

# Silica and silica-alumina composite monoliths with a hierarchical pore structure containing the MFI-type zeolitic films

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## ABSTRACT

Pre-shaped amorphous silica and silica/alumina monoliths containing an extensive system of meso-/macropores were used as parent solids for the preparation of a new type of hierarchical porous systems. Impregnation of the monolith pore walls with a template solution and subsequent hydrothermal recrystallization resulted in the formation of materials consisting of amorphous silica or silica/alumina carcass covered with a thin layer of the MFI crystals. The differences in the porous structure of the parent monoliths appeared to have critical effect on the porosity and deposition of the zeolitic phase in the prepared composites. The results of characterisation of both parent and modified monoliths carried out by XRD, N<sub>2</sub> adsorption and SEM are discussed.

**Keywords:** monoliths, hierarchical pore structure, zeolitic films

## 1 INTRODUCTION

The size of micropores in zeolites may significantly hinder or even restrain transport of bigger reactants inside the crystals. Synthesis of new catalysts containing an active phase in the form of fine and dispersed zeolite crystals and a system of meso- and macropores (serving as arteries for unrestricted transport of the molecules) could overcome such limitations.

Previous research on the preparation of the multimodal porous materials containing zeolitic phase showed the possibility of introducing nanodomains of the desirable microporous phase (FAU, BEA, MFI) into the meso/macroporous aluminosilicate structure via partial recrystallization of amorphous walls [1, 2]. The present work aimed to apply this method to the preparation of a new type of porous solids using pre-shaped silica and silica/alumina monoliths, with very well developed system of the meso/macropores [3-5]. Application of these materials, which retain the size and shape after recrystallization, should eliminate costly and time-consuming shaping step in the preparation of more efficient zeolite-based catalyst.

## 2 EXPERIMENTAL

The synthesis of the silica monolith was carried out according to the procedure reported previously [6]. The same procedure was applied to obtain silica/alumina monolith.

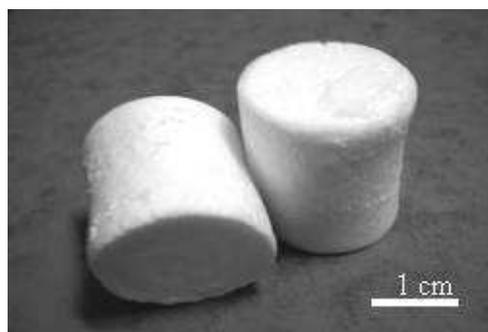


Figure 1. Parent silica (left) and silica-alumina (right) monoliths with a hierarchical pore structure.

In this case, 0.95 g of aluminium nitrate nonahydrate (Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) was used as alumina precursor (Si/Al molar ratio of the product equal to 40). After dissolving the aluminium source in 1M nitric acid, the polyethylene glycol (PEG), tetraethoxysilane (TEOS) and cetyltrimethylammonium bromide (CTABr) were subsequently added. The gels obtained were aged at 40°C for 6 days and then dried at 60°C for four days and finally calcined in air at 550°C for 5h. The synthesis procedure used for the preparation of the silica and silica/alumina monoliths enabled to tailor their size and shape (Figure 1). The applied process of recrystallization consisted of: impregnation of a dry monolithic sample with 40 wt% tetrapropylammonium hydroxide solution (TPAOH), ageing the impregnated monolith for up to 1.5 h, and its heating at 175°C for the period ranging from 12 to 44 h. The products i.e., partially recrystallized monoliths (composites) were calcined for 12 h at 550°C in dry air.

