Fabrication of Iron/Silica/Polyethylene Composite Particles by Polymerization-Filling Method (Postprint)

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Abstract

Fe/SiO2 composite particles prepared by the sol-gel method were used as a support to load bis(cyclopentadienyl)zirconium dichloride (Cp2ZrCl2), and Fe/SiO2/PE composite particles were prepared by catalytic ethylene polymerization using the polymerization filling method. The composite particles were analyzed and characterized by scanning electron microscopy (SEM), X-ray energy dispersive spectroscopy (EDS), infrared spectroscopy (IR), inductively coupled plasma spectrometer (ICP), thermogravimetric analyzer (TGA), laser particle size analyzer, and gel permeation chromatography (GPC). The results show that the outer SiO2 layer of the Fe/SiO2 composite particles is completely coated and can be used as a support for Cp2ZrCl2; the Fe/SiO2/Cp2ZrCl2 catalyst system exhibits high activity in the ethylene polymerization process and can polymerize ethylene to obtain Fe/SiO2/PE composite particles; the catalytically active component does not detach from the Fe/SiO2 composite particles during the polymerization process, and the produced polyethylene is well-coated on the support surface; the Fe/SiO2/PE composite particles exhibit obvious agglomeration during the polymerization process; both the Fe/SiO2/Cp2ZrCl2 catalyst particles and the Fe/SiO2/PE composite particles have irregular shapes, and there is a replication effect between them; varying the polymerization time and polymerization pressure can regulate the Fe content in the Fe/SiO2/PE composite particles; the polyethylene produced by ethylene polymerization with the Fe/SiO2/Cp2ZrCl2 catalyst has a narrow molecular weight distribution.

Full Text

Preamble

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Preparation of $Fe/SiO_2/PE$ Composite Particles Through Polymerization Filling Technique

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Abstract
Fe/SiO_2 composite particles were first prepared via a sol-gel method and subsequently used as supports to deposit zirconocene dichloride (Cp_2ZrCl_2), forming a $Fe/SiO_2/Cp_2ZrCl_2$ catalyst. $Fe/SiO_2/PE$ composite particles were then produced through polymerization filling technique using ethylene and the $Fe/SiO_2/Cp_2ZrCl_2$ catalyst. The obtained composite particles were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), infrared spectroscopy (IR), inductively coupled plasma spectroscopy (ICP), thermal gravimetric analysis (TGA), laser particle size analyzer, and gel permeation chromatography (GPC). The results demonstrate that the Fe/SiO_2 composite particles feature a complete SiO_2 coating layer on the outer surface, making them suitable as supports for Cp_2ZrCl_2. The $Fe/SiO_2/Cp_2ZrCl_2$ catalyst system exhibited high activity during ethylene polymerization, successfully producing $Fe/SiO_2/PE$ composite particles. The catalytic active components did not detach from the Fe/SiO_2 composite particles during polymerization, and the generated polyethylene coated the support surface effectively. Significant agglomeration of $Fe/SiO_2/PE$ composite particles occurred during polymerization. Both $Fe/SiO_2/Cp_2ZrCl_2$ catalyst particles and $Fe/SiO_2/PE$ composite particles exhibited irregular shapes with a replication effect between them. The Fe content in $Fe/SiO_2/PE$ composite particles could be adjusted by varying polymerization time and pressure. The polyethylene obtained using the $Fe/SiO_2/Cp_2ZrCl_2$ catalyst displayed a narrow molecular weight distribution.

Keywords inorganic/organic composites, $Fe/SiO_2/PE$ composites, polymerization filling technique, metallocene catalysts

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Introduction

Metal powder-filled thermoplastic polymer composites represent important engineering materials widely applied in thermal conduction, electromagnetic shielding, and electric heating applications [1-5]. Iron powder offers high magnetic permeability, high saturation magnetization, and good electrical conductivity, while polyethylene provides advantages such as abundant monomer availability and excellent properties. Modifying polyethylene with iron powder can enhance its physical and mechanical properties [6], and the resulting Fe/polyethylene composites exhibit high magnetic permeability and high dielectric constant, showing promising applications in electromagnetic shielding [3] and microwave transmission [7].

