



## Ordered mesoporous materials with MFI structured microporous walls – Synthesis and proof of wall microporosity

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### ABSTRACT

Ordered mesoporous materials (OMMs) of 1-dimensional hexagonal and 3-dimensional cubic symmetry of the pore systems were synthesized via well-established soft templating routes starting from precursor solutions of MFI-type zeolites (Silicalite-1, TS-1). The products were characterized by XRD, nitrogen and argon physisorption, DTG/DTA, IR, UV–vis spectroscopy, XANES, TEM, <sup>129</sup>Xe NMR, and determination of the pair distribution function (PDF) in order to elucidate their structure, in particular to prove the presence of microporosity in arrays smaller than the coherence lengths of XRD, i.e. in the pore walls. The mesoporosity of the OMMs was well supported by physisorption studies and by TEM while the regularity of the structure was documented by XRD, which also served to exclude the presence of microporous crystalline grains. Instead, microporosity was detected by adsorption/desorption of water on tetrahedrally coordinated Ti-sites (XANES), by <sup>129</sup>Xe NMR, by the comparison of the PDF with those of amorphous and of MFI-type solids, and by sequential decomposition of the structure directing agents for meso and micropore systems. From comparison of XRD and physisorption data and from the TEM micrographs, the thickness of the microporous mesopore walls was concluded to be  $\approx 1.5$  nm. Therefore, the failure of Ar physisorption to detect pores of sizes typical of MFI structures was attributed to the small micropore volume and the very short pore extension. The structural integrity of OMMs with 1-dimensional hexagonal pore system could be improved by a hydrothermal post-treatment despite the microporous nature of their pore walls, which resulted in more narrow mesopore size distributions peaking at somewhat larger pore sizes.

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### 1. Introduction

Redox zeolites have attracted wide attention as highly selective catalysts for liquid-phase oxidations. Titanium-substituted zeolites have even found industrial application in various reactions, and research is ongoing with them and with Ti-containing mesoporous materials [1–3]. Titano-zeolites, in particular zeolite TS-1, show high product selectivity with small alkene reactants and allow using aqueous H<sub>2</sub>O<sub>2</sub> as an oxidant for epoxidation reactions.

However, zeolite micropores are not accessible for bulkier molecules, which excludes those from the applications. Mesoporous Ti-containing materials elude the micropore limitation [4,5] but, unfortunately, suffer from insufficient thermal and steam stability of the silicate framework for applications under hydrothermal conditions. In addition, they are hydrophilic, which prevents the use of aqueous solutions of the oxidant in many applications.

A combination of the favorable properties of microporous TS-1 with the structural organization of ordered mesoporous systems like MCM-41 or MCM-48 would be an attractive approach to improved liquid-phase redox catalysts. However, simple physical mixtures or hybrid phases consisting of massive grains of the two materials are not suited to overcome the above-mentioned problems of activity, stability and hydrophilicity. Recently, different groups reported the successful synthesis of ordered mesoporous materials (OMM) built from of TS-1 subunits as constituents of the mesopore wall as an appealing alternative for the assortment of micro- and mesoporosity [6–14].

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In this paper we describe the synthesis and the extensive characterization of hexagonal and cubic materials assembled from preformed Silicalite-1 and TS-1 precursors. Some preparations based on TS-1 precursors have been described earlier in a paper focused on the microporous character of the walls, which was proven by XANES at the TiK edge, and on the catalytic properties in alkene epoxidation [11]. These materials are now considered in a broader context that includes silicalite-based materials and the application of new techniques for the demonstration of wall microporosity –  $^{129}\text{Xe}$  NMR and the analysis of the Pair Distribution Function (PDF) from high resolution PXRD data. As in [11], our materials are designated as mime-1h(Silicalite-1), mime-1h(TS-1), mime-3c(Silicalite-1) and mime-3c(TS-1), and they are meant to contain micropores and mesopores. “1h” refers to the 1-dimensional channel in hexagonal symmetry, “3c” stands for 3-dimensional and cubic, and the structure of the seed is added in parentheses. The materials were characterized with XRD, TEM, IR-spectroscopy, UV-vis spectroscopy, Thermal Analysis (DTA/TG), Argon- and  $\text{N}_2$ -physisorption, selected samples also by  $^{129}\text{Xe}$  NMR and by synchrotron-based XRD to derive the PDF.

For regular MCM-41 and MCM-48 with amorphous pore walls, it is known that their structural attributes can be changed after synthesis using a hydrothermal post-treatment. Although not all mechanisms of this method are fully understood, it is a welcome opportunity to enhance the thermal stability of MCM-materials [15,16]. In addition, hydrothermally modified materials usually show a higher degree of order, a narrower pore size distribution and a larger pore diameter [15–17]. Hydrothermal post-treatment was also used by Kao et al. for micro-meso materials [18] as a step in the synthesis route, however, without comparison of properties between the treated and untreated materials. In this study we apply the hydrothermal post-treatment to hierarchical mime-1h and mime-3c structures that are assembled from preformed Silicalite-1 and TS-1 precursors and compare their structural and functional properties with those of the untreated material.

