Chem. Mater. **2001,** *13,* 3915−3919 3915

Cyclodextrin-based Porous Silica Materials as in Situ Chemical “Nanoreactors” for the Preparation of Variable Metal−Silica Hybrids

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Received February 5, 2001

Inclusion complexes of cyclodextrins with organometallic coordination compounds of Pd, Pt, Rh, Fe, Ni, and Ru have been used to produce porous metal−silica hybrid materials. The cyclodextrins are templates for the structure of the silica and lead to a uniform “worm-type” pore system. After the templating step the organometallic compounds can be employed as in situ precursors for the preparation of metal nanoparticles within the pore system, thus leading to a one-step synthesis of silica-supported metal catalysts. These new materials are characterized and how the chemical confinement of the silica pores can influence the size, structure, and distribution of the nanoparticles is studied.

Introduction

Two of the many applications of mesoporous silica materials[1−3] since their discovery in 1992 by Beck et al.[4] are their use as reactors in “nanochemistry” [5,6] and—related to this—as catalytic materials or catalyst carriers. The “nanochemical” effort is concerned with how chemical reactions are influenced due to the confinement in the silica pores. Chemical transformations under confined conditions are omnipresent in nature (e.g. cell compartments), and it is important to extend this principle to technical processes such as catalysis. For catalysis the pure silica materials are not sufficient, but active metal “additives”, mostly metallic or oxidic nanoparticles, are needed.

In this paper, a simple but powerful approach toward chemistry under confined conditions in special types of porous silicas (namely cyclodextrin-based silicas)[7] and the corresponding variety of new metal−silica hybrid materials is presented. Instead of utilizing a preformed porous silica material, filling this with the precursors, and then creating the metal−nanoparticles by reduction (route I)[8] we follow a recently introduced approach[9] to choose porogens that simultaneously have the potential to act as a template and metal precursor in one (route II). The starting molecules exhibit two properties: They are the structure-directing agent for the porous silica and template cavities of their own molecular shape. Then (without any removal) they act as precursors for the catalytic particles by chemical transformation of their interior load.

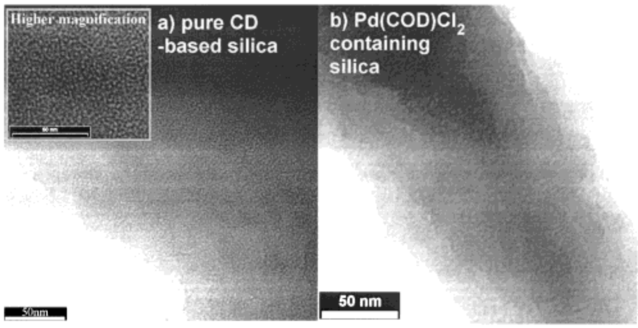

Figure 1. TEM image of a calcined, pure βM-CD-based porous silica material (a) and the corresponding. βM-CD/βM-CD•Pt(COD)Cl$_2$-containing silica (b).

In a recent work we have shown[7] that, using the nanocasting concept,[10] supramolecular cyclodextrin assemblies can act as templates for the production of porous silica materials with pore sizes exactly resembling the cyclodextrin diameters (1.5−2 nm) and a bicontinuous “worm-type” pore structure (Figure 1). Our findings concerning the unusual aggregation of cyclodextrins that leads to this porous structures are described elsewhere.[7] Other authors have named the resulting pores in the size range between micro- and mesoporous “supermicroporous”.[11] The pores are very uniform, and no further microporosity is found, as is the case when silica is prepared by templating of block copolymers.[12]

