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Synthesis of hierarchical porous silicas with a controlled pore size distribution at various length scales

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Abstract

Hierarchically structured porous materials are of great interest to catalysis, where an accurately controlled pore texture at different length scales can help to reduce or otherwise control transport limitations. A method is presented to synthesize bimodal structured silicas, with an independently controlled small meso- and large meso-to macroporosity. Small primary MCM-41 particles assemble around micelles formed by a tri-block copolymer surfactant that is added as a low-concentration ethanolic solution to the particles, while these still form a flexible gel. Cross-linking of the particles in an autoclave, followed by drying and calcination, leads to bimodal materials with the controlled small mesopores of MCM-41, and a larger meso- to macropore size distribution that depends on the micelle shape and size. The latter is a function of the conditions in the second step, such as the amount and composition of the surfactant, the aging time, the temperature, the pH and the type of solvent. Fine tuning of this procedure, application to other primary structured particles, and combination with other structuring methods, should enable to construct multi-structured hierarchical materials with a desired texture at all scales.

Keywords: Hierarchical porous silicas; MCM-41; MAS–NMR

1. Introduction

Recent years have seen great progress in nanotechnology, and in particular in the design of porous materials with a controlled nanostructure [1,2]. However, as nature teaches us, not only the nano-scale matters. Hierarchical channel or pore network structures are ubiquitous in nature, one reason being that while the main biophysico-chemical processes are principally controlled at the molecular (or nano-)scale, the easy accessibility of cells, small capillaries or other building blocks, i.e., an efficient link between the micro- and the macro-world, is equally important, because many of these processes are transport limited. We can learn from this to design more efficient porous catalysts.

Some preliminary calculations and simulations were performed to demonstrate that, if diffusion limitations were to exist in a catalyst with unisized nanopores (i.e., micro- or small mesopores), the catalytic process would occur more efficiently in a material that is, on the one hand, characterized by a regular unisized nano-scale and, on the other hand, by a broad, typically fractal-like meso- to macropore size distribution [3,4]. Such a pore network allows better access to features at the nano-scale, than if all pores were narrow or if the pore size distribution were bimodal with only one type of nanopores and macropores. The optimal distribution depends on the application. This is quite similar to nature, where branched, hierarchical, fractal-like distribution of

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channels are frequent; examples are branch, leaf and root systems, as well as the vascular or the respiratory network of animals. The process details are governed by what occurs at the, typically regular, molecular or nano-scale, while the accessibility to that nano-scale is efficient and scalable. A self-similar, fractal-like structure interpolating between the micro- and the macro-scale, turns out to be a facile, maybe even optimal route to transport molecules from one point or a small area to reach a very large surface area or volume in a controlled, uniform way [4–6]. It should be noted that many natural porous materials, such as bone, also have a hierarchical porous structure. Cities are made more accessible in a similar way, through a hierarchical network of roads and streets of different sizes.

This motivates the design of new hierarchical porous catalysts that do not only have a controlled structure at the micro-scale (molecular or nano-scale, such as microporous and mesoporous molecular sieves), but also at scales ranging from the micro- to the macro-scale [7]. A first step is the independent control of pore sizes at two length scales, but, for the above mentioned reasons, we would eventually like to control all length scales. In the last few years, various physical templating methods have been used to create macropores of a few hundred nanometers: latex sphere dispersing [8,9], oil/formamide emulsions [10], colloidal crystal templates [11], and two-dimensional micro-molding [12]. Most recently, carbon particles were used as templates to create large mesopores in zeolite crystals [13]. The implementation of some of these techniques on a larger scale may be difficult or expensive, and it would in any case be interesting to have access to chemical templating techniques that could create, in a controlled way, larger meso- to small macro-pores (i.e., the range 10–100 nm) in solids with a controlled micro- or small meso-porosity (i.e., scales <10 nm).

A new, chemical synthesis method is presented here to prepare multi-structured porous materials through a fully chemical route that allows to control the smallest pore size and the larger meso- or macropore sizes independently. Such methods, possibly applied in a hierarchical way or in combination with physical templating methods, should eventually enable the tailored design of catalysts, the optimized pore network structure of which was calculated a priori. Our synthesis method operates by cross-linking primary particles of a nanostructured material, prepared through a conventional template-based route, in a way preserving the nanostructure yet creating a controlled (regular unisized, broad or continuous) pore size distribution at larger scales [14]. The method is illustrated here with the mesoporous sieve MCM-41 as the primary, starting material [1].

