versus $\omega^{-1/2}$ graph, ca. 0.7 mA cm^{-2}) is comparable to the rate of substrate transfer within the PC film (ca. 0.8 mA cm^{-2}),[9] the latter process is the plausible TDS at the plateau.[14] In contrast, the TOF of an electrode-adsorbed catalyst is limited by the rate of the catalytic cycle, not charge or substrate transfer, at all potentials.[6b]

As expected for catalysis under limited electron availability, the PC-dispersed catalyst degrades more than 100 times faster than the electrode-adsorbed analogue during O_2 reduction at 100 mV. Intra- or intermolecular oxidation of the organic ligand is likely in a PC matrix when other reductants (Fe^{II}, Cu^{I}, or the electrode) are inaccessible to complete the O_2 reduction cycle. Indeed, the very low stability of the Cu-free, NMeFe-only catalyst in the PC matrix appears to account for the lack of a well-defined catalytic wave in this system.[9] This result contrasts with only minor differences in the catalytic properties of the FeCu and Fe-only complexes adsorbed on the electrode.[6b]

In summary we presented a biomimetic system that reproduces a key aspect of terminal oxidases reactivity. The synthetic heme/Cu analogue dispersed in a PC matrix catalyzes O_2 reduction: 1) at physiological potentials, 2) under diffusion-limited electron flux, and 3) without releasing partially reduced oxygen by-products into the bulk medium. In contrast to electrode-adsorbed systems,[6b] notable differences in the catalytic behavior of the FeCu and Cu-free analogues in a PC matrix illustrate the benefit engendered by an additional readily accessible reductant (Cu^{I}) within the catalyst molecule. This system mimics the proposed role of Cu_B as an electron reservoir at the catalytic site. The use of a PC matrix should allow meaningful studies of the catalytic properties, under steady-state turnover, of heme/Cu analogues containing a phenol moiety. In cytochrome oxidase, a tyrosine residue (Tyr 244 in Figure 1 A) is involved in catalysis when the availability of electrons is limited[15] (for example, O_2 reduction by a mixed-valence enzyme). Whereas such conditions are inaccessible for an electrode-adsorbed functional analogue, they are realized for a PC-dispersed complex.

Received: May 24, 2002 [Z19386]

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Taking Nanocasting One Step Further: Replicating CMK-3 as a Silica Material

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Bernd Spliethoff, Bernd Tesche, and Ferdi Schüth*

Dedicated to Professor Dieter Fenske
on the occasion of his 60th birthday

The replication of nanoscale structures by a direct templating process has been used in recent years in several creative ways for the synthesis of carbon replicas of zeolites[1] or ordered mesoporous carbons, such as CMK-1[2] or SNU-1.[3] Such processes rely on the fact that an ordered pore system, provided by the zeolite or ordered mesoporous silica, can be filled with a carbon precursor which is pyrolyzed and the silica leached with NaOH or HF solution. However, the technique is difficult to apply to the synthesis of framework compositions other than carbon, since the leaching of the silica typically also affects the material which is filled into the silica pore system. This problem could possibly be circumvented by not using the silica as the mold, but to instead go one step further and use the mesoporous ordered carbons as templates, which could then easily be removed by combustion or other techniques, as suggested recently.[4] On the macroscale, that is, for the production of photonic crystals, similar approaches are well known, where latex spheres are used as templates which can be removed by calcinations.[5] Also carbon black has been used as a "template", for instance to synthesize mesoporous zeolite single crystals, in which the pores, however, are disordered.[6]

In a first attempt to show the feasibility of using ordered mesoporous carbon to synthesize ordered mesoporous oxides, we decided to template mesostructured silica by using an ordered mesoporous carbon. Although this brings one only back to the starting point, that is, a mesoporous silica, it

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demonstrates the principle possibility to use ordered porous carbons to template ordered inorganic materials. The usefulness of such a templating procedure to create nanoparticles has been shown in the synthesis of various high surface-area oxides by impregnating activated carbons with highly concentrated metal nitrate solutions and subsequent combustion of the carbon.[7] Silica was chosen because tetraethoxysilane (TEOS) has 1) a relatively high ratio between the central atom and the hydrolyzable groups, which allows high filling of the pore system of the carbon and 2) a moderate susceptibility to hydrolysis, which avoids a too rapid and vigorous reaction. However, it is expected that under properly chosen conditions with adapted precursors many other inorganic frameworks can be templated with carbon.

