

Synthesis and Catalytic Applications of Mesoporous Polymer Colloids in Olefin Hydrosilylation

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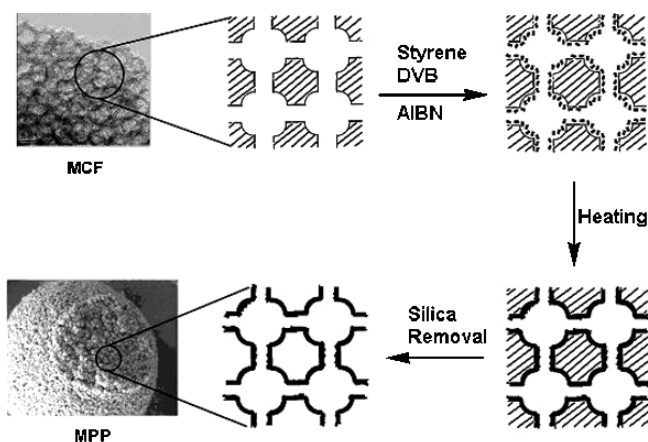
Abstract: Mesoporous polymer particles (MPPs) have been synthesized by using the spherical microparticles of siliceous mesocellular foam (MCF) as a hard template. The MPPs possessed a robust structure with ultralarge mesopores, and a clean and inert surface. The surface properties of the MPPs could be tailored for various applications by using different functionalized monomers. An imidazolium-pyrrolidine ligand was successfully immobilized onto MPPs and used as a supported platinum organometallic catalyst in olefin hydrosilylation. The MPP-supported catalyst provided superior activity and selectivity for this reaction as compared to the MCF-supported catalyst.

Keywords: catalyst support; heterogeneous catalysis; hydrosilylation; mesoporous materials; platinum

Polymers and porous silicas are commonly used materials for catalyst supports.^[1–4] Mesoporous silicas have superior physical properties; they have a robust porous structure with high surface areas. For example, mesocellular foam (MCF)^[5] has ultralarge cell-like pores (up to 50 nm) that are interconnected by windows; this pore structure minimizes the diffusion limitation problem in heterogeneous catalysis.^[6–8] However, silica supports consist of surface silanol groups that tend to interact strongly with catalytic complexes. Surface modification may not fully address this issue.^[6,9] Thus, the catalysts would require a multi-step immobilization process, and frequently suffer from a decrease in activity and/or selectivity after immobilization on silica supports.^[9] Polymer supports do not show these challenges, but are not characterized by well-defined, ultralarge pores.^[10] Diffusion limitation and polymer swelling remain as drawbacks,^[11] despite the development of large-pore resins,^[12] low-swelling

polymers,^[10–12] and mesoporous polymers.^[13] It would be of great interest to develop new materials that possess all the important properties, such as ultralarge pores, uniform spherical particle morphology, and clean/inert surface. Herein, a new type of material, low-swelling mesoporous polymer particles (MPPs), has been synthesized for the first time by using spherical siliceous MCF microparticles^[7] as hard templates. MPPs retained the excellent physical properties of the mesoporous silica template, without the challenges associated with surface silanol species. The surface property of MPPs could also be easily modified for a wide range of potential applications.

Various approaches have been developed for synthesizing porous polymers, such as solvent-controlled macroporous polymers,^[10] mesoporous polymers prepared with hard templates^[12,14] and soft templates,^[15] etc.^[16] However, deriving uniform micron-sized polymer particles with interconnected mesopores of >10 nm remains a challenge. We have selected siliceous MCF microparticles of 2–10 µm in diameter^[7] as a hard template to generate MPPs. These spherical MCF microparticles have a BET surface area of 504 m² g^{−1} and an open pore structure with 30 nm pores that were connected by 18 nm windows. The MPPs were prepared by modifying Ryoo's polymer coating process^[17] and Hyeon's nanocasting strategy.^[18] As illustrated in Scheme 1, styrene, divinylbenzene (DVB) cross-linker and α,α'-azoisobutyronitrile (AIBN) were wet-impregnated onto MCF. A uniform polymer layer was coated on the MCF framework by direct polymerization of the monomers that were adsorbed on the MCF pore walls. MPPs were obtained after removing the silica matrix using a hot solution of NaOH, ethanol and water. The photoacoustic Fourier-transform infrared (PA-FT-IR) spectrum of MPPs showed the disappearance of silica bands in the range of 700–1300 cm^{−1} (see Supporting Information). Elemental analysis and thermal gravimetric analysis (TGA) further confirmed that the silica template was completely removed. The resulting MPPs showed



Scheme 1. Synthesis of MPPs.