2. Experimental

In a first step, MCM-41 is prepared following a literature synthesis method [1]: tetra-ethyl orthosilicate (TEOS), template cetyltrimethylammonium bromide (CTAB), water and ammonia are mixed at room temperature in a molar ratio 1:0.2:160:1.5. The primary product is filtered and repeatedly washed with distilled water. The MCM-41 structure, after drying and calcination, is verified by XRD and nitrogen adsorption. In a second step, part of the filtered product, prior to drying, is immersed in a basic (pH $\sim$ 10) 5 wt.% solution of a tri-block copolymer surfactant in a solvent (base case: ethanol). The surfactants are pluronics, of which the hydrophilic head and tail blocks are oligomers consisting of m units of ethylene oxide, and the core block is a more hydrophobic n-unit propylene oxide oligomer; base case is P-123, with $m = 20$ and $n = 70$: $HO(CH_2CH_2O)_{20}(CH_2CH_2CH_2O)_{70}(CH_2CH_2O)_{20}H$. The gel is aged for up to 2 weeks (base case: 2 days) in an autoclave at 100°C. Finally, the product is filtered, repeatedly washed with distilled water, dried for 3 h at 120°C in air, and calcined in air by heating at a rate of 1°C/min to 500°C, at which temperature it is kept for 6 h. Products are analyzed using nitrogen adsorption/desorption, XRD, TEM, SEM and MAS–NMR.

3. Results and discussion

BJH-analysis of nitrogen adsorption/desorption isotherms shows that bimodal silicas are formed, with the smaller pores having a size of about 3 nm, and the larger pores having a size in the range 10–100 nm, depending on the exact synthesis conditions. An example is shown in Fig. 1. The small, “primary” pores correspond to those found in the primary, MCM-41 material, while the “secondary” pores are new and

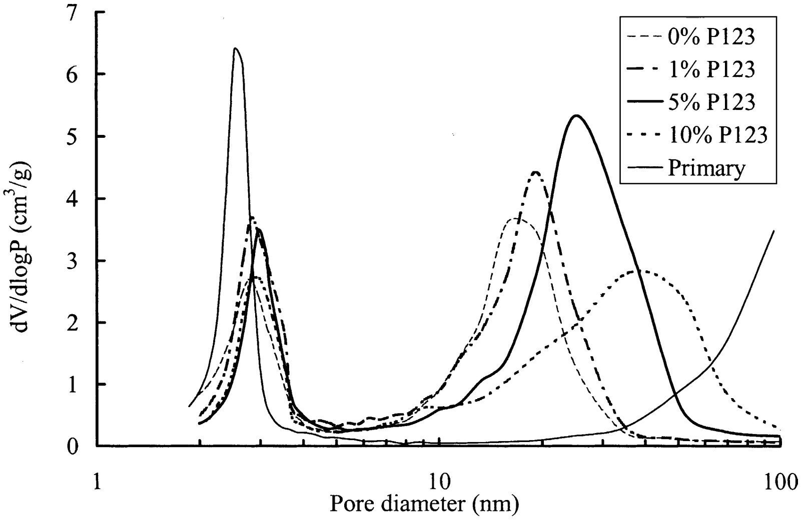

Fig. 1. Effect on the pore size distribution of the amount of P123 surfactant added in the second step. The pore size distributions are based on the BJH-model for the desorption branch of the nitrogen isotherms.

different from the large inter-particle pores found in a dried and calcined primary MCM-41 material. For the "base case" (5 wt.% P123 in ethanol, pH ∼ 10, 100°C, 2 days aging), e.g., the larger, secondary mesopores are around 25 nm in size, the surface area is 960 m^2/g, and the total pore volume is 2.6 cm^3/g with 0.6 cm^3/g as primary and 2.0 cm^3/g as secondary pores.

This is a typical example, yet a change in temperature, copolymer surfactant (different number of units m and n to change the hydrophilicity/hydrophobicity of the surfactant), aging time or acidity in the second synthesis step changes the position and width of the larger peak in the pore size distribution. Changing the amount of tri-block copolymer in the range 0–10 wt.% (base case: 5 wt.%) has a drastic effect (Fig. 1). If no copolymer is used at all ("blank" with 0 wt.%), a bimodal material with 3 and 16 nm pores is formed after the second step. The secondary pores are of the same order of magnitude as the primary nanoparticles (∼20 nm), but in the presence of a surfactant, the secondary pore size may increase because the surfactants form micelles around which the primary particles aggregate. The pores of the basic, primary MCM-41 material are slightly widened from 2.6 to 3 nm because of swelling in the ethanol solvent used in the second step [15]. For a given solvent, however, the primary pore size is largely independent of the conditions used in the second step. The solvent used in the second step has a significant influence on the texture: when water is used instead of ethanol, the average secondary pore size increases to 54 nm, while the use of the nonpolar solvent benzene shifts the secondary pore size to 16 nm with a width of 10 nm, exactly the same as if no copolymer were used in the second step at all, because no templating micelles are formed, so that the secondary pores are completely determined by the size of the aggregating primary nanoparticles. In the latter case, the primary pore size, however, does not remain 3 nm, but shifts to 5.4 nm, because of swelling of the hydrophobic core of CTAB in the primary pores, while the pluronic has no effect, as a comparison with the blank shows.