We chose to employ CMK-3,[8] the replica of SBA-15, as the mold, because the relatively large pore size of this carbon should make its pore system very accessible. SBA-15 appears on first sight only to be a hexagonal array of cylindrical pores in a silica matrix. However, the cylindrical mesopores are connected by micropores in the walls, which result in a 3D pore system.[9] Only thus is it possible to obtain the carbon negative of SBA-15 as a stable structure. SBA-15 was synthesized with Pluronics 123 according to published procedures.[10] Figure 1a shows a small-angle X-ray diffraction (XRD) pattern of a calcined aluminum-containing SBA-15 with a specific surface area of 760 m^2g^{-1}. The lattice parameter is $a = 10.7$ nm, the pore size, determined by nitrogen adsorption and Barrett, Joyner, Halenda (BJH) analysis from the adsorption branch of the isotherm, is 6.9 nm, from which the wall thickness of the SBA-15 is calculated to approximately 3.8 nm. The pores of the material were impregnated with a carbon precursor by adsorption of furfuryl alcohol, according to Shin et al.[8] Carbonization of the carbon precursor in the pores at 850 °C under nitrogen atmosphere and subsequent removal of the silica with hydrofluoric acid led to the formation of CMK-3, the XRD pattern of which is shown in Figure 1b. The lattice parameter of that CMK-3 is $a = 10.5$ nm. The pore size derived from nitrogen sorption and BJH analysis of the adsorption branch corresponds to 3.8 nm, well in agreement with published data on such materials and the wall thickness of the SBA-15 precursor. To check the completion of the silica removal, the carbon was combusted and the amount of ash determined. The ash content of the sample was less than 0.5 wt%, thus demonstrating almost complete removal of the silica, which is important to check the success of the next step.

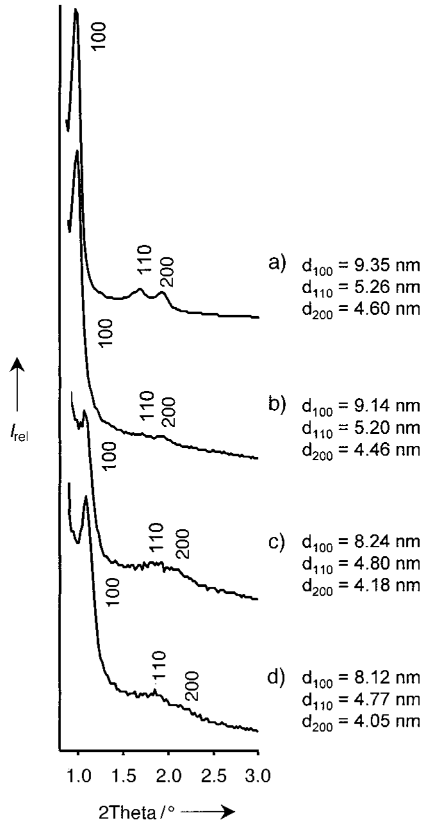

Figure 1. XRD-patterns of a) Al-SBA-15 ($S_{BET} = 676\ m^2g^{-1}$, $D_{BJH} = 6.9$ nm), b) CMK-3 ($S_{BET} = 764\ m^2g^{-1}$, $D_{BJH} = 3.8$ nm) synthesized from the SBA-15 in (a), c) NCS-1 ($S_{BET} = 272\ m^2g^{-1}$, $D_{BJH} = 7.2$ nm) replicated from the CMK-3 in (a), and d) NCS-1 ($S_{BET} = 557\ m^2g^{-1}$, $D_{BJH} = 4.9$ nm) replicated from another CMK-3 ($S_{BET} = 1043\ m^2g^{-1}$, $D_{BJH} = 3.7$ nm) obtained from a Al-SBA-15 ($S_{BET} = 680\ m^2g^{-1}$, $D_{BJH} = 5.8$ nm) with smaller pore size (S_{BET}: BET surface area, D_{BJH}: pore diameter according to BJH).

