Zeolites from Plant Leaves

Biomineral-Silica-Induced Zeolitization of *Equisetum Arvense*[**]

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The performance of bulk materials often depends on the size and habit of the primary particles, and their ordering into hierarchical structures. In the area of catalysis and separation processes, ordered materials with well-defined periodic structures and controlled sizes are highly desired. Hierarchical porous structures combine the benefits of each pore-size regime and are expected to lead to higher efficiency and new applications in catalytic and separation processes, biomolecular separations, and chromatographic supports.[1] The most commonly used approach for the fabrication of such materials is the application of sacrificial templates, which after the synthesis of the inorganic framework are dissolved or volatilized by heating. The template approach, first employed for the preparation of zeolite-type materials, where small organic molecules are used for directing the microporosity,[2] was extended to the formation of mesoporous[3] and macroporous[4] structures. By employing dual templates, hierarchical porous materials with combinations of micro-/meso-

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pores,[5] meso-/macropores,[6] micro-/macropores[7] and micro-/meso-/macropores[8] were synthesized. Thus, a high level of control was achieved and materials with up to three different pore sizes were synthesized, however, the morphology of these hierarchical structures is far from being controlled.

Nature provides many examples of biological specimens with complicated morphologies and hierarchically built anatomies that are completely petrified, and in which the organic structures are substituted by minerals. Laboratory simulation of this process may provide materials where complex anatomy is combined with specific macromorphology. Recently, laboratory zeolitization of silica cells from diatoms (single-celled algae) providing a micro-/macroporous material was reported.[9,10] Crystallization of the zeolite was induced from seeds, since the reactivity of the fossilized biogenic silica seems to be very low, which does not allow direct crystallization of the zeolite. In addition, by the adsorption of zeolite nanocrystals followed by a hydrothermal treatment, wood cellular structures were transformed into micro-/macroporous zeolite structures.[11] Aggregation of silicalite-1 nanocrystals on biological macrotemplates was used for the preparation of micro-/macroporous fibers[12] and spongelike monoliths.[13] Previous studies have shown that the utilization of biological templates requires the application of zeolite seeds. On the other hand, the most perfect replication of biogenic materials in nature is by silica that is transported in solution and deposited in an amorphous form.[14] Although zeolites are silicates and water transport is an important stage in their formation, successful laboratory zeolitization of biological templates without the use of seeds has not been reported. Thus, the application of zeolite seeds appeared to be indispensable for the synthesis of zeolites on biological macrotemplates.

Herein, we report the in situ zeolitization of a vegetal macrotemplate, induced by the biogenic silica of a fresh plant. The content of silica in dry *Equisetum arvense* used for the present study was about 13 wt%, and is deposited in discrete knobs and rosettes at the epidermal surface.[15] The ^{29}Si NMR spectrum of the freeze-dried plant is typical of amorphous silica.[16] Thus, *Equisetum arvense* offers a perfect surface for zeolitization where easily accessible, highly reactive amorphous silica is exposed.

Leaves of the plant were subjected to hydrothermal treatment with a precursor solution that yielded silicalite-1 (MFI-type structure) crystals.[17] The crystallization of silicalite-1 was accomplished after 24 h treatment. A series of experiments that varied the duration of the hydrothermal treatment from 4–24 h was performed. Analysis of the biological macrotemplate and the mother liquor showed that zeolite formation at the surface of *Equisetum arvense* overtook that observed in solution. The first trace of silicalite-1 on the surface of the plant was detected after 6 h hydrothermal treatment, followed by a rapid increase of the zeolite content. In contrast, silicalite-1 crystallization in the mother liquor took place over the 12–24 h period, which is in good agreement with literature data.[18] The enhanced nucleation on *Equisetum arvense*, in comparison with that in the solution, clearly showed that the epidermal surface of the plant was not a simple support for nucleation and subsequent zeolite formation. The high rate of zeolite formation on the epidermal surface of the plant results from the interaction of the highly reactive initial mixture with biogenic silica, which induces a fast and uniform nucleation. Figure 1 shows the effect of one- and two-step hydrothermal treatments on the amount of crystallized zeolite. The halo emanating from the organic part of the composite decreased after the second crystallization procedure. Only pure, highly crystalline silicalite-1 was observed in the calcined material (600 °C for 5 h).

