One-Step Synthesis of Mesoporous Metal—SiO₂ Particles by an Aerosol-Assisted Self-assembly Process

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Spherical mesoporous silica particles with entrapped metal nanoparticles are synthesized from a one-step aerosol-assisted self-assembly process using sols of an alkoxysilane, ethanol, surfactant, water, HCl, and metal precursors (e.g., salts or complexes). Utilizing nitrogen as a carrier gas, the sol is sent through an atomizer, producing aerosol droplets, which are passed through a tubular furnace heated to 400 °C. Solvent evaporation from the droplets enriches the nonvolatile components and results in the coassembly of silicate and surfactant into 3-dimensional mesostructures with incorporated metal precursors. Lamellar, cubic, and hexagonal mesostructures are achieved by using different surfactants. Subsequent calcination of the surfactant and reduction of the metal result in spherical mesostructured porous silica particles with supported metal nanoparticles. Nitrogen sorption techniques, transmission electron microscopy, scanning electron microscopy, and X-ray diffraction are used to characterize the particles. Mesoporous silica particles with 0.5% Pd are tested as a catalyst in the hydrodechlorination reaction of 1,2-dichloroethane and exhibit $\sim 100\%$ conversion above 350 °C and $\sim 100\%$ ethylene selectivity, demonstrating the potential of such nanocomposites as catalysts.

Introduction

Surfactant-templated mesoporous materials have attracted considerable attention in the past decade due to their unique properties, such as controllable pore structures, high surface areas, narrow pore size distributions, and potential applications. ^{1–6} These materials are typically synthesized by assembling surfactant molecules and inorganic species such as silicates into nanocomposites that contain lamellar, hexagonal, or cubic lyotropic liquid crystalline mesostructures followed by surfactant removal. The synthesis procedure involves either a solution precipitation route^{7–9} or a solvent evaporation induced self-assembly (EISA) route. ^{10,11} In the solution precipitation route, inorganic precursors such as tetraethox-

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vsilane (TEOS) are reacted in a highly acidic or basic aqueous solution containing surfactant with concentrations often exceeding critical micelle concentrations. Spontaneous coassembly of the inorganic species and surfactant results in the formation of mesostructured materials precipitated from the solution.⁷ The EISA approach utilizes homogeneous precursor solutions that contain inorganic species and surfactant. The concentrations of surfactant are often below the critical micelle concentration. Solvent evaporation during a coating, 10 aerosol, 12 or inkjet printing 13 process enriches the nonvolatile silicates and surfactant and induces their coassembly into ordered mesostructures.¹¹ Compared with the solution precipitation route, the EISA route combines the simplicity of the sol-gel process with the efficiency of surfactant self-assembly, allowing rapid synthesis of mesostructured thin films, particles, and arrays with the morphology and mesostructure controlled. In particular, the nonequilibrium feature of the EISA process allows the incorporation of various nonvolatile components such as functional organic molecules, particles, and polymers within the self-assembled mesostructures, providing a general and flexible approach for nanocomposite fabrications. 14-16

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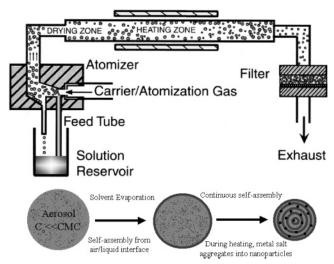


Figure 1. Schematic of the one-step aerosol process and the formation of a mesostructured metal/silica particle from an aerosol droplet.

In this research, we explored the nonequilibrium synthesis feature of the EISA method to fabricate mesoporous silica/ metal nanocomposite particles using a one-step aerosol process. Porous inorganic/metal materials, such as porous silica supported platinum and palladium, are of great interest for catalyst applications.¹⁷ In general, porous inorganic/metal materials are synthesized by introducing metal precursors or colloidal metal nanoparticles within preformed inorganic porous materials through impregnation,⁶ ion exchange, ¹⁸ or interactions between metal precursors and functional ligands¹⁹ or by directly incorporating metal precursors or particles into sols that are subsequently converted into porous inorganic gels.²⁰ These conventional methods often lack the capability of simultaneously controlling the metal loading and pore structure. For example, a high loading of metals produced using an impregnation method may decrease the porosity and deteriorate pore accessibility. In contrast, the aerosol process continuously produces particles in a one-pot synthesis where the metal is incorporated into the inorganic support in situ without destroying the mesostructure. As illustrated in Figure 1, different loadings of metal precursors can be added into the starting silicate/surfactant solution. The aerosol atomizer generates droplets containing silicates, surfactant, and the metal precursors. Solvent evaporation at the air/liquid interface enriches the aerosol droplet in surfactant and silicates, resulting in their cooperative assembly into liquidcrystalline mesophases that dynamically grow from the interface to the interior of the droplet. As the assembling particles pass through the heating zone of the process, further drying and silica condensation result in the formation of mesostructured particles incorporating palladium salt. Subsequent or in situ metal reduction reaction reduces the palladium ions into Pd⁰ and converts the counterion Cl⁻ into HCl that is released from the particles. Further surfactant removal leads to the formation of mesoporous silica/metal