The pore system of CMK-3 was then filled with TEOS and hydrolysis of the TEOS in the pore system initiated by treatment with an HCl solution of pH 1. The sample was left to stand for 10 min, and then placed in a box furnace which was first kept at 40 °C and then 80 °C for 3 h each, to remove the products, such as water and ethanol which result from the hydrolysis of the TEOS and subsequent condensation from the system. This procedure was repeated several times to achieve full loading. Depending on the pore volume of the starting CMK-3, an SiO_2 content of about 60—70 wt% could be achieved in the final material. In some cases, the amount of silica was too high for the pore volume of the CMK-3 material by about 10%, assuming a silica density of 2.2 $g\,cm^{-3}$, which indicates the presence of some externally deposited silica. The detailed procedure is described in the Experimental Section. After the last thermal treatment, the sample was transferred to a horizontal tube furnace with a quartz tube and heated under flowing nitrogen at a heating rate of 0.5 °C min^{-1} to 250 °C, and then with 1 °C min^{-1} to 700 °C where it was kept for 4 h, to complete the silanol condensation as far as possible. The carbon was removed in a box furnace within 5 h at a temperature of 550 °C. Alternatively, the carbon was removed in a fluidized bed reactor in flowing air at a temperature of 550 °C to avoid temperature hot spots which could damage the structure of the forming silica. This procedure results in enhanced adsorbed volume and a better defined capillary condensation step in the isotherm.

Figure 1c shows the diffraction pattern of the white material (designed as NCS-1 for nanocasted silica No. 1) recovered after calcination. There is a low-angle-feature centered at an angle of 1.07° 2θ ((100) reflection), with a relatively weak intensity. In addition, intensity is observed at higher angles with reflections at about 1.85° and 2.10° 2θ, which correspond to the (110) and (200) reflections of the usual hexagonal mesostructure. The relative intensity of the (100) reflection compared to the (110) and (200) reflections is lower than for the normal mesostructured materials, but the typical hexagonal pattern is clearly discernable. The successful casting of an ordered silica from the carbon is even more clearly demonstrated, if the sorption isotherm (Figure 2) and the TEM (Figure 3) are analyzed. The adsorption step in the isotherm is rather steep, which suggests a narrow pore-size distribution.

If an SBA-15 with smaller pore size (5.8 nm) is used, also the lattice parameter and the pore size of the resulting NCS-1 is changed (Figure 1 d and Figure 2 c). The pore size calculated from the adsorption branch of Figure 2 c is 4.9 nm, the lattice parameter corresponds to 9.4 nm. In addition, the better developed steps in the isotherm demonstrate that fluidized-bed calcination, which was used for the sample represented by Figure 1 d and Figure 2 c, is beneficial with respect to sample quality. Most convincing with respect to the ordered pore system are the TEMs of all the obtained materials. All sections of the samples look like the one displayed in Figure 3 a and Figure 3 b, which clearly shows channels similar to the ones present in SBA-15 viewed sideways as well as the hexagonal pattern if the sample is viewed along the six-fold axis; also quite indicative are the noodle-shaped particles which are often observed for SBA-15 and CMK-3. The repetition unit (8–9 nm) observed in the TEM corresponds well to the repeat distance calculated from the XRD experiments.

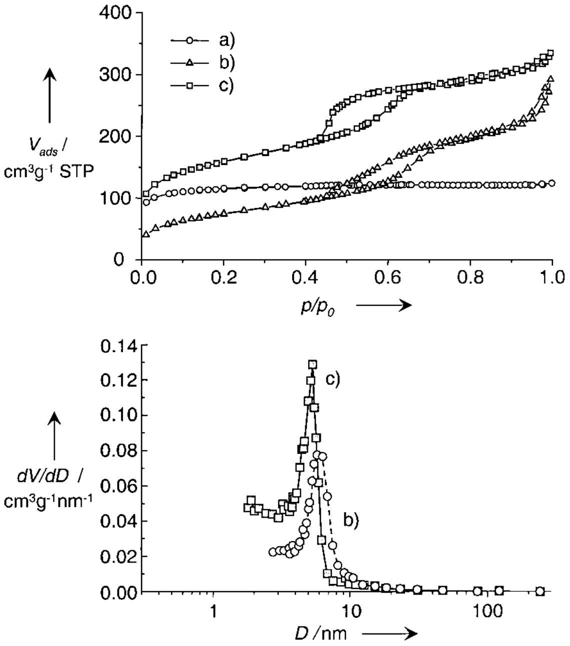

Figure 2. Nitrogen adsorption isotherms (top) and pore-size distributions (bottom) of a) a composite of silica and CMK-3 after treatment in nitrogen at 700 °C, b) NCS-1, the diffraction pattern of which is given in Figure 1 c, c) NCS-1, the diffraction pattern of which is given in Figure 1 d. STP = Standard temperature and pressure.

