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Ice templating – an alternative technology to produce micro-monoliths

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Abstract

Hierarchical ceramics with porosities defined at multiple length scales are of particular interest as catalyst support materials. In fixed-bed reactors, catalytically active particles or porous pellets are packed in the reactor. A combination of high specific surface area, accessibility to the active sites and mechanical strength is therefore required and yet difficult to achieve. This problem is tackled using the ice templating process. Two approaches are investigated to obtain micromonoliths combining macro- and mesoporosities. Ice templating of boehmite suspensions provides materials with macropores ranging from 10 to 26 μm and mesopores from 3.6 to 6.2 nm throughout the entire volume of the sample. Total porosity of the samples ranges from 70 to 98%, and specific surface areas from 170 to 300 $\text{m}^2 \text{g}^{-1}$ can be reached. The mesopore characteristics can be adapted by modifying the particle size and the freezing rate. However, the mechanical properties are not sufficient for application as catalyst carriers. An alternative method based on wash-coating a mechanically resistant ice templated monolith is described. These monoliths have 64% porosity and straight, continuous, 4.5 μm diameter channels. Uniform 100 to 200 nm thick coatings, with a 360 $\text{m}^2 \text{g}^{-1}$ specific surface are deposited without altering the initial mechanical strength of the monolith: 134 ± 30 MPa. We expect such architectures, combining high specific surface area, low pressure drop, and high mechanical strength, to be of special interest as catalyst carriers.

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Ceramics with porosities defined and controlled at multiple length scales are currently investigated for various energy-related applications. In fixed bed reactors, for example, catalytically active particles or porous pellets are packed in the reactor volume and only the easily accessible part of the catalytic sites are chemically active. Simply decreasing the particle size in order to increase the available catalytically active surface necessarily decreases the pore size, which corresponds to the inter-particles space in this case. This results in an excessive increase of the pressure drop across the catalytic bed making it unsuitable for some applications. Currently, the solution to this problem has been using packed beds of porous pellets in which the catalytic phase is dispersed on the internal surface of the pellets. However most conventional porous pellets used in packed bed reactors have a monomodal porous structure. With such microstructures, it is thus difficult to combine at the same time a high dispersion of the catalyst and a low diffusion path for the reactant. It is therefore of interest to use a hierarchical pore system comprising macro-, meso-, and/or micropores. Meso- and micropores will provide high specific surface area, required for a good dispersion of the catalytic sites. Macropores are necessary for rapid fluid distribution and pressure drop limitation. Their size, shape, and interconnectivity must be controlled in order to facilitate both mass transport through the macrochannels and local diffusion to the catalytic sites. Monoliths with monodispersed macroporous channels on the order of a few to tens micrometers, oriented along the flux of reactants and products, are thus of particular interest if they can be connected to high surface area mesopores. This configuration should allow rapid access to the catalytic sites, advantageous diffusion path, and limited pressure drop.

Ice templating is a simple way of making such macroporous channels in a pellet. In this process, first reported for ceramics by Fukasawa *et al.*,¹ unidirectional freezing of an aqueous suspension or gel triggers ice crystal growth along a thermal gradient. Rejection of the particles by the growing crystals concentrates the particles between the ice crystals. Subsequent sublimation of the ice leads to a porous body where the porosity is the replica of the ice crystals. The morphologies and characteristics of the ice crystals depend on the process and formulation parameters. As ice templating is mostly based on physical interactions and mechanisms, materials can be templated independently of their nature. To date, metals, polymers, and ceramics starting either from slurries, suspensions or gels have been ice-templated. Several reviews of this process give a detailed description of the process and its potential applications.^{2, 3}

Hierarchically porous silica obtained by ice templating has been investigated by Nishihara and Mukai.⁴⁻⁶ Starting either from hydrocolloids or hydrogels, they obtained silica monoliths with 10–15 μm sized macropores possessing micro- and mesoporosity

resulting from the packing of the colloidal silica particles between the ice crystals. Ice-templated systems of mixed nanoparticles with specific properties were also investigated, adding zeolites, graphite, or photo-catalytically active TiO_2 to the colloidal silica, which in this case acted as a binder.⁷ Mixed alumina-silica⁸ and titania-silica monoliths⁹ were also reported. Ohshima and coworkers¹⁰ introduced monodispersed poly[styrene-(*co*-2-hydroxyethyl methacrylate)] latex particles into a silica sol and obtained a beautiful reverse opal structure in the walls between the macroporosity.