particles. This technique has three major advantages: (1) various metal nanoparticles can be incorporated into the silica frameworks at different loadings during this in situ process, (2) pore structures and pore sizes can be easily controlled by the surfactant/silicate coassembly process, and (3) this aerosol-assisted assembly process allows continuous, efficient production of mesoporous metal/silica particles on a large scale.

Experimental Section

All commercial chemicals and surfactants were used as received. The surfactants chosen for this study were Brij-58 ($C_{16}H_{33}(OCH_2-CH_2)_{20}OH$; from Aldrich), P123 ($EO_{20}PO_{70}EO_{20}$; from BASF), and F127 ($EO_{106}PO_{70}EO_{106}$; from BASF). EO and PO are used to designate ethylene oxide and propylene oxide, respectively. Tetraethyl orthosilicate (TEOS; from Aldrich), ethanol, and deionized water were used in the synthesis of the silica particles, and 5 wt % palladium(II) chloride in 10 wt % HCl (from Aldrich) and tetraammine palladium(II) nitrate (Strem) were used as the palladium precursors.

Pd-SiO₂ mesoporous particles were produced using an aerosolassisted self-assembly process. A typical silica sol was prepared by adding 8.3 g of TEOS to a solution of 40.5 g of ethanol, 3.6 g of water, and 3 g of P123 or F127 surfactant (for Brij-58 solutions, 8.3 g of TEOS, 48.2 g of water, and 2 g of surfactant were used). Varying amounts of palladium(II) chloride dissolved in HCl (an aqueous solution containing 5 wt % PdCl2 and 10 wt % HCl) and tetraammine palladium(II) nitrate with added HCl (pH was maintained around 2.8) were added to the solution to give the desired Pd concentrations. The palladium loadings were calculated on the basis of the amounts of palladium precursors added. The solutions were sonicated for 30 min to allow for hydrolysis and condensation reactions of the TEOS. An aerosol process first described by Lu et al. 12 and shown schematically in Figure 1 was used to synthesize the Pd-SiO₂ mesoporous particles. As shown in the figure, nitrogen at 40 psig draws the sol into the atomizer, resulting in the generation of aerosol droplets that are carried through a glass tube (1 in. inside diameter) heated to 400 °C. In this research, the aerosol reactor was operated at a volumetric flow rate of 2.6 L (STP)/min, in which the N₂ flow is laminar. During the drying zone of the process, solvent evaporation from the aerosol droplets results in the selfassembly of surfactant and silicates into ordered mesophases. As the droplets pass through the heating zone (around 2 ft long) of the process, rapid silica condensation results in surfactant/silica nanocomposite particles with entrapped metal salt crystals that are collected on a filter heated to 80 °C. The particles are then calcined at 425 °C for 3 h at a heating rate of 1 °C/min and further reduced using forming gas (8% H₂ in N₂) at 400 °C for 1 h to form palladium metal nanoparticles dispersed within the mesoporous silica particles.

