interstitial voids in the DM-L-303 silica indicates that MAO will only diffuse through the mesopores which are uniformly distributed throughout the particle. Thus, no preferential immobilization in larger macropores occurs, and each pore is equally reduced from the presence of MAO.

5.3.5.2 Changes to Pore Volume and Surface Area

Changes to the pore size distribution and average pore diameter will also affect the surface area and pore volume of the silica. Both variables impact the local active site environment such as the active site density and pore volume around the active site which is believed to have an impact on the growing polymer chain. **Figure 5.8** shows

the surface area of the supported catalysts and the percent change to the pore volume. The surface area of each silica decreased from their initial value of 300 m²/g. For 2408HT silica, the surface area does not change much with the amount of MAO loading whereas for two other silicas (P10 and DM-L-303), surface area decreases with MAO loading. Figure 5.8b shows that the overall pore volume decreases by about 40 to 75%. These results are consistent with the literature that report the decrease in the surface area and pore volume of the original spherical amorphous silica supports after immobilization of MAO and metallocene compounds.^{101, 136, 209, 210}

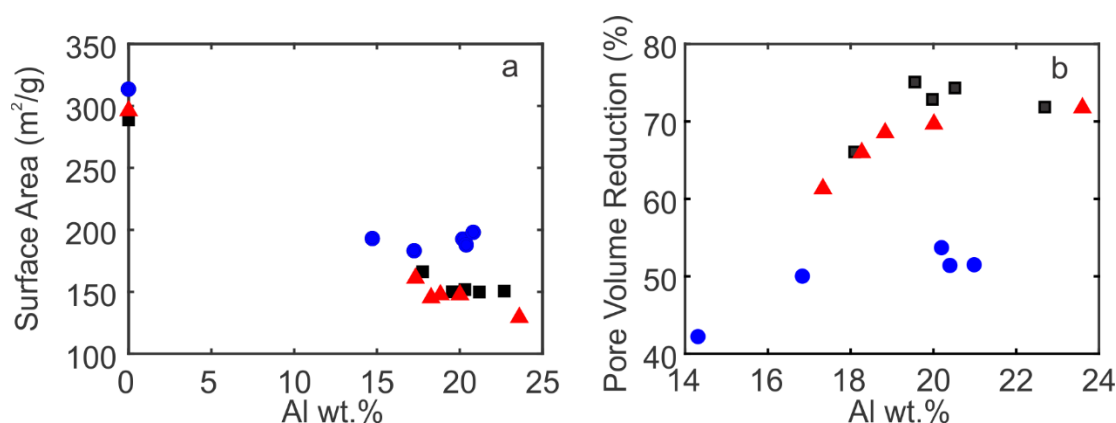


Figure 5.8. (a) Changes to surface area (b) and pore volume of the initial silica based on the immobilized Al concentration for P-10 (black squares), 2408HT (blue circles) and DM-L-303 (red triangles).

5.3.6 Polymerization Activity

Ethylene polymerization experiments in slurry and gas phase were performed with the supported catalysts prepared with the three different commercial silica particles. The instantaneous reaction rate was calculated using the flow rate of ethylene gas to the reactor while the time-averaged polymerization rates of the supported catalysts were calculated using the final weight of the polymer produced along with the initial weight of the catalyst.

Figure 5.9 shows the instantaneous polymerization rate profiles of X-30-2 and X-5-2 where X represents the silica used in preparation. These two were chosen because they represent the supported catalysts with the highest and lowest polymerization activities for the set of catalysts prepared with the same silica and Zr concentration. The difference between X-30-2 and X-5-2 is the immobilized Al content with X-30-2 having higher amounts. Despite similar amounts of immobilized MAO and metallocene compounds between catalysts P-10-30-2, 2408HT-30-2, and DM-L-303-30-2 and P-10-5-2, 2408HT-5-2, and DM-L-303-5-2, the instantaneous activities are dependent on the types of the silica used as the support. Among the three silica-supported catalysts, the highest instantaneous activity was obtained with the P-10 silica-supported catalyst, followed by the 2408HT support, and the DM-L-303 supported catalyst showed the lowest activity. This is regardless of the Al concentration (X-30-2 vs X-5-2) and in both slurry and gas phase reactions. For all supported catalysts, the maximum activity was reached after 20 minutes of reaction and the polymerization activity slowly decreased afterward in both slurry and gas phase reactions.

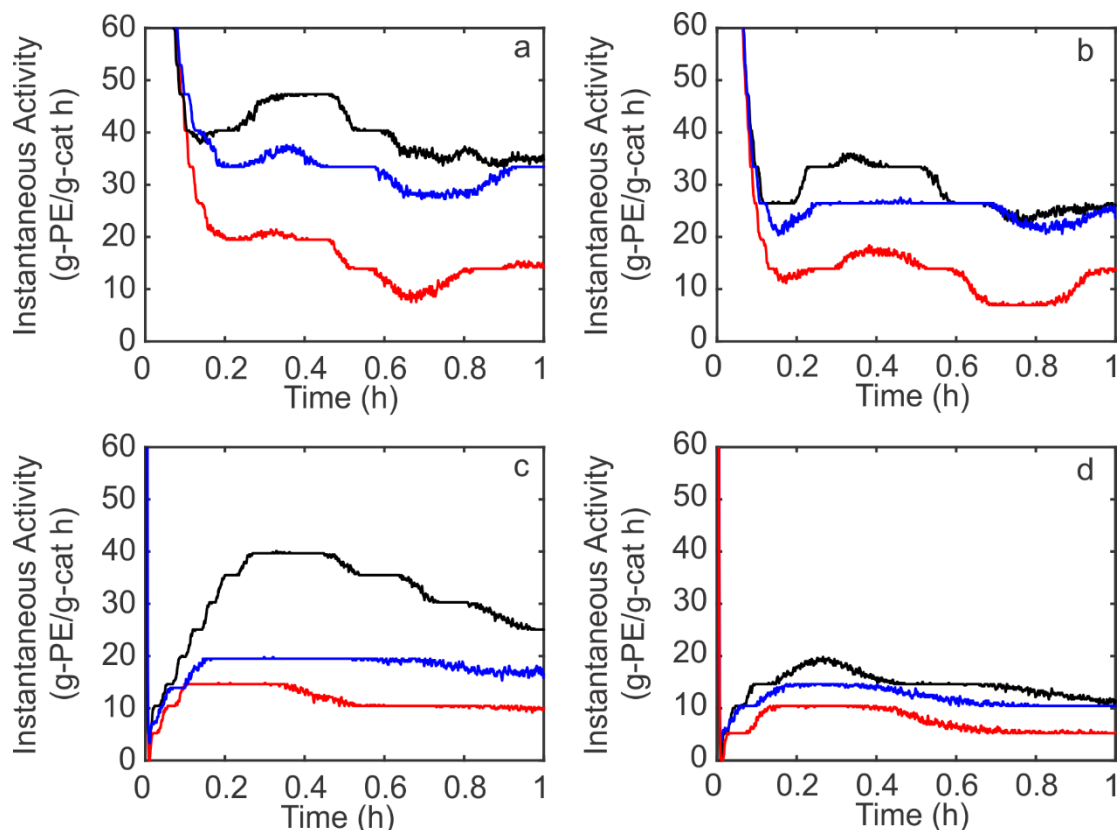


Figure 5.9. Slurry phase kinetic profiles showing the (a) X-30-2 catalysts and (b) the X-5-2 catalysts. Gas phase kinetic profiles showing the (c) X-30-2 catalysts and (d) X-5-2 catalysts. X represents the silica trade name: P-10 (black), 2408HT (blue), DM-L-303 (red).

The grade of silica used to preapre the supported catalyst will also affect the time-averaged polymerization activities. **Table 5.6** shows that supported catalysts prepared with the P-10 silica generally had higher polymerization activities, followed by 2408HT and then DM-L-303. These results correspond to those seen in the instantaneous activity of the supported catalysts. It can be seen that the supported catalysts with higher amounts of Zr content achieved higher polymerization activity for all grades of silica. However, no clear universal trend is apparent between the polymerization activity and the Al content immobilized onto the supported catalyst for all grades of silica.

Table 5.6. Time-averaged polymerization activities

Supported Catalyst ^{a)}	Slurry phase polymerization activity (g-PE/g-cat.h)			Gas phase polymerization activity (g-PE/g-cat.h)		
	P-10	2408HT	DM-L-303	P-10	2408HT	DM-L-303
X-5-1	20.68	20.93	8.05	7.42	18.94	4.13
X-10-1	20.80	11.95	11.15	14.83	9.38	5.89
X-15-1	23.00	10.84	12.93	18.72	7.10	5.06
X-20-1	23.69	11.92	14.06	18.90	4.80	8.79
X-30-1	18.28	10.75	12.88	8.79	5.75	9.11
X-5-2	33.52	28.84	9.19	15.99	20.79	5.76
X-10-2	42.99	27.24	12.60	22.40	18.46	5.97
X-15-2	37.05	21.72	12.17	30.98	16.82	12.72
X-20-2	33.40	17.01	19.62	22.47	8.68	13.90
X-30-2	34.76	21.92	18.54	17.98	9.78	11.09

Instead, qualitative trends are seen for supported catalysts prepared with the same grade of silica. For supported catalysts prepared with the DM-L-303 silica, an increase in the MAO solution concentration and the total immobilized Al concentration within the supported catalysts led to higher polymerization activities in both slurry and gas phase. However, for supported catalysts prepared with the 2408HT silica, increased MAO solution concentration decreased the polymerization activity. Despite similar Al and Zr content between supported catalysts prepared with the P-10 and DM-L-303 silica, supported catalysts prepared with P-10 silica exhibit almost double the activity of the catalysts prepared with DM-L-303. This discrepancy might be due to how the immobilized MAO affects the pore structure of each silica differently. For further insight, the time averaged activity was plotted against the pore diameters of the supported catalysts. **Figure 5.10** shows a qualitative trend of increasing polymerization activity as the pore diameter decreases due to the immobilization of higher amounts of MAO. This is seen for both slurry phase and gas phase polymerization of ethylene.

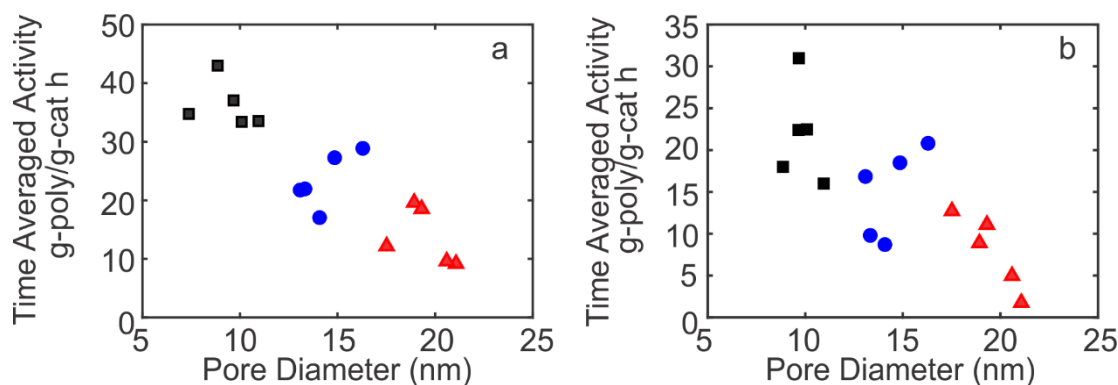


Figure 5.10. (a) Time averaged activity in slurry phase based on pore diameter. (b) Time averaged activity in gas phase based on pore diameter. Silica: P-10 (black squares), 2408HT (blue circles) and DM-L-303 (red triangles).

