

Synthesis of Pd-SiO₂ aerogel inverse opals in supercritical CO₂

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Pd-SiO₂ aerogels inverse opals were prepared in supercritical CO₂ (scCO₂) using a colloidal crystal templating technique. Monodisperse spherical polymer particles (latex) were arranged in 3D-arrays (colloidal crystals) and used as templates. Two different approaches are compared. In the first approach, the templates were reacted with tetraethylorthosilicate (TEOS) and Palladium hexafluoroacetylacetonate dissolved in scCO₂. In the second approach, the templates were impregnated with a small amount of PdCl₂ in the liquid phase before assembling the colloidal crystal, which was then reacted with TEOS in scCO₂. In both cases, the reaction was carried out at 40°C and 85 bar. After removal of the template, porous materials replicating the structure of the original template were obtained. Palladium incorporation into the materials is different depending on the method employed.

INTRODUCTION

Supported Pd catalysts are used in reduction and oxidation reactions as well as in hydrogenation, dehydrogenation, debenzoylation, hydrocracking, carbonylation and other carbon-carbon coupling reactions [1]. In order to improve the catalytic activity and selectivity of the catalyst, the metal must be evenly dispersed on a large surface area support, such as a mesoporous SiO₂ aerogel. The presence of macropores in the catalyst facilitates the transport of the reactants to the catalyst surface. Furthermore, preparing structured catalysts of defined geometry and pore size distribution is necessary to model catalytic processes.

A new technique to produce structured porous SiO₂-aerogels in supercritical CO₂ (scCO₂) has been developed at our laboratory [2-4]. Monodisperse polystyrene (PS) polymer particles modified with carboxylic acid groups on their surface are arranged in 3D-ordered arrays and used as the templates. The polymer particles have sizes in the range of the visible wave-length and the colloidal crystals exhibit opalescence; these materials are called opals. The polymeric template is reacted with a ceramic precursor dissolved in scCO₂. The low viscosity, high diffusivity and very low surface tension of scCO₂ promote infiltration of the precursor into the template. After calcination or dissolution of the template, highly porous materials replicating the structure of the original template are obtained (inverse opals). In this communication we show that the method can be extended to produce Pd-SiO₂ aerogels inverse opals.

MATERIALS AND METHODS

For the synthesis of the polymeric templates, reagent grade materials from Sigma-Aldrich and distilled water were used. Tetraethylorthosilicate (TEOS, 99+% pure), benzenesulfonic acid (BSA, 99+% pure), p-toluenesulfonic acid (pTSA, 98.5+% pure) and Palladium(II) hexafluoroacetylacetonate (Pd(hfac)₂) were obtained from Aldrich. Anhydrous Palladium Chloride (59-60% as Pd) was obtained from Riedel-de Haën. CO₂ purity >99.99% was supplied by Air Liquide. All chemicals were used as received.

PS particles modified with methacrylic acid (MA) or both MA and itaconic acid (IA) groups on their surface were prepared by surfactant-free emulsion copolymerisation in water [5]. The molar ratios of styrene (S) to MA in PS-MA samples were 7:1 and 47:1, yielding particles of 160 and 385 nm, respectively. S:IA:MA monomer ratio in PS-IA-MA was 50:1:2.

The experiments were carried out in a ca. 70 mL custom-made stainless-steel high-pressure reactor in the batch mode [4]. The reactions were carried out in scCO_2 at 40 °C and 85 bar for 1-6 hours, followed by depressurization. Two different approaches are compared. The experimental procedure is summarized in **Figure 1**.