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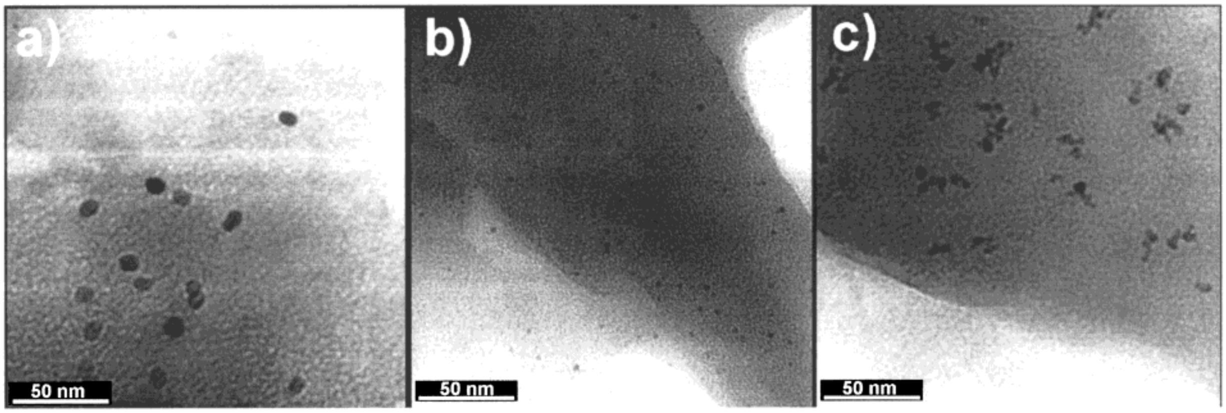

Figure 2. TEM images of three βM-CD/βM-CD•guest [Pt(cod)Cl_2 (a), Pd(cod)Cl_2 (b) and $Rh_2(cod)_2Cl_2$ (c)] based silica materials after one-step treatment to 500 °C.

Cyclodextrins (CDs) are macrocyclic sugars consisting of several glucose units arranged in a way such that the exterior surface of the CDs is covered by hydroxyl groups and is hydrophilic while the cavity of the CD ring is hydrophobic. Because of the ability of the cyclodextrins to build a vast number of inclusion complexes[13−15] with molecules of low water solubility, they should be ideal candidates to act as simultaneous precursors and templates (route II). The stability of the complexes depends on many factors such as size fit, hydrophobic character, or solvent composition. For further details of the complexation mechanism we refer to the literature.[13−15] A solubilization of organometallic compounds in water has also been reported several times by different authors.[16−20]

Results and Discussion

As porogens, methylated β-cyclodextrins (βM-CDs) are used. Instead of using only the pure cyclodextrins as in ref 7 (see Figure 1), a fraction is modified by building inclusion complexes with organometallic coordination compounds of the desired metals. The metal precursors are suspended in a solution of an excess (e. g. 5 times the molar amount) of βM-CD in aqueous hydrochloric acid (40 wt % CD, 60 wt % HCl (aq); pH = 2) at room temperature until a clear solution is obtained.[13−20] An excess of CD with respect to metal precursor is necessary to preserve solubility throughout the following silica sol−gel procedure. After filtration (syringe filter 5 μm) this solution can be employed without further treatment for the nanocasting.[10] Tetramethyl-orthosilicate (TMOS; 2 times excess) is added under stirring. After homogenization, the methanol formed by hydrolysis is removed under vacuum until transparent gels are obtained. The gels are aged in open flasks at room temperature.

As a model, we discuss the organometallic compounds Pt(cyclo-octadiene)Cl_2 [=Pt(cod)Cl_2], Pd(cod)Cl_2, and $Rh_2(cod)_2Cl_2$. Initial characterization of the as-prepared materials was performed with transmission electron microscopy (TEM) (Figure 1b).

The TEM images verify the optical impression that the material is homogeneous, i.e., no demixing occurred. Also no chemical transformation or destruction of the organometallic precursors is found. The typical “worm-type” structures for cyclodextrin-based porous silica materials, as described elsewhere,[7] (see Figure 1a,b) could be seen. The pores are homogeneously filled with the mixture of βM-CD and βM-CD•guest, which only reduces the imaging contrast in TEM, and no reduction has yet occurred. The inclusion complexes are stable under the conditions of nanocasting.

In preliminary experiments we observed that cyclodextrins act as reducing agents during their thermal decomposition. No additional agent for reduction was employed and the zerovalent state of the metals is reached in situ by the thermal decomposition of the cyclodextrin while a thermogravimetric analysis (TGA) experiment is performed.