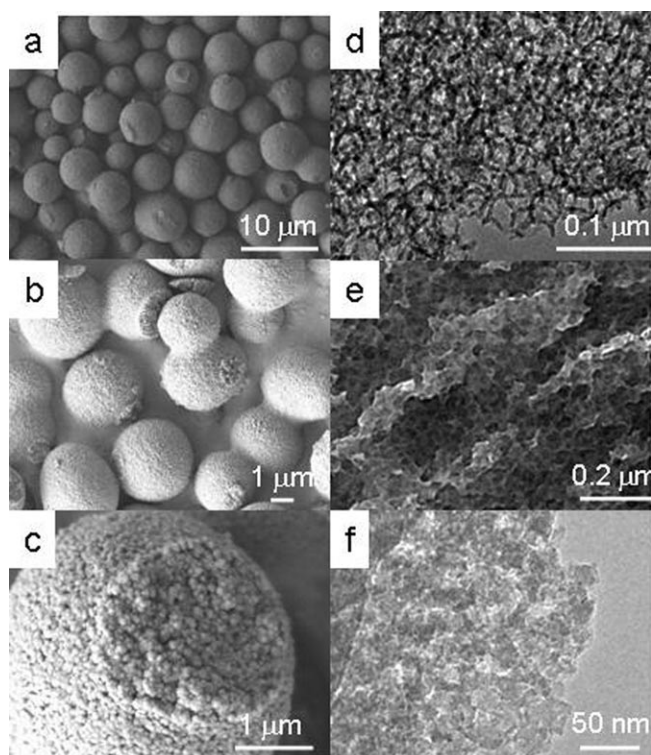


Figure 1. (a–c) SEM and (d–f) TEM images of (a, d) spherical MCF microparticles and (b, c) MPP-Cl1, (e) MPP-A, and (f) D after the first reaction run.

> 99% weight loss when heated to 500°C due to its organic nature (see Supporting Information).

The synthesis of robust MPPs required the use of a high cross-linker/monomer molar ratio (> 1:1).^[10] The resulting polymer coating was highly cross-linked, and rigid and robust enough to retain the porous MCF framework after removing the silica template. The MPPs also possessed the same particle size and morphology of the hard template (see Figure 1). The porosity of MPPs could be adjusted by using different amounts of monomers. The surface areas of MPPs were controlled to be between 100 and 550 m² g^{−1}. The presence of mesopores was noted in the N₂ sorption isotherms of the MPPs (Table 1 and Supporting Information). The size distribution of the mesopores in MPPs was not expected to be the same as in MCF since MPPs were derived from the polymeric coating onto the MCF matrix, followed by removal of the MCF template. As shown in Table 1, to synthesize MPP-A, 0.6 mL of styrene and 0.6 mL of DVB (for a total of 1.1 g of monomer) were used for casting on 1 g of MCF. The surface area of the resulting polymer particles (532 m² g^{−1}) was slightly larger than that of the MCF template (504 m² g^{−1}). The pore volume of MPP-A was 0.76 mL g^{−1}. When more monomer was used with the same amount of MCF template (MPP-B), the surface area and pore volume were reduced substantially. The porous structure was associated with the mesopores of the MCF template, and was also derived from the removal of the silica pore walls of the cast. A scanning electron microscopy (SEM) image (Figure 1c) of MPP-Cl1 showed that the micron-sized MPP particles consisted of interconnected nanoparticles of ~30 nm, which were associated with the cell size of the MCF template. The MPP-A was also ultramicrotomed to thin slices of ~100 nm, and examined by transmission electron microscopy (TEM). Figure 1e illustrates the mesoporosity of the MPP particles (MPP-A in Table 1). The surface properties of MPPs could be modified by using various functionalized monomers. When 4-vinylbenzyl chloride was co-polymerized with DVB, the resulting MPPs (MPP-Cl in Table 1) would have benzyl chloride surface groups, which could be very useful towards catalyst immobilization and be easily converted to ammonium groups with positive charges. When

Table 1. Syntheses and characteristics of MPPs.