The influence of the pore diameter on the polymerization activity is well known. Qualitatively similar observations have been reported by Sano et al.^{122, 287, 288} and Kumkaew et al.¹²³ where higher polymerization activities were achieved with supports with pore sizes around 10 nm compared to supports with larger pore sizes. Both studies proposed that smaller pores are able to selectively immobilize smaller MAO compounds that are more active and stabilize the MAO/metallocene active site. Silveira et al.²¹⁹ proposed that the pore diameter of the support will influence the structure of the metallocene catalyst through measuring the Zr-C interatomic distance. While MAO was not used in that study, it is possible that the MAO layer within each supported catalyst will also affect the structure of the immobilized active site. **Figure 5.11** shows that the pore volume of the supported catalyst per the Zr content. It can be seen that in general, reducing the pore diameter decreases the amount of open void space around the active site. The amount of pore space around active sites was lower for supported catalysts prepared with the P-10 silica while those prepared with the 2408HT and DM-L-303 silica were similar. The reduction of space around the active site might also

affect the fragmentation behavior of the supported catalyst. Pore volume and pore diameter are believed to impact the fragility of the silica support and decreased pore space around the growing polymer chain lead to a faster buildup of hydraulic pressure and increased rate of fragmentation.^{211, 254, 289}

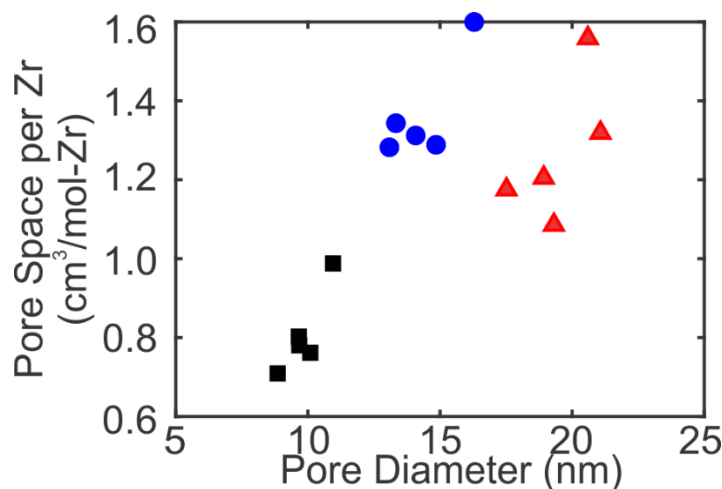


Figure 5.11. Pore volume of supported catalyst per Zr content. Silica: P-10 (black squares), 2408HT (blue circles) and DM-L-303 (red triangles).

5.3.7 Polymer Morphology

SEM images of polyethylene particles formed after 1 h of reaction were used to observe the effect of the pore structure on the fragmentation behavior of the supported catalyst. It was expected that the polymer morphology would be affected by the silica pore properties (e.g., pore volume and pore size distribution or mean pore size). **Figure 5.12** and **Figure 5.13** show the morphologies of polymer formed with the two types of silica used as catalyst supports: 2408HT and DM-L-303, respectively.

After the reaction time of 60 min, the size of the final polymer particles produced from the 2408HT silica are spherical in shape, ranging from 100 to 200 μm in diameter (Figure 5.12a). Figures 5.12b and c show some roughness on the exterior

surface of the particle with polymer aggregates comprising the surface of the particle and macropores present. Figure 5.12d shows the cross-section of the polymer particle and the presence of a thick 25 μm layer near the surface of the particle. However, a large void space as large as c.a. 20 μm inside the particle suggests that the monomer diffusion resistance in such void space will be very small for this supported catalyst (Figure 5.12d and e). Large polymer aggregates of around 20 μm are seen at the center of the particle. Figure 5.12f shows the edge region of the particle cross-section where we can see the aggregates of polymer sub-particles of around 5 μm in diameter.

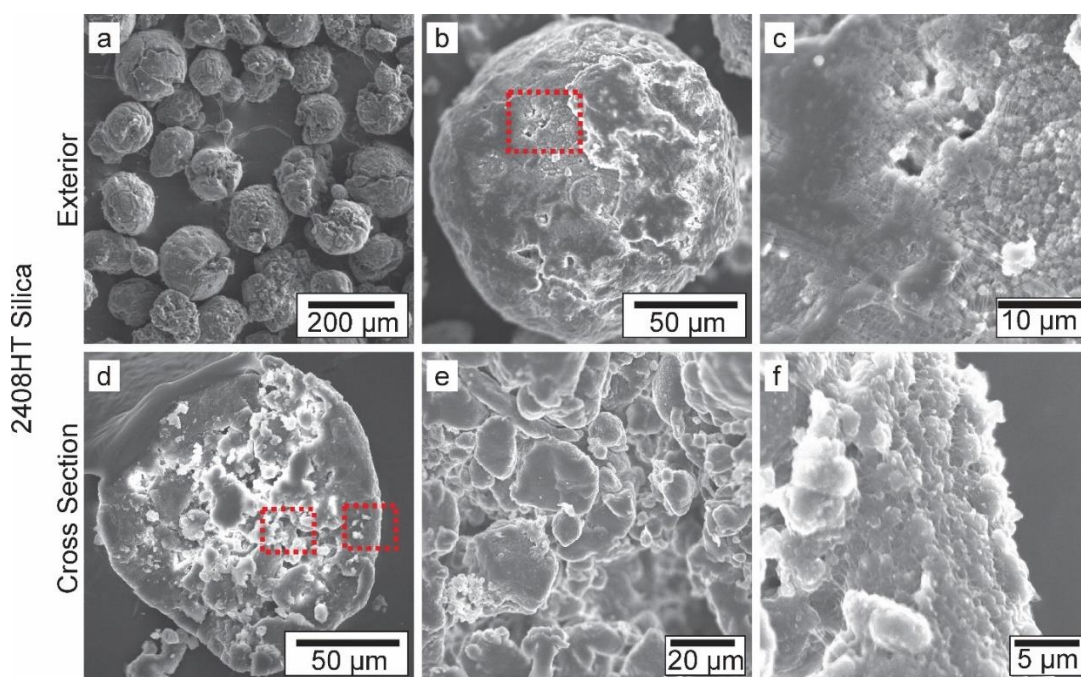


Figure 5.12. SEM images of polyethylene particles from slurry phase polymerization using 2408HT-30-2. Squares represent enlarged zones. Reaction time: 60 min.

For the DM-L-303 silica-supported catalyst that showed the lowest polymerization activities among the three set of silica-supported catalysts studied, the final polymer particles were smaller than the other two cases and they range between 75 and 150 μm (Figure 5.13a). The particles are mostly spherical with smooth exterior

surfaces that is comprised of polymer aggregates of about 1 μm in diameter (Figure 5.13b,c). In the magnified image of Figure 5.13c, we can observe the large patches of polymer on the surface of the particle exterior. These patches are composed of slightly larger polymer aggregates $\sim 5 \mu\text{m}$ in diameter. The cross section of the polymer reveals an extremely dense particle with no macropores seen (Figure 5.13d). Thus, monomer diffusion resistance might be higher for these particles and explain the low growth. The interior of a polymer particle is made up of polymer aggregates between 1 and 2.5 μm in diameter (Figure 5.13e). Figure 5.13f shows that the particle surface is dense with the packing of smaller polymer microparticles.

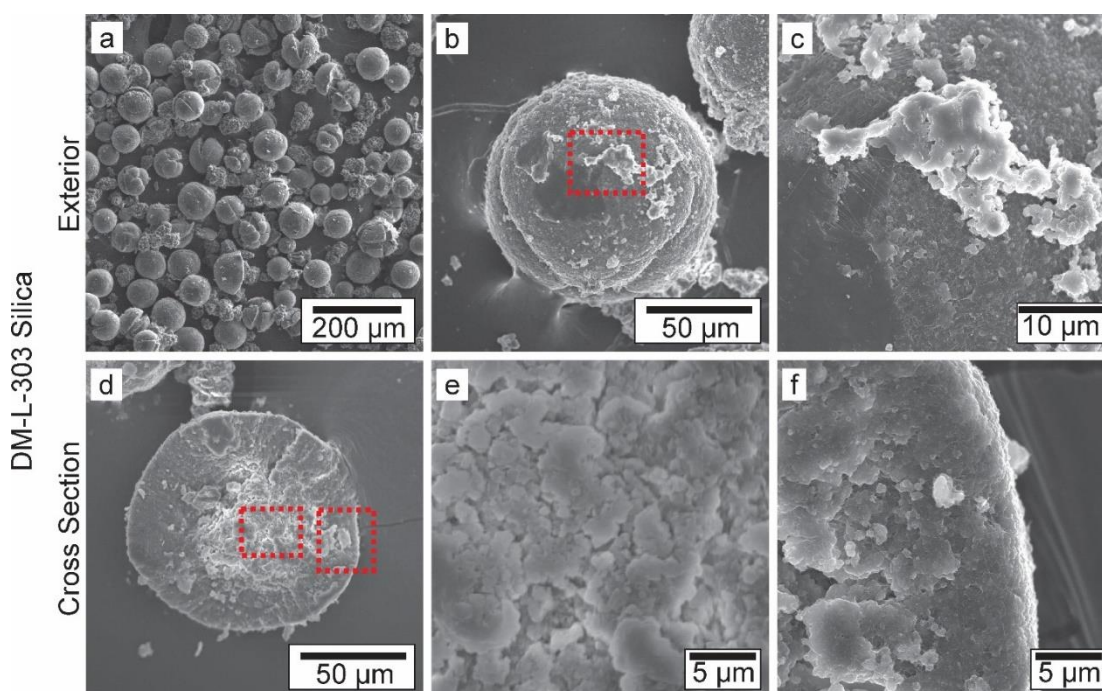


Figure 5.13. SEM images of polyethylene particles from slurry phase polymerization using DM-L-303-30-2. Squares represent enlarged zones. Reaction time: 60 min.

From the images of the cross-sections of the initial silica particle and the final polymer particle, it is shown that the internal morphology of the silica may influence

that of the polymer particle. From Figure 5.2, it is shown that the internal morphology of the 2408HT silica has a large number of interstitial voids, making the particle relatively porous. In contrast, the internal morphology of DM-L-303 is extremely compact with the silica aggregates in close arrangement with one another. From Figure 5.12, polymer particles produced from 2408HT-30-2 have a relatively porous interior while from Figure 5.13, polymer particles produced from DM-L-303-30-2 have extremely dense interior with minimal pore space between the polymer aggregates. These results qualitatively agree with the conclusion reached by Weickert et al.¹⁹⁸ who reported that the initial fragmentation of the silica support influences the final morphology of the polymer particle. During the reaction, polymer will preferentially form at the active sites at the catalyst particle exterior and on the surface of interstitial voids and macropores due to smaller diffusion limitation compared to active sites within the particle that require passage through the tortuous pore structure. As seen in Figure 5.2, large interstitial voids approximately 5 μm in diameter along with silica aggregates around 1 – 2 μm were seen throughout the interior of the 2408HT silica particle. It is believed that during the polymerization these aggregates near the surface of the particle were able to completely disintegrate, forming the dense polymer shell. The expansion of the particle from the growth of polymer led to the creation of large 20 μm void spaces that allowed monomer access to the interior active sites and continued growth.

However, no interstitial void spaces were seen in the cross-section of the DM-L-303 silica particle (Figure 5.2). Likewise, no large pores were seen in the polymer particles produced from supported catalysts that utilized DM-L-303 (Figure 5.13). It is

seen that polymer aggregates around 2 to 5 μm are present throughout the polymer cross-section from the original silica aggregate size of around 100 nm. This suggests that polymer growth was uniform throughout the particle during the reaction. However, the presence of a very dense polymer shell at the surface might have caused a strong diffusion resistance to the monomer. The lack of the large interstitial pores in the silica might have inhibited the access of monomer to the active sites due to the filling of the mesopores with polymer. Thus, the overall polymer particle is smaller than those produced with the 2408HT silica and no increase in polymerization activity is seen. Di Martino and McKenna proposed that a stress gradient, whether arising from regions with different polymerization or crystallization rates, is necessary for fragmentation to occur.^{162, 163} Similarly, McDaniel et al.²⁵⁴ proposed that Cr/silica-titania catalyst particles that are composed of primary particles in close proximity to one another will strengthen the overall particle and prevent fragmentation. It was seen from the cross-section of the DM-L-303 silica that the primary particles were packed tightly together with no interstitial voids present (Figure 5.2). After the reaction, the cross-section of the polymer particles shows similar packing of polymer aggregates. It is possible that this packing prevented fragmentation and further growth of the particle.

5.3.8 Effect on Polymer Properties

The thermal properties of the polymer formed from the supported catalyst were analyzed by differential scanning calorimetry (DSC). The DSC endotherms shown in **Figure 5.14** indicate that the polymers obtained with the same metallocene catalysts supported on different silica supports have different crystallinity and melting points. It

is important to note that these endotherms do not show the crystallization of polymer during the polymerization.