In a first set of experiments we heated the samples to 500 °C in one step under a flow of nitrogen. After this process the materials have changed in color. Depending on the precursor color, a transformation to different shades of brown is observed. To determine the size and the structure of the resulting metal particles in the silica, TEM was performed (Figure 2a−c).

As expected, a porous SiO_2 with the typical “worm-type” structure can be seen, but the Pt particles (Figure 2 a) do in no way follow the original pore geometry.

The particles are too large [5−7 nm for Pt, 3−5 nm for Pd (Figure 2 b); see also data from the wide angle X-ray scattering (WAXS) in Figure 4] and spherical in shape, in contrast to the pores which were “wormlike” and $d \approx 1.5$ nm in dimension. The question why no strict confinement effect by the size of the silica pores is found for this case will be answered below. For catalysis, these species are nevertheless interesting model cases, because they contain a porous “transport” system with all the advantages of cyclodextrin-based silicas (uniform pore size, no disturbing microporosity, bicontinouity) and the “active” metal centers in the form of nanopar-

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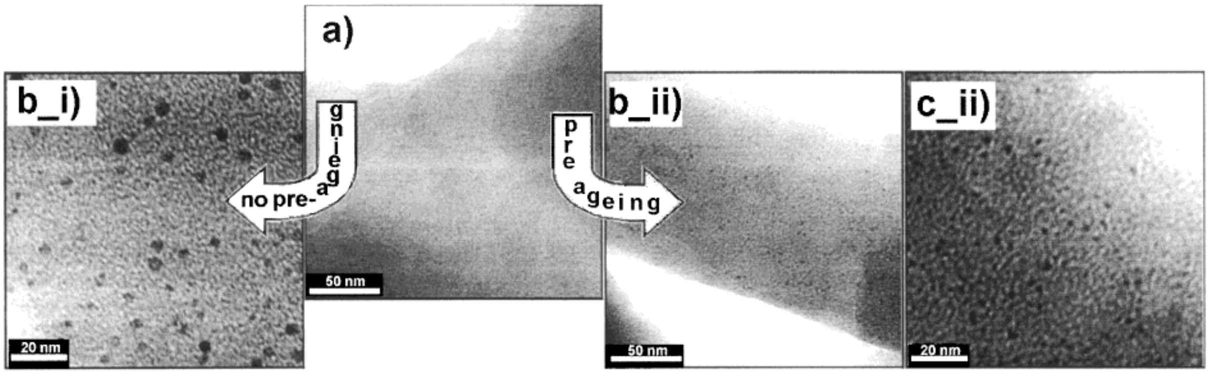

Figure 3. Evolution of Pd metal nanoparticles under different conditions for Pd(cod)Cl_2: TEM image of the first nucleation at a final temperature $T_e = 250$ °C of the in situ transformation process (a), behavior for the nanoparticles in a sample not pretreated at $T_e = 350$ °C (b_i) and the pre-aged sample (chemical confinement) at $T_e = 350$ °C (b_ii) and $T_e = 500$ °C (c_ii).

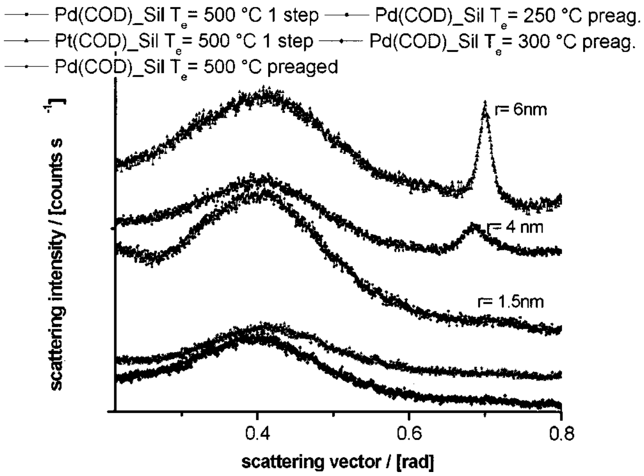

Figure 4. WAXS diffractograms of metal-containing silica under different confinement conditions for Pd and Pt.

ticles (Figure 1a,b), fixed in the porous system, too large to be leached out during applications. After removal of all organic matter via O_2 calcination, the materials show a BET surface area, determined with N_2 sorption, of 400−500 m^2/g.

