



Surface structuring of mesoporous materials by controlled synthesis of nanocavities



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ABSTRACT

A process for the creation of uniform nanocavities on the surface of mesoporous materials using atomic layer deposition (ALD) and nanotemplate surface patterning is presented. Prior to grafting the organic nanotemplate, the surface of silica SBA-15 was pre-treated with an ALD coating of one monolayer of TiO₂. The templates were then surrounded by Al₂O₃ as wall material using further ALD treatment. Template removal is achieved at moderate temperatures by reaction with ozone preventing damages to the structure which might occur at higher temperatures. By this approach a homogeneous distribution of uniform nanocavities of conical shape with 1–2 nm diameter, reflecting the size and geometry of the calixarene template molecules, was obtained. To monitor the various steps of the synthesis detailed characterization using N₂ adsorption/desorption isotherms, FTIR, UV–Vis, and XP spectroscopy as well as thermal analysis and TEM was applied. Results from FTIR and UV–Vis spectroscopy reveal the successful formation of a covalent template-to-substrate binding, which remains unchanged during wall formation but breaks up during ozone treatment. Supporting XPS and TGA measurements give insight into the changing composition of the modified SBA-15 surface during synthesis and template removal in particular.

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1. Introduction

Atomic layer deposition (ALD) is well known for its excellent qualities in creating homogeneous conformal coatings of a large variety of materials on nearly arbitrary surface morphologies. Its nature of self-limiting layer-by-layer deposition and linear film growth with the number of ALD cycles allows for the fabrication of thin films with precise thickness control on a sub-nanometer scale with the limitation of one monolayer. In most applications, ALD is separated into two half-reactions – one for the deposition of each of the two precursors in an ABAB-type like process [1]. Less common is the use of three or even four precursors (ABCABC- and ABCDABCD-type) and further variations like ABCB-type processes [2,3]. By choosing suitable precursors different materials like metals, oxides, nitrides, sulfides and carbides can be deposited [2]. In contrast, other coating techniques like chemical vapor deposition (CVD) do not employ separated precursor exposures and thus cannot reach the ALD conformity standards due to the lack of self-

limiting layer growth thus making ALD unique in this regard [2,4]. Thus atomic layer deposition finds its use in a wide field of applications tuning chemical, physical and electrical properties of the support material. Some of those are catalysis, sensing, microelectronics, photovoltaics, separative membranes as well as nanostructuring of surfaces [2,5,6].

Recent advances in nanotechnology enable the fabrication of tailored catalysts for a variety of applications. It would be e.g. highly desirable to improve catalysts properties such as activity, selectivity and catalyst stability by rational design to provide short reaction times, a minimum amount of unwanted byproducts and waste, and a long lifetime of the catalyst [2]. Hereby, ALD represents a powerful tool providing access to the controlled preparation of nanoparticles, protective or functional overcoatings, as well as other complex nanostructures [2–8]. It has been shown that protective coatings with insulating layers (e.g. core-shell catalysts) may enhance the stability of underlying active sites with respect to temperature, pressure or solvents [2]. If the protective film is thin enough, as can be managed by the precise thickness control of the ALD process, the catalytic activity of the covered material is maintained. In case of conformal coatings, a temperature treatment

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can be applied to produce a porous structure ensuring access to the active species [2,3]. As discussed recently, ALD also represents a promising method for the functionalization of large surface-area substrates like mesoporous materials with catalytically active coatings [2,9].

Other ALD approaches employ the use of templates combined with etching or dissolution of porous membranes or fiber. Using such processes, nanostructures like nanotubes, nanowires or nanoparticles of uniform thickness can be generated [2–4,7,10,11]. This is possible since ALD allows to conformally coat substrate surfaces of various geometries with high aspect ratio [4,10,11]. Regarding surface modification a variety of techniques have been developed [4]. Some employ the (reversible) grafting of template blocking agents or lithographic methods to create a nanopatterning [4,5]. Thus ALD can selectively be applied to a target area in order to generate a lateral structuring of the substrate surface. However, most of these techniques are limited to planar substrates making it difficult for applications in catalyst tailoring, where large surfaces are desirable [2,4]. Various patterns generated by such area-selective ALD approaches were reported exhibiting structures with some ten nanometers in diameter [4,5]. A new method not limited to planar substrates was first presented by Canlas et al. creating nanocavities of 1–2 nm in diameter by the use of *p*-*tert*-butyl-calix[4]arene (calixarene) as a sacrificial nanotemplate [5]. By grafting calixarene onto the surface of titania P25 followed by ALD deposition of inert wall material and template removal uniform nanocavities were obtained. The dimension of the cavity size is of great interest as it enables to increase the shape-selective conversion of organic molecules e.g. in photocatalytic reactions. Thus ALD is a powerful tool with versatile applicability and flexibility for different types of surface modifications.