However, there is only limited work on hierarchical ice-templated alumina or boehmites. Winnubst and coworkers¹¹ reported meso-macroporous alumina monoliths starting with a mixture of sub-micrometer sized α -alumina and nanometer sized γ -alumina. The nanosized γ -alumina is used as a binder; the samples consequently do not require freeze-drying and can be dried under room pressure and temperature conditions.

In the present work, we investigate the ice templating of nanosized boehmite particles aqueous suspensions, chosen for their wide use as catalyst carriers.¹² More specifically, the impact of the boehmite particle size and the freezing speed on the porous structure is investigated. An alternative method is described, to produce monoliths with hierarchic porous structure resulting from the deposition of a mesoporous boehmite washcoat in sintered ice-templated monoliths.

1. Experimental

1.1. Boehmite Micromonoliths with Mesoporous Walls

Boehmite micromonoliths with mesoporous walls are manufactured by directional freezing of boehmite suspensions and gentle thermal treatment to avoid densification by sintering. Three types of boehmite powders were tested: Disperal, Catapal B from Sasol, and boehmite synthesized following the procedure described by Yoldas.¹³

Suspensions of Disperal and Catapal B are prepared by dispersing 35 wt% of the commercial powder in deionized water (DI). The suspension pH is adjusted to 4 using nitric acid (69 wt%, Sigma–Aldrich). Dispersion is promoted by ultrasound application.

Colloidal boehmite is synthesized following the Yoldas method. 3.7×10^{-2} mol of aluminum tri-sec butoxyde (Sigma–Aldrich, 97%) is first refluxed with 34 ml of DI water. After 15 min refluxing at 90 °C, 2.6×10^{-3} mol of nitric acid (Aldrich, 69%) is added for peptization. A transparent sol is obtained and refluxed for 45 min.

The suspension is poured into PTFE moulds and cooled from the bottom using a copper rod cooled by liquid nitrogen. The cooling rates are adjusted through a thermocouple and a ring heater placed around the copper rod. After complete freezing, ice crystals

are removed by sublimation using a commercial freeze dryer (FREE Zone 2.5Plus, Labconco, Kansas City, Missouri, USA). The samples are maintained at low temperature ($-82\text{ }^{\circ}\text{C}$) and reduced pressure (0.42 mbar) for at least 48 h in order to ensure complete removal of the ice crystals. The boehmite samples were then thermally treated at $550\text{ }^{\circ}\text{C}$ for 2 h. Throughout the paper, the samples are referred to using the starting boehmite powder and the freezing speed.

1.2. Zirconia Micromonolith with Mesoporous Boehmite Layer

In a first step, yttria stabilized zirconia (YSZ) monoliths are prepared following the experimental procedure described in ref. ¹⁴. The as prepared zirconia suspensions are poured into a 21.5 mm diameter and 25 mm height PTFE mould. Freezing and sublimation are performed as described previously. Samples are thermally treated at $1350\text{ }^{\circ}\text{C}$ for binder removal and sintering. The sintered monoliths are machined to a 5 mm thickness. To remove cutting debris, they are extensively cleaned ultrasonically with large quantities of DI water.