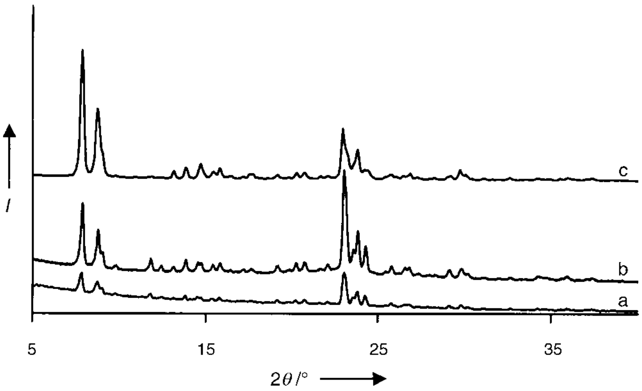

Figure 1. X-ray diffraction patterns of silicalite-1/*Equisetum arvense* composites obtained by one- (a) and two-step (b) synthetic procedures, and the pure silicalite-1 replica (c) of the plant obtained after calcination of the two-step material.

The amounts of silicalite-1 deposited after one and two synthesis steps were determined by thermogravimetric analysis (TGA). After one step, a weight loss of 50.1 wt% was recorded, of which 6.02 wt% was attributed to the loss of water, and the remaining 44 wt% results from thermal degradation of the plant tissues and the tetrapropylammonium (TPA) template. After two hydrothermal steps the total weight loss was about 36.9 wt%, where the weight loss through water was only 0.7 wt%, while that resulting from the decomposition of TPA and the biological macrotemplate was about 36 wt%. It is difficult, however, to evaluate the content of each of the templates because of the overlapping of the corresponding peaks.

Figure 2 shows the zeolitized *Equisetum arvense* leaves, viewed at various magnifications by scanning electron microscopy (SEM), after the hydrothermal treatment and calcination procedure. The morphology of the leaves is maintained after combustion of the organic tissue (Figure 2 a,b). It can be seen that the silicalite-1 replica (Figure 2 c) retains much of the detail observed in the original plant structure (Figure 2 d). Also of note are the extremely small silicalite-1 crystallites that grow on the surface, the size of which is approximately at the resolution limit of the SEM instrument; according to dynamic light scattering (DLS) measurements, the size of the silicalite-1 crystals formed in the solution is approximately 90 nm. An investigation by transmission electron microscopy (TEM) showed that crystallites grown at the epidermal surface of *Equisetum arvense* are much smaller, and range from 20 to 40 nm (Figure 2 e,f). The TEM images reveal that