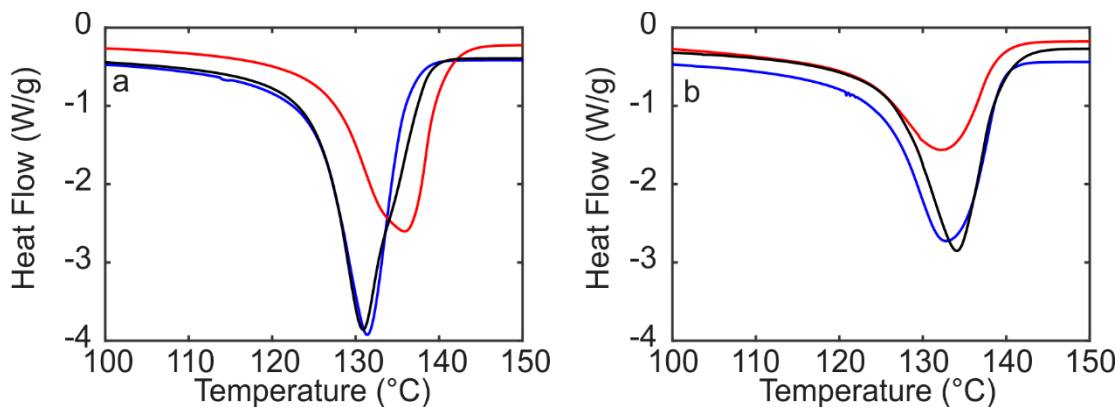


Figure 5.14. DSC curves of polyethylene formed using different supports with (a) Catalysts X-30-2 and (b) Catalysts X-5-2. X represents the silica used: P-10 (black), 2408HT (blue) and DM-L-303 (red).

Figure 5.14a shows the endotherm for the polymer with the highest crystallinity while Figure 5.14b shows the endotherm for the polymer with the lowest crystallinity for the three silicas. These represent polymer produced with supports with smaller and larger pore diameters respectively. Each endotherm has a single broad peak centered at the peak melting temperature suggesting a single site catalyst system. However, peaks for the lowest crystallinity are broader compared to those of the highest crystallinity. This can be attributed to either the occurrence of some form of branching or the presence of different types of active sites.²⁹⁰⁻²⁹² Polyethylene produced with supports with bimodal pore size distributions was seen to have lower crystallinity compared to those produced with supports with unimodal pore size distribution.^{264, 293} The original pore size distributions in those studies were extremely narrow and the bimodal pore size distribution broadened the distribution. Those studies proposed that more than one type of active site present, one in narrow pores and one wider pores. Each type of active site

would produce polymer with a different microstructure (i.e. crystallinity) and that the observed DSC graph are the combination of the endographs of both types of polymer.²²⁴ It is seen that while the pore size distribution will narrow from their initial states after the immobilization of MAO, the breadths of pores present in the supported catalysts are still fairly broad with supported catalysts that utilized P-10 and 2408HT ranging between 10 and 40 nm and supported catalysts that utilized DM-L-303 range between 10 and 80 nm. This difference in pore diameter may lead to the formation of different active sites within the particle, especially for those on DM-L-303. Further study into the molecular weights of the polymer produced would be needed.

Analysis of the endotherms shows that the polymer obtained with the supported catalysts will have differing crystallinity and melting points based on the silica the metallocene was supported on (**Figure 5.15**). The results presented in Figure 5.15 can be interpreted in the context of the activity and fragmentation behavior seen in the previous section. The crystallinity of the polymer is believed to be dependent on the local environment of the growing chain such as the density of active sites and the pore space surrounding it. Loos et al.^{163, 294} proposed that high density of active sites will lead to highly entangled polymer chains and impact the formation of amorphous and crystalline regions. These amorphous and crystalline regions will affect the diffusion of monomer through the polymer layer as well as the fragmentation behavior of the particle. It is thought that high fractions of amorphous phase polymer (i.e. lower crystallinity) facilitate overall mass transfer of monomer to reach active sites as well as being more mobile.^{295, 296} Amorphous regions consist of deformable polymer chains and generates less stress on their surroundings. Thus, fragmentation would be lower in

particles with high amounts of amorphous polymers. Figure 5.15b shows that the peak melting point increases with a decrease in the pore diameter of the supported catalysts. As melting temperature is directly influenced by the crystallinity, this is expected. Interestingly, the polymer produced with silica with interstitial voids (P-10 and 2408) show a strong correlation between the melting point and the pore diameter. However, polymer produced by DM-L-303 have a high melting point, but low crystallinity. This might be due to the tight packing of polymer aggregates seen in the cross-section of the polymer particle.

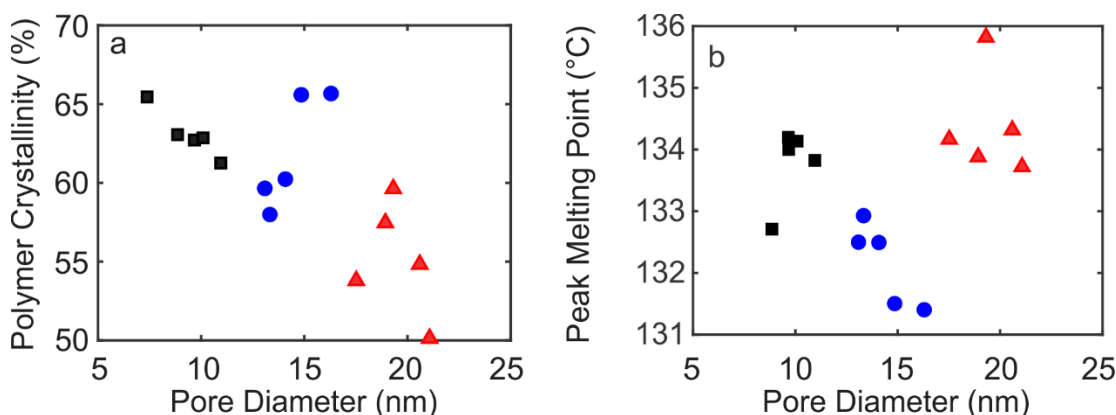


Figure 5.15. (a) Polymer crystallinity and (b) Peak melting point based on pore diameter of supported catalysts prepared with different silicas. Silica: P-10 (black squares), 2408HT (blue circles) and DM-L-303 (red triangles).

The tight packing of polymer aggregates seen within the cross-section of the polymer particle might be a result of the density of active sites. It is seen from Table 5.4 that the Zr contents of supported catalysts prepared with DM-L-303 is relatively higher than supported catalysts prepared with other types of silica despite having similar surface areas. It has been proposed that high density of active sites will result in highly entangled polymer chains preventing crystallization leading to lower overall

crystallinity.^{163, 294} It has also been reported that higher Zr content of supported catalysts have lower activity either due to the formation of dimers through bimolecular deactivation or lowered local Al/Zr ratio which prevents the total activation and stabilization of the cationic active site.^{70, 78, 104} Thus, the Zr density of supported catalyst prepared with DM-L-303 might explain the polymerization activity and thermal characteristics seen

5.4 Concluding Remarks

In this work, we have shown that the pore diameter of the silica particle will change based on the amount of immobilized MAO. This was found to be the case for all three commercial silica used in this study. The three commercial silica used were produced using different methods including sol-gel process (P-10), spray-drying process (2408HT), and emulsion-based process (DM-L-303). It was observed that the silica structure such as the primary particle aggregate size, the presence of interstitial voids, and surface roughness are different. Due to these differences, the amount of immobilized MAO and the changes to the pore size distribution and average pore diameter vary despite having similar initial surface area, pore volume, and pore size distribution values. Increasing the amount of immobilized MAO between 14 to 22 Al wt. % reduced the pore diameters by 20 to 60% and the pore volumes by 40 to 70% of their original values. The pore size distributions of the P-10 and DM-L-303 silica changed from a unimodal distribution to bimodal distribution after the immobilization of MAO. However, MAO had difficulty accessing pores smaller than 10 nm for all types of silica. This study shows that the immobilization of MAO does not affect all

silica equally and that the final pore size distribution of the supported catalysts along with other physical characteristics such as surface area, average pore diameter, and pore volume changing significantly from the original silica particles.

Strong correlations between the pore diameters of the supported catalysts and the polymerization activity and polymer crystallinity were seen. Smaller pore sizes from the immobilization of more MAO led to higher polymerization activity and higher polymer crystallinity. Physically, the pore walls restrict of the orientation of the polymer chains and lead to a higher degree of orientation and crystallization.²⁹⁷ Crystalline polymer regions are more rigid and exert higher amounts of stress on their surroundings as they cannot easily deform and absorb the compressive stress.¹⁶³ This in turn would lead to higher fragmentation as stress accumulates within the pores. Larger pore diameters and pore volumes lead to a higher fraction of amorphous polymer as the polymer chains have more space to entangle together and form amorphous regions. The role of interstitial voids within the silica was also examined. The presence of these voids led to higher activity and larger polymer particles formed. This is due to their ability to facilitate the mass transfer of monomer during the reaction to interior active sites. However, the lack of these voids produced polymer with high melting point with low crystallinity. Further study with silica particles without interstitial voids should be considered.

Chapter 6. Morphological Study of Nascent Growth of α -Olefin

Polymers on Spatially Unconstrained Silica Surfaces

6.1 Introduction

Heterogeneous polymerization of α -olefins has been well known by its unique catalyst particle fragmentation or breakup phenomena that have a tremendous impact on the catalyst performance. The growth of polymer chains inside micropores of support materials for Ziegler-Natta and metallocene catalysts is an intriguing physico-chemical process that has been the subject of research in several decades. However, due to the fragmentation of support materials and subsequent encapsulation by polymers during the polymerization, direct observations of the formation and growth of polymers at/near the catalyst sites over a solid support surface have been difficult. The growth of polymer at the active site is of particular interest due to its role in fragmentation.

For industrial use, metallocene catalysts are supported on micrometer-size silica particles (c.a. surface area of 200-500 m²/g, $\sim$ 30 μ m particle diameter and 20-30 nm average pore size) for the control of polymer morphology and stable reactor operations. The fragmentation of silica supported catalyst and the resulting morphology of olefin polymer depend upon many factors such as silica morphology, catalyst loading, and reaction conditions as seen in this dissertation. As a result, inconsistent results of polymer morphology are frequently obtained even with the same type of silica supported catalysts as seen in the previous chapters. Most of the polymerization occurs within the pores of the silica particle. The pores in a typical silica micro-particle used

as a catalyst support are very complex in nature because a silica micro-particle is essentially the aggregates of silica nanoparticles formed during the sol-gel process as seen in Chapter 5. For example, for a typical industrial silica gel used as a catalyst support (e.g., WR Grace 952), the smallest silica primary particle size is 10-50 nm and these unit particles form larger aggregates of 200-500 nm.^{98, 298} The interstices between the smallest particle units and the interstices between their aggregates are the actual pore space where active sites are formed and monomer will access during the reaction. Polymer formed at the active sites on the silica primary particle will fill the interstices and then the breakup or fragmentation of silica occurs and with the polymer particle expanding. This is similar to what is seen with Ziegler-Natta supported catalysts where Kakugo et al.¹⁶⁵ reported that each primary particle contains a catalyst crystallite as a core which will form polymer that entirely encapsulate the crystallite and grow. Although the general aspects of catalyst particle fragmentation and polymer growth with silica-supported metallocene catalysts are conceptually well accepted, the actual polymer morphologies are often hard to understand and control due to the many factors that affect their formation.

The nature of complexity of silica support particles and the difficulties in measuring catalyst site distribution on the silica surface are two of the main reasons why predicting polymer particle morphology is difficult. Understanding the exact mechanisms of polymer particle morphologies at different reaction environment and at different reaction time is a difficult and challenging problem. Thus, there is a need to understand the morphogenesis of nascent polymer growth at the catalyst site level in the holistic approach of developing an understanding of particle morphology. The

control of polymer particle morphology and particle size distribution is not only of a scientifically interesting and important problem but also of a significant industrial relevance. In industrial processes, for example, very fine particles $< 100\ \mu\text{m}$ are commonly produced during the polymerization. These fine polymer particles can cause serious reactor operational problems such as reactor fouling, poor reactor heat transfer, and poor polymer properties.

The exterior and interior structures of polymer particles have been analyzed by many researchers using scanning and transmission electron microscopy as well as this dissertation. However, direct observation of the growth of polymer at the catalyst sites and understanding of how the polymer growth leads to specific particle morphology has been a difficult problem. To observe the nascent morphology of olefin polymers in the proximity of catalyst sites, specially designed catalyst support materials will be useful. For example, flat surface silica can be used as a catalyst support and other support geometries such as spherical solid silica nanoparticles and silica nanotubes have also been used. Since these support materials do not have complex internal or secondary structures, the deposition of catalyst is possible only on the exposed solid surfaces. Therefore, the effect of silica fragmentation can be eliminated and the direct observation of nascent polymer morphology is possible.²⁹⁹⁻³⁰⁵ When ethylene was polymerized over metallocene catalysts deposited on solid silica nanoparticles and silica nanotubes, it was observed that the basic polyethylene morphology was a nanofibril of diameter 30-50 nm.^{306, 307} However, the curvature of the solid nanoparticle and nanofibril make it difficult to accurately view the growth of the polymer at longer reaction times.