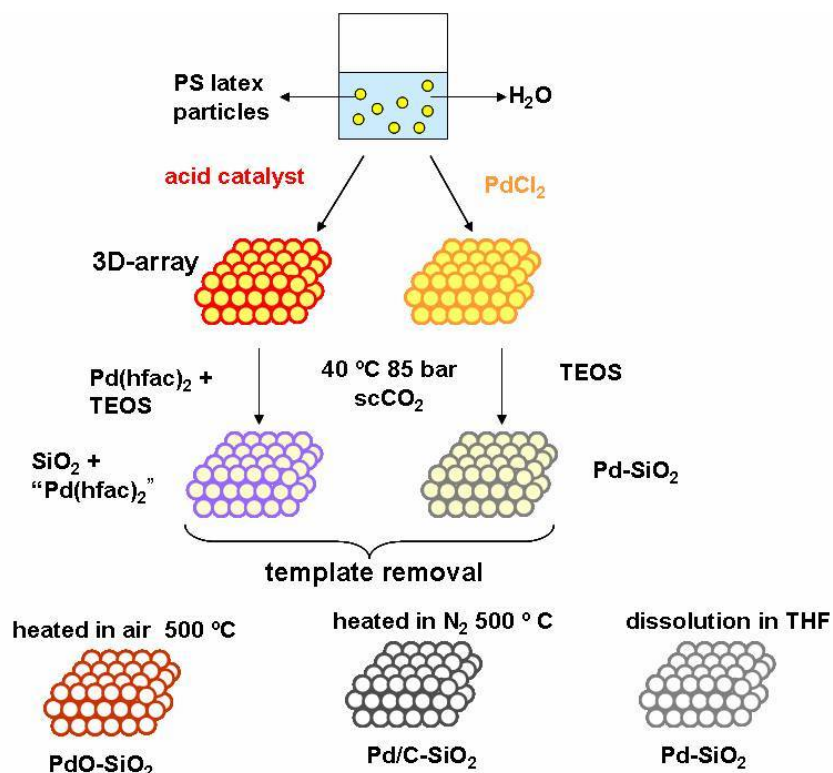


Figure 1. Synthesis of Pd-SiO₂ inverse opals in scCO_2 .

In the first approach, the template is impregnated with a small amount of an acid catalyst (BSA or pTSA) in the liquid phase (0.01-0.001 mM pTSA/g latex) and the colloidal crystal is formed by centrifugation or evaporation. This template is reacted with a mixture of TEOS and Pd(hfac)₂ in scCO_2 at 40 °C and 85 bar.

In the second approach, the template is impregnated with a small amount of PdCl₂ in the liquid phase, and the mixture is centrifuged and washed several times to remove excess Pd. After drying, the template is reacted with TEOS in scCO_2 at 40 °C and 85 bar. At these conditions SiO₂ deposits on the surface of the template and the metal is reduced.

The template can then be easily removed by thermal treatment in air or N₂ at 500 °C yielding PdO-SiO₂ or Pd/C-SiO₂ inverse opals, respectively, or it can be dissolved in THF to give Pd-SiO₂ (with some leaching of Pd). Materials replicating the structure of the original template were obtained.

Materials were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier Transform-IR (FTIR) and X-ray diffraction (XRD). SEM images

were taken on a JEOL-6400 electron microscope working at 20 kV. Prior to analysis, samples were gold coated or evaporated with graphite if elemental analysis was conducted. TEM were carried out on a JEOL 2000FX electron microscope operating at 200 kV equipped with a double tilting ($\pm 45^\circ$) and a JEOL-JEM 3000F electron microscope operating at 300 kV equipped with a double tilting ($\pm 25^\circ$). Samples were dispersed in water or 1-butanol over copper grids and dried in air. Energy-dispersive Detection X-ray analysis (EDX) was conducted on selected samples using both SEM and TEM microscopes. FTIR spectra of the powdered materials were recorded as KBr pellets on an IR-PRESTIGE-2 spectrometer. XRD patterns were collected using a Siemens D5000 diffractometer with Cu K_α radiation.

RESULTS

PS-MA (160 nm) or PS-IA-MA (350 nm) latex particles were impregnated with pTSA or BSA in the liquid phase and arranged in 3D-ordered arrays. These templates were reacted with a mixture of TEOS and Pd(hfac)₂ ($\leq 5\%$ mol Pd) in scCO₂ at 40 °C and 85 bar for *ca.* 3 hours. The material turned from white to light blue or blue/brown. After removal of the template in air, the material became brown, which indicates the incorporation of Pd into the inverse opal (SiO₂ inverse opals are white). XRD analysis of the samples showed a very broad band at 2θ *ca.* 20 due to amorphous SiO₂ and weak reflections at 2θ values *ca.* 34 and 42 ascribed to PdO. SEM images of the samples showed that the material replicates the structure of the template. Pd content was, in most cases, below 1 % mol as determined by EDX.

TEM images of the material obtained using the PS-MA template (**Figure 2**) showed small clusters of 1-2 nm, homogeneously distributed throughout the SiO₂ matrix.

