Spherical Polyolefin Particles from Olefin Polymerization in the Confined Geometry of Porous Hollow Silica Particles

Ines Freudensprung, Daejune Joe, Sven Nietzel, Doris Vollmer, Markus Klapper,* Klaus Müllen

Porous hollow silica particles (HSPs) are presented as new templates to control the product morphology in metallocene-catalyzed olefin polymerization. By selectively immobilizing catalysts inside the micrometer-sized porous hollow silica particles, the high hydraulic forces resulting from polymer growth within the confined geometries of the HSPs cause its supporting shell to break up from the inside. As the shape of the support is replicated during olefin polymerization, perfectly spherical product particles with very narrow size distribution can be achieved by using HSPs exhibiting a monomodal size distribution. Furthermore, the size of the obtained product particles can be controlled not only by the polymerization time but also by the size of the support material.

1. Introduction

The combination of metallocenes with methyl alumoxane (MAO) has opened a new era of producing polyolefins with tailor-made properties. In contrast to traditional Ziegler–Natta systems, metallocene catalysts exhibit single-site character of the active species which generates polymers with relatively narrow molecular weight distributions (MWD) and high stereo selectivity. Despite these outstanding properties, the polymers produced from homogeneous olefin polymerization via metallocenes are obtained as materials with low bulk density and irregular particle shape. To achieve better morphology control with higher bulk densities of the obtained particles and to avoid reactor fouling, metallocenes have to be supported on solid carriers. Additionally, the use of a supporting material is the only known way to run metallocene-based polymerizations without a solvent in the gas phase. It is desirable to produce final polyolefin products with a particle size distribution as narrow as possible and with an almost perfect spherical shape, thereby generating a flowable powder and obviating the step of making pellets for subsequent processing steps. Commercially applied supports are usually composed of nanometer-sized nonporous granulates (primary particles) of solid or hollow silica, as well as polymer-based organic materials, compounded into micrometer-sized agglomerates (secondary particles) with a wide range of sizes and shapes. This irregularity in support shape/size is replicated in the as-produced polyolefin particles limiting processability. As the support particles remain in the produced polymer as inorganic impurities, they can affect the physical properties and chemical stability of the product.

To achieve polyolefin particles with the desired spherical shape and narrow particle size distribution, either specially designed support systems or polymerization techniques have to be employed. Therefore, we introduce in this study micrometer-sized porous hollow silica particles (HSPs) with spherical shape and monomodal particle diameters as supports for metallocene catalysts. By the exclusive immobilization of metallocene catalysts on the internal surface of the hollow silica particles, olefin polymerization only occurs within the confined geometries of the HSPs. Contrary to some work being conducted...
from Kageyama et al.\textsuperscript{[13]} and Zhang et al.\textsuperscript{[14]} where they produced crystalline poly(ethylene) nanofibers and 3D ordered macroporous poly(ethylene) through exclusive template design, we persecuted the idea of producing individual, uniform, and spherical polyolefin particles for generating a powder with enhanced processability, employing this novel way of porous, hollow templates, and selective catalyst immobilization.

The high hydraulic forces resulting from polymer growth within the HSPs cause its supporting silica shell to break up from the inside. Hereby, the fragments of the support material are located on the surface of the product particles. This support system provides better shape control of the final polyolefin product with a very narrow size distribution.

2. Results and Discussion

To achieve a monomodal size distribution and a uniform shape in the polyolefin products, spherical silica particles possessing porous shells and empty cores were investigated as “mini-reactors” for olefin polymerization. These porous HSPs were synthesized via Stöber synthesis on poly(styrene) templates according to a literature procedure.\textsuperscript{[15,22]} To introduce empty cores to the silica particles, the PS template particles, which can be conveniently removed, were first prepared with a monomodal size distribution by copolymerization of styrene and acrylic acid as controlling functional group on the surface of the poly(styrene) particles (Figure 1a). The size of the silica nanoparticles, as well as the degree of porosity, can be tuned by the amount of tetraethoxysilane (TEOS) used for the modified Stöber synthesis with hydrolysis of TEOS and ammonium hydroxide in ethanol (Figure 1b). After removal of the PS core through washing with tetrahydrofuran, the HSPs were obtained with a monomodal size distribution and a mean diameter of 1.1 \( \mu \text{m} \pm 35 \text{ nm} \). To verify the formation of a hollow and porous structure, the HSPs were studied by transmission electron microscopy (TEM), revealing the empty core and an internal diameter of ca. 1.0 \( \mu \text{m} \) (Figure 1c) which matches the original size of the PS template particles. As further evidence of the HSP geometry, they were cryo-sectioned with a thickness of around 60 nm. The cryo-TEM image clearly demonstrates the formation of porous hollow silica particles with a wall thickness of approximately 50 nm (Figure 1d).