To elucidate the growth of polymer at the catalyst surface, a flat surface silica is a convenient means to support metallocene catalysts.¹⁸¹⁻¹⁸⁹ The characteristics of catalyst crystallites and polymer growth with CrOx/flat-SiO_2 , $\text{rac-[Me}_2\text{Si(2-Me-4-(1-Naph)Ind)}_2\text{]ZrCl}_2(\text{CH}_3\text{AlO})_x\text{/flat-SiO}_2$, and Ziegler-Natta catalyst/flat-silica catalysts have been reported by Thüne and coworkers.¹⁸¹⁻¹⁸⁴

In this work, flat surface silica has been fabricated using a silicon wafer as a substrate. The wafer is then oxidized to form a layer of silica on the wafer surface. The oxidized wafer is then heat treated before a MAO layer is immobilized. Afterwards, metallocene catalyst is immobilized to the MAO layer forming active sites. **Figure 6.1** illustrates the procedure for the preparation of flat silica supported catalyst. In what follows, we shall present the experimental analysis of polymer growth on flat surface silica support with $\text{rac-Et(Indenyl)}_2\text{ZrCl}_2$ catalyst for propylene and ethylene polymerization in liquid and gas phases.

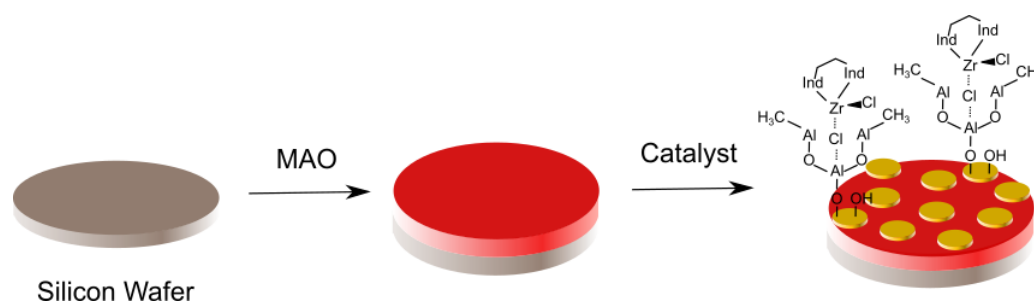


Figure 6.1. Preparation of flat silica-supported catalyst.

6.2 Experimental

6.2.1 Preparation of Flat Surface Silica-Supported Catalysts

A silicon wafer (University Wafer, P-type (100)) was calcined in a furnace at 250°C for 24 h, rinsed in acidic piranha solution and water, and dried *in vacuo*

overnight. The treated wafer with surface silica layer was then immersed in a MAO solution (10 wt.%, Sigma-Aldrich) for 8 h into to immobilize MAO compounds to the surface. Afterwards, the wafer was rinsed with toluene several times to remove unbound MAO compounds prior to immersing the wafer in a catalyst solution (*rac*-Et(indenyl)₂ZrCl₂) (EBI catalyst, Sigma Aldrich) at 70°C for 24 h. Again, the wafer was rinsed with toluene several times to remove unbound metallocene compounds. **Table 6.1** summarizes the properties of flat surface silica and other silica support materials for comparison. The Zr concentration was measured by inductively coupled plasma mass spectrometry (ICP-OES, ACTIVA, JY HORIVA). We note that the amount of Zr per flat silica surface area (mol/m²) is about two orders of magnitude larger than the spheroidal commercial silica microparticles.

Table 6.1. Properties of silica-supported catalysts

Support material	Diameter (μm)	Surface area (m ² /g-cat)	Zr (mol/g-cat)	Zr (mol/m ²)
Flat-silica	-	0.015	8.56 x 10 ⁻⁸	5.71 x 10 ⁻⁶
Solid silica nanoparticle	0.4	16.0	3.17 x 10 ⁻⁵	1.98 x 10 ⁻⁶
Commercial micro silica	30-50	250~295.0	(1.88 ~ 2.82)×10 ⁻⁵	(7.52 ~ 9.56)×10 ⁻⁸

6.2.2 Slurry and Gas Phase Polymerization

Ethylene and propylene polymerization experiments were carried out in a 500 mL high pressure glass reactor. For slurry phase polymerization experiments, the supported catalyst, MAO (Sigma Aldrich), and toluene (Fisher Scientific) were charged into a glass reactor bottle in a dry box under argon atmosphere. For gas phase polymerization experiments, no solvent was added to the reactor. The reactor assembly was then removed from the dry box and installed in a ventilated fume hood. The reactor

temperature was controlled by immersing the reactor bottle in a constant temperature bath which was controlled within $\pm 2^{\circ}\text{C}$ accuracy. Since the size of flat surface wafer and the amount of catalyst sites was small, the reaction exotherm was quite negligible and the isothermal reaction condition was well maintained during the course of polymerization. The polymerization was started by supplying monomer gas to a desired monomer partial pressure in the reactor. The reactor pressure was maintained constant by the pressure controller. After polymerization, the reactor was vented and the wafer was retrieved and quenched with a 10 vol.% HCl/methanol solution to stop the reaction. For the scanning electron microscopy analysis (SEM, Hitachi SU-70), the wafer-polymer samples were coated with gold layers using a Hummer X Sputter Coater to improve image quality.

6.3 Results and Discussion

6.3.1 Slurry Phase Propylene Polymerization

Propylene was first polymerized on a flat silica-supported catalyst. In conducting the polymerization experiments, several preliminary experiments were carried out to find the favorable reaction conditions that would allow for the good observations of polymer growth at the catalyst surface. If the reaction rate is too high (e.g., high reaction temperature or high monomer partial pressure), polymer growth is too fast and observing the intimate morphology near the active sites was difficult because the silica surface is covered with too much polymer. On the other hand, if the reaction rate is too low, polymer does not grow to its full morphological structure. Thus,

a considerable amount of time has been spent to find the right reaction conditions for the observation of polymer growth and polymer morphology.

Figure 6.2 illustrates the experimental results of polypropylene (PP) morphologies at the flat silica surface catalyst in liquid toluene at different time points. The polymerization experiments were carried out in toluene at 30°C at 50 psig of propylene partial pressure for 0.75 and 3h respectively for Figures 6.2a-b and 6.2c-d. Figure 6.2a shows that PP initially forms a primary micro-globule of size 3-7 μ m at the surface. We can see from the magnified view (Figure 6.2b) a PP nanofibril with a diameter of approximately 100 nm protruding from the surface of the primary micro-globule. Over time, these nanofibrils will form secondary micro-globules on the surface of the primary micro-globule. As can be seen in Figure 6.2c (reaction time: 3 h), these interconnected micro-globules will form a layer of thickness larger than 20 μ m. The magnified view (Figure 6.2d) shows an interesting morphology. First, a close observation of the polymer micro-globule at the silica-polymer interface shows that a large number of polymer nanofibrils emanate from the flat surface of silica and they penetrate into the bottom of the micro-globule. It is believed that the micro-globule size increases as these polymer nanofibrils are supplied from the silica surface. Secondly, we can observe a nascent secondary growth of a micro-globule about 1.0 μ m on the surface of a larger micro-globule (Figure 6.2d).

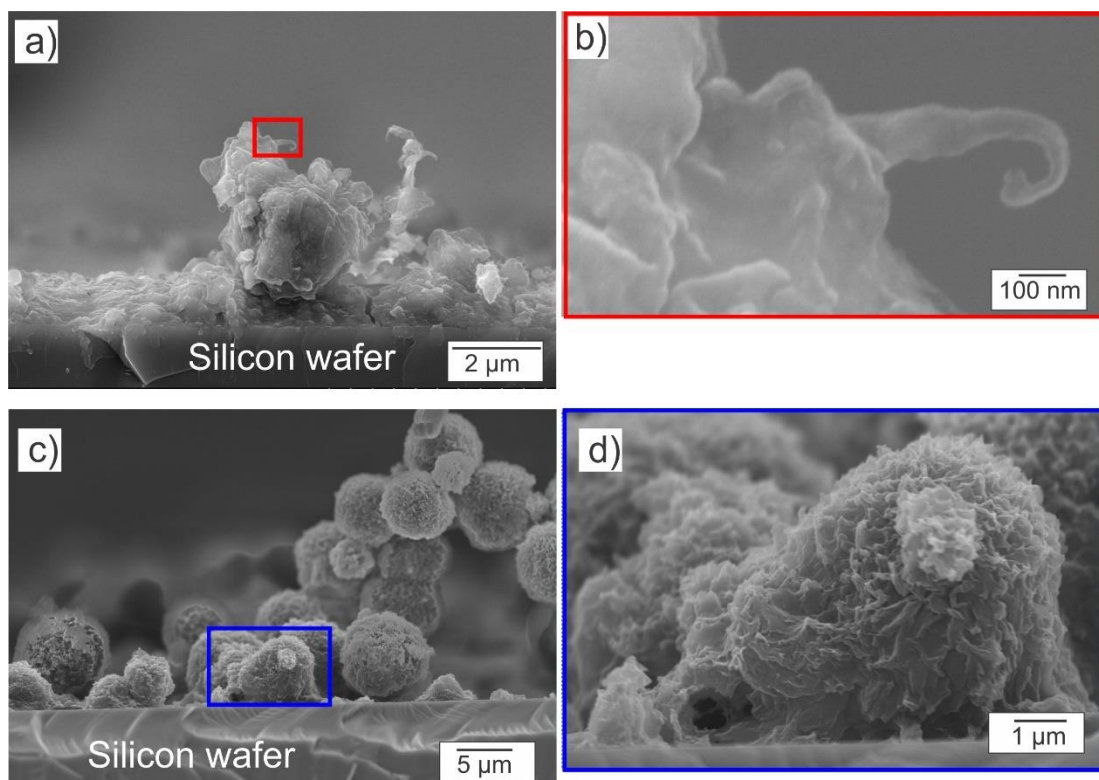


Figure 6.2. Polypropylene near the catalyst surface in a liquid phase polymerization after (a-b) 0.75h and (b-c) 3h at 30°C. Colored boxes represent magnified views.

From this, we find that initial growth of PP is that of nanofibrils. Due to the low reaction temperature employed in our experimental study, the rate of polymerization of PP and the growth of the nanofibrils were relatively slow, allowing us to observe the fine details of the morphological developments. The SEM images presented in the above suggest that nanofibrils emanating from each active site collapse upon themselves and form the micro-globules. **Figure 6.3** shows SEM images of a single PP micro-globule. Indeed, we observe that the interior of the micro-globules is quite porous and it is comprised of intertwined nanofibrils approximately 100-300 nm in diameter (Figure 6.3a). These larger nanofibrils are thought to have been initially nanofibrils of approximately 50 nm in diameter (Figure 6.3b), similar to those seen by Guttman and Guilett with crystalline α -TiCl₃ catalyst.^{306, 307}

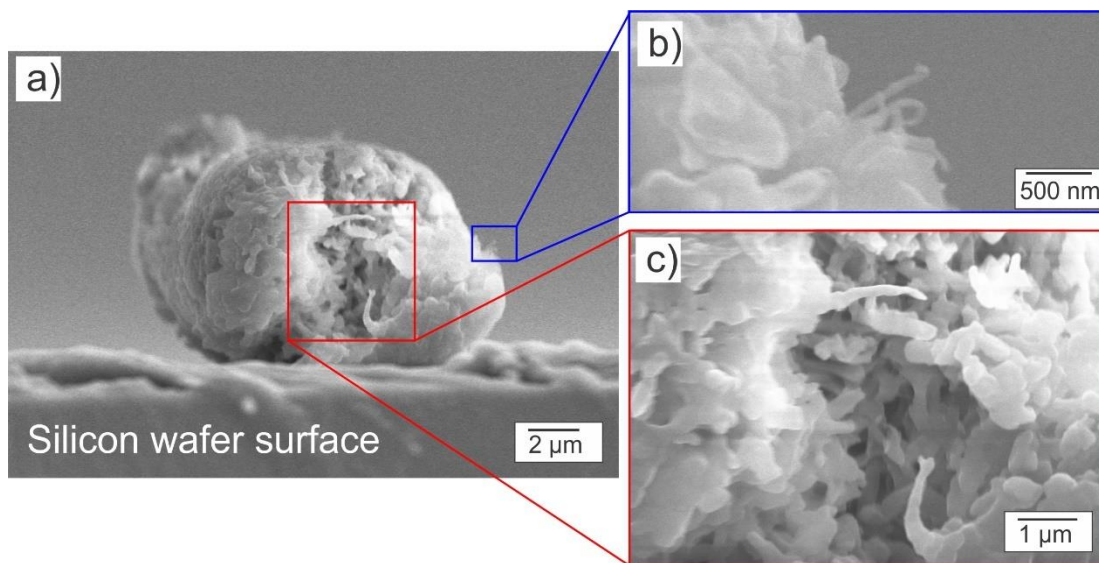


Figure 6.3. (a) Polypropylene microglobule highlighting (b) nascent nanofibril growth, and (c) interior structure in a liquid phase polymerization after 3h at 30°C.