## 2. Experimental

### 2.1. Synthesis

#### 2.1.1. Silicalite-1 precursor solution

In a typical synthesis, 8.03 mL (35.84 mmol) TEOS (Aldrich, 98% GC) were added dropwise under stirring to 6.36 mL (12.64 mmol) of a 40 wt.% TPAOH-solution (BASF, alkalifree). The reaction vessel was cooled in a water bath, because hydrolysis of TEOS is exothermic. After the addition of TEOS the mixture was stirred at room temperature for 30 min. Then, 6.11 mL (339.44 mmol) of distilled water were added. The resulting zeolite precursor solution had the molar ratio TEOS:TPAOH:water = 1:0.35:15.45. It was aged at 20 °C for 24 h.

#### 2.1.2. TS-1 precursor solution (see also (11))

In a typical synthesis 8.03 mL (35.84 mmol) TEOS (Aldrich, 98% GC) were added dropwise under stirring to 6.36 mL (12.64 mmol) of a 40 wt.% TPAOH-solution (BASF, alkalifree). As hydrolysis of TEOS is exothermic, the reaction vessel was cooled in a water bath. After the addition of TEOS the mixture was stirred at room temperature for 30 min. Then 0.21 mL (0.55 mmol) TBOT (Tetra-*n*-butylorthotitanate) (Merck) were added dropwise under vigorous stirring. Stirring was continued for 10 min. Then 6.11 mL (339.44 mmol) of distilled water were added. The resulting zeolite precursor solution had the molar ratio TEOS:TPAOH:TBOT:water = 1:0.35:0.02:15.45. It was aged at 20 °C for 24 h.

#### 2.1.3. Synthesis of the mesoporous matrix

For the synthesis of mime-1h(Silicalite-1) and mime-1h(TS-1), 60 g of a 10 wt.% cetyl-trimethyl ammoniumbromide-solution, i.e. 16.46 mmol CTAB (Aldrich), which was kept at 80 °C, were added to the zeolite precursor solution under stirring. Stirring was continued at room temperature for 20 min. For mime-3c(Silicalite-1) and mime-3c(TS-1), 20 ml of distilled water (1111 mmol) and 6 g CTAB (16.46 mmol) were added. The mixture was kept at 100 °C for 3 days to conclude the synthesis. Then the solid pro-duct was separated by filtration, washed several times with distilled water and dried at 60 °C for 24 h.

Afterwards CTAB was removed by extraction with ethanol (Riedel de Haën, p.a.). For this, 1 g of the product was mixed with 80 ml ethanol and 0.16 ml (2.77 mmol) acetic acid (Merck, p.a.) and re-fluxed at 77 °C for 1 h. The procedure was repeated twice, however, only 0.08 ml of acetic acid was used for the second treatment. The extracted product was dried at 60 °C for 24 h. The remaining TPA<sup>+</sup> cations were removed by calcinations of the product, first at 300 °C for 1 h, then at 450 °C for 1 h, with a heating rate of 1 K/min applied.

### 2.2. Hydrothermal post-treatment

For the hydrothermal post-treatment 2 g as-synthesized mime-1h(TS-1), mime-1h(Silicalite-1), mime-3c(Silicalite-1), or mime-3c(TS-1) were mixed with 120 ml distilled water and put in an autoclave at 140 °C for 1 day. After filtration and drying, the samples were treated the same way as described for the unmodified products in paragraph 2.1.3.

The different treatments of the samples will be abbreviated by the following labels. The material still containing all structure-directing agents (SDA) will be referred to as **as-made**, the hydrothermally treated samples as **hytr**, the extracted samples as **ex**, the hydrothermally treated and extracted samples as **hytr-ex**, the extracted and calcined samples as **ca** and the hydrothermally treated, extracted and calcined samples as **tc**. Materials which were gently calcined (1 K/min) will be labeled **gc**.

### 2.3. Sample characterization

Powder XRD experiments were performed with a conventional diffractometer in Bragg–Bretano geometry on a flat plate sample holder with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Additional XRD measurements were carried out with a Huber Imaging Plate Guinier Camera 670 with Cu K $\alpha_1$  radiation using a Ge(111)-monochromator ( $\lambda = 1.54056 \text{ \AA}$ ). High energy powder X-ray experiments for PDF analysis were carried out at beamline B2 at the DORIS synchrotron in the HasyLab in Hamburg ( $\lambda = 0.123984 \text{ \AA}$ ). The samples were kept in glass capillaries of 0.3 mm diameter.

AAS measurements were made with a Varian SpectrAA 220. ICP-OES analyses were carried out on a Philips PU 7000 ICP Spectrometer.

DRIFT spectra were measured using a Nicolet Protegé 460 FT-IR-spectrometer equipped with a diffuse reflection cell in praying-mantis arrangement (Harrick). The resolution was  $4 \text{ cm}^{-1}$ . The samples were diluted with KBr with a mixing ratio of sample to KBr of 1:500. For each spectrum 500 scans were collected with KBr as a standard. Additional measurements were performed on a Perkin-Elmer 882 IR-spectrometer. For those measurements the samples were diluted with KBr again with a ratio of sample to KBr of 1:500 and pressed to pellets. Measurements were done in transmission mode.

High quality TEM images were taken on JEM-3010 and JEOL-2000FX instruments at acceleration voltages of 300 and 200 kV, respectively.

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