Interestingly, the results concerning metal nanoparticle formation differ for various organometallic compounds, although the "aging" conditions of the silica materials are identical. The particles compared for Pt and Pd were spherical, but the latter one led to significant smaller sizes (Figures 2a,b and 4). In the case of Rh, the particles are slightly smaller (Figure 2c) than for Pd and not spherical in shape. The Rh particles seem to mimic in a certain way the original "worm-type" pore system of the cyclodextrin-based silica. This behavior is attributed to the difference in nobility (tendency to be reduced) in the series Pt > Pd > Rh. Under identical conditions Pt is reduced first, then Pd, and finally Rh. This led us to the hypothesis that the formation time of the metal nucleus is of major importance for the particle morphology in the one-step TGA experiment.

It is assumed that in the one-step procedure the formed particles first experience walls that are not strong enough to confine the growth of the particles. At low temperatures and after short aging, the silica gels are relatively weak due to incomplete condensation of the silanol groups.[3,21] We tested this assumption by a series of experiments where the dependence of particle nucleation and growth of Pd and Pt on the heating program of the TGA experiments (final temperature T_e and rate of heating) were observed. In the following the Pd-containing silicas are discussed, but the findings are equal for Pt. Below $T_e = 200$ °C, no thermal decomposition of the cyclodextrines and included metal complexes is observed at all, as found by TGA and TEM. The pictures look like Figure 1b; only the typical "worm-type" pore system is observed. For final temperatures higher than 200 °C, a complete evolution series of metal nanoparticles can be seen by TEM and be verified by WAXS: At a final temperature of 250 °C, only tiny particles of similar size (1.5 nm) and shape of the silica pore are found (Figure 3a). At $T_e = 300$ °C, these particles are larger (2−5 nm), but a careful investigation at higher magnifications reveals that many of these particles are not massive but still structured in a "wormlike" fashion (Figure 3b_i). To illustrate this Figure 3b_i is shown in higher magnification. Finally, for a heating program with $T_e = 500$ °C, large particles (5 nm) with spherical shape and no substructure are dominant (as already seen in Figure 2b). The exclusive occurrence of larger particles is due to Ostwald ripening, which can be rather strong for bare metal particles without additional additives (high surface energy) at elevated temperatures.

This reveals that a sufficient condensation of the silica walls has to be reached before the precursor decomposition takes place at temperatures above 200 °C. Only in this case a chemical confinement due to the pores of the silica can be expected to lead to a restriction of the metal colloid size. By applying the knowledge of the decomposition behavior of both the organometallic precursors and the cyclodextrin in the silica, an aging procedure for the materials can be established. After the standard treatment at room temperature, the silica gels were pre-aged at 170 °C and $p = 100$ mbar, and then further heating to a final temperature of $T_e = 250$ °C (TEM image shown in Figure 3a), 300 °C (Figure 3b_ii), and finally 500 °C (Figure 3c_ii; also shown in higher magnification) for the in situ reduction followed.

With pre-aging, the Pd(cod)Cl_2-containing cyclodextrin silicas were transformed to materials containing Pd particles of 1.5 nm size according to WAXS and TEM (Figure 3 c_ii). Neither the particle size nor the shape, which mimics to a certain extent the "worm-type" pore

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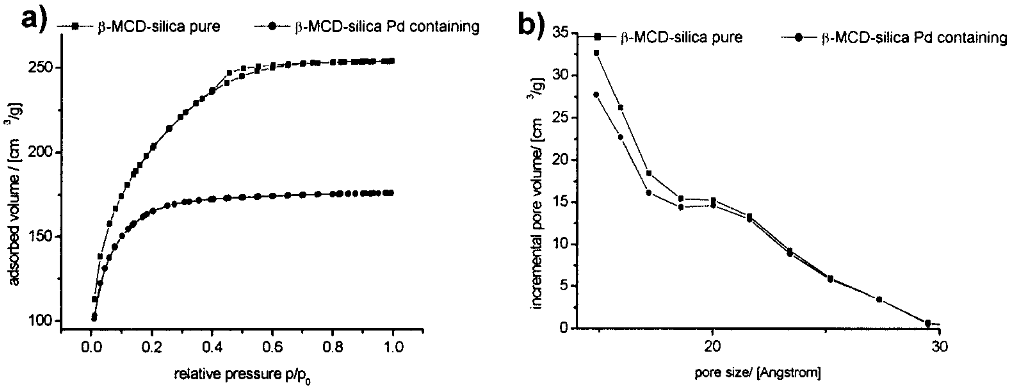