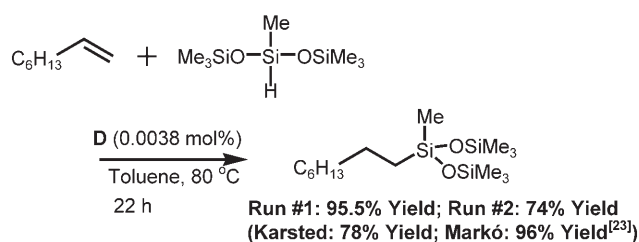
	Monomer ^[a] [mL g ^{−1} of MCF]	Surface area [m ² g ^{−1}]	Pore volume [mL g ^{−1}]	Pore size [nm]
MPP-A	A 0.6, B 0.6	532	0.76	25
MPP-B	A 0.8, B 0.8	248	0.33	21
MPP-Cl1	A 0.95, C 0.25	209	0.25	20
MPP-Cl2	A 0.6, B 0.46, C 0.14	111	0.28	20
MPP-COOH	A 0.6, D 0.6	210	0.26	13

^[a] A: DVB; B: styrene; C: 4-vinylbenzyl chloride; D: acrylic acid.

acrylic acid was co-polymerized with DVB, the resulting MPPs (MPP-COOH in Table 1) would have carboxyl surface groups. The ease with which the MPPs could be derived and the flexibility with which they could be modified in chemical and physical properties provide for a broad range of potential applications.

MPPs were shown to have a robust mesoporous structure with a clean surface, which was important for a catalyst support.^[19,20] We have generated a versatile catalyst system by immobilizing pyrrolidine onto MPPs (MPP-Cl1 in Table 1) through an imidazolium linkage,^[21] a supported ionic liquid.^[22] This system could be flexibly transformed into different types of catalysts. Herein, the MPP-supported NHC/pyrrolidine-Pt catalyst **D** was shown to catalyze the hydrosilylation of olefins (see Scheme 2).

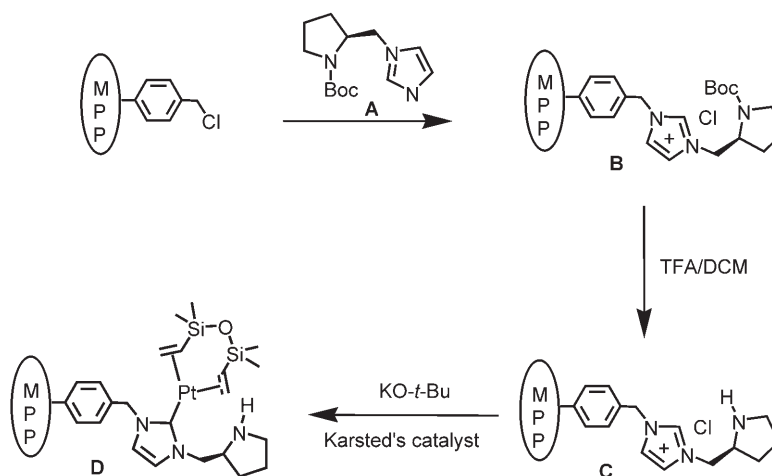
Hydrosilylation is a very important process for producing silicon polymers. Although the hydrosilylation reaction can be catalyzed in many ways, the most popular industrial catalysts are Pt-based systems: Speier's catalyst ($\text{H}_2\text{PtCl}_6/\text{i-PrOH}$) and Karstedt's catalyst [$\text{Pt}_2(\text{dvtms})_3$, dvtms = divinyltetramethyldisiloxane]. However, there are some critical drawbacks for these two systems, such as the formation of a significant amount of undesired by-products, and catalyst decomposition to form platinum particles that gave rise to major product contamination. Markó's group recently



Scheme 2. The catalytic olefin hydrosilylation reaction.

reported an NHC-Pt complex system that successfully catalyzed alkene hydrosilylation reactions, and demonstrated superior selectivity and activity compared to the commercial Speier's and Karstedt's catalysts.^[23,24] The NHC-Pt catalyst showed remarkable efficiency and selectivity, and avoided the formation of platinum colloids. Encouraged by these reports, MPP-NHC/pyrrolidine-Pt catalyst **D** was developed to catalyze olefin hydrosilylation reactions (Scheme 2).