The energy-dispersive X-ray spectroscopic analysis (EDX/EDS, EDAX) has also been conducted. The point scan analysis of the sample as shown in **Figure 6.4** indicates the presence of Zr (2.28 wt.%) in the + marked position of the PP globule (Figure 6.4a). The EDX scan data suggests that Zr in the PP globule might be from metallocene compounds that detached from the silica surface as PP nanofibrils grew. In some other PP globules, the amount Zr varied from near zero to a small wt. fraction. It is not clear whether detached Zr sites in the PP globule continue to be active or they lose activities. If the detached catalyst is still active, it is possible that the PP globules may continue to grow with time. We have also observed that the secondary growth of a globule in Figure 6.4a has also contained a small amount of Zr, suggesting that the secondary globule might have grown from the detached Zr-site. However, it appears that the detached Zr sites have lost catalyst activity rapidly and the secondary globule growth seems to have been terminated before it grows to larger size.

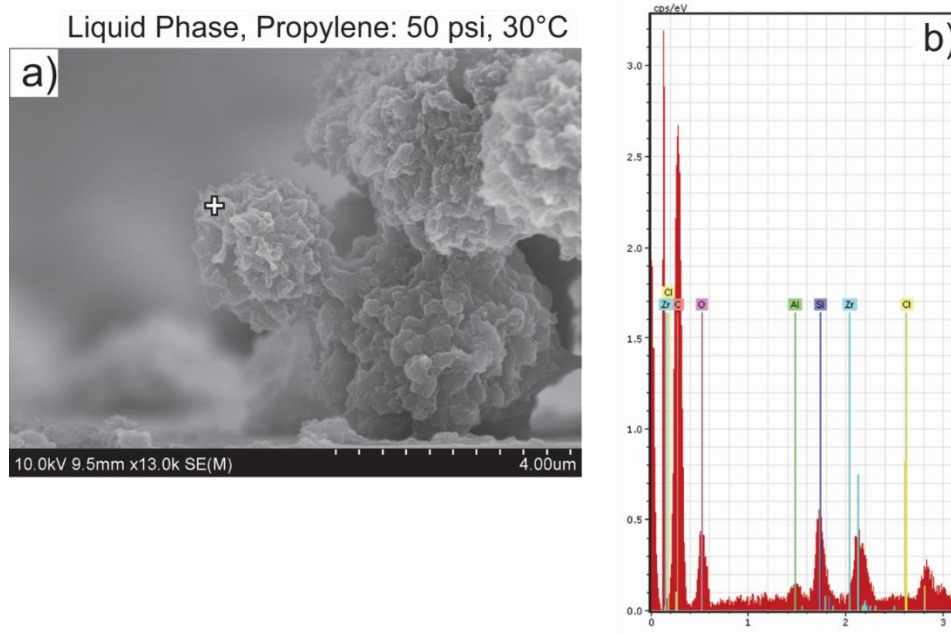


Figure 6.4. EDX elemental point scan (marked by + in (a)) of a PP globule.

6.3.2 Gas Phase Propylene Polymerization

Using the same flat surface silica wafer, we carried out gas phase polymerization at 20°C at 50 psig of propylene partial pressure for 11 and 21 h respectively and the results are shown in **Figure 6.5**. When propylene was polymerized in gas phase, the reaction rate was much lower than in liquid slurry polymerization. This was due to the difference in propylene concentration in toluene (2.29 mol/L) compared to gas phase (0.14 mol/L). Unlike the PP micro-globules formed in liquid toluene phase (Figure 6.2), no layer of discrete micro-globules is observed in gas phase polymerization. Instead, gas phase polymerization results in the formation of PP globules of about 200 nm and their aggregates (Figure 6.5a). These PP globule aggregates are made up of smaller nanoparticles with approximate diameters of 5-10 nm (Figure 6.5b) on top of a rather uniform PP layer just above the flat silica surface. An observation that can be made is that as reaction time progresses, this uniform PP

layer grows thicker. We hypothesize that the PP globules initially grows in a structure similar to the top region. Over time, the reaction progresses in a way that polymerization occurs outwards from the globules parallel to the flat plane faster than polymerization from the globule normal to the flat plane. This “fills in” the gaps between the PP globules resulting in a uniform PP layer above the flat silica surface (Figure 6.5c and 6.5d).

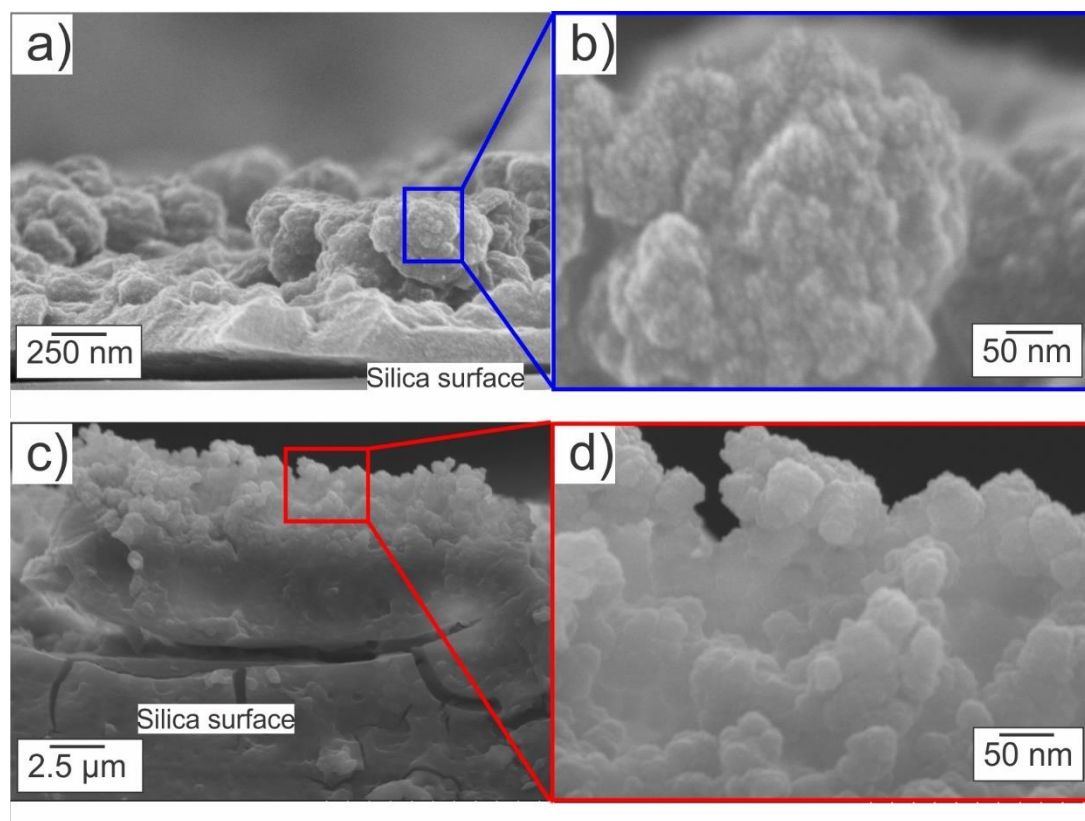


Figure 6.5. Polypropylene near the catalyst surface in a gas phase polymerization over 11h (a and b) and 21h (c and d) at 70°C.

6.3.3 Slurry Phase Ethylene Polymerization:

The nascent growth of polyethylene (PE) in slurry phase has also been investigated using the flat surface silica supported catalyst. The EBI catalyst used in our study is more reactive toward ethylene than propylene. **Figure 6.6** shows the SEM

images of PE formed at the silica surface in liquid toluene at polymerization temperature of 70°C and with 30 psig of ethylene partial pressure for 20 min of reaction time. The dissolved ethylene concentration in toluene is 0.15 mol/L. We observe that the morphology of PE shown in Figure 6.6 is quite different from that of PP shown earlier. Rather than exhibiting the discrete micro-globule structure of PP, PE forms ribbon-like structures and creates a PE layer of thickness about 100 μm . The large layer thickness indicates that the EBI catalyst was very active for ethylene polymerization. The enlarged images (Figures 6.6b for the top portion of the PE layer and c for the bottom layer) show that the PE ribbons consist of PE nanofibrils that are about 25-40 nm diameter. As these PE nanofibrils get close and fuse together, they form rather smooth ribbon-like or curled sheet-like morphology. Due to high polymerization rate when the wafer is immersed in liquid toluene, these ribbons are very mobile and flow easily away from the surface of the silica wafer. This results in a thick layer, but one that is significantly light and sparse.

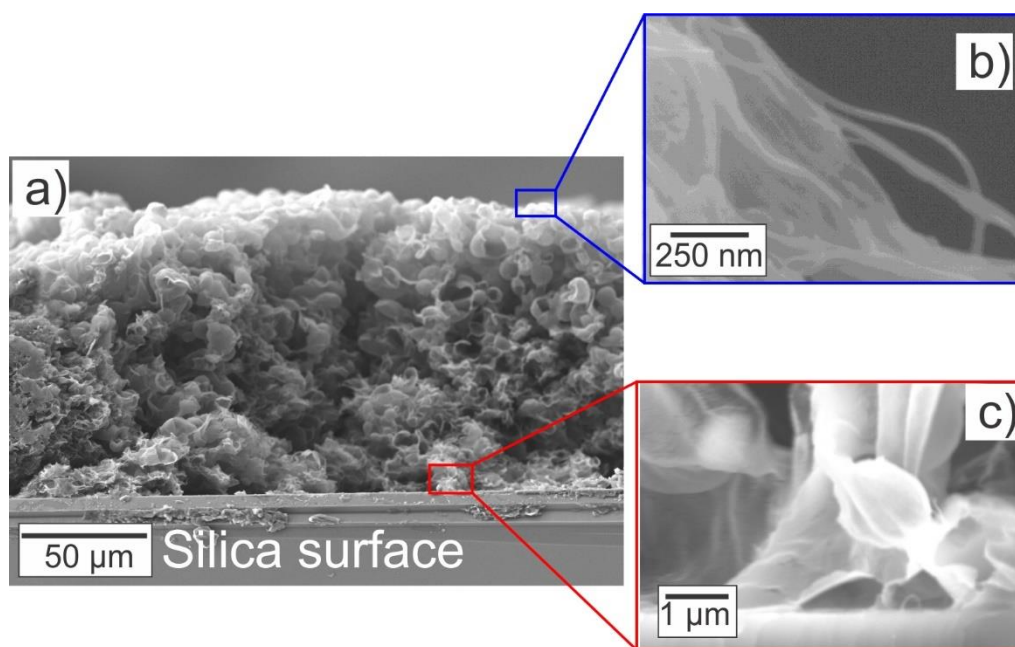


Figure 6.6. Polyethylene on flat silica surface at 70°C, 30 psig, 20 min in toluene.

6.3.4 Gas Phase Ethylene Polymerization

The nascent morphology of PE prepared by gas phase polymerization is shown in **Figure 6.7**. For these samples, gas phase polymerization was carried out at 70°C at 50 psig of ethylene partial pressure for 21 hr ($[E] = 0.121$ mol/L). The PE layer near the flat surface silica consists of the aggregates of PE particles of about 200 nm diameter and the polymer layer shows high porosity. Along the PE layer height of about 3 μ m shown in Figure 6.7, we observe that the size of particle aggregates is much larger in the top region than in the bottom surface region, indicating that as more PE primary particles are formed at the surface, they aggregate and partially fuse to form larger structures. As the catalyst deactivation occurs, the newer polymer particles (particles near the silica surface) do not grow to large size as in the early polymerization period. Unlike in the polymerization in slurry phase (Figure 6.6), no ribbon-like morphology is seen in Figure 6.7. Instead, PE takes a structure similar to PP in gas phase polymerization shown in Figure 6.5. Despite the similarity of gas phase PE morphology to that of gas phase PP globules, a key difference is the absence of a uniform layer at the wafer surface seen in PP gas phase polymerization (Figure 6.6). Due to the increased activity of the EBI catalyst towards PE polymerization, it is believed that this increased growth rate means that new PE particles preferentially grows upward from primary particles away from the wafer surface rather than outwards along the surface.