The particles were characterized using transmission electron microscopy (TEM) (JEOL JSM-2010 operated at 120 kV), scanning electron microscopy (SEM) (JEOL JSM-5410), and X-ray diffraction (XRD) (Phillips Xpert X-ray defractometer using Cu Kα radiation at 1.54 Å). Nitrogen adsorption/desorption isotherms were obtained using a Micromeritics ASAP 2010. The particles were tested for possible applications as catalysts, using the hydrodechlorination reaction of 1,2-dichloroethane as an example. Approximately 200 mg of catalyst prepared with Brij-58 surfactant and with 0.5 wt % Pd was loaded into a Pyrex microreactor equipped with a quartz frit. The catalyst was pretreated with argon to remove any oxygen, reduced with hydrogen gas at 400 °C for 1 h, and cooled to room temperature in argon. Hydrogen gas was

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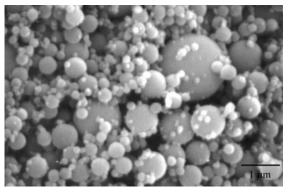


Figure 2. SEM micrograph of polydisperse Pd-SiO₂ mesoporous particles with spherical morphologies.

metered into the reactor along with liquid 1,2-dichloroethane maintained at 0 °C and passed through a saturator using helium as the carrier gas. The effluent gas stream was sampled using an online 5890 Hewlett-Packard gas chromatograph equipped with an FID and a custom Haysep R column to determine the composition of 1,2-dichloroethane, chloroethanes, ethylene, and ethane. The reactions were conducted at 50 °C increments from 200 to 400 °C.

Results and Discussion

The SEM micrograph in Figure 2 shows the size and morphology of the calcined Pd—silica mesoporous particles. The particles are spherical in shape with polydisperse particle sizes ranging from less than 0.1 μ m to greater than 1 μ m in diameter. If desired, monodisperse particles with diameters in the micrometer range can be achieved by using a vibrating orifice aerosol generator (VOAG) instead of the general atomizer used in this study.²¹

1. Mesoporous Structure Control. Controlling the pore sizes and structures of the silica support by using different surfactants is an important component for some applications where molecule size exclusion or diffusion control is important. Figure 3 shows representative TEM images of various mesoporous particles with 2 wt % Pd prepared using P123, Brij-58, and F127 surfactants. The use of P123 surfactant results in vesicular or lamellar pore structures with a nonuniform layer distance (Figure 3a,b). The formation of the nonuniform lamellar structures may be due to the partial collapse of the concentric spheres during surfactant removal. The TEM images in Figure 3a,b also clearly show the formation of palladium nanoparticles entrapped within the mesoporous silica layers. The size of the metal particles is dependent on the synthesis conditions used. For example, in sols with tetraammine palladium(II) nitrate as the metal precursor (Figure 3a), the pH is kept at 2.8, which is above the isoelectric point of silicate (pH of \sim 2.2). In these sols, the silicates are slightly negatively charged, which may allow the Pd cations to attach to the silica and result in 5-7 nm metal particles. When palladium chloride is used as the metal precursor (Figure 3b), the high concentration of HCl in the PdCl₂ solution brings the pH of the sol below the isoelectric point, resulting in a positive charge on the surface of the silicates. This leads to repulsion between the silica and Pd

cations, resulting in the aggregation and formation of large 15-25 nm Pd nanoparticles.

The use of Brij-58 surfactant results in an ordered hexagonal structure with an estimated pore diameter of 3.8 nm and a center-to-center pore distance around 6.6 nm (Figure 3c). When F127 is used as the surfactant template, a cubic mesostructure²¹ with an estimated pore diameter of 7.8 nm and a center-to-center pore distance around 15.5 nm is observed (Figure 3d). Larger 15–25 nm metal nanoparticles are observed in both the F127- and Brij-58-templated particles, which results from the lower pH of the palladium chloride solution as described above.

The ordered mesostructures of the particles are confirmed from low-angle XRD patterns (Figure 4). Particles templated with P123 exhibit two diffraction peaks at $d_{100} = 10.1$ nm and $d_{200} = 5.1$ nm, consistent with the distance between the layers observed. Particles templated with F127 show two diffraction peaks ($d_{110} = 11.2$ nm and $d_{211} = 6.6$ nm), consistent with an fcc structure typically formed from F127.²¹ Brij-58-templated particles result in a single diffraction peak at a d spacing of 5.9 nm, which may be from the (100) plane of a hexagonal unit cell. However, it is difficult to accurately determine the mesostructure since only one diffraction peak was observed.

