



# Building concept inspired by raspberries: From microporous zeolite nanocrystals to hierarchically porous assemblies



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## ABSTRACT

Hierarchically porous zeolites offer great potential in catalytic and sorptive processes due to the enhanced mass transport properties by the increased diffusivity of the molecules from the bulk phase to the final active sites or sorption sites, respectively. In this contribution we present a simple, 3-step bottom-up preparation route yielding binder-free spherical zeolite material exhibiting a hierarchical pore system. This process consists of zeolite synthesis, aggregation and recrystallization. In this contribution, the process is demonstrated on silicalite-1 (MFI-type zeolite) as a model system. The aggregation process was realized by special spray drying of a complete reaction mixture containing pre-synthesized nanocrystals. The spray drying process results in spherical aggregates which contain amorphous silica species originating from the unconverted part of the zeolite synthesis mixture and which are acting as an intermediate binder. Steam-assisted crystallization was then applied to convert these amorphous species into crystalline zeolite enabling the overall process to utilize 100% of the initial silicon from the zeolite synthesis mixture.

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## 1. Introduction

Zeolites, being one of the most famous members of crystalline, microporous materials feature remarkable properties in terms of chemical composition (e.g. solid ion, hydrophobicity/hydrophilicity) and structure (micropores of definite pore size). Especially in catalysis and sorption these materials can unfold their potential, serving as a solid acid catalyst, adsorbents and molecular sieve in conventional applications [1–3] and with increasing relevance in green chemistry [4–8]. Even though, it is the well-defined microporosity [9] which is responsible for the outstanding performance of zeolites in the above mentioned applications, their small pore size (micropores per definition <2 nm [10]) “thwarts” the effective kinetic of the overall process by impeding the diffusion of molecules from the bulk phase to the very active sites within the crystalline material. Thus, the mass transport very often is a limiting

factor which, as a consequence, leads to an inefficient utilization of the active material.

On a quantitative level, the utilization of a catalyst system (might be e.g. a single crystal or a catalyst pellet) can be characterized by the so-called effectiveness factor  $\eta$  describing the ratio of the “real” observed (effective) reaction rate  $r_{obs}$  influenced by mass transport phenomena and the intrinsic reaction rate  $r_{intr}$  expected for the absence of any heat- and mass-transport limitations. The effectiveness factor of a mass-transport influenced catalyst system additionally can be described by the Thiele modulus  $\phi$  being a measure for the internal mass-transport limitation within the considered catalyst system. Considering a reaction rate of  $n^{\text{th}}$  order in reactant concentration  $c$ , catalysed by a (spherical) system of the characteristic length  $L^* = V_{app}/A_{app}$ , Thiele modulus  $\phi$  and effectiveness factor  $\eta$  are coupled according to the following equation [11,12]:

$$\eta = \frac{r_{obs}}{r_{intr}} = \frac{3}{\phi} \cdot \left( \frac{1}{\tanh(\phi)} - \frac{1}{\phi} \right) \quad \text{with} \quad \phi = L^* \cdot \sqrt{\frac{k \cdot c^{n-1}}{D_{eff}}}$$

Obviously, process parameters such as reaction temperature

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might be used to decrease the Thiele modulus (e.g. *via*  $k$  and  $D_{\text{eff}}$ ) but in order to decrease  $\phi$  from the very basic, materialistic side of the system, it is  $L^*$  (measure for the effective diffusion path length) and the effective diffusion coefficient  $D_{\text{eff}}$  which is of great interest in academic and industrial research [13]. While  $L^*$  results from the morphology of the system (external surface area versus volume),  $D_{\text{eff}}$  is strongly affected by the inner structure of the material (pore size, pore distribution, pore arrangement). For zeolite-based systems, different principles are discussed in literature to achieve the objective of increasing  $D_{\text{eff}}$ : Besides the development of ordered mesoporous materials in the 1990's (e.g. MCM 41 [14,15]) and more recently the development of new zeolite materials having well defined pores in the mesopore-regime (e.g. ITQ 39 [16]), especially the generation of a hierarchical porosity by introducing a hierarchically connected, additional meso- and/or macropore system to the inherent zeolitic micropores is in the focus of current research.

Several attempts have been made to introduce such a hierarchically arranged pore system into the pristine microporous zeolite material, serving as transport pores in order to increase the reactants' diffusivities [13,17–19]. Even though it has been shown that hierarchically porous zeolites outperform their microporous counterparts in catalysis [20,21], it is worth mentioning, that a detailed characterization of their hierarchical nature is still a challenging task [22–24]. The preparation attempts discussed in literature mainly can be assigned to (i) post-synthetic introduction of mesopores in zeolite crystals *via* extraction of framework constituents [25], (ii) *in-situ* generation of meso- and/or macropores by using hard or soft templates [26–28], (iii) downsizing the crystals in one dimension (sheets [29–31]) or all three dimensions (nanocrystals [32]), (iv) introducing additional porosity by novel synthesis approaches [27,33] or advanced aggregation of nanocrystals [34–36]. All these attempts are facing some economical/ecological drawbacks [22,37,38] in terms of (1) the need of an additional and/or an elaborated intermediate component which eventually has to be removed (e.g. hard and soft templates), (2) following a top-down approach whereupon a readily synthesized material has to be partly destroyed (extraction) and (3) in terms of achieving only a low space-time-yield in zeolite synthesis (nanocrystal) and the necessity of an elaborated processes for the separation of the nanocrystals from the reaction mixture.

