Processing and performance of zeolites for efficient carbon dioxide separation
Arto Ojuva
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Arto Ojuva
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Department of Materials and Environmental Chemistry
Stockholm University
SE-10691 Stockholm
Sweden

Cover illustration:
Schematic illustration of a mixture of carbon dioxide, which is selectively adsorbed, in nitrogen, which flows through a freeze-cast monolith.

Faculty opponent:
Professor Viveka Alfredsson
Department of Chemistry
Lund University

Evaluation committee:
Professor Håkan Engqvist
Department of Engineering Sciences
Uppsala University

Docent Mattias Grahn
Department of Civil, Environmental and Natural Resources Engineering
Luleå Technical University

Dr. Feifei Gao
Department of Materials and Environmental Chemistry
Stockholm University

Substitute:
Muhammet Toprak
Division of Functional Materials
KTH

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“How can I tell what I think
till I see what I say?”

*E M Forster*
Abstract

We have structured zeolites from powders of zeolite 13X and 4A into hierarchically porous monoliths for efficient carbon dioxide capture by tailoring the pore dimensions to facilitate rapid gas uptake and release. Freeze-casting was used for the first time to shape adsorbents into a lamellar structure. Lamellar walls with thicknesses and spacing in the range of 10 µm were found to be the best combination between rapid gas transport and a short diffusion distance in the zeolite-containing walls for rapid carbon dioxide uptake and release.

Compressive strength measurements of the freeze-cast zeolite-based monoliths showed that monoliths with small pores, thin walls and a lot of interconnectivity between the walls were stronger than monoliths with large pores and thick walls. Image analysis of the structures together with modelling of the deformation behavior suggests that the failure mechanism of freeze-cast monoliths is dominated by buckling.

Binder-free zeolite Y and ZSM-5-based monoliths were produced by pulsed current processing (PCP) into strong, hierarchically porous monoliths with minimal loss of crystallinity. Ranges for the maximum PCP processing temperatures for the zeolites with different aluminium contents were identified by powder x-ray diffraction (PXRD) with full-profile fitting analysis.

Matching the thermal expansion behavior of the supports with the zeolite film is important to minimize the risk of thermally induced cracking of zeolite membranes. Zeolite supports with a macroporous structure was prepared by PCP and the thermal expansion coefficient was determined by PXRD and compared to traditional alumina substrates. It was found that the slightly negative thermal expansion coefficient of the zeolite supports matched the thermal expansion of the zeolite films very well, whereas the alumina support would induce large stresses upon fluctuating temperatures.

Methylcellulose-directed synthesis of zeolite 4A produced nano-sized crystals with a narrow size distribution, which could be tuned by adjusting the methylcellulose content. The crystallinity of the synthesized 4A was controlled by PXRD and found to be very high, and the gas uptake capability performed well in comparison with available micron-sized zeolites.
List of publications


   I did the planning, writing and data analysis with assistance from the co-authors, all practical work, excluding the compressive testing which was performed by co-authors and the gravimetric uptake measurements which were outsourced to Institut für Nichtklassische Chemie, Leipzig, Germany.


   I did the planning and writing with assistance from co-authors. I also prepared the majority of the structured zeolite monoliths and ion-exchange of the zeolites, analyzed the breakthrough data and combined and analyzed the results from image analysis and strength measurements.


   In this study, which was based on my diploma thesis, I analyzed the densification during PCP and did the PXRD measurements and full-profile refinement.


   I studied the PCP-processed supports, commercial alumina supports, and membrane material with in-situ PXRD analysis and, with the help of full-profile fitting, calculated the thermal expansion coefficient of the materials and components.


   I assisted with the writing and performed the PXRD analysis of the nanocrystals.
Publications not included in this thesis:


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## Abbreviations

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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>CCS</td>
<td>Carbon dioxide Capture and Storage</td>
</tr>
<tr>
<td>D4R</td>
<td>double four-membered ring</td>
</tr>
<tr>
<td>dwb</td>
<td>dry weight basis</td>
</tr>
<tr>
<td>FAU</td>
<td>Faujasite</td>
</tr>
<tr>
<td>LTA</td>
<td>Linde Type A</td>
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<tr>
<td>MFI</td>
<td>Mobil Flve</td>
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<tr>
<td>MTZ</td>
<td>mass transfer zone</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular Weight</td>
</tr>
<tr>
<td>PCP</td>
<td>Pulsed Current Processing</td>
</tr>
<tr>
<td>PEG</td>
<td>Poly Ethylene Glycol</td>
</tr>
<tr>
<td>PSA</td>
<td>Pressure Swing Adsorption</td>
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<tr>
<td>PXRD</td>
<td>Powder X-Ray Diffraction</td>
</tr>
<tr>
<td>QPA</td>
<td>Quantitative Phase Analysis</td>
</tr>
<tr>
<td>SBU</td>
<td>Secondary Building Unit</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
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\( m_\infty \)  
equilibrium uptake
\( a \)  
major cross-sectional axis of a pore
\( a' \)  
empirically determined rheology scalar
\( A_w \)  
cross-sectional area of the wall \((d \times a)\)
\( b \)  
minor cross-sectional axis of a pore
\( b' \)  
empirically determined rheology factor
\( C \)  
empirical deformation constant
\( d \)  
cross-sectional wall thickness
\( D_c \)  
diffusion coefficient in a spherical crystal
\( E \)  
elastic modulus
\( I \)  
moment of inertia
\( k' \)  
degree of constraints for the attachment points of the wall
\( L \)  
length of a wall section
\( m \)  
Weibull modulus
\( m_t \)  
uptake at time \( t \)
\( M \)  
mass of the formula unit
\( n \)  
a flow parameter
\( p \)  
pressure
\( P_s \)  
probability of survival
\( q \) empirical surface roughness factor  
\( r \) radius  
\( S_j \) scale factor for phase \( j \)  
\( t \) time  
\( V \) volume of the unit cell  
\( W_j \) weight fraction for phase \( j \)  
\( Z \) number of formula units per unit cell  
\( \alpha \) linear thermal expansion coefficient  
\( \gamma \) surface tension  
\( \eta_r \) relative viscosity  
\( \theta \) angle incident radiation relative to the sample surface  
\( \theta_c \) contact angle between a liquid and a solid  
\( \rho \) density  
\( \rho_s \) density of a bulk material  
\( \sigma \) compressive strength  
\( \sigma^* \) compressive strength of a porous monolith  
\( \sigma_0 \) characteristic strength for which the survival probability is \( 1/e \)  
\( \sigma_{el} \) elastic buckling strength  
\( \sigma_s \) compressive strength of a bulk material  
\( \varphi \) solids loading of a suspension  
\( \chi \) pore cross-sectional aspect ratio \((a/b)\)
Introduction

The need for carbon dioxide capture

We are doing better than ever before. Human kind is progressing in numbers, life expectancy and scientific and technological achievements, but while we are gaining ground with new advances, we also do need to keep up with our energy output in order to sustain development. Our most abundant energy source by far is the sun, which supports and bolsters Earth’s biomass that is dependent on photosynthesis.

The most straightforward way for humans to utilize the energy from the sun has traditionally been to harvest either the biomass or its condensed and fossilized form, such as oil and coal, and burn it. However, with our energy demands escalating since the beginning of the industrial era, combustion of fossil fuels has started to make a global impact. Combustion produces mainly water and carbon dioxide, both of which are very stable molecules, but while water will eventually condense and rain down, carbon dioxide has a tendency of accumulating in the atmosphere. As was concluded as early as 1896 by Svante Arrhenius,\textsuperscript{1} atmospheric carbon dioxide does affect the heat balance of Earth, and this has been corroborated by more current research, summarized in five comprehensive assessment reports by the Intergovernmental Panel on Climate Change since its founding in 1991. The energy supply sector is the largest contributor to global anthropogenic greenhouse gas emissions. More specifically, coal combustion is responsible for a major part of it, with emissions averaging to 1 kg of carbon dioxide equivalent gases per kWh of electricity.\textsuperscript{2}