Bis(methylcyclopentadienyl) zirconium (IV) dichloride (MCP, Figure 2a) was used as metallocene catalyst to produce poly(ethylene) from gaseous ethylene. In order to support the catalyst exclusively on the internal HSP surface, a special procedure was employed to transfer the catalyst through the open pores into the confined geometry of the HSPs. This protocol must be outlined in greater detail. Therefore, no pretreatment with MAO as a scavenger was applied on the HSPs, since MAO structures

\textbf{Figure 1.} SEM images of a) uniform PS template particles with an average diameter of 1 \( \mu \text{m} \) and b) grown silica nanoparticles on the PS template particles, with an overall particle diameter of 1.1 \( \mu \text{m} \). TEM micrographs of c) porous hollow silica particles and d) cryo-sectioned HSPs, showing the wall thickness of ca. 50 nm.
might block the pores of the HSPs. After preliminary drying steps of the support material, the preactivated MCP/DMAO-solution was added under vacuum to the HSPs and the flask mounted overnight on a shaker, to enable diffusion of the activated metallocene complex into the HSPs. Following this, the HSPs were washed three times with toluene, which removed MCP from the outer surface of the HSPs. Due to geometric limitations, the cage-like MCP/DMAO species within the HSPs have a stronger interaction with the silica and among each other, whereby they are “trapped” inside the HSPs and hence retained during the washing procedure (Figure 2b).

After drying, the prepared MCP/DMAO-containing HSPs were ready to catalyze ethylene polymerization in a gas phase reactor at 3 bar ethylene pressure and a temperature of 60 °C.

Since the catalyst is selectively immobilized on the inner wall of the HSPs, ethylene growth starts within the HSP shells. After longer polymerization times, the outer silica shell starts to fragment due to induced pressure from the growing PE chains (Figure 2c).[16]

According to the replication effect, the catalyst support acts as a shape template for the product particle formation, with the relative size of the polymer product particle being determined by the catalyst productivity and polymerization time.[17,18] By using spherical HSPs with monomodal particle size distribution as catalyst support material, PE particles which are uniform in their size and shape were indeed obtained (Figure 3). After polymerization times of 60 min, the hollow silica particles with a mean diameter of 1.1 μm produced in different runs in the gas phase reactor uniform, spherical PE particle sizes between 2.5 and 3.5 μm (Figure 3a–d). Moreover, the PE particles reached sizes around 1.8 μm after polymerization times of 30 min (Figure 3e), confirming the capability of controlling the size of the produced polyolefin particles by adjusting the polymerization time. Independently from the polymerization times, the poly(ethylene) particles always showed a uniform spherical shape, replicated from the HSP template. The particle size distribution ranged for different experiments from 2.5 ± 0.1 μm (Figure 3a, first 60 min polymerization) to 3.4 ± 0.2 μm (Figure 3b) and 3.5 ± 0.3 μm (Figure 3c) during the second and third 60 min polymerization runs, respectively. The small silica fragments from the remaining HSP template, which are found at the exterior of the poly(ethylene) particles (Figure 3a–e), are a solid evidence that the MCP/DMAO-catalytic system was immobilized at the interior of the HSPs. Figure 3f shows the profile of grown PE particles (60 min polymerization time) after a FIB cross-section, revealing completely filled HSPs by poly(ethylene). To the best of our knowledge, spherical polyolefin particles in such a quality could only be obtained by using the confining geometry of nonaqueous emulsions.[6,19] However, those polyolefin particles did not possess a comparably narrow and monomodal size distribution as reported here. In addition, the product particle sizes obtained from emulsion polymerization are in the nanometer range, which targets different applications.

To investigate their long-time polymerization stability, the MCP/DMAO-loaded hollow silica particles were used to perform ethylene polymerization in the gas phase reactor for 30, 60, and 90 min under 3 bar ethylene pressure at 60 °C. For each reaction time, comparable productivities between 5 and 7 gPE gHSP⁻¹ h⁻¹ were found (Table 1), demonstrating long-time stability for the investigated catalytic system. However, MAO-activated MCP on conventional silica supports exhibits a 10 times higher productivity of 47.7 gPE gCatalyst⁻¹ h⁻¹ for ethylene polymerization at 60 °C in the gas phase reactor.[20] Compared to conventional silica supports and metallocene/MAO catalysts, there are fewer active catalyst sites on the...
HSPs, which explains the lower productivity. For instance, some fraction of the catalyst species might not be firmly anchored at the inner surface of the hollow silica particles due to the lower DMAO concentration being applied and therefore not yielding into active sites. Another explanation for the inferior productivity is that parts of MCP/DMAO are simply washed away during the preparation steps and therefore resulting in less active catalyst being immobilized inside the HSPs.