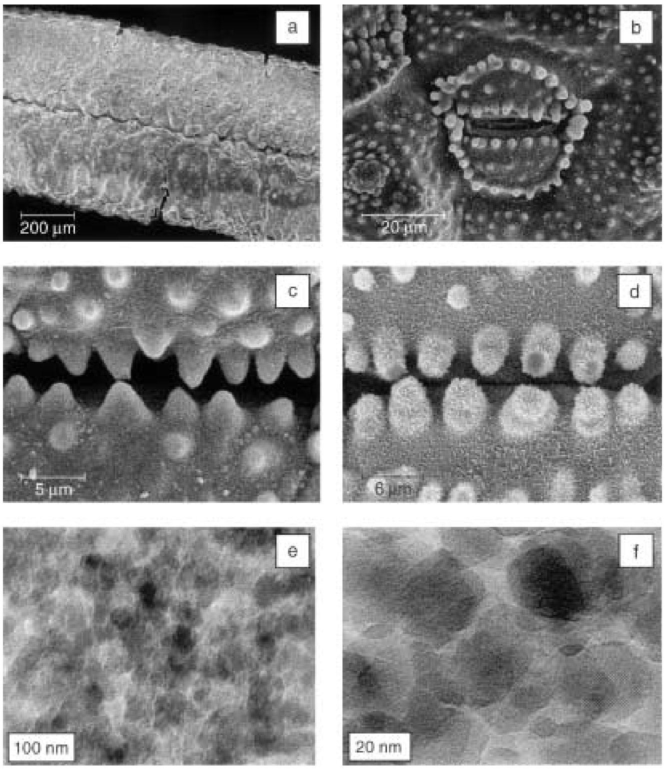

Figure 2. Low-(a) and higher (b) magnification views of the silicalite-1 replica of a leaf of *Equisetum arvense*. The silicalite-1 replica of a stomata structure (c) is compared with the original plant structure (d), where fine filaments covering the leaf can be seen; e,f) TEM images at two magnifications show the lattice fringes of the silicalite-1 nanocrystals within the homogeneous zeolite layer.

the crystals are fairly uniform in size (Figure 2e). These results prove that the reactive biomineral silica promotes zeolite nucleation at the epidermal surface. Thus, a very homogeneous fine silicalite-1 film is formed, and even the nanometer-scale morphological details of the plant are replicated.

Initially, the leaves showed a relatively high Brunnauer–Emmet–Teller (BET) surface area (3.9 m^2g^{-1}) for a dense centimeter-sized material, which is probably a result of the nanosized silica particles exposed throughout the epidermal membrane. After a single-step hydrothermal synthesis, the BET surface area of the as-synthesized product increased to 58 m^2g^{-1}. This value is indicative of the very small nanocrystallites formed on the biological template. After calcination, the sample showed a BET surface area of 217 m^2g^{-1}, which is two orders of magnitude higher than natural *Equisetum arvense* leaves. This value, however, is lower than that of a highly crystalline MFI-type material, which reveals that after the one-step synthesis, a dense material with low specific surface area is still present. The second synthesis step substantially reduces the amount of non-zeolite material, and the calcined sample showed a BET surface area of 383 m^2g^{-1}, which is in accordance with a highly crystalline MFI-type material. However, a total single-point pore volume of 0.92 cm^3g^{-1} was measured for the two-step material (of which the micro- and mesopores contribute 0.13 and 0.79 cm^3g^{-1}, respectively), which does not correspond to that of a microporous MFI-type material. The value corresponding to the micropore volume is somewhat below that of a highly crystalline sample of silicalite-1 (about 0.18 cm^3g^{-1}), which reveals the presence of some non-zeolitic material after the second hydrothermal synthesis. The type I adsorption/desorption isotherms of the calcined samples synthesized by one- and two-step hydrothermal treatments show the microporous character of the materials (Figure 3a and b). A steep rise in the gas uptake at low relative pressures corresponds to the filling of micropores with N_2. In contrast to pure microporous materials, the steep uptake at low relative pressures is not followed by a flat curve. Instead, an inclination of the curve with an increase of the pressure can be observed. At high relative pressure the upward turn with a hysteresis loop is indicative of the generation of intercrystalline mesoporosity. Thus, the zeolitization of *Equisetum arvense* yields a material with combined micro- and mesoporosity.

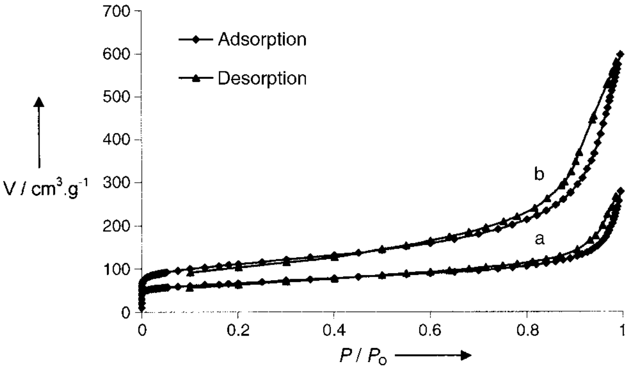

Figure 3. Adsorption/desorption isotherms of the calcined samples prepared by one- (a) and two-step (b) synthetic procedures.