There are a number of alternative energy production methods where the amount of released carbon dioxide is reduced or eliminated, such as solar-, wind- and hydropower, nuclear power, natural gas and also biofuels where the combustion material is taken from regenerating biomass rather than carbon stored in oil deposits. While many developed countries have the luxury of choosing between these alternatives, many emerging economies have no choice but to implement the cheapest form of power generation available, or leave people without energy. Even in Europe and the USA there are still a number of coal-burning power plants with high emission rates: a medium-sized coal power plant operating at 500 MW will generate almost 500 tonnes of carbon dioxide every hour. Thus, a first obvious step to mitigate the growing emissions of carbon dioxide would be to target point sources of high
emission density, such as coal-fired power plants, refineries, cement plants and steel mills$^{2-6}$ with carbon dioxide emission exceeding roughly 0.1 Mt/year, and capture the carbon dioxide from their flue gas stream (Figure 1), which consists mainly of nitrogen and typically has a carbon dioxide content of 10-15%. The captured carbon dioxide could, as a first step, be injected into a suitable geological structure, at least 800 m below surface, where the pressure will be so high that it will assume a liquid form.

\[ \text{Figure 1: Retrofitting a coal-burning power plant with a selective carbon dioxide separation unit (orange cylinder).} \]

**Post-combustion capture**

Unless carbon dioxide can be utilized, post-combustion separation of carbon dioxide from flue gas (nitrogen) is not adding anything of immediate value. Hence, it has to be motivated either by legislation or by financial means, such as an implementation of an emission tax or a reimbursement. The ideal solution, however, would be to combine the carbon dioxide capture and utilization (CCU), and use the separated product, chemically pure carbon dioxide, to produce useful chemicals and fuels.$^{7,8}$ Carbon dioxide is already being widely used for example in fire extinguishers, or as a protecting gas and as a refrigerant in food industry. The use of supercritical carbon dioxide as a solvent in advanced material synthesis has also been attracting increasing interest.$^{9-11}$ A successful separation will produce carbon dioxide in vast amounts, and a future challenge will indeed lie in finding the pathways to utilize it.

The separation has nevertheless to be as inexpensive as possible, using low-cost materials with small or no maintenance or running costs, resulting in a capture of at least 90-95% of the carbon dioxide. Various technologies have been proposed, including cryogenic separation$^{12}$ and amine scrubbing,$^{13}$ but both of these methods are associated with a large energy cost either to
perform the separation or to regenerate the separation medium. Solid sorbents with a high surface area have an advantage in that they have a high selectivity but still a relatively weak physical interaction to carbon dioxide. Solid sorbents can stand thousands of adsorption/desorption cycles as they are, and are normally neither hazardous nor toxic. They are therefore a strong candidate as a choice for a robust and well-established separation technology. Potential sorbent materials include metal-organic frameworks, mesoporous silica, microporous silicates, porous polymers and activated carbon, with zeolite adsorbents being probably the most well-known and widespread group of adsorbents that is already in use within many applications of gas separation.

The capture occurs mainly by physisorption, which demands relatively little energy for the regeneration of the adsorbent, typically 40-50 kJ/mol of adsorbed species. Among the most studied materials for carbon dioxide capture are the low-cost zeolite 13X and zeolite 4A, both possessing a good combination of high carbon dioxide uptake capacity, high carbon dioxide over nitrogen selectivity, and good thermal and mechanical stability.

One notable disadvantage with zeolites 13X and 4A is that they are very hygroscopic, a result of their high aluminium content which also increases their acidity. Although a trace amount of water has been shown to increase the uptake of carbon dioxide in zeolites, a gas flow with a high concentration of wet gas, such as unprocessed flue gas, can result in water getting selectively adsorbed in the zeolite, which in turn may hinder the uptake of other gas molecules. It is also well-known that water will slowly degrade the typical zeolites and zeolite-binder composite pellets, which will have adverse effects on the gas transport through the bed. Therefore, carbon capture from flue gases using beds of 13X or 4A will greatly benefit from a preceding dehydration step. Other zeolites with less hydrophilic character, such as zeolite Y or ZSM-5, do not suffer that much from interactions with water, but they have also smaller affinity towards carbon dioxide.

The gas separation in a pressure swing adsorption (PSA) process is achieved by leading the flue gas through a sorption column. The set-up typically consists of several sorption columns operating in parallel, where one (or several) is adsorbing while another (or others) is being purged and regenerated, in order to keep up with the continuous incoming gas flow. The sorption column, typically several cubic meters in volume, is loaded with the adsorbent in a suitable form. The gas mixture (flue gas) is let in from one end, and while it passes through the adsorption column, one species (carbon dioxide) will be selectively adsorbed while the other one (nitrogen) will pass through. Just before the carbon dioxide would break through on the opposite end and the bed is saturated, the column is closed and purged by drawing a vacuum, which will desorb the carbon dioxide, and a counter-current of a purge gas (nitrogen) is flowed against the initial direction in order to clean the bed. When the bed is purged, the flue gas is once again let in and a new
cycle is started. The cycle time depends on the application, regular PSA cycles are in the order of 10 minutes, while a rapid PSA cycle is normally 30 seconds or less.\textsuperscript{44} 

\section*{Structuring of the adsorbent}

The adsorbent in a pressure swing adsorption unit is usually in the form of small extruded rods or beads (2-5 mm),\textsuperscript{20,45} which are placed on trays or packed as a bed in the adsorption column. During separation of vast volumes of gas, such as the flue gas from a coal-based power plant, the column has to allow for large volumes of gas to pass unhindered. Therefore, a packed bed with narrow, tortuous passages will not do; the column has to rely on smart design, such as a rotating bed system,\textsuperscript{46} or simply an effective packaging of the adsorbent which utilizes the entire volume of the adsorbent. Cost-effective gas separation will gain advantage from shaping of the adsorbent powder into a shape which allows for high flow and rapid mass transfer, and is at the same time mechanically strong enough to be able to resist the gas flowing back and forth.\textsuperscript{47,48} 

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{A packed bed of granules (left) and lamellar sheets (right). The granules are easy to make and pour in the cylinder, but the lamellar structure will provide unhindered flow and rapid saturation of the sheets, leading to improved efficiency.}
\end{figure}

Structured adsorbent materials have recently attracted increased interest, and laminate structures, such as are shown in Figure 2, have been predicted to be the ultimate solution for adsorbent packaging needs.\textsuperscript{48-51} The laminate walls should be thin in order to minimize the diffusion time to the middle of the sheet, and ideally they should not be separated by more than 200 µm in order
not to contain too much void space. In this way, the adsorbent loading, external surface area and the flow will be optimized.

The structuring of self-supported adsorbents can be done by a range of methods; one can extrude honeycombs\textsuperscript{52}, make ceramic foams\textsuperscript{53}, or use sacrificial templating\textsuperscript{54,55} where the template can be polymers\textsuperscript{56}, surfactants\textsuperscript{57}, carbon\textsuperscript{58}, sponges\textsuperscript{59} or ice\textsuperscript{50}. Ice templating, commonly known as freeze-casting, is an emerging approach to produce monoliths with an ordered open porosity and a lamellar or columnar structure. Figure 3 shows that directional freezing of a ceramic suspension results in oriented segregation of ice crystals and dense particle-rich domains. The ice can be separated by subliming the ice, resulting in a porous powder compact which can be heat treated to increase the mechanical strength. The increase of the volume during water to ice transformation exerts a pressure to the particle-rich domains, which is enough to densify them but without doing any damage, as might otherwise be the case with uniaxial pressing\textsuperscript{61}. By controlling the suspension concentration and cooling rate, the mean size and shape of the formed pores can be tuned within certain limits\textsuperscript{62–64}. A lot of research has been done in preparing strong porous scaffolds and bioceramics\textsuperscript{65,66}, but reports on the use of freeze-casting to shape structured adsorbents are still sparse\textsuperscript{67}.

![Figure 3: The essential part of a freeze-casting unit is a mold where an adsorbent suspension is frozen from the bottom. An image, pooled from several scanning electron micrographs, shows the resulting oriented ice-templated structure.](image-url)
Zeolites and CO₂ separation

Microporous crystalline aluminosilicates, or zeolites, were discovered in their natural form by Axel F. Cronstedt in 1756. He noticed that his new-found mineral Stilbite frothed when heated, which was caused by boiling of adsorbed water in its pores. He then called them for a “ζεω λιθος”, a “boiling stone” in Greek. The pores, inherent in the crystal structure, are the heart and core of zeolites, and have found numerous applications in many fields such as laundry detergents, oil refining and petrochemical industries, adsorbents, gas separation, agriculture, etc. The International Union of Pure and Applied Chemistry defines all pores below 2 nm as micropores, 2-50 nm as mesopores, and above 50 nm as macropores. All zeolites, which traditionally may contain only silicon, aluminium and oxygen in their framework, belong to the category of microporous materials.