These sintered zirconia monoliths are washcoated with a boehmite suspension, prepared by dispersing commercial boehmite powder (Disperal, Sasol) in DI water. Dispersion is promoted by ultrasound and pH adjustment to 3.5 with nitric acid (69 wt%, Sigma–Aldrich). A binder solution containing polyethylene glycol (PEG2M, Sigma–Aldrich) and isopropanol is then added. Final mass percentages are: 2.29 Disperal/90.64 DI water/0.55 PEG2M/6.52 Isopropanol. Washcoating is performed by immersing the YSZ monoliths into the boehmite suspension under vacuum. This serves to outgas the air from the channels of the monolith and promote suspension infiltration. After this washcoating step, excess solution is eliminated from the monolith surfaces and the sample is dried in a controlled atmosphere oven at $40\text{ }^{\circ}\text{C}$ and 80% relative humidity. The samples are thermally treated at $550\text{ }^{\circ}\text{C}$ for 2 h.

1.3. Sample Characterization

Dispersed particle size is measured by quasi elastic light spectroscopy (Zetasizer, Malvern), by dilution of the slurry used for ice templating at constant pH. Specific surface area and pore size distributions are determined using nitrogen adsorption/desorption at 77 K (Micromeritics-ASAP 2010) after outgassing at $280\text{ }^{\circ}\text{C}$ for at least 2 h. Hg intrusion is measured using an AutoPore IV from Micromeritics, the pressure range varied between 0.44 and 30 000 psi. SEM observations are performed using either a TM1000 from Hitachi or a Nova NanoSEM 230 from FEI. Boehmite samples made following the first method are prepared by cutting the frozen monoliths at half height before lyophilization and thermal treatment. Samples obtained following the second method were either machined (views perpendicular to freezing direction) or

fractured (views along freezing direction) after thermal treatment. Transmission electron microscopy (TEM) observations are performed on crushed samples on a FEI Tecnai G2 20. Compressive strength (test equipment from Lloyd) was measured on five samples (10 mm diameter for a 15 mm height), with a 150 kN sensor and a crosshead speed of 0.5 mm s^{-1} .

2. Results and Discussion

In a first approach, hierarchical micromonoliths with mesoporous walls are synthesized by directional freezing of boehmite suspensions. The impact of the powder granulometry on the mesoporosity is studied using powders with increasing size in the nanometer-range: commercial powders from Sasol (referred to hereafter by “Catapal” and “Disperal”) as well as a boehmite suspension synthesized following Yoldas method (referred to hereafter by “Yoldas”). The mean particle sizes of dispersed Catapal and Disperal, as indicated in the technical data sheet from Sasol, are, respectively, 100 and 80 nm. A 28 nm particle size value is measured for the Yoldas powder, using quasi-elastic light scattering.

Using aqueous suspensions of these powders, monoliths are frozen at a constant freezing rate of $10 \text{ } \mu\text{m s}^{-1}$. A gentle heat treatment at $550 \text{ } ^\circ\text{C}$ is chosen to avoid the sintering and transformation of the boehmite into α -alumina. The final porosity characteristics are thus directly related to particle packing during the freezing process. The ice crystallization seems to occur similarly for the three powders, yielding elongated and highly dendritic macropores, as shown on the SEM images in Figure 1. A lamellar macroporous structure is obtained at the micrometer scale with a mean pore width of approximately $10 \text{ } \mu\text{m}$. These values are confirmed by Hg intrusion measurements: the measured mean macropore diameters for Catapal and Disperal samples are, respectively, 10 and $10.3 \text{ } \mu\text{m}$. The use of commercial powders with larger particle size leads to denser walls than Yoldas samples. In this case, the primary macropores are separated by bundles of sheets generating a second level of macropores. Due to lower mechanical resistance towards the Hg pressure, the macropore size was not assessed with Hg intrusion. It can be noticed that for the monolith produced from the Catapal powder, dendrites are only situated on one side of the sheets, whereas in the case of Yoldas, the sheets appear smooth.

