

## Synthesis of Advanced Mesoporous Materials by Partial Pseudomorphic Transformation

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**Abstract:** The structure of porous silica particles can be reorganized without alteration of the particle size and shape by the process of pseudomorphic transformation. Partial pseudomorphic transformation leads to ordered mesoporous silica with bimodal pore size distributions and bottleneck pores. Compared to the classical pathways of mesoporous silica synthesis, pseudomorphic transformation implies less compromise between pore structure and particle shape, while enabling the preparation of complex pore architectures.

**Keywords:** Bottleneck pores · Mesoporous silica · Pseudomorphic transformation · Silica gel

### Introduction

A pseudomorph is a material formed by the chemical or structural change of another substance without alteration of its original external shape. The general principles of pseudomorphism – well-known in the field of mineralogy – have recently been applied to develop novel synthesis pathways for mesoporous silica.<sup>[1,2]</sup> The preparation of ordered mesoporous silica from a silica gel by pseudomorphic transformation thereby relies on carefully balancing the dissolution and reprecipitation of the silica framework in the presence of a structure-directing agent (SDA). Fig. 1 shows an example of a pseudomorphic transformation. A commercial silica gel (Kromasil, 300 Å, 5 µm) was transformed in the presence of hexadecyltrimethylammonium. The conversion of the broad pore size distribution of the original silica gel to a narrow distribution centered at 4.15 nm was accompanied by an 8-fold increase of the specific surface area.<sup>[3]</sup> The spherical morphology and the size of the original Kromasil particles were largely retained during the transformation.

### Bimodal Mesoporous Silica

Pseudomorphic transformation can also be accomplished with ordered mesoporous starting materials, provided that the SDA is small enough to fit into the pores. Partial pseudomorphic transformation of an ordered mesoporous silica such as SBA-15 (Santa Barbara Amorphous)<sup>[4]</sup> leads to a material featuring a pore size distribution with two distinct maxima (Fig. 2). This so-called bimodal mesoporous silica consists of two pore size domains, where the size of the larger pores is determined by the pore size of the starting material. The volume contribution and the size of the smaller pores can be controlled by the pH and by the size of the SDA.<sup>[2]</sup> Detailed analysis of the nitrogen (77 K) and argon (87 K) adsorption/desorption hysteresis

reveals that the two pore size domains are interconnected, thus leading to bottleneck pores.<sup>[2,5]</sup> Small-angle X-ray scattering (SAXS) patterns of the partially transformed materials show a well-distinguishable mesoscopic ordering of the two pore size domains.<sup>[5]</sup>

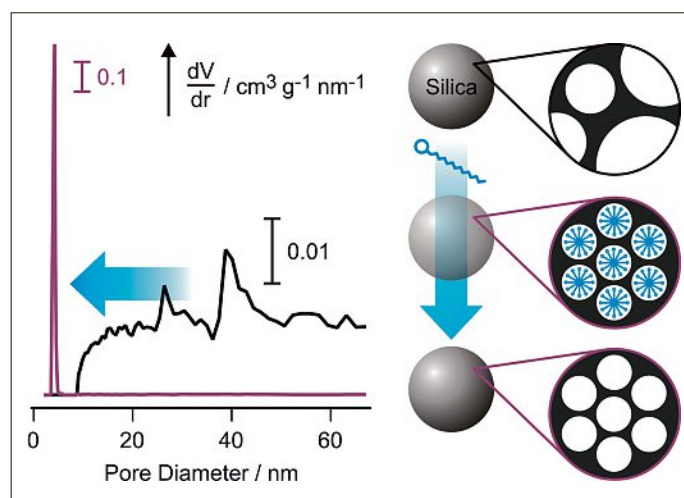


Fig. 1. Pore size distribution of Kromasil before (black curve) and after (purple curve) pseudomorphic transformation. The scheme illustrates the basic steps of the transformation: The large and disordered pores of Kromasil are rearranged into an ordered pore system with a well-defined pore size by balancing the rates of silica dissolution and reprecipitation in the presence of a structure-directing agent (SDA). The latter is typically an alkyltrimethylammonium surfactant, which is ultimately removed by calcination or extraction.<sup>[3]</sup>