Zeolites are composed of corner-sharing tetrahedra with aluminium(+III) or silicon(+IV) as the central atom and oxygen at the corners. From that simple primary building unit a number of secondary building units (SBUs) can be created, and the arrangement of the SBUs, together with a structure-directing agent during the synthesis, results in the formation of the zeolite with a well-defined framework. The framework is crystalline with a translational symmetry, and has an extremely well-defined pore structure. The pore sizes typically range between 0.3 and 1.0 nanometres with very small variations in the pore dimensions, less than 0.01 nm.

The number of ways that the silicon or aluminium – oxygen tetrahedra and their SBUs can be combined is very large, and in order to keep track of them a database has been established of the found framework structures by the Structure Commission of the International Zeolite Association. The
number of unique frameworks is steadily increasing, during the time it took to write this thesis it grew from 218 to 225.

An example of a framework, Faujasite, is shown in Figure 5. The framework only describes the connectivity of the tetrahedra, showing only the central atoms and omitting the oxygen atoms, and it doesn’t concern with the Si/Al loadings of the structures. Thus there are many more zeolites than frameworks, since, for example, the framework Linde Type A (LTA) is available as 3A, 4A or 5A, depending on the charge-balancing cation, and Faujasite (FAU) is known as HSX (High-Silica X), zeolite Y or zeolite X, depending on the Si/Al-ratio.

![Figure 5: A Faujasite framework (zeolites 13X and Y), showing the accessible pores and kinetically inaccessible cages (close-faced polyhedra). For simplicity, only the tetrahedral central atoms (Si or Al) are shown, the bridging oxygen atoms have been omitted. The blue area shows the supercage inside the framework, the open accessible window size is 0.9 nm.](image)

A zeolite can consist only of silicon and oxygen, and some frameworks have been constructed with this composition (for example Silicalite-1, HSX, ITQ-29), but typically zeolites always have some aluminium present, since it lowers the energy of formation. Many high-silica zeolites are made by leeching the aluminium out of the network after the zeolite is synthesized. Substitution of silicon(+IV) to the similarly sized aluminium(+III) results in a net negative charge of the framework, equal to the amount of aluminium present. This charge is usually compensated by cations, usually group I or II ions, or cationic molecules like NH$_3^+$, leading to weak Lewis (electron pair
acceptor) or strong Brønsted-Lowry acidic (hydrogen ion donor) sites.\textsuperscript{71,72} Bearing in mind that each aluminium atom adds one negative charge, the aluminium content is directly proportional to the acidic properties of the zeolite, directly influencing its hydrophilicity.

The aluminium content of zeolites is not unlimited. The bonding of the Al-O and Si-O networks favour Al-O-Si –bonds, and while Si-O-Si –bonds are possible, Al-O-Al bonding is typically not seen in zeolites. This is known as the Lowenstein’s rule, and a direct result of this is that the silicon to aluminium ratio (Si:Al) cannot be lower than 1.

The carbon dioxide capture properties of acidic zeolites are well-known,\textsuperscript{37,73,74} and the mutual exclusion of nitrogen, which is the dominant species in flue gas, makes acidic zeolites very promising as a material for carbon dioxide separation. The different affinity for the two gases stems to a large extent from the interaction between the zeolite’s acid sites and the quadrupole moment of the adsorbent molecule, which for carbon dioxide is nearly four times as high as for nitrogen.\textsuperscript{75}

Figure 6: Uptake of carbon dioxide on pure powders of 13X and 4A, and a comparison uptake of nitrogen on a freeze-cast 4A monolith (10.2% K-exchanged NaKA)

The field of microporous crystalline aluminosilicates, or zeolites, is rather large and no exhaustive discussion about zeolites in general is provided in this thesis. The interested reader can find plenty of good overviews over catalysis\textsuperscript{76} or adsorption in zeolites\textsuperscript{36} or more comprehensive works, such as the book from Čejka et al.\textsuperscript{77}
The aim of the work

This work has been motivated by the need to develop sustainable methods for carbon dioxide capture from large point sources, mainly coal-based power plants. The primary aim was to facilitate it through gas separation using pressure swing adsorption, which is an established and very promising technology for carbon dioxide capture. Next generation structured macroporous adsorbents are needed in order to meet the huge volumes of flue gas processed directly at the source. The structured adsorbents have to maintain a short diffusion time, and the macropores have to be accessible in dimensions suitable for rapid gas flow, while still keeping the volumetric packing of the adsorbent high. Therefore, to fully utilize their potential, the pores and walls alike should not exceed the lower micrometer range to ensure an uptake time in the order of seconds.

The goal of creating a new generation of structured adsorbents has to rely on affordable and preferably green methods in order not to create new problems. A promising approach was made via freeze-casting process, detailed in papers 1 and 2, where an aqueous suspension containing the active ingredients is frozen in a controlled fashion, so that the formation of ice packs the suspended particles into thin lamellar sheets in the micrometer range. The ice is then sublimated away, leaving a macroporous structure in the optimal size range for gas flow and uptake, and the challenge was to identify the conditions for creating an adsorbent monolith with rapid gas uptake and sufficient mechanical integrity. The choice and proportions of materials also had a large effect which was equal to the structural properties, since also the amounts of active and binding materials affect both the uptake and strength.

The monolith properties had also to be quantified in a relevant fashion. Measurements had to assess the whole monolith in a sufficient volume to include the effects coming from having a lot of material; measurements on the particle level would only characterize the material itself, not the structure it was formed into. The most important properties, gas uptake and strength, had to be quantified and linked to the structural parameters. A successful property determination, able to link together the structural parameters, uptake and strength, was therefore pursued.

Binderless routes to create macroporous monolith were another target, where the total volumetric capacity is more important than very fast gas transport. Although zeolites are normally sensitive to high temperatures and collapse before they are sintered, very rapid heating during only a few minutes will consolidate the zeolite particles without sacrificing the zeolite crystallinity. Finding the right conditions is an important task, and determining what changes in the zeolites and how during the treatment is a crucial goal. It is not enough to follow the dimensional changes in the consolidated body, such as shrinkage, but one has to quantify the relevant properties, such as surface area and crystallinity of the zeolite.
Gas separation can also be approached via membranes. Ceramic membranes, which selectively allow the passage of one type of molecule, are susceptible to thermally induced stresses and delamination. Preparing the support discs out of a material with similar thermal behavior to the membrane, such as a zeolite membrane on a support made out of another type of zeolite, will greatly reduce the thermal mismatch effects, and allow for an effective separation with little or no running costs. The characterization of the membrane support has to be focused on the thermal expansion, which, in the case of zeolites, is a complex relationship. Measurements of how the atomic coordinates in the crystals vary during heating were invaluable in following the thermal expansion properties.

The gas diffusion into the adsorbent material itself could also be improved by reducing the particle size. The synthesis of zeolite nano-crystals, which allow potentially for a much faster gas uptake than regular, micron-sized crystals, was therefore an obvious target for rapid carbon dioxide separation applications. Control over the particle size distribution was also important and novel synthesis systems with a confined space for nucleation and growth was an object for investigation. Characterization of the formed zeolites depended then, aside from size distribution determination, also largely on confirmation of their correct crystal structure and high crystallinity.
Materials and methods

Raw materials
Commercially available materials were chosen for freeze-casting, Figure 7. Zeolite 13X with a particle size of 3-5 µm and zeolite 4A with a particle size of 2-4 µm were obtained from Luoyang Jianlong Chemical Industrial Co., Ltd (Yanshi, Henan, China). Bentonite clay and the intermittent binder polyethylene glycol (PEG, MW = 8000) were both obtained from Sigma-Aldrich Chemie GmbH (Buchs, Germany). The water used in freeze-casting was regular de-ionized water.

Freeze-casting
The freeze-casting unit consisted of a vessel for liquid nitrogen with a protruding cold finger, which is essentially a copper rod that functions as the heat sink during freezing, Figure 8 a. The suspension to be freeze-cast was placed in Teflon die (20 mm inner diameter) that was mounted on a thin copper bottom piece, and the mold was placed on the top of the finger. The top also featured a thermocouple and a heater, both of which were connected to a control unit, allowing the user to control the temperature of the rod and change it according to a predetermined ramp (typically 0.5-20 °C/min).