Thermal analysis of the products was performed via DSC to classify the obtained polyethylene. The melting points ($T_m$) for all polyethylene products ranged from 136 to 139 °C (see Table 1). These are characteristic values for high-density polyethylene (HDPE), indicating that there is very little to no branching in the polyethylene product. By GPC analysis in trichlorobenzene versus polystyrene

standards, a number-average molecular weight of 225 000 g mol$^{-1}$ with a molecular weight distribution of 3.3, which is common for ethylene polymerization by metalloccenes, was found.$^9$ Hence, the DMAO-activated

![Figure 3. SEM images of polyethylene particles after gas phase polymerization for a)–d) 60 min from different runs using porous hollow silica particles loaded with MCP/DMAO, showing the fragmented silica shell on the outside and e) 30 min using hollow silica particles loaded with MCP/DMAO. f) SEM image of PE particles after 60 min of polymerization time after FIB cross-section, revealing the PE-filled spheres.](image)

Table 1. Results of ethylene polymerizations with MCP/DMAO-supported HSPs.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reaction time [min]</th>
<th>Productivity [gPE/gHSP h$^{-1}$]</th>
<th>$T_m$[°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>7.0</td>
<td>136</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>7.0</td>
<td>139</td>
</tr>
<tr>
<td>3</td>
<td>90</td>
<td>5.0</td>
<td>137</td>
</tr>
</tbody>
</table>

$^a$Polymerization under 3 bar of ethylene at 60 °C in a gas phase reactor; $^b$Determined by DSC.
and selectively immobilized MCP performs within the HSPs like conventional silica-supported MCP in gas phase polymerizations.

In contrast to conventional silica or MgCl₂ supports, the application of HSPs is an excellent solution to obtain polyolefin products with well-defined particle morphology and very narrow size distribution. The perfect spherical shape of our polyethylene particles provides, similar to the polyolefin particles obtained from nonaqueous emulsions, a better flowable product which, in turn, results in improved processability.

3. Conclusion

The results presented here show a way of producing nearly perfectly spherical polyolefin particles with very narrow size distribution from porous hollow silica particles, which act as “mini-reactors” and enable controlled polymerization within their confined geometry.

Preparation of monomodal HSPs having an empty core was accomplished via the Stöber method using polystyrene templates, which were then used as supports in metallocene-catalyzed olefin polymerization. After ethylene polymerization for 30–90 min, small fragments of the HSPs were found at the surface of the polyethylene particles with a mean diameter of around 2.5–3.5 μm for 60 min polymerizations and 1.8 μm for 30 min of ethylene polymerization. This indicates that catalytic species of MCP/DMAO were selectively immobilized inside the HSPs and the produced polyethylene broke the HSPs by induced pressure.

It is essential for the present concept that metallocene/DMAO is selectively supported inside the HSPs to afford polyolefin particles with a uniform and well-controlled morphology. The very narrow size distribution of these polyethylene particles even exceeds that obtained from ethylene polymerization in nonaqueous emulsions or other approaches. Since the supports, i.e. the fragmented silica shell, are exposed, support removal procedures such as by mechanical shearing would be more convenient than within the cases of conventional silica supports, where the support fragments are encapsulated by the growing polymer.

4. Experimental Section

4.1. General Procedure and Materials

All air and water sensitive reactions were performed in a glovebox or under standard Schlenk techniques. Dried toluene (Acros) was used after distillation over sodium and benzoephone for the immobilization of the metallocene catalysts on the hollow silica particles. Bis[methylcyclopentadienyl]zirconium (IV) dichloride (MCP) was purchased from Aldrich and used as received. Dried methyl alumoxane (DMAO) was obtained from 10 wt% MAO solution (Sigma–Aldrich) after evaporation and drying under high vacuum. Ethylene gas (Gerling Holz & Co.) was purified by passing through columns with 5 Å molecular sieves and Superpure-O for deoxygenation (both Sigma–Aldrich). The purified ethylene was used for ethylene polymerizations in a gas phase reactor.