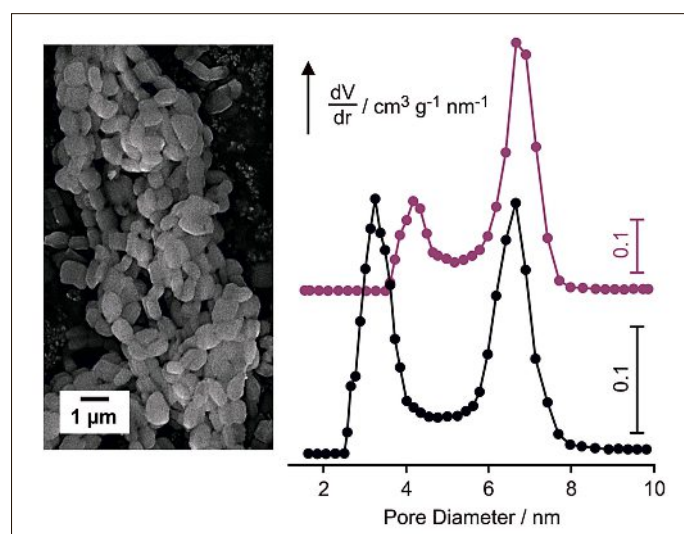


Fig. 2. Left: Scanning electron microscopy image of mesoporous silica SBA-15. The characteristic particle morphology is preserved after the pseudomorphic transformation. Right: Pore size distributions (offset for clarity) of two partially transformed SBA-15 samples. The larger pore size corresponds to the pore size of the SBA-15 starting material, whereas the smaller pores are introduced during the partial transformation.<sup>[2]</sup>

## Bottleneck Pores

Accessibility tests provide further experimental evidence for the presence of bottlenecks in partially transformed mesoporous silica. Our pore accessibility tests are based on the confocal laser scanning microscopy (CLSM) imaging of the spatial distribution of a fluorescent probe within a micrometer-sized porous particle.<sup>[6]</sup> Fig. 3 illustrates the outcome of such an accessibility test. Mesoporous silica spheres with a particle size in the range of 4 to 7  $\mu\text{m}$  and an average pore size of approximately 6 nm were used as the starting material for the partial pseudomorphic transformation. The respective pore size distribution (Fig. 3, top) shows contributions from the primary mesopores (1) and secondary intrawall mesopores (2). Partial pseudomorphic transformation eliminates the secondary mesopores and introduces domains with a well-defined pore size centered at 4.2 nm (3). Poly(amidoamine) (PAMAM) dendrimers coupled with fluorescein isothiocyanate were used as fluorescent probe molecules for the accessibility tests. Optical slices through the center of the particles show that generation 1 PAMAM (G1, 1.9 nm in diameter) is able to pass through the small pore domains and can therefore access the entire particle. However, generation 3 PAMAM (G3, 3.6 nm in diameter) is blocked after partial pseudomorphic transformation, leading to the conclusion that the newly introduced small pore domains are located close to the external particle surface.