The highest cooling rate practically attainable was found to be 20 °C/min, for which the time to freeze the contents of the mold was around 10 minutes, the rate was limited mainly by heat transfer in the copper finger and heat convection from air which would warm the protruding parts. The lowest cooling rate used was 0.5 °C/min, and although the cooling can theoretically...
go much slower, this took typically more than an hour and we felt no need to explore the extents of very slow cooling. An observed versus expected temperature curve, Figure 8 b, shows that the temperature follows the preset ramp very precisely. Only in the fastest setting, 20 °C/min, does the temperature lag behind a few degrees, but the rate of temperature change, or the slope of the curve, is still the same.

![Figure 8: In (a) a photograph of the freeze-casting apparatus. The control unit monitors the temperature at the thermocouple and adjusts the heater in order to maintain the programmed temperature at the top of the copper rod, which is immersed in liquid nitrogen. In (b) a plot of different cooling ramps (lines) and corresponding measured temperatures (open symbols). The filled symbols at the end of the series indicate the points at which a 20 mm tall mold filled with pure water was completely frozen.](image)

The suspension was mixed on the previous day and it consisted of water, zeolite, inorganic binder (bentonite) and intermittent binder (PEG), that was keeping the frozen and dried piece together until it could be consolidated. The relative amounts of bentonite and PEG to the zeolite were always kept constant. The suspension was ball-milled overnight, after which it was subjected to low vacuum under stirring for a few minutes to de-air the liquid, and then it was kept stirred in a closed vessel until it could be cast. All concentrations were alkaline (pH 9-10) and stable for at least 6 h when stirred.
After the suspension in the mold was completely frozen, the mold was removed from the copper rod and the bottom plate was pried away. The frozen composite was then removed from the die using a punch and a mallet, and placed in a freeze-drier. There it was kept at below 200 Pa for 48 h, after which it could be moved to a furnace and consolidated. The furnace was first heated to 550 °C at 2 °C/min and held there for five hours in order to remove the intermittent binder PEG, and then to 750 °C (zeolite A) or 780 °C (zeolite 13X) at 10 °C/min, after which it was immediately allowed to cool to room temperature. The maximum temperatures were chosen so that the bentonite would be activated, but the zeolite would still be unaffected.

Rheology

The viscosity of the aqueous zeolite suspensions was determined with a Paar Physica MCR301 (Anton Paar GmbH, Graz, Austria) using a concentric cylinder geometry. The measurement volume was 20 ml, and the suspension had been through the same procedure as suspensions immediately before freeze-casting, so it had been ball-milled and de-aired. The temperature during the measurements was controlled by a Peltier element, and prior to the measurements the suspensions were pre-sheared at 50 s⁻¹ for 3 minutes and then allowed to rest for 30 seconds.

The steady-shear measurements consisted of two cycles where the shear rate was first increased and the viscosity measured at several intervals, from 30 s at 0.1 s⁻¹ to 2 s at 1000 s⁻², and then decreased with same values in decreasing order. The reported viscosity for the suspensions was taken from the Newtonian region of the steady-shear measurements; at 100 s⁻¹ for suspensions containing 13X (Paper 1), and at 200 s⁻¹ for suspensions containing 4A (Paper 2).

Powder x-ray diffraction

X-rays are electromagnetic radiation with a wavelength \( \lambda \) between ultraviolet and \( \gamma \)-rays, roughly between \( 10^{-8} \) and \( 10^{-12} \) m. Usually, and in all the measurements in this thesis, the bombarded element is copper, and the ionization which we are most interested about is the expulsion of 1s –electrons that leads to the relaxation of a 2p –electron, giving out a monochromatic wavelength at 0.15 nm known as the CuKα-radiation. CuKα is actually a doublet, consisting of two distinct sharp peaks, of which the main one, CuKα₁, is at 1.540598 nm, and a second with 50% intensity from the first one, CuKα₂, at 1.544426 nm. The difference comes from relaxation to slightly different spin states, and the second peak is sometimes stripped in order to get a single sharp wavelength. These wavelengths are close to the distances between
atoms in crystals, which makes them diffract at distinct directions and making it possible to accurately calculate the positions of the atoms in the crystal according to the Bragg’s law. Bragg’s law relates the distance of planes of atoms $d$, the angle of the incident radiation relative to the sample surface $\theta$, and the wavelength multiplied by an integer $n\lambda$:

$$2d \sin \theta = n\lambda$$  \hspace{1cm} (1)

Powder X-ray diffraction (PXRD) was conducted using a PANalytical X’pert PRO MPD diffractometer, Figure 9, equipped with a Pixel detector and copper radiation source with a Kβ filter, emitting either CuKα$_1$ or CuKα – radiation, depending on the instrument (Figure 9 features the CuKα – emitting apparatus). The measurements were carried out typically between 5-100° 2θ, using reflection mode with a 10 mm mask and automatic divergence slits that kept the illuminated area at 1 cm$^2$. The pure samples were ground in an agate mortar into a fine dust and, if enough material was available, loaded into back-filled stainless steel sample holders. If only a small amount of sample was obtained, it was ground into powder, suspended in 95% ethanol and applied onto a zero-background silicon wafer using a pipette.

*Figure 9: The PANalytical diffractometer, equipped with a reaction chamber.*
Thermal expansion analysis

In-situ PXRD analysis was used to follow the crystallographic changes in the unit cells of zeolites at varying temperatures. In Paper 4, Silicalite-1 membrane supports were investigated, but various zeolite powders were also studied in a separate thesis work. The membrane supports were investigated both as large pieces of the supports themselves, and as crushed support powder. Silicon powder (Sigma Aldrich Chemie GmbH, Germany) with an average particle size of 44 µm was used as an internal standard to correct for sample displacement caused by heating of the sample and sample holder.

The investigated powder was mixed and ground with a small amount, approximately 10 wt%, of silicon powder, then mounted on a Macor holder inside a reaction chamber, and measured at various temperatures in vacuum. The heating was usually done at 10 °C/min, with a holding time of 15 minutes before a 30 minute measurement.

For the membrane support pieces, the disc-shaped, pulse current processed, membrane was broken into a piece, approximately 2 cm², which could then be mounted on either a Macor holder for an in-situ measurement, or for a regular measurement on an open stainless steel holder with a piece of clay, that was holding the piece level at correct height. The surface of the membrane was rough, so a very thin layer of silicon could easily be applied in the grooves with a finger for zero-point correction purposes.

Quantitative phase analysis

The quantitative phase analyses (QPA) of zeolites 13X and 4A were made by taking the sample to be analyzed, either 13X or 4A, and carefully weighing an estimated equal amount of the other zeolite, 4A or 13X, respectively, and mixing the powders together with a mortar and a pestle before analysis.

While the diffraction pattern theoretically contains all information about the arrangement of atoms in the investigated sample, extracting the data is often challenging. Especially in powder patterns, where the data from the entire bulk powder is overlapping, different effects, such as crystallite size and strain, amorphous fractions, impurities and filler molecules, micro-absorption effects and the sample displacement will affect the final diffractograph. Traditional QPA is done by comparison method, comparing the heights or areas of a few selected peaks to either an external or an internal standard. For the reasons mentioned above, this brings a lot more uncertainty in zeolite QPA. Especially filler molecules, i.e., template or water, may have a notable influence on selected peak intensities in porous powders.

The QPA and microstructural characterization in Papers 3 and 5 were made using the Rietveld full-profile refinement with the program FullProf 2k, version 5.30. A diffraction pattern, which was calculated from a model of the crystal structure, was fitted to the measured pattern and their squared
difference was minimized by refining the model and issues during measurement. The typical parameters to refine consisted of a general scale factor, the zero point error, polynomial background parameters, unit cell parameters, profile parameters for the pseudo-Voigt function, two asymmetry parameters and the overall temperature factor. Each phase \( j \) in a mixture of phases \( i \) is contributing to the overall diffraction pattern by their own pattern multiplied by a scale factor \( S_j \). The weight fraction \( W_j \) of that phase is then given by

\[
W_j = \left( S_j(ZMV)_j \right) / \sum_i (S_i(ZMV)_i)
\]  

(2)

In where \( Z \) is the number of formula units per unit cell, \( M \) is the mass of one formula unit, and \( V \) is the volume of the unit cell.