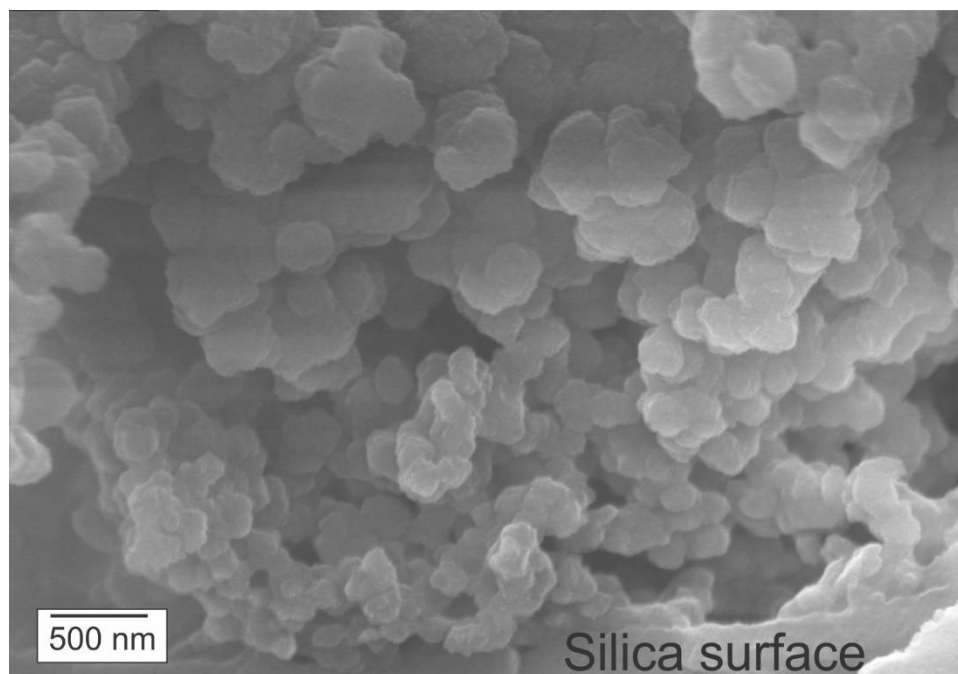


Figure 6.7. PE globules near the flat silica surface in gas phase polymerization.

6.3.5 Sequential Polymerization of Propylene and Ethylene:

During the polymerization of propylene, we observed the detachment of active site from the wafer surface and secondary formation of polypropylene globules. In order to determine if the majority of growth occurs from these detached active sites or active sites immobilized on the silica surface, sequential polymerization of propylene and ethylene was performed. The different polymer morphology of both polypropylene and polyethylene would be easy to distinguish the regions of growth. First, propylene was polymerized in toluene at 30°C at 50 psig of propylene partial pressure ($[C_3H_6] = 2.29 \text{ mol/L}$) for 8 h to achieve a thick layer and then the reactor was vented to remove dissolved propylene. Then, ethylene was supplied to the reactor at 50 psig of ethylene partial pressure ($[C_2H_4] = 0.15 \text{ mol/L}$) and the temperature was raised to 70°C for 20 min of reaction time. **Figure 6.8** shows the SEM images of the polymer at the flat silica

surface. From Figure 6.8 we can see that there are two regions of different morphologies. The top region consists of micro-globules with diameter 3-7 μm , and the bottom region consists of nanofibrils and ribbons. These respectively correlate to polypropylene and polyethylene which were previously described. Similar to PP homopolymerization, smaller secondary micro-globules can be seen on the surface of larger micro-globules. For the second stage of ethylene polymerization, we see ribbon-like structures and nanofibrils emerging from the surface of the silica wafer underneath the layer of PP globules. Because the growth of PE is restricted by the layer of PP, PE is confined to a smaller window compared to ethylene homopolymerization. Polyethylene will grow from the Zr active sites on the surface until there is enough to “push” the PP micro-globule layer away. This results in a PE layer that is very open as PE growth is concentrated at specific areas and creates spaces where there was no PE growth. Previously, we described how detachment of Zr sites from the silica surface might have occurred and formed secondary micro-globules followed by loss of activity. However, we do not see any morphological features of PE at the top of the PP micro-globule layer where detached Zr sites would likely be indicating probable deactivation. In other words, ethylene polymerized mostly at the active catalyst sites immobilized on the wafer surface.

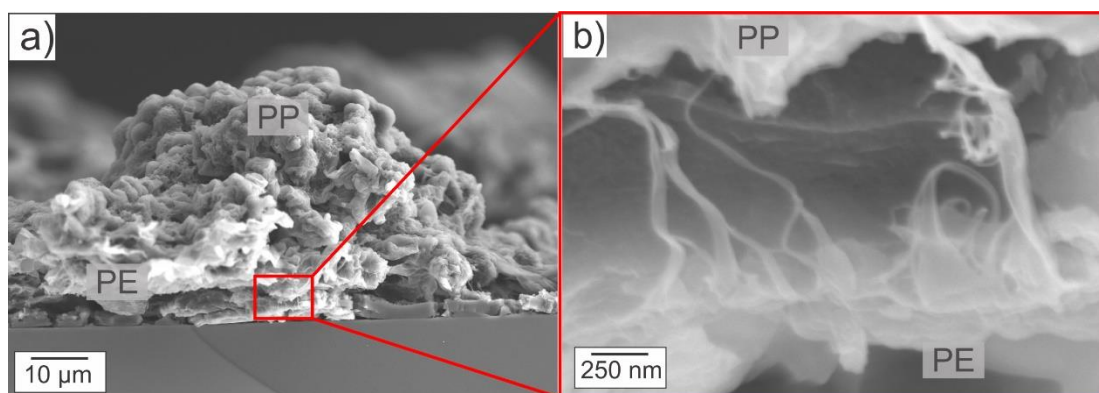


Figure 6.8. Sequential polymerization of propylene and ethylene in liquid toluene.

We have also performed the sequential polymerization in reverse order by polymerizing ethylene in toluene first at 50 psig of ethylene partial pressure at 70°C for 20 min. The reactor was then vented to remove dissolved ethylene and transferred to a secondary temperature bath at 30°C. Propylene was then supplied at a partial pressure of 50 psig and was left to react for 8 h. The results are shown in **Figure 6.9**.

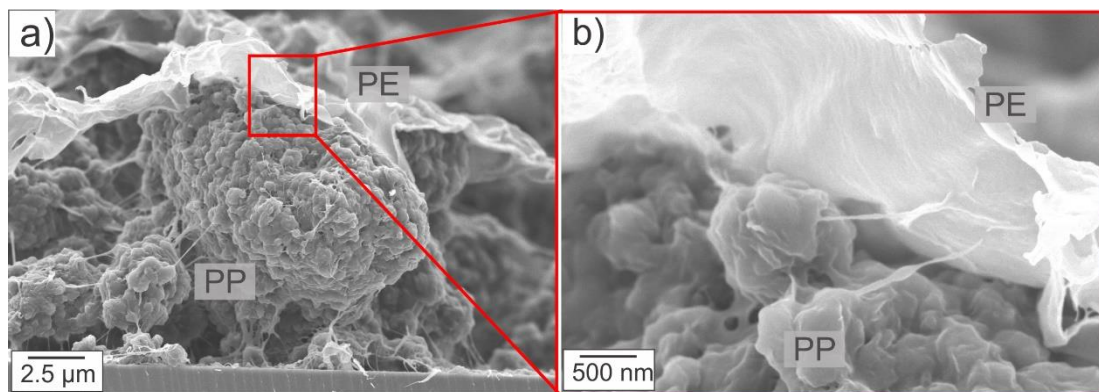


Figure 6.9. Sequential polymerization of ethylene and propylene in liquid toluene.

Again, we observe two regions of differing morphologies. The top region, which has a sheet appearance, corresponds to the PE growth, and the bottom region, which comprises of micro-globules, corresponds to the PP growth. Somewhat unusually, the PE growth is restricted only to a single sheet at the top of the polymer layer. A closer look at the PP micro-globule layer provides a possible explanation as to why the distinct PE ribbon morphology is missing. Previously, a homopolymer PP layer exhibited only micro-globule morphology. However, the PP micro-globules formed after PE homopolymerization are smaller and exhibit fibrils emanating from them. One can also see long fibrils at the wafer surface where Zr active sites are theorized to be located. We have seen that a homopolymerization of ethylene is a very

light ribbon formation. It is hypothesized that as polypropylene globules are formed at the wafer surface, they push the polyethylene ribbons out of the way and grow in spaces between the ribbons. The PE ribbons restrict the growth of the micro-globule causing them to be smaller than those previously seen. The PE ribbons surrounding the PP micro-globule would then be draped over the PP micro-globule.

6.4 Concluding Remarks

In this chapter, we have presented the experimental study of nascent morphological development of polypropylene and polyethylene over EBI catalyst supported on flat surface silica. The morphologies of PP and PE synthesized in liquid toluene and gas phase were investigated. It was observed that PP layer on the silica surface consists of micro-globules of 3-7 μm and the basic structural unit of micro-globules is PP nanofibrils emanating from the catalyst site on the silica surface. The detachment of some Zr sites has also been observed from the EDX point scan analysis of PP micro-globules that are far from the silica surface. The observed secondary growth of PP micro-globules is believed to have occurred by the detached Zr site, but it is speculated that these Zr sites have lower activity to result in smaller secondary PP micro-globules. In the gas phase polymerization of propylene, the formation of discrete PP micro-globules was not as prominent as in the presence of liquid toluene phase. The PP globules are smaller and more compact, probably due to less mobility of PP nanofibrils near the catalyst sites to form micro-globules in the absence of liquid medium.

Ethylene polymerization in liquid toluene yield PE with ribbon- or curtain-like morphology. Polyethylene nanofibrils grown from surface catalyst sites fuse together to form a thin layer, instead of forming a three-dimensional globular structure as in propylene polymerization. It is likely that PE is more flexible than PP and the rate of PE formation is much faster than that of PP to form flatter morphological structures as observed. However, the PE synthesized in gas phase polymerization show globular morphology and no ribbon-like morphology is observed. It is possible that the gas phase polymerization rate for the reaction conditions employed was too low to form a ribbon- or sheet-like structure. The sequential polymerization experiments of propylene/ethylene and ethylene/propylene have also been conducted and the resulting morphology of each polymer was quite similar to that of homopolymer case. The results of sequential polymerization experiments suggest that if the polymerization occurs in a multigrain model framework, a distinct two-layer polymer particle is expected to be formed with the first polymer in the outer layer and the second polymer in the center.

In interpreting and extrapolating the results of morphological study presented in this paper, it is important to note that there was no spatial constraint for the growth of polymers from the catalyst sites on silica surface. If conventional silica microparticles are used as catalyst supports, the resulting morphology near the catalyst sites can be different from what we have observed in this work because the space above active sites within a fragmented and growing polymer particle will be constrained and certainly the growth of polymer will be affected by this factor.

Chapter 7. Conclusions and Recommendations for Future Work

7.1 Conclusions

In this dissertation research, we initially focused on the effects of intraparticle mass transfer within the particle which were directly affected by the preparation conditions. The variables used in the preparation of supported metallocene catalysts for this purpose included the volume (amount) and concentration of the MAO solution, the concentration of the metallocene solution, the contact time in those respective solutions, and the silica pore structure. It was found that these factors will not only affect the distribution of active sites, but also the pore structure of the supported catalyst and ultimately the fragmentation behavior and polymer properties.

In Chapter 2, we investigated the effect of uniform and non-uniform distribution of active sites within the supported catalyst on gas phase ethylene polymerization. Catalysts with non-uniform distributions led to increasing number of fine particles, some of which have active sites while others do not. It was found that the distribution of active sites was directly related to the contact time used during the preparation process. Our experimental results concluded that a uniform distribution is needed to mitigate the formation of fine particles.

In Chapter 3, the preparation conditions were varied so that supported catalysts with varying pore diameters and distribution of active sites were prepared and used in both slurry and gas phase polymerization of ethylene. It was shown that the pore diameter of the supported catalyst will be altered from the silica's original value based on the Al concentration or the amount of immobilized MAO. Catalysts with narrower

pore sizes led to higher polymerization activity and increased fragmentation in both slurry and gas phase. The distribution of active sites within the particle led to different kinetic behavior such as the induction time between the start of the reaction and maximum instantaneous activity. Our results illustrate the need to carefully tailor the preparation of the catalysts for the appropriate polymerization process.