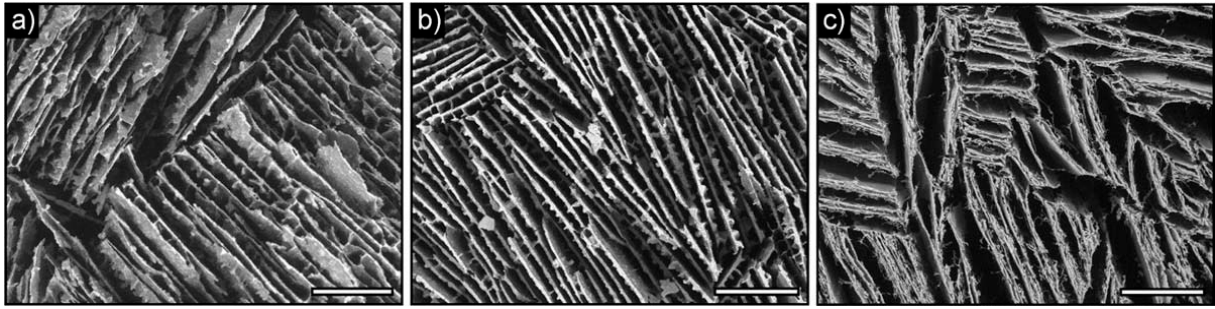


Figure 1 : SEM images of ice templated monoliths manufactured using (a) Catapal B, (b) Disperal, and (c) Yoldas. Scale bars 250 μm .

Mesoporosity is assessed by N_2 adsorption–desorption measurements (Figure 2). The resulting textural properties together with particle size and freezing conditions are summarized in Table 1. As expected, increasing the particle size leads to a decrease of the specific surface area of the monoliths from 292 to 174 $\text{m}^2 \text{g}^{-1}$. High values of specific surface area are measured for all starting boehmite particles, showing that loose contact occurs between particles in the monolith walls. The mesopore diameter calculated from N_2 adsorption–desorption measurements is, respectively, 4.8, 5.4, and 6.2 nm for Yoldas, Disperal, and Catapal monoliths, but otherwise pore volume of the walls is equivalent for the three types of boehmite powders. When Yoldas boehmite particles are used as the starting material, a typical type IV isotherm is obtained (Figure 2). The initial part of the isotherm indicates the presence of microporosity, unlike Catapal and Disperal samples. In Figure 2b, one can see that mesopore size distribution is narrow for Yoldas and much larger for Catapal and Disperal monoliths. This can explain why the pore volume is almost constant due to the contribution of the largest pore size. A TEM image (Figure 3) of a Yoldas monolith obtained at a freezing speed of 10 $\mu\text{m s}^{-1}$ shows the mesoporous structure of the walls formed by the nanosized Yoldas particles. The pore size is in agreement with the value obtained from N_2 adsorption–desorption whereas typical platelet morphology of boehmite particles can be seen on this image.