Figure 5. (a) N_2 isotherms of the pure silica CD-based materials and the Pd-containing analogues and (b) the corresponding DFT pore-size distributions.

structure changes also after longer thermal storage in the TGA at temperatures of even 500 °C. This shows that the silica structure of aged and nonaged samples are indeed different and that the metal particles formed too early in the process indeed create their own cavities that are later solidified.

These processes of evolution and control of particle size were also characterized by WAXS, as shown in Figure 4, where five samples are compared.

The broad maximum at $2\theta = 0.40$ rad is due to the structure of the amorphous silica, as is well-known from many experiments. The small upriding peaks at 0.70 and 0.68 are indicative of elementary Pt and Pd.

The Pt-containing silica, which was prepared by one-step heating to $T_e = 500$ °C, shows a relatively sharp maximum at 0.70 rad. The Scherrer equation was used to calculate the particle sizes from the half-width of this peak,[22] and a mean diameter of 6 nm was obtained. For the comparable Pd-containing sample, the maximum at $2\theta = 0.68$ rad is broader and corresponds to particles 4 nm in diameter. The Pd-containing sample originating from the optimized pre-aging process is characterized by an extremely broad peak (becomes visible only in logarithmic plots) in the region significant for palladium. A fit of these maxima, taking the structured scattering background into account, led to particle diameters of 1.5 nm. No metallic species at all are seen for the unreduced precursor species.

Therefore, WAXS fully confirms the results already presented by TEM. As soon as the cyclodextrin-based silica pores are able to confine the growth of the particles, no change can be observed under different conditions. Although most of the nanoparticles are spherical, some grow also along the channel and adopt the "wormlike" character of the pore system.

The strategy of nanocasting cyclodextrin inclusion complexes and in situ transformation can in principle be extended to all organometallic precursors that are able to form such inclusion complexes with cyclodextrins. So far we have successfully applied our approach to prepare Pd (with the aid of Pd(cod)Cl_2), Pt (with the aid of Pt(cod)Cl_2), Rh (with the aid of $Rh_2(cod)_2Cl_2$), Fe (with the aid of ferrocene, $Fe(Cp)_2$), Ni (with the aid of $Ni(Cp)_2$), Ru (with the aid of $Ru(Cp)_2$), and also Cu (with the aid of Cu(II) ethylhexanoate)[23] containing silicas. Silica materials of variable metal contents can be produced; however, they are limited by the solubility of the precursor. According to our experiments, an average ratio of 30 mol % in relation to the total cyclodextrin content is the maximum to be reached without additional cosolvents (as DMSO). This corresponds to about 1.5 wt % for Fe and 5 wt % Pt in the final silica hybrids.

To a certain extent the metal loading effects the porosity. Pure CD-based silica materials without metal but with the same amount of porogen exhibit surface areas of ≈800 m^2/g.[7] The metal-containing silicas show qualitatively the same sorption behavior (same type of isotherms) and, therefore, the same type of pore system, but lower surface area values of ≈500 m^2/g after removal of the organic part. This is proven by the isotherms and the corresponding density functional theory derived pore-size distributions shown in Figure 5. It is seen that the absorbed volume is significantly smaller for the Pd-containing material, while the pore-size distributions are very similar and show the typical small maximum at pore diameters of ≈2 nm, which is significant for the CD pores. Even for the material with the incorporated larger metal particles, the isotherms (not shown) have the same shape and no additional porosity in the meso-scale range appears. This verifies the TEM impression that the large metal nanoparticles are truly incorporated into the CD-based pore system.