Apart from nitrogen adsorption, XRD patterns confirm the preservation of the MCM-41 pores, which are the primary, smaller pores in the new bimodal silicas, although the pores have been deformed (note the small shift of the (1 0 0) peak and the decrease of a higher order peak in Fig. 2). In summary, MCM-41 based materials have been formed, with primary pores around 3 nm in size, a more or less (depending on the conditions) broad distribution of mesopores with an average around 10 to more than 50 nm in size, a high to very

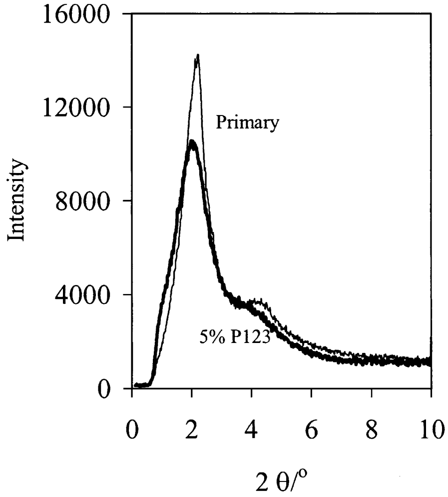

Fig. 2. XRD patterns for the primary material and a representative secondary, bimodal material (5 wt.% P123 in ethanol).

high N_2 BET surface area (~1000 m^2/g), and a relatively high porosity (2.5 cm^3/g). The larger pore size can even be extended to more than 100 nm by adding a modifier in the first step. For a detailed discussion of all these conditions and their effect, we refer to upcoming communications [14]. Here, we focus on the general observations and mechanism behind the formation of the bimodal silicas.

Tri-block copolymer surfactants such as P123 form micelles, around which the primary particles assemble when immersed in a solution of the surfactants. Note that at the low surfactant concentrations used here and in ethanol solution, the micelles do not form a liquid crystal phase, but form disordered spherical to flexible rod- or worm-like micelles [16]. The primary MCM-41 gel particles are still soft and deformable in this stage; surface silanol groups exposed to the micelles form hydrogen bonds with the hydrophilic heads of the surfactants, while silanol groups of nearby particles condense around the micelles at the higher temperatures in the autoclave. When there are no micelles, such as in benzene or in the absence of surfactants, the secondary pores have a minimal size, determined by the space between the primary particles. ^{29}Si MAS–NMR confirmed the continued condensation through an increase of the Q^4:Q^3:Q^2 ratio. Scanning electron microscopy (SEM) images showed a smoother morphology compared with the particulate morphology of the primary material, while transmission electron microscopy (TEM) images clearly revealed the formation of a new material with a tunable, bimodal pore size distribution [14].

Finally, the "base case" sample was Ti-grafted and used as a catalyst in the epoxidation of cyclohexene with tetra-butyl hydroperoxide. An eight times higher turnover frequency (TOF) at a reaction temperature of 40°C and a reaction time of 6 h was observed compared to a Ti-MCM-41 sample prepared by direct synthesis [17], and the TOF was even higher than with a pure grafted Ti-MCM-41 sample. This suggests not only a high dispersion of the tetrahedral Ti-centers in the pores [18], but also the benefits induced by a well-connected hierarchical pore network.

4. Conclusions

A flexible, fully chemical synthesis method was presented to prepare structured bimodal silicas with an independently controlled pore size at the small meso- and the larger meso-to macropore scale. This method is based on controlled cross-linking of primary porous particles using tri-block copolymer micelles as templates; the mesoporous sieve MCM-41, with 3 nm pores, was chosen as an example for the primary material. Template and solvent are removed by controlled heating, and it was found that the small-scale structure can be conserved during the second step that leads to spatial structuring on larger scales. This methods opens the way to the controlled synthesis of multi-structured materials, which at the same time have a high internal surface area and pore volume, and a very good molecular accessibility of their area through a well-defined network of pores. This is very important to reduce or control transport limitations in catalysis. The preparation method is flexible and the used structure-directing agents are readily available, inexpensive, and can be easily removed by simple calcination or extraction after the inorganic network has been formed. Nanoporous particles other than MCM-41 could be used as building blocks to design more general tailor-made spatially structured materials, to combine the desired catalytic function with an improved, fine-tuned molecular accessibility through a controlled hierarchical pore network.

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