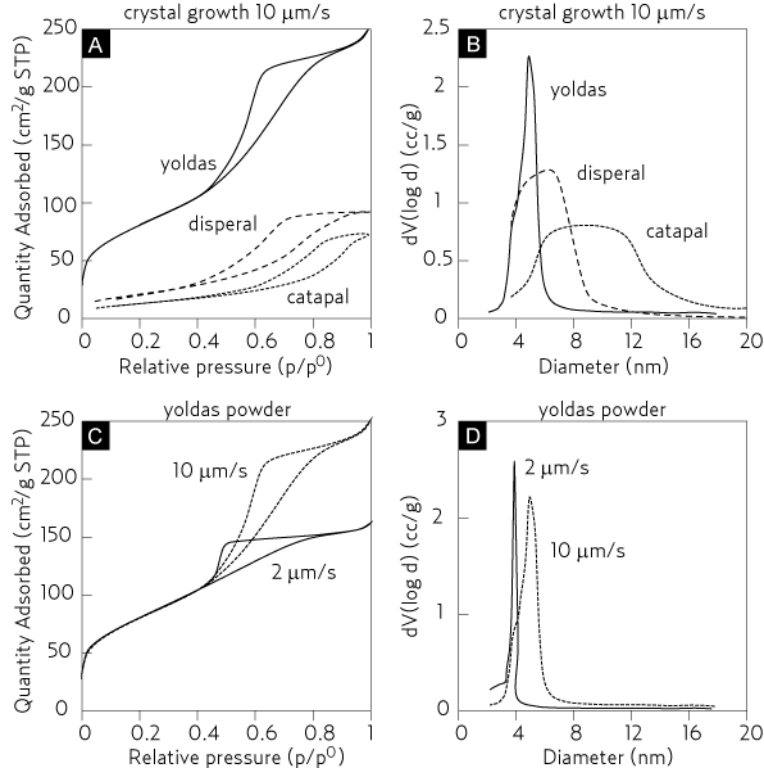


Figure 2: N₂ adsorption/desorption isotherms and corresponding pore size distribution. (a, b) Impact of boehmite powder: Yoldas, Dispersal, and Catapal powders. (c, d) Impact of freezing kinetics, crystal growth velocity of 2 and 10 μm s⁻¹.

Table 1. Particle size, freezing conditions, and samples characteristics.

| Boehmite powder | Dispersed particle diameter [nm] | Ice front velocity [μm s ⁻¹] | SSA [m ² g ⁻¹] | Mesopore diameter [nm] | In-wall pore volume [cm ³ g ⁻¹] |
|-----------------|----------------------------------|--|---------------------------------------|------------------------|--|
| Yoldas | 28 | 2 | 293 | 3.6 | 0.20 |
| Yoldas | 28 | 10 | 292 | 4.8 | 0.37 |
| Disperal | 80 | 10 | 224 | 5.4 | 0.39 |
| Catapal | 100 | 10 | 174 | 6.2 | 0.38 |

The freezing speed, or correspondingly the ice crystal growth velocity, impacts the redistribution and packing behavior of the particles. In the case of Yoldas boehmite suspensions, decreasing the freezing speed from 10 to 2 μm s⁻¹ decreases the pore diameter from 4.8 to 3.6 nm. The corresponding pore volume of the walls also decreases from 0.37 to 0.20 cm³ g⁻¹ showing that lower freezing speed allows particles to arrange in a closer manner. As reported in Table 1, the specific surface area is not affected by this reorganization of the porous structure. One explanation could be the contribution of the microporosity, almost identical for both samples. These ice-templated monoliths exhibit a high specific surface area and a hierarchic porosity, which are of potential interest for catalyst carriers. However the one step process used for their preparation

leads to very brittle pellets with insufficient mechanical strength for applications in a catalytic bed.

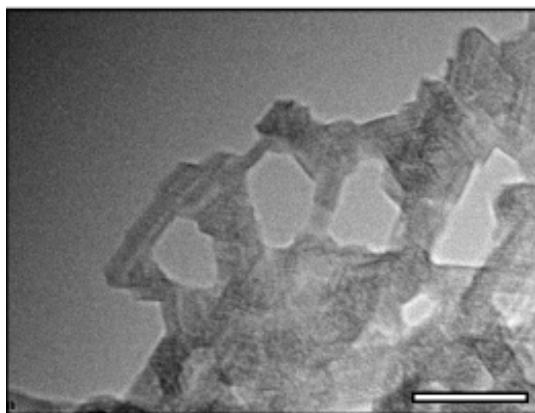


Figure 3 : TEM image of the wall mesoporous structure in a Yoldas monolith obtained at a freezing speed of $10 \mu\text{m s}^{-1}$. Scale bar 10 nm.