Conclusion

A variety of porous silica materials containing different metals and various amounts of metals can be prepared by using cyclodextrin-inclusion complexes of organometallic species as templates in a one-pot reaction. The pores are "wormlike" in structure and possess diameters of 1.5 nm. For the in situ production of the materials two situations have to be distinguished (see Figure 6).

If the nanoparticle nucleation is faster than the condensation of the silica, the walls are not strong enough to restrict the particle growth. In this case the

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[22] Klug, H. P.; Alexander, L. E. *X-ray diffraction procedures*, 2 ed.; John Wiley & Sons: New York, 1974.

[23] Due to the extremely low solubility of Cu(II) ethylhexanoate in water, building the inclusion complex is a very slow process. Our approach using one-pot conditions with only water as solvent is not applicable for copper. Instead, Cu(II) ethylhexanoate can be bound by βM-CD in DMSO as solvent. Then the DMSO is removed under low pressure and the inclusion complex is directly taken for the nanocasting.

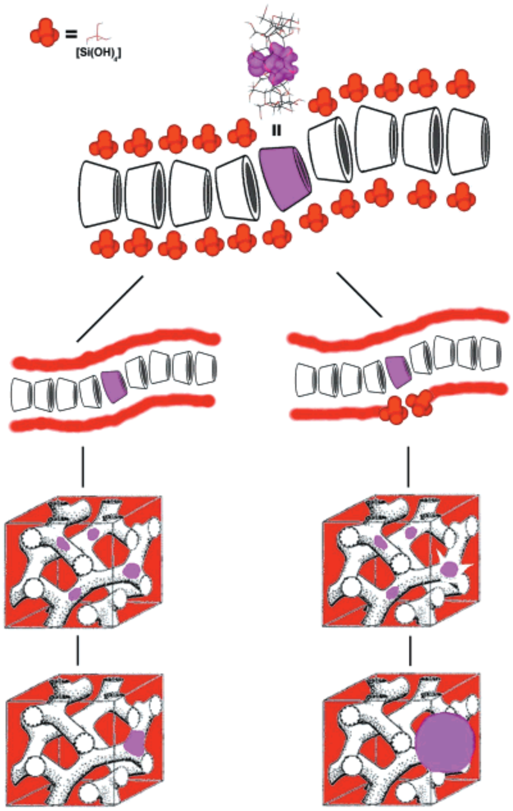

Figure 6. Schematic representation: cyclodextrins build inclusion complexes with organometallic compounds (violet) that can be used for silica nanocasting. The cyclodextrins are assembled to “worm-type” structures. To demonstrate the dependence on the aging conditions, the silica walls are fully condensated before the metal particle nucleation and growth starts (left side) or after (right side).

whole evolution of spherical particles is dependent on the external conditions, yielding from small to 5−10 nm particles. The metals are incorporated into the silica and bicontinuously interconnected by the silica pores.

If the silica materials are pretreated so that the condensation of the silica walls occurs prior to nucleation, the geometric confinement by the pores becomes effective. In this case the particle size is restricted by the 1.5 nm wall-to-wall distance and even the shape of the particles often mimics the “worm-type” morphology. Future work will focus on the synthesis of other metallic species and performing catalytic experiments with these new materials.

Experimental Section

*β*M-CD was obtained from the Wacker AG/Germany, the organometallic precursors were obtained from ABCR−Chemicals/Germany, and all other standard chemical were from Aldrich. All the chemicals mentioned above were used without further purification.

The procedure to obtain the metal-containing silica materials is described in the text.

TEM images were acquired on a Zeiss EM 912Ω at an acceleration voltage of 120 kV. Samples were ground in a ball mill and taken up in acetone. One droplet of the suspension was applied to a 400 mesh carbon-coated copper grid and left to dry in air. TGA measurements were performed with a Netzsch TG209 cell. WAXS patterns were collected on an Enraf Nonius FR590 diffractometer. Ball-milled samples were irradiated for about 5 h. Nitrogen sorption ($T = -196$ °C) data were obtained with a Micromeritics Tristar. Isotherms were evaluated with density functional theory.[24−26]

Acknowledgment. We would like to thank the Wacker AG for the donation of the *β*-methyl cyclodextrins and the Max-Planck society for funding.

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