Primary preparation methods for inorganic/organic composites include mechanical blending [6], sol-gel method [8], and polymerization [9-13]. Polymerization methods can be further categorized into emulsion polymerization [9,10], suspension polymerization [11], interfacial polymerization [12], and polymerization filling technique [13]. Yang et al. [7] prepared Fe/SiO_2/PDMS composites with high magnetic permeability and dielectric constant by dispersing Fe/SiO_2 composite particles in polydimethylsiloxane (PDMS) elastomer via mechanical blending, adjusting the magnetic permeability and dielectric constant by controlling Fe content. However, mechanical blending suffers from non-uniform filler distribution. Chen et al. [9] prepared monodisperse gold nanoparticles via phase transfer method using chloroauric acid as precursor, dodecanethiol as stabilizer, and sodium borohydride as reducing agent, subsequently producing nano-gold/polystyrene composite particles through emulsion polymerization. Majidi et al. [10] synthesized Fe_3O_4/polystyrene magnetic nanoparticles via soap-free emulsion polymerization using azobisisobutyronitrile as initiator and hexadecane as hydrophobic agent. Suslick et al. [14] prepared Fe/PVP composite particles by decomposing organometallic precursor $Fe(CO)_5$ in octanol solution containing polyvinylpyrrolidone (PVP) under ultrasonic irradiation. However, Fe/PVP composite particles prepared by this method tend to separate due to weak interfacial interaction between Fe and PVP.

Polymerization filling technique is a polymerization method that introduces fillers during the polymerization stage. This approach allows inorganic particles with catalytic functions to enter the polymer matrix center, with polymers directly chemically bonded to or strongly adsorbed on the inorganic particle surfaces. Roberta Sulcis et al. [13] prepared rubber tire/high-density polyethylene (HDPE) composite materials through polymerization filling technique, confirming strong interaction between rubber tires and HDPE, with significantly improved stress-strain properties compared to conventional mechanically blended rubber tire/HDPE composites. This paper employs polymerization filling technique to prepare Fe/SiO_2/PE composite particles, using Fe/SiO_2 composite particles prepared by sol-gel method as supports for metallocene catalysts to catalyze ethylene polymerization.

1.1 Experimental Reagents

Nano-iron powder (99.9% purity, 79 nm); KH-792 silane coupling agent ($NH_2(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$); Tetraethyl orthosilicate (TEOS, chemically pure); Methylaluminoxane (MAO, 10% toluene solution); Cp_2ZrCl_2 (99% purity), prepared as 1 g/L toluene solution; Ethylene (polymerization grade), purified through copper molecular sieve and 0.4 nm molecular sieve to remove water and oxygen before use; Ammonia water (analytically pure); Toluene (analytically pure), soaked in 4 Å molecular sieve for 72 h before use, then purified through a solvent purification system to remove water and oxygen.

All operations involving water- and oxygen-sensitive materials were performed under anhydrous and anaerobic conditions using Schlenk technique.

1.2 Preparation of Fe/SiO_2 Composite Particles

Since iron powder surfaces lack hydroxyl groups unfavorable for SiO_2 deposition, KH-792 silane coupling agent was first used for surface modification. 1.92 g of iron powder was added to 400 ml ethanol-water solution (volume ratio 1:1) and heated to 40°C with stirring for 0.5 h. Then 15 ml KH-792 ethanol solution (volume ratio 1:2) was added, followed by 20 ml ammonia water to make the solution alkaline after uniform mixing. Subsequently, 25 ml TEOS was slowly added and stirred for 3 h. The sample was then filtered, washed with ethanol, and vacuum-dried at 70°C for 24 h.