The results clearly show, that the structure of CMK-3 is transferred to the silica replica. The hexagonal order of the channels is visible in the TEM in many sections, the sorption isotherm also corresponds to a highly ordered pore system. The X-ray diffraction pattern is not as well developed as for the starting SBA-15. However, a complete filling of the CMK-3 pore system with silica can not be expected. Even if impregnation with TEOS is repeated several times, the last TEOS introduced is still decomposed, and part of the material in the pores leaves the pore system. Thus, additional micropores are created in the silica part which are detected in the sorption isotherm of the SiO_2/CMK-3 composite heat treated at 700 °C in nitrogen, which is given for comparison in Figure 2 a. The distribution of matter in the unit cell will thus be rather different compared to SBA-15, which can lead to strong deviations of the relative intensities of the low-angle reflections.[11] This explains the variation of the XRD patterns of the materials.

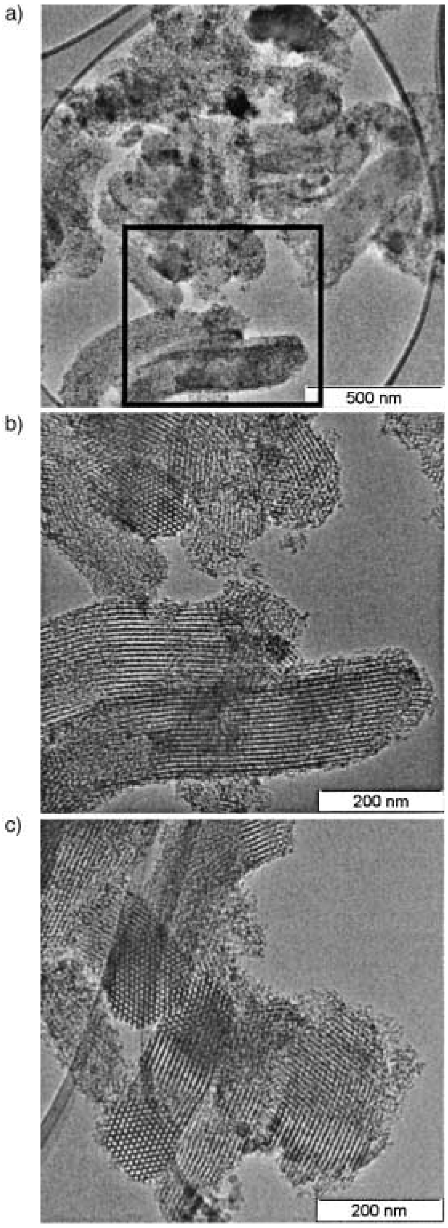

Figure 3. Typical TEM images of a) NCS-1, b) magnification of the section marked with a box in (a), and c) section showing the well-defined hexagonal ordering of the pores.

We have shown that it is in principle possible to take nanocasting one step further and use the nanocasted carbon CMK-3 as a matrix for the production of an ordered mesoporous silica. It should be possible to extend this approach to other carbon templates, such as CMK-1 or SBU-1, or to other inorganic framework compositions. The carbon has been removed by an oxidation process in the example presented here, which would suggest, that only stable oxides or oxidation-resistant compositions could be obtained following this pathway. However, carbon can also be removed by other reactions, such as high-temperature hydrogenation, which should allow the synthesis of compounds which are not stable against oxidation.

Experimental Section

Materials: The following materials, tetraethylorthosilicate (TEOS, 98%, Aldrich), furfuryl alcohol (98%, Fluka), trimethylbenzene (THB, 98%, Aldrich), and hydrochloric acid 37%, were used as received without further purification.

Synthesis of SBA-15: The synthesis of the SBA-15 was performed following published procedures[10] by first heating the reaction mixture at 40 °C for 4 h, followed by aging at 80 °C for 24 h. The filtered samples were calcined at 550 °C for 5 h with a heating rate of $1\,°C\,min^{-1}$ to the final temperature. To improve the carburization, the SBA-15 (12 g) was stirred for 12 h in a solution of $AlCl_3$ (2 g) in ethanol, collected by filtration, and washed with ethanol.