NHC/pyrrolidine ligand was immobilized by direct alkylation of *N-tert*-butoxycarbonyl (Boc) protected pyrrolidine-substituted imidazole (**A**), followed by deprotection with trifluoroacetic acid (TFA) (see Scheme 3).^[21] The loading of pyrrolidine was in the range of 0.1–0.5 mmol g⁻¹, depending on the different procedures used. Compared with MPP or MPP-Cl, **C** showed stronger PA-FT-IR peaks for NH species (3300 cm⁻¹) and quaternary ammonium (1000–1200 cm⁻¹) (see Supporting Information). This indicated that pyrrolidine groups were successfully immobilized onto MPPs, which was further confirmed by elemental analysis. Catalyst **D** (with 0.016 mmol of Pt/g) catalyzed the model hydrosilylation reaction (Scheme 2) to give the desired product in excellent yield (95.5% and 74% yields in the first and second runs, respectively). For comparison, the homogeneous counterpart^[25] and the MCF-supported NHC/pyrrolidine-Pt catalyst were also prepared^[26] and tested. The homogeneous catalyst with 0.0020 mol% of Pt loading gave 97% of product in 22 h (incomplete reaction was noted when a lower Pt loading was employed). This illustrated that NHC/pyrrolidine was an excellent ligand for Pt in the hydrosilylation of olefins, providing similar selectivity as Markó's catalyst.^[23] The MCF-supported catalyst provided conversions of only 11% and 1% for the first and second runs, respectively, under the same reaction conditions. While catalyst **D** was less active than its homogeneous counterpart



Scheme 3. Synthesis of MPP-supported chiral pyrrolidine and NHC-Pt catalysts.

and Karstedt's catalyst, its reaction rate was still impressive at a Pt loading of 0.0038 mol%. It also provided similar chemoselectivity (>95%) as the homogeneous NHC-Pt catalyst in both the first and second runs. Inductively coupled plasma-mass spectrometry (ICP-MS) analysis indicated that platinum leaching to the liquid phase was negligible. No platinum was detected in the reaction solution. Furthermore, a hot filtration experiment was conducted.^[27] The hot mother liquor (filtrate) obtained from the reaction mixture after 5 h of reaction with ~30% of conversion was kept at the reaction temperature for another 15 h; no further reaction was observed. Compared to the MCF-supported catalyst, the MPP-supported catalyst **D** was superior in activity and selectivity, and yielded the desired product with negligible Pt contamination. The lower yield of the recovered catalyst might be due to some catalyst deactivation when the sensitive and very small amount of catalyst was recycled. Elemental analysis confirmed that Pt leaching was not the case here; the same amount of Pt was found in the solid catalyst before and after the reaction. A TEM image of catalyst **D** after the first reaction run did not show any Pt particles (Figure 1f). The challenge for this reaction was to be able to separate the Pt catalyst from the product to avoid product contamination. MPP-NHC/pyrrolidine-Pt represents the first solid-supported NHC-Pt catalyst. It retained the excellent activity and selectivity of the homogeneous catalyst, while effectively tackling the product purification and Pt contamination challenges.

In summary, MPPs have been synthesized by using spherical MCF microparticles as a hard template. The MPPs possessed a robust structure with ultralarge mesopores, and a clean and inert surface. The surface properties of the MPPs could be tailored for different applications by using different functionalized monomers. An imidazolium-pyrrolidine ligand was successfully immobilized onto MPPs, and used as a supported platinum organometallic catalyst in olefin hydrosilylation. The MPP-supported catalyst provided superior activity and selectivity as compared to the MCF-supported catalyst in this reaction. This study demonstrated the MPPs as a new class of materials with interesting potential for catalytic applications.

Experimental Section

All solvents were used as received from commercial suppliers, unless otherwise noted. Centrifugation was performed on Eppendorf Centrifuge 5810R (4000 rpm, 10 min). PA-FTIR spectra were obtained with a Digilab FTS 7000 Series using a photoacoustic cell (MTEC Model 300). Gas liquid chromatography (GLC) was performed on Agilent 6890N Series gas chromatograph equipped with a split-mode capillary injection system and flame ionization detector using

Bodman ChiralDEX γ -TA column (0.25 mm \times 30 m). C, H, N analyses were obtained with EAI CE-440 Elemental Analyzer. N₂ adsorption isotherms were obtained at 77 K using a Micromeritics ASAP 2020M system. SEM images were obtained with a JEOL JSM-7400F electron microscope (10 kV). TEM was conducted on a FEI Tecnai G² F20 electron microscope (200 kV). TGA was performed on Perkin-Elmer Pyris-1 Thermogravimetric Analyzer. ICP-MS was performed on ELAN 9000/DRC system.