1.3 Preparation of $Fe/SiO_2/Cp_2ZrCl_2$ Catalyst

The prepared Fe/SiO_2 composite support was further treated for water and oxygen removal. The Fe/SiO_2 composite support was heated at 110°C under vacuum for 4 h, with subsequent operations performed under nitrogen protection. 2.09 g of Fe/SiO_2 composite support was dispersed in 50 ml MAO and heated at 40°C with stirring for 4 h. After settling, the supernatant was decanted, and the residual solid was washed with toluene three times, then vacuum-dried at 60°C for 2 h to obtain black solid powder.

The catalyst precursor Cp_2ZrCl_2 was then loaded onto the solid powder. The powder was placed in a 250 ml three-neck flask, and 100 ml toluene and 62 ml Cp_2ZrCl_2 toluene solution were added, followed by heating at 40°C with stirring for 8 h. After settling, the supernatant was decanted, and the residual solid was washed with toluene.

1.4 Ethylene Polymerization Evaluation

Ethylene slurry polymerization was conducted in a 1 L Swiss Buchi AG pressure reactor to evaluate the catalytic performance of $Fe/SiO_2/Cp_2ZrCl_2$ for ethylene polymerization. The reactor can withstand temperatures up to 250°C and pressures up to 6 MPa, and features a visual window. Data acquisition software enables remote operation and data storage, with jacket temperature control ensuring temperature fluctuations within $±$2°C during polymerization. For experiments, the reactor was first dried, evacuated under 95°C circulating water bath for 3 h, then purged three times with nitrogen and three times with ethylene. After cooling to 50°C, toluene (350 ml) and cocatalyst MAO (Al/Zr molar ratio of 4055) were added sequentially, with stirring speed set at 350 r/min. Once temperature stabilized at 40°C, catalyst (100-300 mg) was added, and ethylene was continuously fed for polymerization with total pressure maintained at a set value. Ethylene consumption rate was recorded in real-time using an ethylene mass flow meter. After a specified reaction time, ethanol was added to terminate the reaction. The slurry solution was removed, filtered, and the polymer product was washed multiple times with ethanol, then placed in a vacuum oven and dried at 60°C for 24 h.

1.5 Material Characterization

Elemental analysis of composite particle surfaces was performed using X-ray energy dispersive spectroscopy (EDX) attached to a Hitachi S-4700(II) field emission scanning electron microscope (SEM). Zr content in the catalyst was determined using inductively coupled plasma spectroscopy (ICPE-9000). Fe/SiO_2 and $Fe/SiO_2/PE$ samples were mixed with potassium bromide for preparation, and infrared spectra were measured on a Nicolet 5700 Fourier transform infrared spectrometer. Thermogravimetric analysis of $Fe/SiO_2/PE$ composite particles was conducted under nitrogen flow using a TGA/SDPA851e analyzer from 25°C to 800°C at a heating rate of 10°C/min. Average particle size and size distribution curves of Fe/SiO_2 composite particles, $Fe/SiO_2/Cp_2ZrCl_2$ catalyst particles, and $Fe/SiO_2/PE$ composite particles were measured using a Malvern laser particle size analyzer (Mastersizer 2000). Molecular weight (MW) and molecular weight distribution (MWD) of polyethylene products were determined using an Alliance GPC2000 gel permeation chromatography (GPC) instrument at 150°C, with polystyrene as standard, trichlorobenzene as solvent, and flow rate of 1.0 ml/min.

2.1 Fe/SiO_2 Composite Particles

Fe/SiO_2 composite particles were prepared by hydrolysis and polycondensation of TEOS in alkaline ethanol-water solution to coat a SiO_2 layer on nano-iron powder surfaces. [Figure 1: see original paper] shows the SEM image of Fe/SiO_2 composite particles. The particles exhibit irregular shapes with micron-scale diameters, significantly larger than the original nano-iron powder (79 nm). Due to the extremely high surface free energy, nano-iron powder readily undergoes spontaneous agglomeration and solidifies during TEOS hydrolysis and polycondensation [7], resulting in each Fe/SiO_2 composite particle containing several nano-iron particles. [Figure 2: see original paper] presents the surface elemental analysis results of Fe/SiO_2 composite particles, revealing the presence of Si, O, C, and Fe elements, with Si and O contents substantially higher than Fe content. This indicates that nano-Fe powder was essentially completely coated by SiO_2. The characteristic peak to the right of Si originates from Pt element from gold sputtering treatment.