In Chapter 4, a dynamic mass transfer and complexation model was developed to obtain a better understanding of the experimental observations. The model was used to study the effects of particle size and contact time on the spatial distribution of catalyst active sites. The results of the model qualitatively correlate with observed experimental values and can be used to prepare supported catalysts with better performance.

In Chapter 5, the impact of interstitial voids within the silica particle on the immobilization of catalytic compounds and the fragmentation behavior were examined. The pore diameters of both spray-dried and emulsion-based silica particles were changed based on the amount of immobilized MAO. Each silica had different adsorption behavior based on their original pore structures. However, qualitatively similar trends were observed where polymerization activity and crystallinity of the polymer depend on the pore diameter of the catalyst.

In Chapter 6, the flat silica model was produced that would allow the view of active sites on the surface of the silica wafer during polymerization. The experimental results demonstrated that polyethylene and polypropylene have different morphologies following the initial polymer chain growth. Active sites could possibly leach away from the surface leading to further growth in slurry phase. This demonstrates the importance of having metallocene compounds firmly immobilized to the silica surface as these

growths could lead to poor morphology of the overall polymer particle. In addition, the results illustrate the importance of the presence of the liquid phase on the morphology of the polymer at the active site and how the buildup of polymer at the active site during polymerization contributes to fragmentation.

7.2 Recommendation for Future Work

7.2.1 Effect of Mechanical Strength of Silica Particles on Fragmentation

The mechanical strength of the silica particle is an essential property that influences the fragmentation process. However, mechanical strength of the particle such as crushing strength, stiffness, or hardness are rarely reported. One possible avenue to research these properties is the use of nanoindentation. Nanoindentation has been used to measure the mechanical properties of electrodes in batteries,^{308, 309} aggregated and single nanoparticles,^{310, 311} coatings,³¹² and biomedical applications.³¹³⁻³¹⁵ In this analysis, a hard tip is pressed into a sample for a given depth. The load needed to impress the tip and the indentation area would be recorded to provide mechanical properties of the sample.

McDaniel et al.²¹² studied how the deposition of silicate oligomer onto silica gel narrowed the pore diameter. This led to higher activity and higher molecular weight of the polymer formed. However, this deposition strengthened the silica as the silicate oligomer bonded to the silica surface and strengthened the particle, preventing fragmentation. Using an experimental setup to test crushing strength of milliparticles, Zakeri et al.³¹⁶ analyzed copper-zinc catalysts on different alumina particles with different catalyst loading. They found that as porosity of the initial particle increased

from 10 to 50%, the crushing strength decreased. After the immobilization of the catalyst, the crushing strength was less than the original alumina presumably due to mechanical and thermal stresses during the immobilization process and the drying process. Despite similar changes to the silica particle, opposite effects on the mechanical strength were seen. In Chapter 5, we have shown that the pore diameter decreased upon MAO immobilization by up to 20 nm and the pore volume decreased by up to 75%. In Chapter 4, we saw that supported catalysts with a narrower pore diameter led to extensive fragmentation in gas phase ethylene polymerization. We hypothesized that this might be due to smaller pore volume leading to the same amount of polymer exerting more hydraulic stress onto its surroundings compared to wider pore diameters.

In future work, mechanical properties of the initial silica and supported silica with increasing amount of immobilized MAO can be investigated using the nanoindenter. The impact of interstitial voids within the particle on the mechanical strength will also be the subject of future study to improve the understanding of the polymer growth and particle fragmentation.

7.2.2 Investigating the Effect of Pore Size on Other Polymer Properties

In Chapter 5, we saw the pore size of the supported catalyst after immobilization of MAO influenced the crystallinity and melting point of the polymer produced. Using the supported catalyst with a larger pore size obtained polymer with lower crystallinity. It was proposed that due to the larger pore size, the polymer chain will have more freedom to move around and form the amorphous regions leading to lower crystallinity.

In addition to the crystallinity, the pore size of the support was found to affect different properties of the polymer. Molecular weight is an important parameter for polymers as it has a direct effect on their mechanical and rheological properties. While metallocene catalysts inherently produce polymer with narrow molecular weight distributions, these are more difficult to process in their molten state. Currently, the molecular weight of metallocene produced polymers can be controlled either through the use of multiple types of metallocene compounds on the same support or the use of hydrogen.^{85, 317-320} Using various mesoporous supports, Silveira et al.^{130, 219} was able to obtain a wide range of molecular weights with an increased pore diameter leading to lower molecular weights though no clear trend was apparent. McDaniel et al.²⁵⁴ produced their own silica-titania supports and saw a general increase in molecular weight and decrease in long chain branching as pore diameter decreased, presumably due to steric effects from the narrower pore walls. It is important to note though that the original silica was treated in a way that strengthened the supports and might have mitigated fragmentation.

In order to produce elastomers and linear low-density polyethylene, ethylene is usually polymerized with other α -olefins such as 1-hexene. Use of a comonomer usually leads to higher activity and easier fragmentation. It is believed that there is a comonomer effect where the incorporation of comonomer into the polymer chain will decrease the crystallinity. Lower crystallinity allows easier access of monomer to the active site. The incorporation of 1-hexene also leads to lower molecular weight and a broadening of the distribution. Kumkaew et al.¹²⁹ investigated molecular sieves with varying pore sizes on ethylene-1-hexene copolymerization. They found that sieves with

larger pores sizes incorporated more 1-hexene comonomer. This might be due to either more space for the 1-hexene comonomer to access the active site or higher crystallinity of polymer in narrower pore sizes which prevents access. Paredes et al.³²¹ performed a similar investigation with different pore sized zeolites and obtained complementary results. They proposed that based on the zeolite structure and pore geometry, there are two different regions of growth. The region at the surface would lead to a less crystalline polymer chain with more comonomer incorporation while the region inside the pore would be more crystalline due to steric effects.

Future work would further investigate the effect of catalyst pore dimension after the immobilization of MAO on ethylene-1-hexene copolymerization in gas phase. Supported catalysts with varying pore sizes will be produced following the outline given in Chapter 5 and used in copolymerization reactions. The molecular weight of the polymer will be analyzed using high temperature gel permeation chromatography. The incorporation of 1-hexene can be analyzed using ^{13}C NMR. The goal is to determine if changes in the pore diameters of the supported catalysts due to the MAO-metallocene layer would lead to appreciable differences in these properties.

Appendix I: Mass Transfer of Gaseous Ethylene into Hexane Diluent

To study the kinetics of supported catalysts in ethylene polymerization, a small laboratory scale reactor is used. While the reactor can be used in both gas and slurry phase, the catalytic performance in slurry and gas phase experiments can be different due to the differences in the physical and chemical reaction environment which were detailed in Chapter 3, primarily due to the presence of the liquid diluent in slurry phase reactions. In slurry phase polymerization, the supported catalyst is initially suspended in a liquid solvent such as hexane or toluene. Gaseous monomer is supplied to the reactor through the headspace of the reactor which then diffuses across the gas-liquid interface to be dissolved in the liquid phase. Then the dissolved monomer must diffuse toward the active sites present on the catalyst to start polymerization. In this sequence of events, mass transfer is commonly overlooked as it is assumed that mass transfer of the monomer gas into the liquid phase is near instantaneous. Mass transfer is represented by the volumetric mass transfer coefficient $k_L a$ which has two terms. The first term is the mass transfer coefficient which represents the how fast the diffusion of gaseous monomer occurs at the gas-liquid interface. The second term represents the area over which the mass transfer occurs.

In the experiments detailed in this dissertation, the reactor was operated in a semibatch mode where ethylene gas was supplied to the reactor to maintain the reactor pressure at 50 psig during the reaction. However, it can be difficult to determine whether the flow of ethylene is due to equilibration between ethylene in the gas and liquid phase or due to catalytic reaction. Thus, in order to measure the mass transfer of gaseous ethylene across the gas-liquid interface, blank runs where no catalyst is present

were performed. A reactor with a certain volume of hexane diluent (180 mL) is charged with monomer gas with the partial pressure of 39 psig and then sealed (i.e., the gas supply is shut off). Thus, the reactor was operated in batch mode. The pressure within the reactor will start to decrease as the monomer diffuses into the liquid until a state of equilibrium is reached as stated by Henry's Law. As no catalyst is present, the decrease in pressure is solely due to mass transfer. The purpose of these blank tests was to observe the time needed for the sorption equilibrium to be reached, i.e., when the measured pressure stops decreasing. A similar experimental procedure was performed to observe the effect of the reaction rate on the measured reactor pressure by adding 0.075 g of supported catalyst. A schematic of the experimental setup is seen in **Figure A-1**.

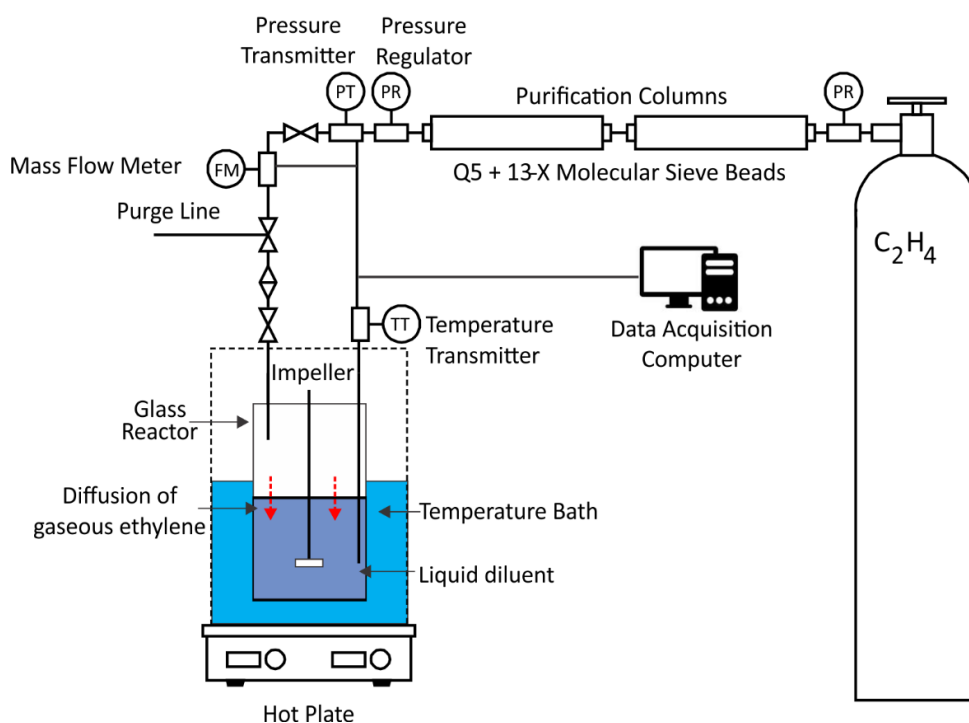


Figure A-1. Schematic of experimental setup for mass transfer experiments.

Figure A-2 shows the decrease in pressure over time in blank runs (labeled “Blank”) and runs with catalysts present (labeled “Batch”). It is shown that equilibrium is reached within ~2 minutes and remains constant in blank runs. It is shown that for runs with catalysts present that similar decrease in pressure is seen within 2 minutes and continual decrease in the pressure after 2 minutes is seen. The further decrease in pressure is due to the polymerization reaction and removal of dissolved ethylene, necessitating the mass transfer from the gas phase into the liquid phase.

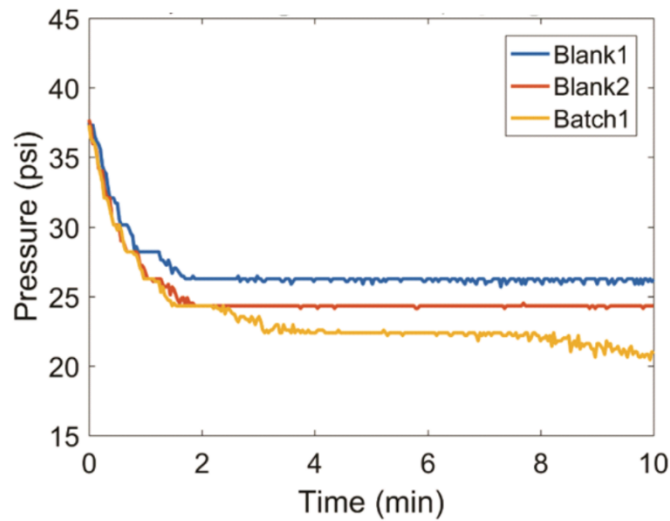


Figure A-2. Change in partial pressure of ethylene over time during blank runs and runs with catalyst present.