Results of small-angle X-ray scattering (SAXS) analysis are in good agreement with the TEM observations and the N_2 adsorption measurements, that is, uniform nanoparticles and a secondary porosity were detected. SAXS data obtained for dried *Equisetum arvense* leaves do not show fractal behavior nor microporosity features (Figure 4a). In contrast, SAXS data obtained after hydrothermal treatment of the fibers exhibits three $\boldsymbol{Q}$-vector domains in the ranges $\boldsymbol{Q} < 5 \times 10^{-3}$ Å^{-1}, $5 \times 10^{-3} < \boldsymbol{Q} < 2 \times 10^{-2}$ Å^{-1}, and 2×10^{-2} Å$^{-1} < \boldsymbol{Q}$ (Figure 4b). These $\boldsymbol{Q}$-vector domains correspond to scattering from mesopores (or small macropores), micropores, and the surface of the crystallites, respectively. The slope deviation observed in the log–log plot of the SAXS curves at 5×10^{-3} Å^{-1} indicates a mean nanocrystallite size of about 30 nm. The power law behavior of the scattering intensities (that is, a linear increase with decreasing $\boldsymbol{Q}$ with a slope equal to -4) for $\boldsymbol{Q} > 2 \times 10^{-2}$ Å^{-1} suggests that these particles possess a smooth surface.

Although no special tests were performed, the difference in the strength of the silicalite-1 replicas prepared by one- and two-step synthesis procedures is easily distinguishable. The one-step synthesized material retained the macromorphological features of the plant leaves. However, the fibrous structure easily disintegrates when a simple laboratory

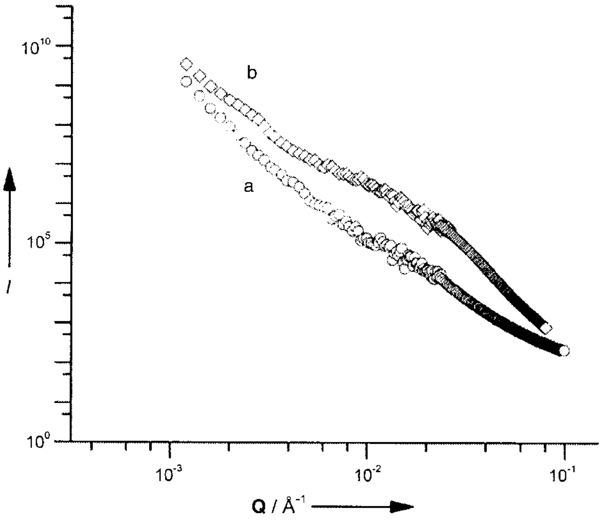

Figure 4. SAXS profiles of *Equisetum arvense* leaves before (a) and after (b) hydrothermal treatment.

operation is performed. In contrast, the replicas obtained by the two-step synthesis are stable, rigid, and can be destroyed only under applied pressure; no destruction was observed during the laboratory manipulations performed with this material. Further increase of the strength of *Equisetum arvense* silicalite-1 replicas might be achieved either by an additional synthetic step, or by a hydrothermal treatment with a precursor gel that does not contain an organic structure-directing agent. In the latter case, subsequent calcination to open the zeolite microporosity is not necessary, and thus flexible fibrous zeolite/*Equisetum arvense* composites might be prepared.

In conclusion, highly reactive silica in plants can promote zeolite crystallization. The large amount of silica found in the epidermal surface of *Equisetum arvense* facilitates zeolite nucleation providing homogeneously and densely distributed zeolite nuclei. Thus a micro-/mesoporous material which retains all of the morphological features of the plant was obtained.

This study opens up routes for the zeolitization of silica-containing plants and the preparation of materials with controlled porosity and specific macromorphological features. The large variety of microporous aluminosilicates and numerous silica-containing plants present tremendous possibilities for tailoring such materials. The reactivity of biomorphous silica can most probably be used to promote the nucleation of other silicate materials that crystallize under soft hydrothermal conditions.

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[17] *Equisetum arvense* was collected from the campus of the University of Haute Alsace (Mulhouse, France). After being dried at room temperature, the leaves were subjected to one or two hydrothermal treatments with a precursor mixture containing 9TPA:25SiO_2:420H_2O:100EtOH. The syntheses were performed at 100 °C for 24 h.

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