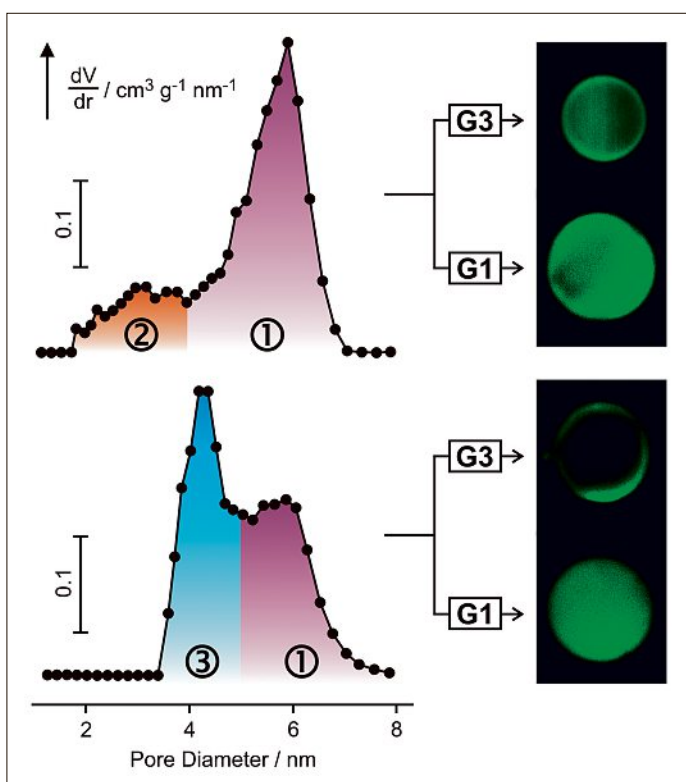


Fig. 3. Pore size distribution and accessibility tests of spherical SBA-15 before (top) and after (bottom) partial pseudomorphic transformation. The CLSM images were taken at the center of the respective particles and show that the parent material is fully accessible for PAMAM G1 and G3, whereas the particle core of the transformed material has become inaccessible for PAMAM G3 due to the presence of bottleneck pores close to the external particle surface. The numbered areas under the pore size distribution curves indicate the approximate contributions from primary SBA-15 mesopores (1), secondary SBA-15 mesopores (2), and bottleneck pores introduced during the transformation (3).<sup>[2]</sup>

## Transformation and Functionalization

The functionalization of preformed mesoporous silica is typically accomplished by a reaction of the surface silanol groups with suitable alkoxy- or chlorosilanes. This post-synthetic or post-condensation pathway often leads to a non-uniform distribution of functional groups in the porous material.<sup>[7,8]</sup> The alternative method of adding the functional silanes at the start of the silica framework formation (co-condensation) produces uniform functional group distributions, but the relative amount of functional silane can have a substantial influence on the size and shape of the silica particles. Combining pseudomorphic transformation and co-condensation allows for better control of particle size and shape, while promoting a uniform functional group distribution. As an example of this concept, we have shown that the pseudomorphic transformation of Kromasil in the presence of 3-aminopropyltriethoxysilane yields an amino-functionalized mesoporous silica with a narrow pore size distribution, fully accessible pores, and the unaltered spherical morphology of the Kromasil particles.<sup>[3]</sup>

## Conclusions

Pseudomorphic transformation opens new possibilities for the synthesis of mesoporous silica-based materials, including the independent adjustment of particle morphology and pore structure, the generation of multimodal pore size distributions, and the control of the spatial distribution of different pore size domains. Potential applications of such materials are as catalyst supports, adsorbents or drug carriers. On a more fundamental basis, the availability of materials with complex, yet well-defined pore structures is essential regarding the development of advanced characterization methods for porous materials.

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- [1] T. Martin, A. Galarneau, F. Di Renzo, F. Fajula, D. Plee, *Angew. Chem. Int. Ed.* **2002**, *41*, 2590.
- [2] M. J. Reber, D. Brühwiler, *Dalton Trans.* **2015**, *44*, 17960.
- [3] M. J. Reber, D. Brühwiler, *Part. Part. Syst. Charact.* **2015**, *32*, 243.
- [4] D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, G. D. Stucky, *J. Am. Chem. Soc.* **1998**, *120*, 6024.
- [5] N. Zucchetto, M. J. Reber, L. Pestalozzi, R. Schmid, A. Neels, D. Brühwiler, *Microporous Mesoporous Mater.* **2018**, *257*, 232.
- [6] M. Ince, N. Gartmann, C. G. Claessens, T. Torres, D. Brühwiler, *Org. Lett.* **2011**, *13*, 4918.
- [7] D. Brühwiler, *Nanoscale* **2010**, *2*, 887.
- [8] N. Zucchetto, D. Brühwiler, *Dalton Trans.* **2016**, *45*, 14363.