The nitrogen adsorption/desorption isotherms, pore size distributions, and BET surface areas of the mesoporous particles with 2% Pd prepared using different surfactants are displayed in Figure 5. The particles respectively exhibit high surface areas of 508, 566, and 753 m²/g when surfactants P123, F127, and Brij-58 are used. The Brij-58-templated particles show a type IV adsorption/desorption isotherm with little hysteresis, indicating a narrow pore diameter distribution. Consistently, the BJH pore size distribution (inset) of the Brij-58-templated particles shows a narrow pore size distribution centered at 3.5 nm in diameter, similar to the pore diameters measured in Figure 3c. The F127-templated particles show an adsorption/desorption isotherm with significant hysteresis and a pore size distribution centered at 10 nm. The P123-templated particles show an adsorption/ desorption isotherm with a large hysteresis. The broad pore size distribution centered at 22.4 nm results from the unique layered structures shown in Figure 3a,b.

2. Control of the Metal Loadings. The aerosol technique not only allows pore structure control by the choice of surfactant, but also the control of metal loadings by directly adding designed amounts of metal precursors into the starting sols. Figure 6 shows representative TEM images of Brij-58-templated particles containing 1, 5, and 10 wt % palladium nanoparticles. The particles with an average 1 wt % palladium loading (Figure 6a) contain palladium particles dispersed within an ordered pore network. Increasing the Pd loading results in silica/metal particles with an increased number of palladium nanoparticles without significantly altering the structure of the mesoporous support.

The pore structure of the particles with different metal loadings was further characterized using a nitrogen sorption technique. Figure 7 shows the adsorption/desorption isotherms of the mesoporous particles with 0.5-10 wt %

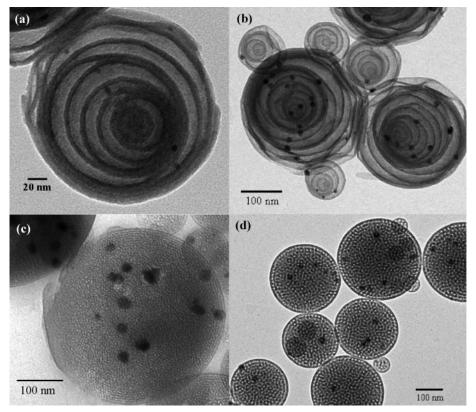


Figure 3. TEM micrographs of 2% Pd-SiO₂ mesoporous particles prepared with (a, b) P123, (c) Brij-58, and (d) F127 surfactants.

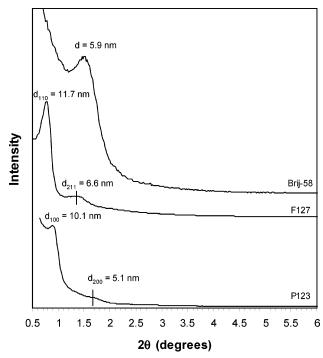


Figure 4. Low-angle XRD peaks for 2% Pd mesoporous silica particles templated with P123, F127, and Brij-58 surfactants.

palladium. It is found that the pore volumes decrease and the surface areas increase (except for 10 wt % Pd) as the palladium content increases. Also, the BJH pore size distributions shown in the inset are centered from 5 to 3 nm in diameter. The decreasing pore diameter with an increasing metal loading results from the partial filling of the pores with palladium or from the altered assembled structure at high ionic strength. A high metal loading may also decrease the

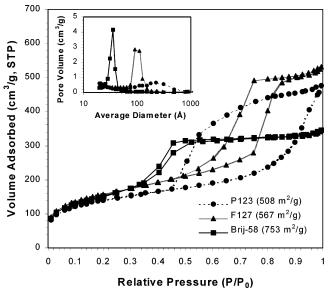


Figure 5. Nitrogen adsorption/desorption isotherms, BJH pore size distributions (inset), and BET surface areas (legend) of 2% Pd-SiO₂ mesoporous particles prepared with surfactants P123, F127, and Brij-58.

silica network strength and connectivity, resulting in more pore structure shrinkage upon calcination and in turn smaller pores. The decrease in pore size with increasing Pd content is also confirmed with low-angle XRD measurements (data not shown). The *d* spacing for the particles are 7.2, 6.8, 5.6, and 5.7 nm from Pd contents of 0.5, 1, 5, and 10 wt %, respectively.