The determination of the mass transfer coefficient $k_L a$ is of considerable interest as the role of mass transfer of gaseous monomer across the gas-liquid interface is unclear. The following mass balance equations were used to fit experimental pressure data from blank runs experiments to obtain values of $k_L a$.

$$\frac{dP}{dt} = -V_s \frac{RT}{V_G} (k_L a) \left(\frac{P}{H} - M_L \right) \quad (\text{A-1})$$

$$\frac{dM_L}{dt} = (k_L a) \left(\frac{P}{H} - M_L \right) \quad (\text{A-2})$$

Where P is the pressure in the reactor (psi), V_s is the volume of the liquid diluent (180 cm³), V_G is the volume of the gas in the headspace of the reactor (600 cm³), R is the gas constant, T is the temperature of the reactor (K), k_L is the mass transfer coefficient (cm/min), a is the interfacial gas-liquid area (cm²), H is the Henry's Law constant (134248 cm³.psi/mol at 60°C), and M_L is the concentration of monomer in the liquid phase (mol/cm³).

The pressure of the reactor being measured by the transmitter is composed of the partial pressure of ethylene (which is diffusing into the solvent) and hexane (which remain constant at a certain temperature). Thus, when processing the pressure measurement, the partial pressure of hexane was removed. However, in order to obtain a value of $k_L a$, we must have measurements of dP/dt . While this can be measured from the pressure data over time, this data is generally noisy and will not give accurate measurements. Thus, after the partial pressure of hexane was removed, the data was fitted to an exponential decay function of the form $P(t) = a * e^{-bt} + c$ so that dP/dt can be easily obtained. **Figure A-3** shows some sample data points and the fitted exponential decay functions.

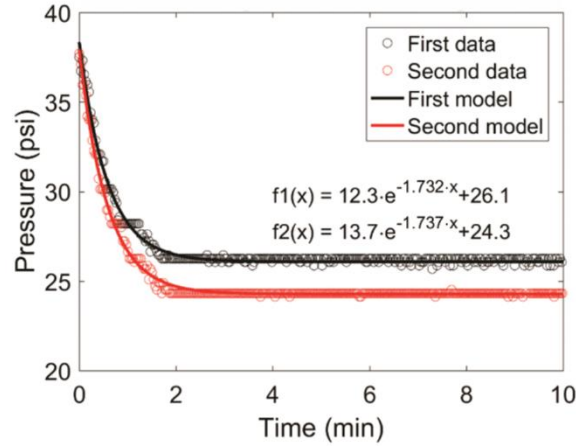


Figure A-3. Pressure data points for blank runs and fitted exponential decay functions.

Although Eq. (A-1) can use the change in measured pressure to calculate $k_L a$, we lack the ability to measure M_L or the concentration of ethylene dissolved in hexane over time. However, because it is a batch blank test, the decrease in pressure from $t=0$ (P_{T0}) represents the ethylene mass transfer rate (which initially is 0). Eq. (A-1) and Eq. (A-2) is set equal each other to obtain Eq. (A-3a). Then, there is a direct correlation between M_L which cannot be measured and pressure at time t (P) which can be measured is obtained as shown in equation (A-3c).

$$\frac{1}{RT} \frac{dP_T}{dt} = -\frac{V_s}{V_G} \frac{dM_L}{dt} \quad (\text{A-3a})$$

$$\frac{1}{RT} (P - P_{T0}) = -\frac{V_s}{V_G} (M_L - 0) \quad (\text{A-3b})$$

$$M_L = \frac{P_{T0} - P}{RT} \frac{V_G}{V_s} \quad (\text{A-3c})$$

Eq. (A-3c) is used in Eq. (A-1) to obtain the following:

$$\frac{dP}{dt} = -V_s \frac{RT}{V_G} (k_L a) \left(\frac{P}{H} - \frac{P_{T0} - P}{RT} \frac{V_G}{V_s} \right) \quad (\text{A-4a})$$

$$\frac{dP}{dt} = -\frac{V_s RT}{V_G H} (k_L a) P + (k_L a) P(t = 0) \quad (\text{A-4b})$$

Figure A-4 shows the equations for dP/dt obtained from the fitted exponential decay functions. These equations and Eq. (A-4b) were used to obtain the $k_L a$ values 1.88 and 1.92 min^{-1} .

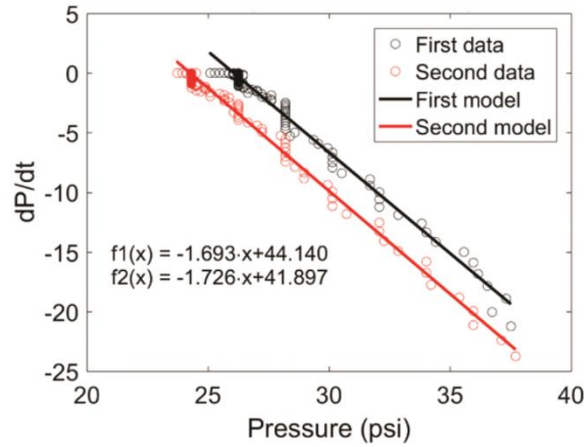


Figure A-4. Equations for dP/dt obtained from the fitted exponential decay function for pressure.

When catalyst is present within the reactor, the pressure will continue to decrease past the initial 5 minutes due to the removal of dissolved ethylene from polymerization. **Figure A-5** shows an example of the decrease in pressure during an experiment conducted with catalyst with the reactor operating in batch mode. The difference between the pressure data from the blank run with no catalyst (red line) and the actual pressure data during polymerization with catalyst (black line) can be used to determine the activity profile over time.

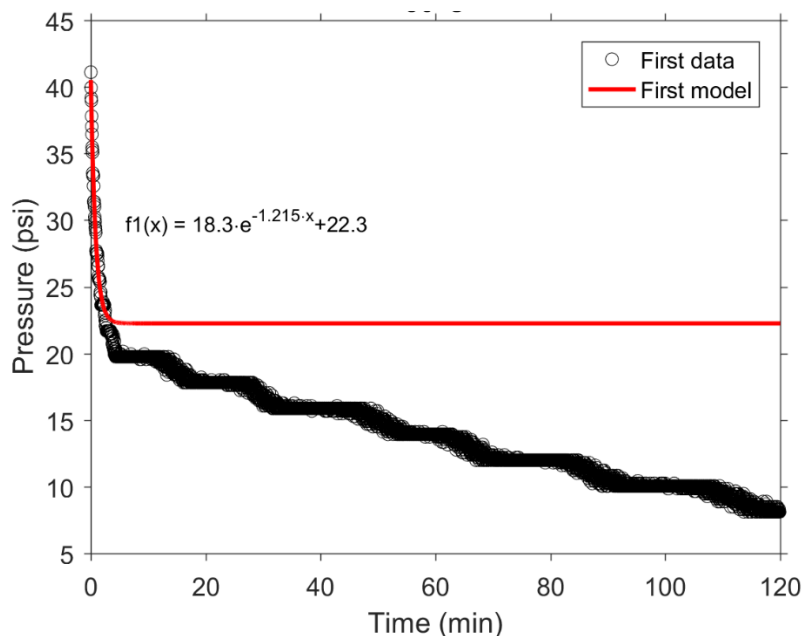


Figure A-5. Measured pressure within the reactor for blank run without catalyst (red line) and with catalyst (black circles).

The effect of mass transfer and the k_{La} value can be seen by varying the values and observing the change to the calculated monomer concentration and pressure. **Figures A-6** and **A-7** show that the pressure profile ($\sim$ polymerization rate profile) and the corresponding monomer concentration in the liquid phase is strongly dependent on the mass transfer parameter values given the same polymerization rate constant. At 60°C, the k_{La} coefficient is 1.5 min^{-1} . Increasing the coefficient does not have much effect with the only difference being that the mass transfer at the beginning of the reaction occurs instantaneously (asymptotic limit).

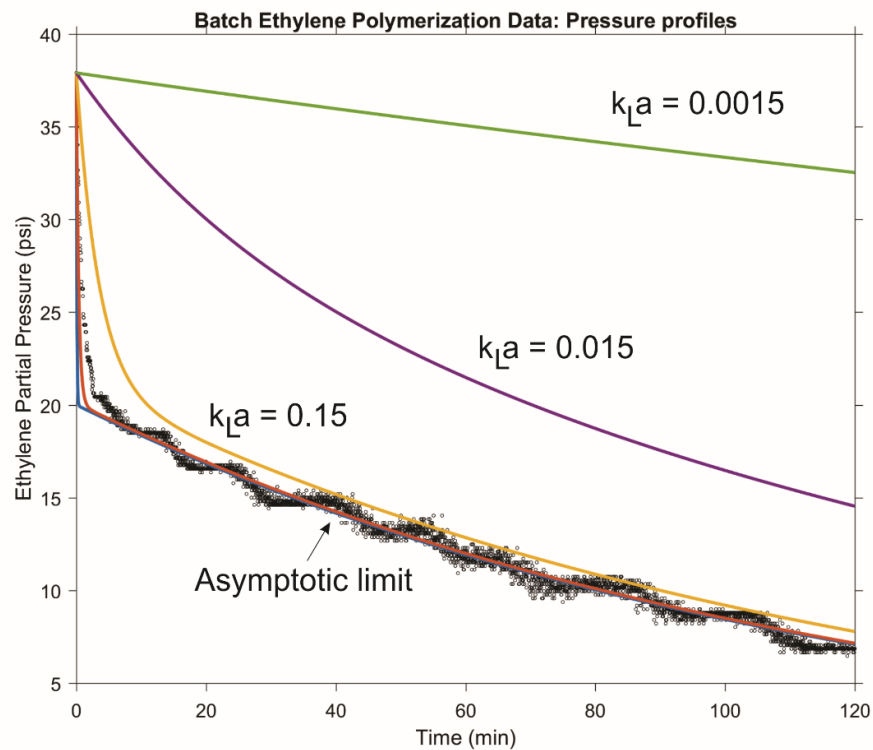


Figure A-6. Effect of different $k_L a$ values on matching the actual pressure data from batch reaction at 60°C using the mass transfer model.

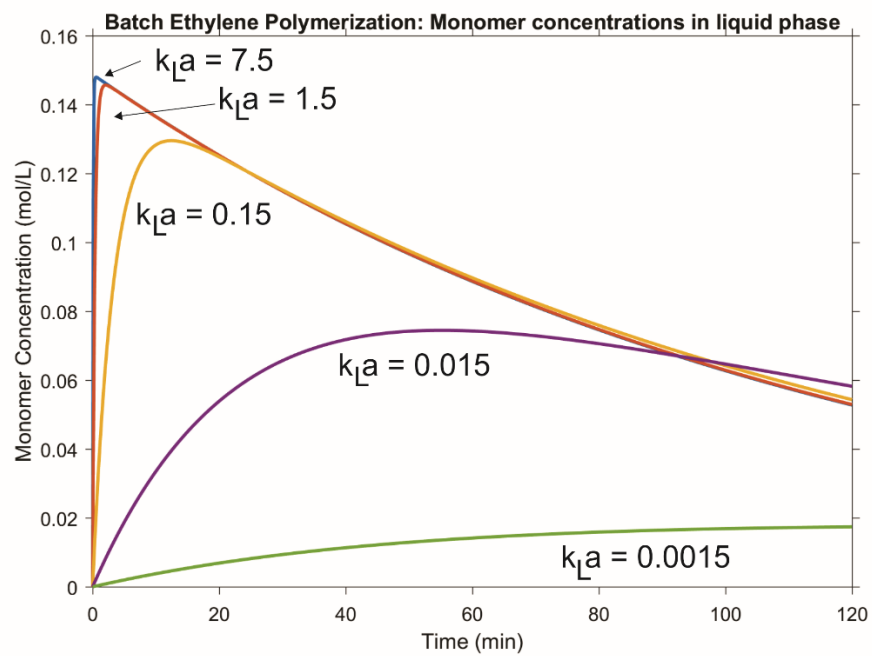


Figure A-7. Effect of different k_La values on monomer concentration in liquid phase at 60°C using the mass transfer model.

The results indicate that the mass transfer coefficient must be considered when performing slurry phase experiments. This is especially important as different studies utilize various reactor setups such as volume of diluent, reactor pressure, and stirring speeds which will impact the mass transfer of ethylene between gas and liquid phases. In the context of the experiments performed in this dissertation, the results show that the initial influx of ethylene gas into the reactor will completely saturate the monomer concentration in the liquid in approximately 5 minutes. During the polymerization, the mass transfer is sufficiently high enough to replenish the dissolved ethylene removed from polymerization as seen from the minimal changes to the pressure or monomer concentration after the initial 5 minutes at higher mass transfer coefficient values.

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