Synthesis of MPPs

This typically involved dissolving 0.6 mL of styrene (Aldrich, 99%), 0.6 mL of DVB (Aldrich, 98%), and 0.05 g of AIBN (Aldrich, 98%) (3% relative to total vinyl group) in 1.0 mL of dichloromethane (DCM). This solution was injected into a flask with 1 g of spherical MCF microparticles, which were synthesized according to previous reports^[7] and used after vacuum degassing at 100°C overnight. After impregnation with the solution, the powder was vacuum dried at -78°C for 4 h to selectively remove DCM, and subjected to freeze-vacuum-thaw cycles several times. The sample was sealed and equilibrated for 6 h at room temperature, and then polymerized by heating at 60°C for 4 h, 80°C for 3 h, and 100°C for 2 h. The resulting material was washed extensively with chloroform and ethanol. It was dried at 80°C, and collected as a white powder. The powder was then mixed with NaOH (4 g) in ethanol (50 mL) and water (50 mL). The mixture was kept at 90°C, and stirred overnight. After filtration, the material was washed extensively with water, methanol and DCM. After drying in vacuum, a white powder was collected as MPP-A. Elemental analysis showed ~99% hydrocarbon components [MPP-A: C 91.02%, H 7.97% (vs. MPP-A with MCF: C 43.38%, H 3.81%); MPP-B: C 90.87%, H 7.99%]. MPP-Cl and MPP-COOH were synthesized by the same procedure with different monomers, as listed in Table 1. Elemental analysis results: MPP-Cl: C 86.78%, H 7.39%; MPP-COOH: C 76.92%, H 6.79%.

MPP-NHC/Pyrrolidine

This was synthesized by adding dimethylformamide (DMF, 30 mL) and catalyst precursor **A** (126 mg, 0.5 mmol) to the dried MPP-Cl (1 g) sequentially. The suspension was stirred at 100°C for 24 h, and filtered. The solid obtained was washed successively with methanol and DCM. After drying in vacuum, the white powder was collected and soaked in TFA (50% in 10 mL of DCM) overnight. The suspension was filtered, and the solid obtained was washed with saturated sodium bicarbonate aqueous solution, methanol and DCM successively. The resulting pale yellow powder was dried and collected as MPP-pyrrolidine (1.02 g). Compared with MPP-A and MPP-Cl, MPP-pyrrolidine showed strong PA-FTIR NH peak (3300 cm⁻¹) and quaternary ammonium peak (1000–1200 cm⁻¹). The loading of pyrrolidine was 0.26 mmol g⁻¹ of MPP based on elemental analysis (C 81.83%, H 7.05%, N 1.12%).

Catalyst **D**

This was prepared by mixing **C** (1 g, 0.26 mmol of imidazolium), potassium *tert*-butoxide (KO-*t*-Bu) (0.1 mmol) with

Karstedt's catalyst [Pt₂(dvtms)₃, 0.03 mmol of Pt] in tetrahydrofuran (THF), and the resulting mixture was stirred at room temperature for 16 h. The solid product was filtered, washed with THF, and dried to obtain a powder **D** (Pt loading = 0.016 mmol g⁻¹ based on ICP-MS analysis); it was used directly in the hydrosilylation reaction.

1-Octene (0.5 mmol), bis(trimethylsilyloxy)methylsilane (MD'M, 0.5 mmol) and platinum catalyst (38 ppm) were mixed in a vial with toluene (1.5 mL). The vial was capped, and the reaction mixture was stirred at 80 °C. After completion of the reaction [as determined by gas chromatography (GC)], the reaction mixture was centrifuged, and the solution was removed. This procedure was repeated at least three times using dry toluene as the wash solvent. The toluene solution was combined and collected for yield determination. The recovered catalyst was used directly for the next run.

Acknowledgements

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- [26] MCF-supported NHC/pyrrolidine catalyst (0.02 mmol Pt/g based on ICP-MS analysis) was prepared by using the same protocol as for the MPP-supported catalyst, except that benzyl chloride-modified MCF [capped with trimethylsilyl (TMS) groups]^[6,9] was used instead of MPP-Cl1 as the starting material.
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