Figure 8 shows the high-angle XRD patterns of the mesoporous silica particles with 0.5–10 wt % palladium. The diffraction peaks shown are consistent with typical palladium fcc crystalline structures, while the broad peak at

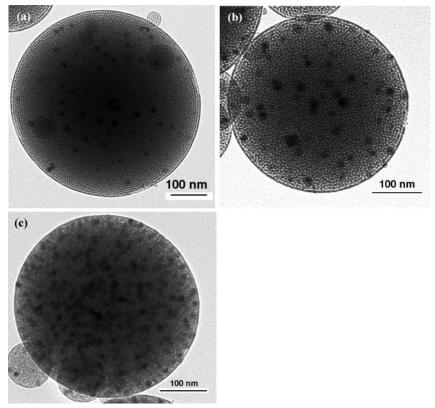


Figure 6. TEM images of Pd-SiO₂ mesoporous particles with varying average amounts of Pd: (a) 1%, (b) 5%, and (c) 10% Pd.

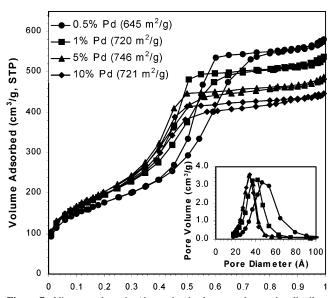
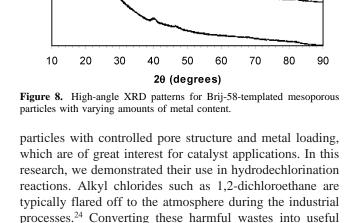


Figure 7. Nitrogen adsorption/desorption isotherms and pore size distributions (inset) of Pd-silcia mesoporous particles with varying amounts of

a 2θ of $\sim 23^{\circ}$ is due to the amorphous silica. The particles with a low palladium loading (e.g., 0.5%) show only weak diffraction peaks, while the peak intensity significantly increases with an increased metal loading. The average palladium crystallite size of the 5 and 10 wt % Pd samples is around 10 nm according to the Scherrer equation, ²² similar to the nanoparticle size observed in TEM observation.

3. Application as Catalysts. The above studies indicate the possibility of synthesizing mesoporous silica/metal



(111)

(200)

(220)

(311)

10% Pd

5% Pd

1% Pd

0.5% Pd

ntensity

products such as ethylene would be beneficial to both the

environment and economic concerns. Shown below is the

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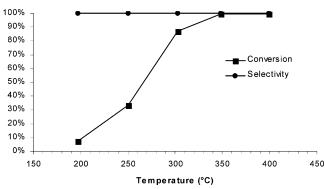


Figure 9. Conversion and selectivity of 1,2-dichloroethane into ethylene as a function of temperature using Brij-58-templated 0.5% Pd-SiO₂ mesporous particles as a catalyst.

reaction scheme of 1,2-dichloroethane hydrodechlorination catalyzed by palladium.

In the presence of hydrogen, 1,2-dichloroethane is sequentially converted into ethylene and ethane. Since ethylene is the more desirable product, selective conversion of 1,2-dichloroethane into ethylene is preferred. Figure 9 displays the conversion of 1,2-dichloroethane into ethane and ethylene and the selectivity of forming ethylene as a function of temperature using a Brij-58-templated 0.5% Pd—SiO₂ catalyst. The conversion and selectivity are defined as

$$conversion = \frac{vol_{ethylene} + vol_{ethane}}{vol_{dichloroethane} + vol_{ethylene} + vol_{ethane}}$$

$$selectivity = \frac{vol_{ethylene}}{vol_{ethane} + vol_{ethylene}}$$

As shown in Figure 9, the conversion of this reaction increases with the reacting temperature while the ethylene selectivity remains $\sim 100\%$ in this temperature range. A conversion and selectivity of nearly 100% can be achieved at a temperature of 350 °C, indicating a good catalytic activity. By no means is this a detailed catalytic study; nevertheless, it does demonstrate the feasibility of using these metal/silica particles for catalytic applications. A comprehensive catalytic study is currently under way.

Conclusions

Mesoporous silica particles with palladium nanoparticles incorporated into the pore framework have been synthesized using an aerosol-assisted self-assembly process. Particles exhibiting vesicular, hexagonal, cubic, or disordered pore structures with high surface areas and narrow pore size distributions can be readily synthesized using different surfactants. The metal content can also be controlled by varying the amount of metal salt added to the precursor solutions. These particles have potential applications as catalysts, which has been demonstrated in the hydrode-chlorination reaction of 1,2-dichloroethane.

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