We therefore propose an alternative method to combine the unique macroporous structure of the ice templated ceramic monoliths and the requirement of high surface area for the active catalytic sites. High mechanical strength monoliths are produced by wash coating mesoporous boehmite layer on a sintered ice templated monolith. This strategy yields pellets combining large continuous macropores, providing access to the catalyst without the usual large pressure drop and lowering the diffusion path, while the boehmite washcoat provides high specific surface area needed for a good dispersion of the catalytic sites. Ice templated YSZ monoliths with a particular macroporosity are used as substrates for the boehmite coating. As recently described by Deville *et al.*,¹⁴ the use of specific ice-shaping compounds in the ice-templating process leads to a honeycomb-like structure with hexagonally shaped pores running continuously throughout the monoliths (Figure 4a and b). The macropores exhibit a smooth and dendrites-free surface (Figure 4d), optimal to minimize the pressure drop. The mean macropore diameter as determined by Hg intrusion is $4.5 \mu\text{m}$, with a narrow pore size distribution (Figure 4c). The measured compressive strength for such monoliths with 64% macroporosity is $134 \pm 30 \text{ MPa}$. In addition, high temperature sintered zirconia are known for their high abrasion resistance. All these characteristics make this substrate well adapted as catalyst carrier pellets for fixed-bed reactors. These substrates are washcoated under reduced pressure using a boehmite suspension to obtain a mesoporous structure. The Disperal powder was chosen to produce mesoporous coatings with high specific surface area. As shown by SEM images in Figure 4, a 100–200 nm thick homogeneous coating is obtained at the surface of the macroporous ice-templated structure. The thin coating only marginally affects the macropore size. The SEM images in Figure 4e–f show close up views of a fractured wall. The YSZ ice-

templated monolith appears as light grey, while the porous boehmite is darker. The coating thickness is indicated by arrows. Specific surface area of the monoliths before and after washcoating increases from 0.2 to 3.8 m² g⁻¹. The boehmite coating represents 1% of the total monolith mass; the SSA of the coating thus can be estimated to be 360 m² g⁻¹. Low transport resistance of the reactants and short diffusion paths to the catalytic sites are expected from pellets based on this architecture. Work is currently under progress for precious metal deposition and catalytic performance evaluation.

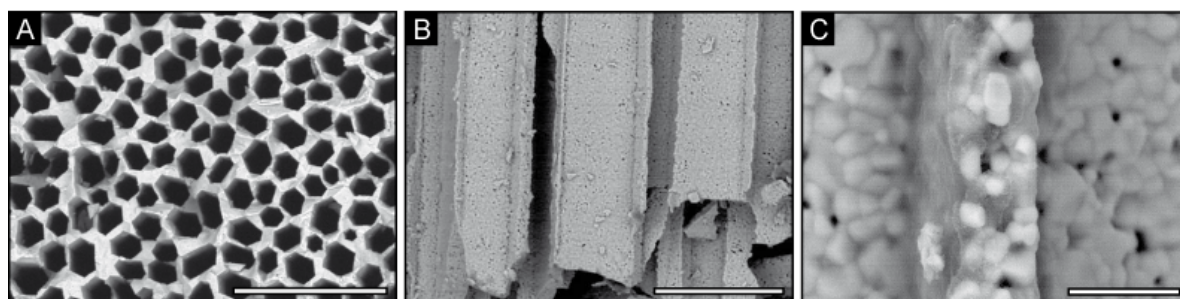


Figure 4 : Macroporous YSZ ice templated monoliths (a) macroscopic view (b) SEM micrograph perpendicular to ice solidification direction, showing the macroporous channels (c) mercury porosimetry results (d) SEM micrograph along ice solidification direction (e) SEM micrograph of the monolith washcoated with boehmite (f) close-up view of the washcoat, the arrows indicates the thickness of the coating. Scale bars (b) 50 μm , (d) 20 μm , (e) 2 μm , and (f) 250 nm.

3. Conclusions

Combining high surface area, accessibility to catalytically active sites, and mechanical strength is a tough requirement for many catalytic carriers. We demonstrate that approaches based on ice-templating can address this requirement, in particular for the fabrication of pellets used in fixed-bed reactors. Boehmite micromonoliths with a hierarchic porosity can be obtained using a one-step process although the mechanical properties do not meet the application requirements. We demonstrate a two-step process in which an ice-templated support with microchannels is prepared, followed by the deposition of a thin mesoporous layer inside the channels. High mechanical resistance, hierarchic porosity, and high specific surface area for catalyst dispersion can thus be advantageously combined. Although the functional catalytic properties remain to be assessed, the combination of continuous and calibrated macropores channels, high strength, and large amount of meso- and micropores is appealing for such applications.

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Table 1: Particle size, freezing conditions and samples characteristics

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