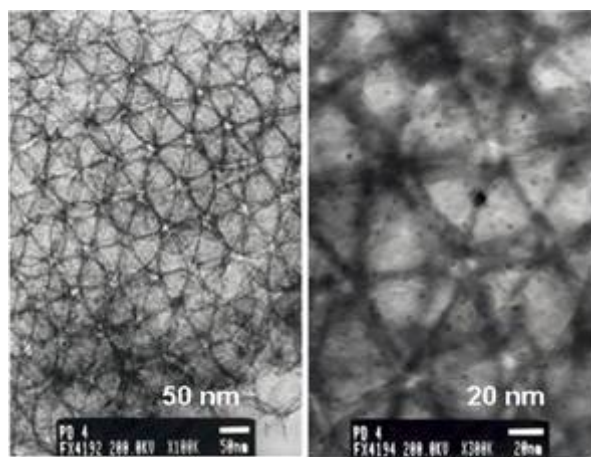


Figure 2. TEM of a PdO-SiO₂ inverse opal obtained from reaction of TEOS and Pd(hfac)₂ in scCO₂.

At the same conditions, Pd(hfac)₂ does not react on these templates in pure scCO₂ or in a supercritical ethanol/CO₂ mixture. The small Pd content in the inverse opal relative to the initial concentration of Pd in the reaction mixture seems to indicate that Pd(hfac)₂ gets only incorporated into the SiO₂ network as it is being formed.

On the other hand, when a template formed by 385 nm PS-MA particles previously impregnated with PdCl₂ was reacted with TEOS in scCO₂ at 40°C and 85 bar for 1.5 hours, a black-grey product was obtained. The weight gain after reaction was significant, proving decomposition of TEOS. XRD analysis of the as-reacted material showed reflections due to metallic Pd at 2θ values *ca.* 39.6. When the template was calcined in air, a heterogeneous white and golden/brown material was obtained. XRD analysis of the calcined sample revealed the presence of strong reflections ascribed to PdO. Pd loading in this case can be quite high, up to 5-10 % mol Pd according to EDX. SEM images showed regions in the material replicating the structure of the original template along with other zones with excess SiO₂ on the surface. TEM images of the inverse opal produced (**Figure 3**) show PdO clusters as large as 20 nm, homogeneously distributed throughout the SiO₂ matrix.

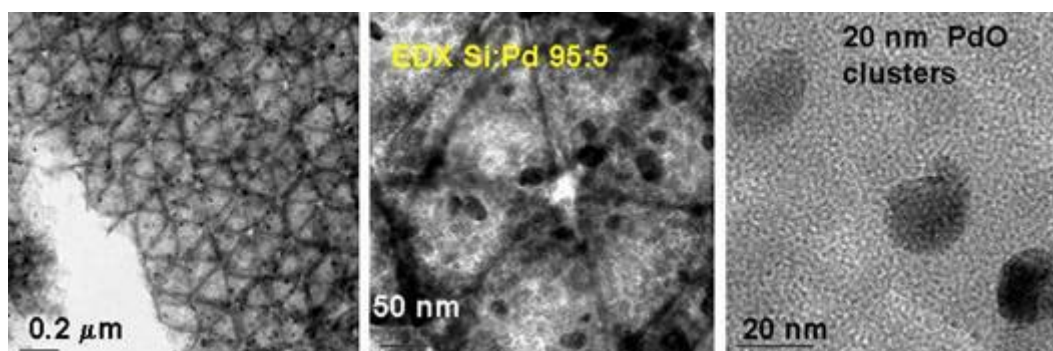


Figure 3. TEM of a PdO-SiO₂ inverse opal obtained from reaction of TEOS in scCO₂ using a PS-MA template impregnated with PdCl₂.

Analysis of the templates by FTIR shows that Pd binds to the carboxylic acid groups at the particle surface. Then Pd catalyses the decomposition of TEOS, SiO₂ deposits on the surface of the template and the metal is reduced. The reaction is very sensitive to the polymer composition and did not proceed readily on other PdCl₂ impregnated latex such as bare PS or PS-MA with a high MA concentration (S:MA 7:1). We are currently investigating the catalysis mechanism.

CONCLUSION

Pd-SiO₂ aerogels inverse opals have been prepared in scCO₂ at 40 °C and 85 bar using PS 3D-latex array templates. In the presence of Pd(hfac)₂, TEOS reacts on the template in scCO₂ but incorporation of Pd into the structure is below 1% mol. If the template is first impregnated with PdCl₂ in the liquid phase and then reacted with TEOS in scCO₂, Pd content increases up to 5-10 % mol. After removal of the template, Pd-SiO₂ porous materials replicating the structure of the original template were obtained. We are exploring the potential of our technique to produce other metal-ceramic composite materials.

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