The composites obtained were structurally characterized by XRD. Their porosity was determined from

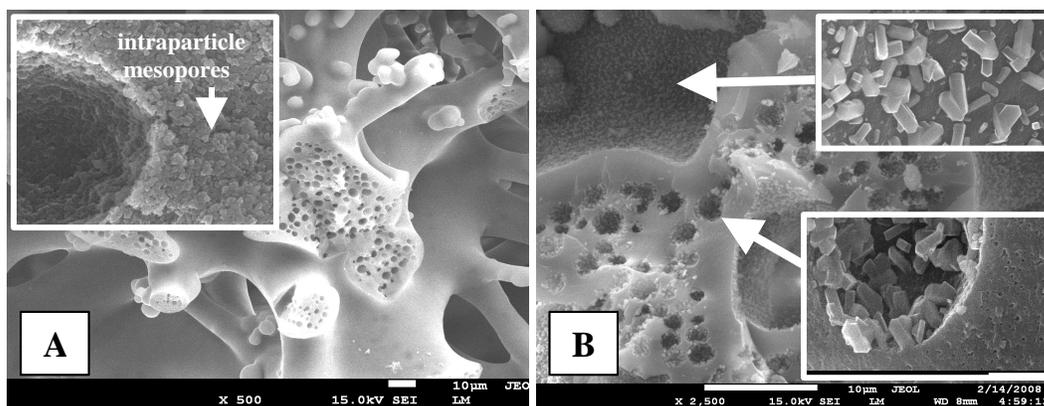


Figure 2. A) Parent silica monolith: “corridor-like” macropores and spherical voids; intra-particle mesopores. B) Recrystallized silica monolith: deposit of silicalite-1 crystals on the walls and inside the spherical void. The bar size is 10 µm.

the N<sub>2</sub> adsorption/desorption isotherms. Scanning electron microscopy (SEM) was applied to study the morphology and architecture of materials and to verify the presence of the zeolite phase.

### 3 RESULTS AND DISCUSSION

#### 3.1 Recrystallization of the silica monolith

The SEM images of the obtained silica monolith showed a developed system of macropores, with interconnected large empty spaces inside a monolith and numerous smaller, spherical macrovoids located in its skeleton (Figure 2A). The adsorption measurements revealed a considerable amount of mesopores, as indicated by the presence of a hysteresis loop (Figure 3A). A careful analysis of SEM images showed, that the mesopores were mainly of an interparticles origin and related to the free spaces between fine silica grains forming the monolith structure (Figure 2A).

The microscopic analysis revealed that the applied process of the controlled recrystallization did not change the initial shape and size of the monolith. The structural analysis (XRD, data not presented) showed, that the MFI was the sole microporous phase present in the material. Recrystallization time of about 12 h proved quite sufficient to obtain the composite product containing a considerable amount of the zeolitic phase. Longer treatment, up to 44 h, did not produce other crystalline phases. The SEM investigations (Figure 2B) showed that the macroporous character of the parent silica monolith was retained in the recrystallized solids. The newly developed microporous phase had a form of fine silicalite-1 crystals (MFI), deposited on the walls of macropores. Similar MFI crystals were also found inside the spherical macrovoids (cf. Figure 2B), which were accessible for the template

molecules through the mesopores present in the pristine material (intraparticle mesopores).

The recrystallization process significantly changed adsorption properties of the modified silica monoliths (Figure 3). The isotherm of composite (B) was shifted upward for low values of the relative pressure ( $p/p_0$ ), in comparison to the isotherm from parent material – A. This signifies the presence of micropores originating from the zeolitic phase. Additionally, the changes in the shape and position of the hysteresis loop registered for the recrystallized material and seen in the pore sizes distributions (results not given) revealed a considerable presence of newly formed smaller mesopores, at the expense of large mesopores, the amount of which considerably decreased. Such modification of porous structure could be explained by the changes in the system of intraparticle mesopores, caused by interaction of the template molecules with silica particles, resulting in their partial dissolution during the hydrothermal process. This idea was supported by the closer inspection of the silica skeleton images in the parent and recrystallized preparations (Figure 2B)

#### 3.2 Recrystallization of the silica/alumina monolith

The SEM analysis of the silica/alumina monolith revealed that introduction of Al and small changes in the synthesis procedure resulted in the generation of less developed pore system with some large macropores. This observation was supported by the adsorption data. The same data (results not given) showed, however, the presence considerable number of irregular micropores. Spherical voids similar to those detected in purely siliceous material were also found in the silica/alumina system. Similarly to the silica monolith, the pure MFI phase was the only microcrystalline phase formed during