2.2 Catalytic Performance of Fe/SiO_2/Cp_2ZrCl_2 Catalyst

Before ethylene polymerization experiments, Zr content on Fe/SiO_2/Cp_2ZrCl_2 catalyst was determined by inductively coupled plasma spectroscopy, showing a loading of 0.256 wt%. The polymerization activity of Fe/SiO_2/Cp_2ZrCl_2 catalyst under different reaction times and polymerization pressures at 40°C and Al/Zr molar ratio of 4055 is presented in . The results show that polymerization activity increases with higher polymerization pressure when other conditions remain constant, while activity decreases with prolonged reaction time, indicating relatively rapid catalyst deactivation. Experimental results demonstrate that the Fe/SiO_2/Cp_2ZrCl_2 catalyst system exhibits considerable activity during ethylene polymerization, with Fe/SiO_2 composite particles serving as effective metallocene catalyst supports to produce Fe/SiO_2/PE composite particles.

A schematic diagram of Fe/SiO_2/PE composite particle formation through polymerization filling catalyzed by Fe/SiO_2/Cp_2ZrCl_2 is shown in [Figure 3: see original paper]. Polyethylene chains grow from active sites on the Fe/SiO_2/Cp_2ZrCl_2 catalyst, gradually coating the Fe/SiO_2 support and ultimately forming Fe/SiO_2/PE composite particles.

2.3 Morphology and Particle Size Distribution of Fe/SiO_2/PE Composite Particles

[Figure 4: see original paper] shows SEM images of Fe/SiO_2/Cp_2ZrCl_2 catalyst and Fe/SiO_2/PE composite particles. Both exhibit irregular morphology. During polyethylene particle growth, catalyst particles serve as templates, with a replication effect between catalyst and polyethylene particles [15,16]. Due to the irregular shape of catalyst particles, the resulting Fe/SiO_2/PE composite particles also display irregular shapes.

The particle size distribution of Fe/SiO_2/Cp_2ZrCl_2 catalyst is shown in [Figure 5: see original paper], while that of Fe/SiO_2/PE composite particles is presented in [Figure 6: see original paper]. The average particle size of Fe/SiO_2/Cp_2ZrCl_2 catalyst is 7.95\$$\pm 1\mu m, and Fe/SiO\{2\}/PE composite particles have an average size of 834.73 \pm 50\mu m. The particle$ composite particles was normalized according to catalyst activity [17], assuming no fines or agglomeration occurred during polymerization. Polymer particle size was normalized using the formula pol,n = [formula], where Y is polymer yield (gpolymer/g-cat), dpol is polymer particle diameter, and dpol,n is normalized polymer particle diameter.

If the normalized polymer particle size distribution curve completely overlaps with the catalyst distribution curve, it indicates good replication effect without fines or agglomeration. If the polymer distribution curve lies to the left of the catalyst curve, fines formation occurred; if to the right, particle agglomeration occurred. [Figure 7: see original paper] reveals significant deviation between the normalized particle size distribution curve of Fe/SiO_2/PE composite particles and that of Fe/SiO_2/Cp_2ZrCl_2 catalyst, with the former positioned to the right of the latter, indicating obvious agglomeration of Fe/SiO_2/PE composite particles during ethylene polymerization.