Zeolites 13X and 4A are very good complementary standards for each other, since they contain very few overlapping peaks, and they consist of similar atoms with almost identical framework density, meaning that x-ray microabsorption effects of the materials do not have to be corrected. Normally, a calibration curve must be made on a series of additions, where the observed \( W_i \) are compared with the calculated values. However, the \((ZMV)_j\) can be calculated so that it contains only the framework atoms, i.e., silicon, aluminium and oxygen (excluding cations and water), which produces a calibration curve with a 1:1 match with no more than 1% deviation, as shown in Figure 10.

Figure 10: The calibration curve for addition of 13X in 4A (a). On the horizontal axis is the added weight fraction of 13X in 4A (determined by balance), and on the vertical axis is the amount of 13X calculated from QPA. The points are measurements with various additions, and the drawn line shows the ideal 1:1 behavior. The deviations of the measured points relative to the line are shown in (b).
Gas uptake and diffusion measurements

The gas uptake measurements provide a direct measurement of surface area and accessibility of the pores in a measured sample, be it a powder or a monolith. Several methods have been employed to determine various qualities.

Manometric methods

The gas adsorption and desorption measurements were done on an ASAP 2020 surface area measurement device (Micromeritics Instrument Corporation, Norcross, GA), Figure 11. The uptake/desorption was determined manometrically; a carefully determined amount of probe gas was released in the sample holder, which had been carefully degassed in vacuum at 573 K for 5 hours prior to the measurement, and given time to adsorb on the sample. When equilibrium is reached, the pressure in the sample holder is measured, and from that the adsorbed amount of the probe gas could be determined. When the kinetic diameter of the probe gas molecule is known, calculating the surface area is straightforward. This procedure is performed usually several times at increasing pressures, until the final target pressure, 100 kPa (saturation pressure of nitrogen at 77 K), was reached. If desorption was needed, the process was then performed from saturation towards vacuum.

Figure 11: The ASAP2020 gas sorption apparatus. The degassing station contains heater socks and a cold trap to degas the sample tube, after which it is transferred to the measurement port for uptake/desorption measurements. The isothermal conditions are kept using an isothermal bath which is elevated to contain the sample during analysis.
Both nitrogen and carbon dioxide has been used as the probe gas. Nitrogen, a very common gas which is widely in use in porosity measurements, provides widely comparable results when measured at its boiling point, -196 °C. However, for some zeolites, such as 4A and its ion-exchanged forms where the kinetic pore diameter is very close to that of the nitrogen molecule, the diffusion of nitrogen at -196 °C may be too slow. For practical purposes, since the materials in use were intended for carbon dioxide capture, carbon dioxide was used instead at 30 °C. In order to determine the carbon-dioxide-over-nitrogen –selectivity, nitrogen was also measured at 30 °C, but since it has a high vapor pressure (and a low uptake), filler rods were always used inside the test tubes in order to minimize the free space and enable the manometric determination of adsorbed nitrogen. The temperatures were controlled by a bath of either liquid nitrogen (-196 °C) or water or silicone oil with a CF31 cryo-compact circulator (Julabo Labortechnik GmbH, Seelbach, Germany) at 30 °C.

Time-dependent uptake was also possible to measure with a kinetic module on the ASAP 2020; instead of waiting until the equilibrium had been reached, the pressure was measured at a set time interval, for example 1 second, up to 500 data points. When interpreting the kinetic uptake data, one would have to account for the decreasing pressure during the uptake due to the small space of the sample tube, leading to artificially reduced uptake at increasing time. Due to this complication, only gravimetric measurements were used for diffusivity calculations.

Mercury intrusion porosimetry
A non-wetting liquid, such as mercury, can be used instead of a wetting gas to measure pore size and volumes. Starting from vacuum, the sample is surrounded by the liquid, which is then subjected to increasing pressure, forcing the liquid to enter into pores of decreasing size. The relationship between the pressure \( p \) needed to force a non-wetting liquid into a cylindrical pore of radius \( r \) is given by the Washburn equation:

\[
p = -\frac{2\gamma \cos \theta_c}{r}
\]

In where \( \gamma \) is the surface tension, which is 0.485 N/m for mercury, and \( \theta_c \) is the contact angle between the liquid and the solid, 130°.

Mercury intrusion porosimetry was done with AutoPore III 9410 (Micromeritics Instrument Corporation, Norcross, GA). The maximum attainable pressure with the instrument is 414 MPa, which corresponds to a pore of radius 3 nm. The samples which were measured with mercury porosimetry were, exclusively, freeze-cast 13X monoliths cut into reasonably small pieces (0.5 g) and degassed in vacuum prior to the measurement.
Gravimetric carbon dioxide uptake measurements

Time-dependent carbon dioxide uptake and release measurements were done complementary to the manometric measurements in a gravimetric fashion with an Isosorp gravimetric device (Rubotherm Präzisionsmesstechnik GmbH, Bochum, Germany) in the Institut für Nichtklassische Chemie, Leipzig, Germany. A freeze-cast zeolite monolith, 3-4 g, was placed in a mesh holder that was open from all sides, and suspended by a wire that was connected to a magnetic suspension balance. The assembly was inside a closed vessel that could be evacuated and heated, and after a degassing for 5 h at 300 °C, carbon dioxide at 140 kPa was released into the vessel, and the increase of the mass of the monolith was measured. After the equilibrium had been reached, the pressure was rapidly reduced to 5 kPa in order to obtain the desorption curve. This uptake/release cycle procedure was repeated a total of three times.

Gas breakthrough measurements

In order to see the uptake behavior of an adsorbent under working conditions, gas breakthrough analysis is an often preferred method. In gas separation the equilibrium uptake itself is unimportant, since the gas flow will be stopped just before the target gas will penetrate the adsorbent bed; instead the relevant measurement is that of the uptake of gas at the moment of breakthrough. The adsorbent was packed in a column with a regulated gas flow of an inert carrier gas (nitrogen), and at the start of the measurement a certain concentration of the target gas was let in the column from one end. The other end will monitor the target gas concentration as a function of time, and the resulting breakthrough curve will contain information on both the uptake capacity (time before the target gas shows on the other side) and the uptake kinetics (the time it takes for the target gas to reach the inlet concentration).

The gas breakthrough tests were performed in Luleå Technical University on freeze-cast monoliths in a stacked column with a total length of 15 cm, as shown in Figure 12. The monoliths were activated under a 0.15 l/min flow of nitrogen at 300 °C for 12 h, after which they were cooled to 25 °C. At time zero, the gas feed was switched from nitrogen to a 1:9 mixture of carbon dioxide in nitrogen using a pneumatic switching valve with the switching time less than 0.1 s. The concentration of carbon dioxide in the gas leaving the column was measured as a function of time using a carbon dioxide analyzer (IR 1507 fast response CO₂ infrared transducer).
Mechanical testing

The freeze-cast monoliths can be delicate and monoliths with a very high porosity may even crumble from a careless touch, so in order to relate the strength between the monoliths, mechanical compressive tests were done parallel to the main pore direction. The compressive test involves a piston or a load which is moving at a constant rate, and a load cell that adjusts the force applied to keep the piston moving. The force is normalized by the area of the sample into pressure (Pa), and plotted against the displacement, normalized by the sample height (mm/mm).

The plot contains information on the failure behavior, viscoelastic properties and the energy that is dissipated in the sample. The most meaningful properties in assessing the strengths of freeze-cast monoliths were the elastic modulus, which is the constant increase in force needed to sustain the compression prior to failure, and the compressive strength, which is the maximum pressure exerted on the structure prior to failing. One should bear in mind, however, that the compressive strength in unidirectionally frozen structures may be many times weaker in the direction perpendicular to the main axis. Different structures with radially ordered walls have been constructed in order to strengthen the monolith, but we were more interested about modelling the mechanical strength rather than ways to overcome the limitations.

The mechanical tests were done with different instruments: the freeze-cast 13X monoliths were tested with a servo-hydraulic testing machine MTS810.
(MTS Systems, Eden Prairie, MN) which compressed the monoliths at 0.20 mm/min, until the monolith broke. The 4A monoliths were measured with an Instron 5967 (Instron, Norwood, MA, USA) mechanical testing device, Figure 13. The initial monoliths were placed on a metal plate in a small plastic bag between two rubber pieces that divided the load more evenly, and compressed with a 2 kN load cell at 10.0 mm/min. In both cases the reported compressive strength was the maximum stress.