In this work, we address the transfer of such ALD approaches to large surface area mesoporous materials. Owing to its large specific surface area, its enhanced hydrothermal stability, and its surface termination with hydroxyl groups, mesoporous silica SBA-15 provides excellent qualities for further modification [12–18]. We present an ALD approach for the generation of nanocavities on the surface of mesoporous materials such as SBA-15. The process is summarized schematically in Fig. 1. For titania-based applications (e.g. size-selective (photo)catalysis), the silica surface is first ALD coated with titania. Subsequently, calixarene is grafted onto the titania surface enabling the area selective deposition of the alumina wall material. Calixarene is chosen for this purpose because of its known qualities as molecular template [5]. Finally, after calixarene removal by ozone treatment, nanocavities are obtained, the dimensions of which are defined by the size and geometry of the sacrificial template. For template removal thermal ozone treatment is the method of choice owing to the moderate temperatures applied (130 °C). A pure thermal treatment requires higher temperatures which might cause morphological changes in the SBA-15 matrix and consequently also in the nanocavity structure. Regarding removal of the calixarene template by thermal ozone treatment, a gradual degradation of calixarene accompanied by formation of the oxidation products CO₂ and H₂O is a plausible scenario.

2. Experimental

2.1. Synthesis of silica SBA-15

For synthesis of silica SBA-15, 4.0 g of Pluronic P123 (EO₂₀PO₇₀EO₂₀, BASF) were dissolved in a mixture of 120 mL of 2 M HCl and 30 mL of deionized water in a polypropylene bottle under stirring at 35 °C. Subsequently, 8.5 g tetraethyl orthosilicate (TEOS, Sigma-Aldrich, ≥99.0%) were added and the solution was stirred for

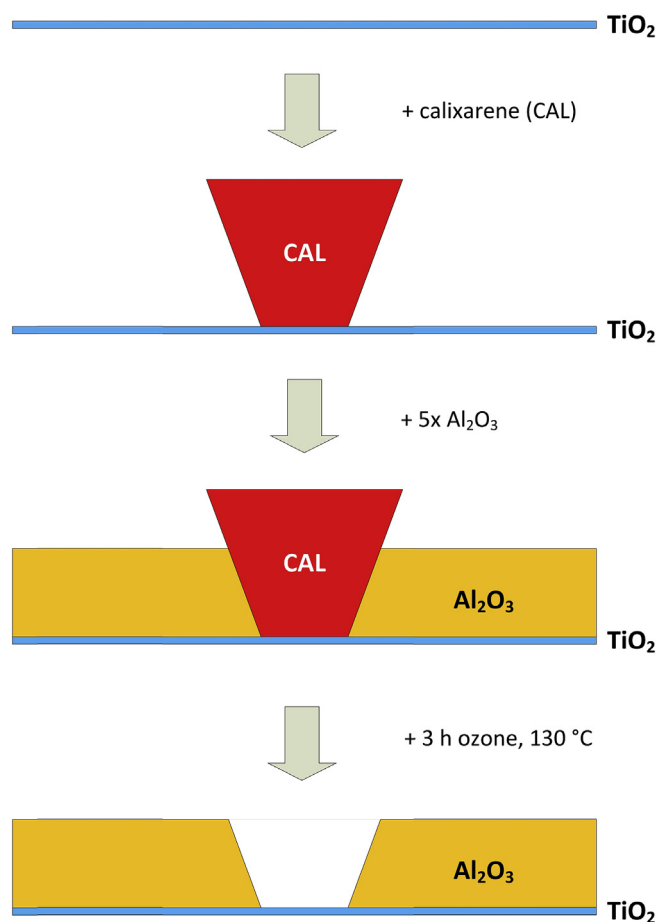


Fig. 1. Scheme illustrating the process of nanocavity formation. For details see text.

20 h at 35 °C. Then the bottle was placed in an oven at 85 °C for another 24 h. The resulting suspension was filtered yielding a white powder. The product was calcined at 550 °C for 12 h [12,14].

2.2. Thermal ALD: TiO₂ coating

ALD coatings were applied by using a self-made stainless steel ALD reactor, which operates at a pressure of 1.3 Torr. Details of the ALD setup were described elsewhere [11]. For the deposition of one monolayer of TiO₂ the reactor walls were heated to 120 °C resulting in a substrate temperature of 115 °C. Up to 200 mg of SBA-15 were placed in the reaction chamber with a volume of 3 L. To ensure the deposition of complete monolayers onto the surface of SBA-15, we applied three successive TiCl₄ (Sigma-Aldrich, 99.9%) precursor pulses followed by three H₂O pulses. Precursors were fed into the reactor by setting the valve opening time to 0.5 s and 0.1 s for TiCl₄ (p ~ 1 Torr) and H₂O (p ~ 8 Torr), respectively. The cyclic ABAB-type ALD process consisted of 1 min exposure time for each precursor separated by 1 min purging with N₂ (99.999%, 200 mL/min). The product will be referred to as TiO₂-SBA-15.

2.3. Surface modification using *p*-*tert*-butyl-calix[4]arene

Nano-structuring of the TiO₂ modified SBA-15 surface was achieved by applying a template-based approach [5]. 100 mg of TiO₂-SBA-15 were added to 50 mL of dry Toluene (Sigma-Aldrich, 99.8%) and 50 mg *p*-*tert*-butyl-calix[4]arene (Sigma-Aldrich, 95%). The mixture was then stirred for 2 h at 125 °C under reflux, yielding

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