4.2. Preparation of Porous Hollow Silica Particles

The porous hollow silica particles HSPs were prepared according to the literature procedure. To introduce empty cores to the silica particles, template polystyrene particles were first prepared by copolymerization of styrene and acrylic acid as controlling functional group on the surface of the polystyrene particles. Ammonium persulfate was used as an initiator in a soap-free emulsion polymerization. This led to polystyrene-co-poly(acrylic acid) particles with monomodal particle diameters, which were employed as templates for the HSPs for a modified Stöber synthesis with hydrolysis of TEOS and ammonium hydroxide in ethanol, whereby the amount of TEOS determines the size of the silica nanoparticles and hence the porosity. The number of silica nanoparticles attached to the surface of the PS template could be tuned by the amount of acrylic acid added to the synthesis of the PS particles. Only at acrylic acid concentrations larger than ~1 wt%, the silica nanoparticles were sufficiently strongly bonded to the surface that they remained attached even after several centrifugation steps. After removal of the PS core through washing with tetrahydrofuran, the HSPs were dried at 300 °C under high vacuum prior to use and their diameter reached uniform 1.1 μm ± 35 nm.

4.3. Selective Immobilization of Metallocene Catalysts

Prior to the immobilization procedure, 50 mg of hollow silica particles were placed in a round-bottom Schlenk flask with 10 mL of toluene. In order to extract the residual water in the HSPs, the flask was mounted on a shaker at 100 rpm and the supernatant toluene removed after 2 h of shaking. This procedure was repeated three times and the HSPs dried under reduced pressure. 5 mg of MCP (15 μmol) were preactivated with 10 mg DMAO in 5 mL of toluene for 10 min and then added to the HSPs under vacuum. The mixture was mounted on a shaker at 100 rpm overnight for immobilization of the catalyst. Afterward, the supernatant catalyst solution was removed and the HSPs washed three times with 5 mL of toluene to remove residual catalyst, especially on the outer surface of the hollow spheres. After drying under reduced pressure, the MCP/DMAO-HSPs were ready to use for olefin polymerizations. The maximum amount of MCP on the HSPs was calculated to be 300 μmolSi/85SiP. The aluminum-to-zirconium ratio was estimated as 150:1.

4.4. Ethylene Polymerization in a Gas Phase Reactor

After delivering the gas phase reactor to a glove box, DMAO solids were placed at the bottom of the reactor and used as scavengers to additionally purify the ethylene gas.

© 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
MCP/DMAO-supported HSPs were deposited on a silver-coated plate in the gas phase reactor. After removal from the glove box, the reactor was connected with a vacuum line which had an internal ethylene supply valve. The line was heated at 300 °C for 5 h under reduced pressure to remove residual moisture. Prior to starting the polymerization, the reactor was heated to 60 °C by an external heating controller. After stabilization of the temperature, the reactor was charged with 3 bar of ethylene. The polymerization was terminated by releasing the monomer after the desired polymerization time, and subsequently, the contents of the reactor were exposed to air to quench the catalysts.

4.5. Characterization of Hollow Silica Particles and Polyethylene

For morphological observations with scanning electron microscopy (SEM), the HSPs or polyolefin particles were placed on a graphite tape and measured at low-voltage using a LEÓ 1530 Gemini, Zeiss. For inner-morphology observations, the particles were embedded in an epoxy resin and sectioned with various thicknesses using a Leica ultracut UCT under liquid nitrogen stream. For cryo-transmission electron microscopy (TEM) images, the ca. 60 nm thick samples were placed on a 300 mesh carbon-coated copper grid and observed with a Zeiss EM912 operating at 80 kV. For a profile of the grown polymer particles, the PE coated copper grid and observed with a LEO 1530 Nanolab Focused Ion Beam Dualbeam operating at 30 kV and 1 nA–100 pA.

The melting points \(T_m\) of the produced polymers were determined through differential scanning calorimetry (DSC) using a heating rate of 10 °C min\(^{-1}\) in the temperature range of –100 to 220 °C. For gel permeation chromatography (GPC) measurements, the obtained polymers from hollow silica particles were dissolved at 120 °C in 1,2,4-trichlorobenzene with a concentration of 1.0–2.0 g·L\(^{-1}\). After filtration through a glass syringe with an attached membrane (Milipore, MillexTM membrane, 5.0 μm LS) to remove the silica residues, GPC was performed on a Waters 150-C gel permeation chromatograph at 135 °C using three TSK gel columns (two sets of TSK\(_{gel}\)GMH\(_{mig}^{HSHT}\) and TSK\(_{gel}\)GMH\(_{mig}^{a-HTL}\) with refractive index detection and calibration versus narrow polystyrene standards.

Acknowledgements: Gabriele Schäfer is gratefully acknowledged for the synthesis of HSPs. The authors are grateful to Gunnar Glasser and Katrin Kirchhoff for SEM and TEM measurements. I.F. acknowledges the support of the Elite Network of Bavaria.

Received: May 20, 2016; Revised: June 30, 2016; Published online: August 24, 2016; DOI: 10.1002/marc.201600295

Keywords: homogeneous size distribution; metallocenes; morphology control; polyolefins; porous hollow silica particles