![Instron mechanical testing device](image)

*Figure 13: Instron mechanical testing device, provided by Tampere University of Technology. The compressive tests were done parallel to the main pore direction.*

**Electron microscopy**

High-resolution SEM images were obtained with a JEOL JSM-7001F microscope (Jeol Ltd., Tokyo, Japan), equipped with a field-emission gun which gives an exceptionally bright electron beam. Some images of the 4A monoliths which could be taken at relatively low magnifications, x1000 and less, were obtained with a Hitachi Analytical TableTop Microscope TM3000 (Hitachi High-Technologies Europe GmbH, Krefeld, Germany). In both microscopes the accelerating voltage was kept low, at 2 kV, in order not to oversaturate the zeolite samples.

Zeolites are tricky materials for SEM because they are non-conductive, the electrons shot at the surface are not led away but stay there for prolonged time and both repel incoming electrons, thereby lowering the resolution, and give random bursts, lighting up parts of the crystals during the measurement. This was mitigated by coating the sample with very thin layer (a few nanometers) of gold, which conducts away the current.
The sample preparation of the highly porous, fragile zeolite monoliths consisted of carefully cutting them into representative pieces which were small enough to fit in the microscope. First, the tall (20-35 mm) monolith was cleaved vertically a couple of times into thin (5 mm), long sections. These sections were then broken by bending in order to obtain a clean and undistorted surface. In the case of monoliths with very isolated lamella, this task was very delicate and required often several tries. Finally, the broken piece was mounted on a 1 SEK coin, which served as an inexpensive sample holder (size, shape and value very close to the U.S. quarter), on top of which a thick layer of a conductive Leit-C carbon cement (Plano GmbH, Wetzlar, Germany), had been deposited. Several pieces (3-5) could usually be mounted on the same holder, after which the coin with the samples was allowed to dry overnight in a desiccator, and then coated with gold.

Pulsed current processing

The hierarchically porous pulse current processed (PCP) ZSM-5 monoliths in Paper 3, and the silicalite-1 membrane support discs in Paper 4, were pro-
duced in Stockholm University using Dr. Sinter 2050 (Sumitomo Coal Mining Co. Ltd., Japan). In Paper 3, the ZSM-5 powder, roughly 1.5 g, was loaded in a graphite die with an inner diameter of 12 mm and placed in between two graphite punches. The die assembly was placed under a hydraulic piston with graphite spacers in a vacuum chamber, and during processing the punches applied a uniaxial pressure of 20 MPa on the powder. At the same time, the die assembly was heated by short pulses (3.3 ms) of direct current at a rate of 100 °C/min up to temperatures between 600 and 1000 °C, with a holding time of 3 minutes. The temperature was monitored by a K-type thermocouple inserted inside the graphite die, and the piston movement was recorded as a function of time.

*Figure 15:* The Dr. Sinter 2050 pulsed current processing device and the inside of its vacuum chamber. The graphite die is loaded in the middle, and the thermocouple is seen in the foreground as a loose wire. The figure is adapted from the author’s master thesis work.\(^{82}\)
Results and discussion

The ultimate goal of this thesis was to advance the field of carbon dioxide capture from a flue gas. The focus is on zeolites, and the scientific input is focused on establishing an understanding on how the adsorbent can be efficiently structured by freeze-casting. An advanced processing method, pulsed current processing (PCP), synonymous with spark plasma sintering (SPS) or field-assisted sintering technology (FAST), has also been used to produce strong permeable zeolite monoliths and zeolite membrane supports to minimize thermally induced stresses. Attention is also paid to synthesis of nano-sized zeolites that can be used for fast uptake or to increase the density in powder mixtures.

Freeze-casting of zeolite monoliths

We have freeze-cast suspensions of zeolites 13X and 4A at various concentrations and cooling rates, which has led to highly porous monoliths with a lamellar or columnar pores structure with different wall thicknesses, pore sizes and shapes. The monoliths have been primarily characterized with respect to the gas uptake kinetics and the compressive mechanical strength.

Suspension rheology

The essence of freeze-casting is the segregation of ice from an aqueous suspension into many tiny, thin, parallel ice veins or crystals. The characteristics of the structure, such as the thickness and shape of the ice crystals, are largely governed by the mobility of the dispersed particles in the suspension before the ice is formed and the structure is set. The mobility of the particles can be inferred by rheological (viscosity) measurements, and it is controlled by the suspension concentration, particle interaction, dissolved species, and, finally, temperature.\(^{83-86}\) A controllable cooling rate enables control of the temperature gradient ahead of the freezing front. A high temperature gradient leads to hindered particle mobility and thin ice crystals, which eventually results in small pores.\(^{87}\)

Zeolites 13X and 4A are both colloidally stable in water due to their negative surface charge, just like bentonite.\(^{88,89}\) That makes zeolites and bentonite an ideal mix to obtain a stable suspension even without surfactants. However,
the suspensions, especially the concentrated ones, have to be kept under constant stirring, lest they start sedimenting (typically in half an hour). The limited stability is actually not a bad thing, since the suspension should be slightly unstable in order to provide gravitational drag against the upwards-proceeding freezing front. Previous work has shown that too stable suspensions will have the particles pushed ahead of the freezing front, creating periodic fluctuations in the solid concentration which will have a deleterious effect on the strength of the formed monolith.\textsuperscript{90}

While zeolite suspensions themselves behave nicely in a classical Newtonian way, the addition of bentonite complicates the rheological behavior. Anisotropic particles, such as platelike clays, lead to a non-Newtonian behavior and high viscosity at relatively low concentrations,\textsuperscript{91} which is a reason to keep the binder content low. Figure 16 shows how the viscosities of suspensions change with the solids loading, temperature and the bentonite content.

![Figure 16: Viscosity versus shear rate in aqueous suspensions containing zeolite 13X, bentonite and PEG. In (a) is the viscosity variation of suspensions with different inorganic content concentration. X22, X24 and X26 refer to](image)

90.\textsuperscript{90}
91.\textsuperscript{91}
Table 1 and correspond to 22, 24 and 26 wt% dwb of the inorganic specie, along with the viscosity of the solvent (water + PEG). The open symbols show a suspension of X24 which had twice the bentonite content as compared to the filled symbols. In (b) the temperature dependency of an X24 suspension is shown from 25, 15 and 5 °C.

The concentration of suspensions for freeze-casting is usually reported as a volume fraction (vol%) of the components relative to the entire volume of the suspension. However, due to the strongly hygroscopic and porous nature of zeolites, this can be misleading since a fraction of the solute will immediately enter the pores of the zeolite and remain there as an adsorbed and immobilized fluid, and not as a free solvent. Therefore, for these studies, the concentration was instead given as weight fraction by dry-weight-basis (wt% dwb), which is the dry mass of a constituent divided by the total mass of the suspension. An example of the water loss of zeolite 4A during heating is given in Figure 17.

![Figure 17: The thermogravimetric measurements of as-received zeolite 4A powder before (black dashed line) and after (full blue lines) conditioning in a humid chamber at 50 % relative humidity at 30 °C. The average mass loss value was taken to be the water content of zeolite 4A after conditioning in the humid chamber. The data are taken from the thesis work of Marcus Bauer.](image)

The concentrations of the zeolite suspensions used for freeze-casting varied between 18 and 32 wt% dwb of the inorganic components (zeolite and bentonite). Solids concentrations lower than that result in freeze-cast monoliths that are structurally too weak to support themselves after sublimation, and concentrations higher than this limit result in viscosities that are too high to freeze-cast. The theoretical upper solids loading \( \varphi \) for suspensions can be predicted from the relationship established by Liu et al.\(^2\):

\[
1 - \eta_r^{-1/n} = a' \varphi + b'
\]

Where \( \eta_r \) is the relative viscosity (viscosity of the suspension divided by viscosity of water+PEG), \( n \) is a flow parameter, where we used the suggested value of 2, and \( a' \) and \( b' \) are empirically determined parameters from the rheology measurements.
From a plot of $1 - \eta_r^{-1/n}$ versus the total solids loading, such as Figure 18 for zeolite 4A, one can determine at which loading the viscosity decreases so much that the suspension stops flowing. For zeolite 4A the maximum predicted loading was 31.4 wt% dwb, although the practical limit for a suspension that could be effectively stirred was slightly below 30 wt% dwb.

Figure 18: The plot of $1 - \eta_r^{-1/n}$ versus the total solids loading in aqueous suspensions containing zeolite A, bentonite and PEG. The circles are measurement points, and the line is linear least squares fit to the measured points. Figure taken from Paper 2.