In this contribution we present a new, technically applicable 3-step bottom-up preparation route towards micrometer sized, all-zeolite binder-free spheres with hierarchical porosity.

## 2. Concept

The three-step preparation route as summarized in Fig. 1, is based on the aggregation of well-defined nanosized zeolite crystals directly from their as-synthesized suspension (steps 1 and 2).

The resulting hierarchical porosity is characterized by at least a threefold pore size distribution whereby the pore sizes are pre-determined by the dimension of the nanosized crystals in the starting suspension and, thus, can easily be tailored to account for the demand of a given application. The hierarchical pore system of these material results from an interplay of the micropores within the nano-sized zeolitic crystals and the meso- and/or macropores originating from the perfect (or imperfect) packing of these zeolitic crystals within the individual (micrometer sized, raspberry-like) assemblies. As mentioned, straightforward the aggregation process starts from the as-synthesized zeolite suspension which eliminates the need of any separation step, resulting in a simple and save handling of the nanosized zeolite material. According to the proposed 3-step preparation process, except for the obligatory structure directing agent (SDA) required for zeolite synthesis, no further template (neither hard nor soft) has to be used. Even more

important, 100% of the silicon atoms, which initially have been provided in the zeolite reaction mixture are utilized to generate the microporous part of the hierarchically organized spheres (*via* recrystallization, step 3). Altogether, from the economical and ecological point of view this 3-step process is very attractive. In particular, the three syntheses and preparation steps are (Fig. 1):

**Step 1:** By conventional hydrothermal synthesis, a stable colloidal suspension of MFI-type zeolite nanocrystals is obtained (nanosized silicalite-1,  $\rightarrow$ nS1).

**Step 2:** The as-synthesized suspension ( $\rightarrow$ nS1-susp) directly serves as a feedstock for the spray drying process. It should be underlined, that the suspension is used without any post-synthetic treatment such as separation of the crystals from the mother liquor or the like. *Via* spray drying, isolated spherical aggregates are formed, within which the individual nS1-crystals are aggregated in a hierarchical manner ( $\rightarrow$ hS1) while being embedded in amorphous  $[\text{SiO}_2]_n$ -species originating from the mother liquor.

**Step 3:** The method of steam-assisted crystallization (SAC) is applied to convert these  $[\text{SiO}_2]_n$ -species into crystalline zeolite ( $\rightarrow$ hS1-SAC). The actual hierarchical porosity is being formed as a result of the transformation of this “intermediate binder” into microporous material which goes along with the generation of intercrystalline voids (“opening of pores”). Eventually, after calcination purely crystalline, spherical, raspberry-like assemblies with a hierarchical pore architecture are obtained.

## 3. Experimental

### 3.1. Synthesis of zeolite silicalite-1 nanocrystals

A sodium-free hydrothermal synthesis procedure for silicalite-1 nanocrystals was adapted from open literature [39,40]. For the preparation of the zeolite synthesis mixture, tetraethyl orthosilicate (TEOS, Alfa Aesar, 98%) and tetrapropylammonium hydroxide (TPAOH, technical grade, 40 wt.-% in water) were used as silicon source and template, respectively, whereas the latter one additionally provided alkalinity. First, 36 g of the template and 45 g of water (de-ionized) were mixed in a 500 ml Erlenmeyer flask while stirring at 400 rpm using a magnetic stir bar. After several minutes 42 g TEOS was added dropwise to the above mentioned solution. This synthesis mixture was stirred at room temperature for 48 h to allow TEOS to hydrolyse completely. The molar ratio in the final mixture was: 1  $\text{SiO}_2$ : 0.18  $\text{TPA}_2\text{O}$ : 19.2  $\text{H}_2\text{O}$ : 4 EtOH. The clear synthesis solution (pH 12.6) was poured into polytetrafluoroethylene (PTFE)-lined stainless steel autoclaves (45 mL, Parr Instrument) and placed into a convection oven for hydrothermal crystallization. After 49 h at 90 °C the autoclaves were cooled down to room temperature.

The as-synthesized suspension (“nS1-susp”, nanocrystals within the mother liquor, pH 13.3) was used as the feedstock for the subsequent spray drying process without any further processing such as separation or the like.

For detailed analysis, a small part of the suspension nS1-susp was further processed to get powdery, isolated silicalite-1 nanocrystals (denoted as “nS1”): *via* several cycles of centrifugation and redispersion in deionized water (10<sup>4</sup> rpm for 15 min (1st run) and 30 min (2nd run and 3rd run)) the nanocrystals were separated from soluble silicon species and dissolved template. Finally, the residues were dried overnight at 75 °C. After this separation procedure, the powder material can be assumed to be free of any amorphous  $[\text{SiO}_2]_n$  species, but obviously still contains template

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