Synthesis of CMK-3: CMK-3 was synthesized by the incipient wetness technique to introduce furfuryl alcohol into the pores of SBA-15 following two different procedures: 1) furfuryl alcohol was introduced as received in the channels of SBA-15, followed by carbonization of the infiltrated furfuryl alcohol with a heating rate of $1\,°C\,min^{-1}$ from 80–150 °C, where the sample was kept at 150 °C for 3 h, then the temperature was increased from 150 °C to 300 °C at a rate of $1\,°C\,min^{-1}$, and, finally, the temperature was increased to 850 °C with a rate of $5\,°C\,min^{-1}$ and maintained at this temperature for 4 h. 2) furfuryl alcohol, diluted with ethanol or TMB was introduced into SBA-15 and then carbonized following the procedure outlined in 1).

Synthesis of NCS-1: Under vigorous agitation CMK-3 (0.15 g) was impregnated drop by drop with TEOS (0.15 mL), then one drop of HCl solution (pH 1) was added under vigorous agitation. After 10 min, the sample was put into a box oven at 40 °C for 3 h and then at 80 °C for 3 h. Subsequently, the sample was removed, cooled, and the impregnation was repeated until the desired amount of TEOS (typically corresponding to a silica loading of 60%) was introduced. The sample was then heated to 700 °C in flowing nitrogen as described in the text, then calcined in a box furnace at 550 °C for 5 h in air with the heating rate of $1\,°C\,min^{-1}$ to the final temperature. After that treatment, a white powder was obtained in a yield of typically 1.5–2 $g\,SiO_2\,g^{-1}$ CMK-3, depending on the pore volume of the CMK-3 starting material.

Characterization: Low-angle X-ray diffraction patterns were recorded with a Stoe STADI P diffractometer in the Bragg–Brentano (reflection) geometry. The step width was $0.02°\,2\theta$ at an acquisition time of 8 s per step. Nitrogen adsorption isotherms were measured with an ASAP 2010 adsorption analyzer (Micromeritics) at liquid nitrogen temperature. Prior to the measurements, all samples were degassed at a temperature of 250 °C for at least 3 h. Pore sizes and pore-size-distribution curves were calculated from the adsorption branch, since calculation from the desorption branch might be influenced by network percolation effects and the instability of the meniscus at $p/p_0 = 0.42$.

TEM images were obtained with a HF2000 electron microscope from Hitachi equipped with a cold field emission gun. The acceleration voltage was 200 kV. Samples were prepared dry on a lacey carbon grid.

Received: June 19, 2002 [Z19566]

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Palladium-Catalyzed Asymmetric Allylic Alkylation of α-Aryl Ketones**

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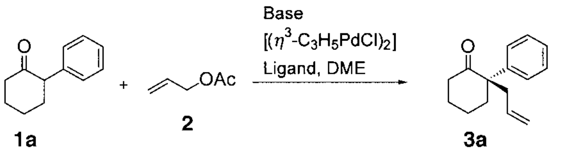
The generation of quatenary chiral centers through catalytic asymmetric alkylation of ketone enolates has been the subject of investigation in recent years.[1] The palladium-catalyzed asymmetric allylic alkylation (AAA) of prochiral nucleophiles represents one such strategy for the creation of quaternary chiral centers.[2] Given the success of stabilized nucleophiles such as β-ketoesters in palladium-catalyzed AAA[3,4] we inquired whether simple ketone enolates, perhaps the most important class of nucleophiles, would function. Previously, we reported the AAA of α'-blocked α-alkylcycloalkanones.[3a] Herein we report the palladium-catalyzed AAA of a series of α'-unblocked enolates: aryl ketone enolates.

Initial studies examined the reaction of 2-phenylcyclohexanone (**1a**) with allyl acetate (**2**) using the conditions developed in our previous work with α'-blocked α-alkylcycloalkanones: 2 equivalents of LDA, 1 equivalent of trimethyltin chloride, 2.5% $[(\eta^3\text{-}C_3H_5PdCl)_2]$, and 5% $\mathbf{L_{ST}}$ in DME as solvent [Eq. (1)]. Unfortunately, under these standard



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[**] We thank the National Science Foundation and the National Institutes of Health, General Medical Sciences Grant GM13598, for their generous support of our programs. G.M.S. has been supported in part by fellowhips form the NSF, the Organic Division of the American Chemical Society, and the Achievement Rewards for College Scientists Foundations. Mass spectra was provided by the Mass Spectrometry Regional Center of the University of California—San Francisco supported by the NIH Divisdion of Research Resources. We thank Chirotech (now Dow) for their generous gifts of ligands.

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