**Freeze-cast structures**

The freeze-casting route is able to form structures with pore diameter and separation (wall thickness) in the range of 5-50 µm, depending on the processing conditions. The suspensions were prepared at various total concentrations while keeping the relative amounts of the suspended components constant. Cooling rates were varied between 0.5 and 10.0 °C/min. The contents of each suspension can be seen in
Table 1: The nomenclature and relative amounts of components in the suspensions of zeolite 13X, data adapted from Paper 1.

<table>
<thead>
<tr>
<th>Suspension ID</th>
<th>X22</th>
<th>X24</th>
<th>X26</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total inorganic content (wt% dwb)</td>
<td>22.6</td>
<td>24.4</td>
<td>26.2</td>
</tr>
<tr>
<td>Zeolite 13X (g)</td>
<td>36.4</td>
<td>40.9</td>
<td>45.5</td>
</tr>
<tr>
<td>Bentonite (g)</td>
<td>3.64</td>
<td>4.09</td>
<td>4.55</td>
</tr>
<tr>
<td>PEG (g)</td>
<td>3.64</td>
<td>4.09</td>
<td>4.55</td>
</tr>
<tr>
<td>H₂O (ml)</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 2: The nomenclature and relative amounts of components in the suspensions of zeolite 4A, data adapted from Paper 2.

<table>
<thead>
<tr>
<th>Suspension ID</th>
<th>A18</th>
<th>A23</th>
<th>A28</th>
<th>A29</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total inorganic content (wt% dwb)</td>
<td>18.4</td>
<td>23.0</td>
<td>27.5</td>
<td>29.3</td>
</tr>
<tr>
<td>Zeolite 4A (g)</td>
<td>26.5</td>
<td>36.2</td>
<td>47.7</td>
<td>53.0</td>
</tr>
<tr>
<td>Bentonite (g)</td>
<td>3.61</td>
<td>4.95</td>
<td>6.51</td>
<td>7.21</td>
</tr>
<tr>
<td>PEG (g)</td>
<td>3.61</td>
<td>4.95</td>
<td>6.51</td>
<td>7.21</td>
</tr>
<tr>
<td>H₂O (ml)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

In simple freeze-casting designs, the suspension to be cast is placed on a cold substrate at a constant temperature. More advanced devices, such as ours, control the temperature of the substrate, and thus the cooling rate, with the help of a thermally conducting material that is in contact with a cold medium (a cold finger) and a heating coil. Ice, however, is a poor heat conductor, and thus it will be more and more difficult to maintain the temperature gradient ahead of the freezing front as its distance from the substrate surface increases. This effect is probably responsible for reports stating that the cross-sectional pore size close to the bottom has been smaller than pores close to the top; however, for our 3.5 cm tall monoliths we found no difference between the bottom and the top, as shown in Figure 19. This shows that the low-density zeolites are generally good materials for freeze-casting, and
that using a set cooling rate instead of a constant substrate temperature is a valid way to ensure the homogeneity of the structure in tall monoliths. Eventually, however, even a linear cooling rate of the substrate is not able to keep the velocity constant, and the most advanced approaches rely on quadratic cooling rates, which can even be applied from the bottom and the top of the sample, in order to keep the ice front velocity constant across a long distance.93

![Figure 19: The comparison of the freeze-cast cross-sectional structure at two different heights in an X24 monolith frozen at 0.5 °C/min. The upper structure (left) is taken approximately 0.5 cm from the top and the lower structure (right) approximately 0.5 cm from the bottom of the monolith. The total height of the monolith was 3.5 cm.](image)

![Figure 20: The cross-sectional SEM images showing the pore structures of freeze-cast zeolite 13X monoliths. The series X22, X24 and X26 correspond to inorganic solids loading of 22.6, 24.4 and 26.2 wt% dwb, respectively, according to Table 1. The graphs are adapted from Paper 1.](image)
The pore morphology has previously been assigned somewhat arbitrarily into various categories, such as lamellar, cellular, columnar and dense. However, in Paper 2 we utilized a digital image analysis of SEM images to determine the average cross-sectional aspect ratio (length / width) of the pores. Based on their mechanical responses, we have then classified structures with the average aspect ratio below three as columnar, and all those above as lamellar.

Figure 20 and Figure 21 show the scanning electron microscope (SEM) images for cross-sections of freeze-cast monoliths containing zeolites 13X and 4A, respectively. Freeze-cast structures in general exhibit increased wall thicknesses at increased solids loadings, and the zeolite monoliths are no different. The increase of the cooling rate will reduce the pore sizes and make the pores more round. For gas transport the size reduction is purely advantageous; it decreases the maximum diffusion distance, and therefore the total uptake time, without affecting the gas flow.

![Figure 21](image)

*Figure 21: The cross-sectional SEM images showing the pore structures of freeze-cast zeolite 4A monoliths. The series A18, A23, A28 and A29 correspond to inorganic solids loadings of 18.4, 23.0, 27.5 and 29.3, respectively, according to Table 2. The graphs are adapted from Paper 2.*
Mechanical properties

When the adsorbent monoliths are physically handled, or experience rapid pressure changes during operation, they are subjected to mechanical stresses and deformations. Although strength is not a major concern in the monoliths, they still do need to be sufficiently strong. Knowledge of their failure mechanisms also helps in predicting the requirements for practical use.

As a first approximation, we expected the freeze-cast zeolite 4A monoliths to behave mechanically as an anisotropic porous solid, such as a honeycomb or cork. The failure strength $\sigma^*$ of these types of porous structures has been studied extensively by Ashby and Gibson, who established a linear relation between the compressive strength $\sigma_s$ of the bulk material and the relative density $\rho/\rho_s$: 

$$\sigma^* = \sigma_s \frac{\rho}{\rho_s}$$

However, when the porosity increases above a certain threshold (typically over 70%) buckling and bending will dominate the failure behavior and cause the material to fail at lower strengths than predicted by equation 7. An empirical equation describing these types of structures has been formulated:

$$\sigma^* = \sigma_s C \left(\frac{\rho}{\rho_s}\right)^{3/2}$$

Where $C$ is an empirical constant depending on the deformation type, for example for brittle foams $C$ equals 0.65.

![Figure 22: Different failure modes, (a) illustrates the compressive failure of a bulk material, where the compressive stress is forcing the material to expand sideways until it fails at its bulk fracture strength, and (b) illustrates the buckling of a thin sheet which will bend and fail sideways long before the bulk strength is reached.](image)
A brittle material is one which will break under stress without significant strain. However, even very brittle materials usually have some elasticity, and when a slender rod or sheet is constructed of the material, it will bend before it fractures at its compressive strength, as illustrated in Figure 22. The failure will then occur at its elastic buckling strength $\sigma_{el}$, according to

$$\sigma_{el} = E I \frac{\pi^2}{k'L^2}$$  \hspace{1cm} (7)

Where $E$ is the elastic modulus of the material, $L$ is the length of the buckling wall or beam, $k'$ describes the degree of constraints for the attachment points of the wall or how freely they are bending from their attachment points, and $I$ is the area moment of inertia of the cross-section of the cell edge or wall:

$$I = 2 \left( \frac{ad}{12} + \frac{A_w(b+d)^2}{4} \right)$$  \hspace{1cm} (8)

Where $a$ and $b$ are the cross-sectional length and width of the pore, respectively, and $d$ is the thickness of the wall. Theoretically, buckling can occur only if the failing element, with a cross-sectional area $A_w$, has a slenderness ratio $L/r'$, where $r' = \sqrt{I/A_w}$, exceeds a minimum value:

$$\frac{L}{r'} > \pi \sqrt{\frac{E}{\sigma^*}}$$  \hspace{1cm} (9)

A simple estimate with generous margins for a weak zeolite monolith, where even the brittle zeolite/bentonite composite material with $E = 500$ kPa, $\sigma^* = 45$ kPa, $L = 500$ µm, $A_w = 400$ µm² and $I = 80000$ µm², gives $36 > 10$, which easily satisfies the condition in in equation 9.