2.4 FTIR Analysis of Fe/SiO_2/PE Composite Particles

[Figure 8: see original paper] presents FTIR spectra of Fe/SiO_2 composite particles and Fe/SiO_2/PE composite particles. The Fe/SiO_2 spectrum contains characteristic SiO_2 absorption peaks at 1047.9 cm^{-1} (Si-O-Si asymmetric stretching vibration) and 450.98 cm^{-1} (Si-O bending vibration). The Fe/SiO_2/PE spectrum shows characteristic polyethylene peaks at 2917.69 and 2849.43 cm^{-1} (C-H stretching vibrations), 1472.92 cm^{-1} (C-H in-plane bending vibration), and 718.53 cm^{-1} (C-H out-of-plane bending vibration), while SiO_2 characteristic peaks nearly disappear. These results indicate that Fe/SiO_2 composite particles were essentially completely coated by polyethylene after polymerization.

When a magnet was placed near Fe/SiO_2/PE composite particles, almost all particles could be attracted by the magnet, as shown in [Figure 9: see original paper]. This demonstrates that the generated polyethylene coated the Fe/SiO_2 composite particles well, with minimal detachment of catalytic active components from Fe/SiO_2 composite particles during polymerization.

2.5 Thermogravimetric Analysis (TGA)

TGA results for Fe/SiO_2/PE composite particles prepared at 40°C reaction temperature, 0.8 MPa pressure, Al/Zr ratio of 4055, and 30 min reaction time are shown in [Figure 10: see original paper]. Weight loss below 200°C corresponds to volatilization of residual organic solvents or moisture. Polyethylene decomposition begins above 450°C, with weight loss reaching 94.5% and the remaining material being non-decomposable Fe/SiO_2 composite particles.

Fe/SiO_2 and Fe contents in Fe/SiO_2/PE composite particles under different reaction times and polymerization pressures at 40°C and Al/Zr molar ratio of 4055 are listed in . The results show that Fe/SiO_2 and Fe contents decrease when polymerization pressure increases or polymerization time extends under otherwise constant conditions, indicating that Fe content in Fe/SiO_2/PE composite particles can be adjusted by varying polymerization time and pressure.

2.6 Molecular Weight and Molecular Weight Distribution of Polyethylene

The molecular weight distribution curve of polyethylene obtained from ethylene polymerization catalyzed by Fe/SiO_2/Cp_2ZrCl_2 at 40°C, 0.8 MPa, Al/Zr ratio of 4055, and 30 min reaction time is shown in [Figure 11: see original paper]. The number-average molecular weight is 269,000 with a polydispersity index (PDI) of 1.71, maintaining the narrow molecular weight distribution characteristic of polyethylene prepared by homogeneous metallocene catalysts. This is attributed to the SiO_2 coating on iron powder surfaces in the form of thin flakes with relatively uniform pore structure, and minimal catalyst particle fragmentation during polymerization, thereby preserving the uniformity of the active center support environment.

Conclusions

1. Fe/SiO_2/PE composite particles can be prepared by loading metallocene catalyst onto Fe/SiO_2 composite particles to catalyze ethylene polymerization. The micron-sized Fe/SiO_2 composite particles prepared by sol-gel method feature complete SiO_2 coating and can effectively support Cp_2ZrCl_2. The Fe/SiO_2/Cp_2ZrCl_2 catalyst system exhibits considerable activity during ethylene polymerization, successfully producing Fe/SiO_2/PE composite particles.
2. Both Fe/SiO_2/Cp_2ZrCl_2 catalyst particles and Fe/SiO_2/PE composite particles exhibit irregular shapes. Agglomeration of Fe/SiO_2/PE composite particles occurs during ethylene polymerization. Catalytic active components rarely detach from Fe/SiO_2 composite particles during polymerization, with generated polyethylene coating the support surface effectively. Fe content in Fe/SiO_2/PE composite particles can be adjusted by changing polymerization time and pressure. Polyethylene obtained from Fe/SiO_2/Cp_2ZrCl_2-catalyzed ethylene polymerization displays narrow molecular weight distribution, maintaining the characteristic narrow

distribution of polyethylene prepared by homogeneous metallocene catalysts.

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