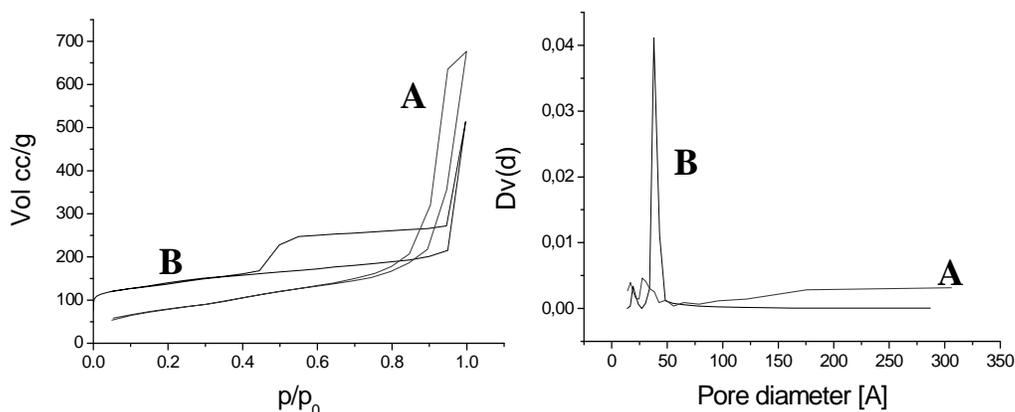


Figure 3. Nitrogen adsorption/desorption isotherms and pore size distribution (calculated on the basis of the desorption branch) of parent (A) and recrystallized (B) silica monolith.

the partial recrystallization. Yet, the synthesis time necessary to obtain a similar level of transformation into the zeolite phase was longer due to more difficult formation of aluminium-containing zeolite phase. SEM analysis of the recrystallized silica/alumina monolith proved, that the zeolite crystals were formed exclusively on the outer surface of macroscopic flow-through “corridors” (Figure 4). No MFI crystals were found inside the isolated spherical voids located in the walls. The lack of mesopores and limited transportation of the template molecules through micropores is the most likely explanation of the lack of MFI crystals inside these empty spaces.

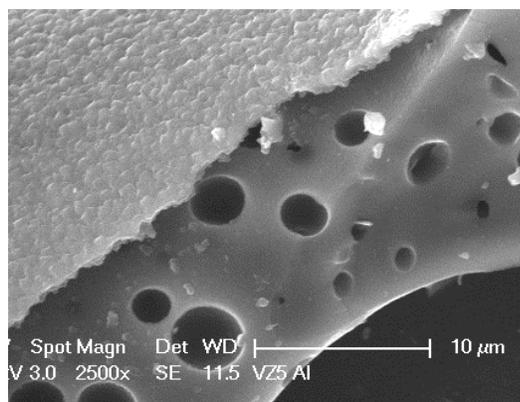


Figure 4. Zeolite MFI laser created on the wall of silica/alumina monolith.

## 4 CONCLUSIONS

The method of controlled hydrothermal recrystallization appears suitable to transform partially the macroporous

skeletons of pre-shaped parent silica and silica/alumina monoliths into a zeolite phase. As a result composite materials containing the layer of fine MFI crystals, deposited in the macroporous structure are obtained. The shape of the parent materials is very well retained. Clear differences in texture of the parent silica and silica/alumina monoliths have a critical effect on the porosity and deposition of the zeolite phase in the prepared composites.

Our future studies will mainly focus on the recrystallization of silica monoliths impregnated with aluminum compounds. This will aim to exploit their vast advantages such as high thermal stability and very well developed meso/macroporosity. We believe that by combining high acidity and shape-selectivity of the zeolites with the highly open structure of silica monoliths we should significantly boost the catalytic performance of these materials.

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