**Compressive mechanical tests for freeze-cast zeolite 4A monoliths**

The mechanical responses of freeze-cast zeolite 4A monoliths were analyzed in detail to elucidate the influence of the solids loading and cooling rate. The first two series investigated the correlation between either total solids loading or cooling rate to the compressive strength, and the final, third series tested the corners of the experimental domain (low/high solids loading and low/high cooling rate), with repeated experiments. All results are shown in Table 3.
The first series in Figure 23 shows the compressive strength data of freeze-cast monoliths prepared out of suspensions A18 to A29. Plotting the strength data versus the solids loading reveals a linear relationship according to equation 5, and linear extrapolation allows us then to obtain the lowest theoretical solids loading at zero strength, 16.5 wt% dwb, and also the strength at the maximum theoretical solids loading (31.4 wt%, taken from equation 4), 1110 kPa.

Figure 23: Compressive strengths and microstructures of monoliths of freeze-cast zeolite A, prepared at a constant cooling rate of 10 °C/min. The bars show the compressive strengths of a series of monoliths made from suspensions A18-A29. The dashed line shows a linear fit which corresponds to equation 5, and the dotted line to equation 6. The SEM graphs show the cross-sections for the corresponding monolith, the scale bar is 100 µm. Figure adapted from Paper 2.

By using calculated maximum solids loading as the substitute for the theoretical bulk strength $\sigma_s$, the common failure model for a highly porous monolith, given by equation 6, could be ruled out. It is not common to estimate the
in this way, since it is a materials property, but in light of the monolith being a composite material which will never be allowed to densify, with a well-defined crystal size and constant binder fraction, this estimate represents well the highest strength that this composition can possess in a dense-packed composite.

Figure 24: Compressive strengths and microstructures of freeze-cast zeolite A-based monoliths prepared from A28-suspension at cooling rates between 0.5 and 10 °C/min, showing the compressive strengths of a series of monoliths. The SEM micrographs show the cross-sections of the corresponding monoliths. The scale bar is 100 µm. Figure adapted from Paper 2.

The second series, which plots the compressive strength versus the cooling rate, is shown in Figure 24. The variation in the cooling rate is quite notable in the structures, where the low cooling rates (0.5 and 1.5 °C/min) feature, not only a distinct lamellar structure, but also compressive strengths that are effectively halved from the monoliths with high cooling rates (5 and 10 °C/min). Since the structure is indeed the only variation between these monoliths, the monoliths containing lamellar pores deviate from the Gibson-Ashby models and fail by a different, inherently weaker, mode than the monoliths with columnar pores.
Finally, the mechanical tests were done in several replicates for four series of monoliths with distinct differences in density and microstructure: both the low-density and the high-density suspensions (A18 and A29) were frozen by cooling them at slow and fast cooling rates (1.5 and 10.0 °C/min). The results, plotted versus the wall thickness in Figure 25, show that, according to the Gibson-Ashby models, the increase in solids loading does indeed provide the dominant contribution to the strength increase, two times as much as the increase in cooling rate, but the effect of the cooling rate is by no means insignificant and warrants further studying and parameterization of the structures.

Figure 25: Compressive strengths versus solids loading and cooling rate on four selected monoliths at the borders of the experimental domain. The green arrows show the multiplier for the increase in compressive strength for cooling rate increase (green) and solids loading increase (purple). The vertical blue thin lines represent standard deviations. The SEM cross-sectional images correspond to the letters in the graph: (a) and (b) are A18 frozen at 1.5 and 10 °C/min, respectively, and (c) and (d) are A29 frozen at 1.5 and 10 °C/min, respectively. The scale bar is 100 µm.
Cross-sectional image analysis of freeze-cast zeolite 4A structures

Digital image analysis was used to quantify the structural features of the porous, freeze-cast monoliths. A computer algorithm, written and ran by Masi Valkonen from the Tampere University of Technology, digitalized a scanning electron micrograph of a cross-sectional area of roughly 900 by 700 µm so that the solid/pore boundaries could be sketched, as shown in Figure 26. Then the pores were fitted with ellipsoids, which gave statistics on the pore minor/major axes, including aspect ratio, cross-sectional area and orientation. The average wall thickness was estimated by measuring 20-40 walls between two arbitrary pores by hand.

![Figure 26: In (a), a cross-sectional SEM image of a freeze-cast zeolite 4A monolith from A29 suspension, frozen at 1.5 °C/min. In (b), the digitized image showing the borders between pore and solid. From images such as these the pore area, width, aspect ratio and orientation are readily obtained. Figure taken from Paper 2.](image)

The digitized pore counting enables the possibility to obtain quantifiable values of pore parameters, which could be grouped together to see their characteristic distribution.

![Figure 27: Counting statistics of important pore parameters from the digitized images. On x-axis are shown (a) the pore width and (b) the pore aspect ratio (length / width), and on y-axis the amount of pores having that value.](image)
Figure 27 features the counting statistics of two important parameters from the SEM-images: pore width and aspect ratio. They are both calculated for featured monoliths (see Figure 25) from representative SEM-images at identical magnifications (such as in Figure 26), and illustrate the different structures: A18 and A29 frozen at 10.0 °C/min both feature small pores, and especially the A29 monolith had quite uniform pore size distribution, as is evident from the high count number which correlates well with the observable SEM-image (Figure 25 d). In comparison the monoliths frozen at 1.5 °C/min have a smaller total number of pores, that are larger and with a wider distribution.

The aspect ratio is useful in relating the mechanical strength to the structure; a small aspect ratio means that the structure resembles more of a honeycomb and the walls will have a large number of interconnecting bridges, while a large aspect ratio relates to few interconnections, leading to isolated walls which are supported mostly from their end points. Bridging the walls is crucial for their stability and for preventing bending and buckling.85,87,100 This is illustrated clearly in Figure 28, which shows pieces of two monoliths with a distinctly lamellar structure, one perpendicular (a) and the other one parallel (b) to the freezing direction. In both pieces the very large and slender sheets can be seen, and especially (b) shows well how the monolith fails in tension, not due to any weakness in lamella but due to the lack of contact points keeping the adjacent layers together. The mechanical failures in columnar monoliths are nowhere near as well-defined.

![Figure 28: Scanning electron micrographs of two monoliths with highly lamellar structures showing fracture surfaces: (a) A18 at 1.5 °C/min taken perpendicular to the freezing direction, the piece is taken from a monolith which was cleaved by initiating a parallel crack with a scalpel and then bending it perpendicularly. In (b) A18 at 10.0 °C/min parallel to the freezing direction, the opening has been caused by a tensile stress, which was exerted when the glue used to mount the piece was drying.](image-url)
The essential structural parameters for the freeze-cast monoliths are listed in Table 4. All the parameters except the wall thickness, which were obtained by hand, were obtained from the digitized image analysis. The reason for this is that the principal component analysis protocol used for the pore parameterization calculated the fitting ellipsoids for each pore individually, but could not relate the ellipsoids to each other.

Table 4: Cross-sectional morphological properties of monoliths prepared from low- (A20) and high (A32) concentration suspensions, frozen at slow (1.5 K/min) and fast (10.0 K/min) cooling rates.

<table>
<thead>
<tr>
<th></th>
<th>A18 1.5 °C/min</th>
<th>A29 10.0 °C/min</th>
<th>A18 1.5 °C/min</th>
<th>A29 10.0 °C/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wall thickness (d) (µm)</td>
<td>8.70</td>
<td>4.33</td>
<td>18.5</td>
<td>7.03</td>
</tr>
<tr>
<td>Pore major axis (a) (µm)</td>
<td>45.1</td>
<td>23.6</td>
<td>32.6</td>
<td>20.2</td>
</tr>
<tr>
<td>Pore minor axis (b) (µm)</td>
<td>11.3</td>
<td>6.70</td>
<td>12.2</td>
<td>8.89</td>
</tr>
<tr>
<td>Aspect ratio (\chi)</td>
<td>3.98</td>
<td>3.52</td>
<td>2.67</td>
<td>2.27</td>
</tr>
</tbody>
</table>

Compressive strength modelling

The compressive strength data and image analysis for the 4A monoliths were combined in order to identify the main factors affecting the strength of the monolith. The relative density of the monolith did have the highest impact on the strength, but the cooling rate did also have a significant contribution to it, and so in order to fit both parameters into a mechanical model, the cooling rate was replaced with a structural parameter, the pore cross-sectional aspect ratio \(\chi\).

The aspect ratio is a direct measure of the interconnectivity of the lamellar walls which provides sideways stability to them, and therefore it is also a derived measure of the possibility for the walls to bend under load. The bending will cause the material to come short of its full potential, since the force needed to bend a long object is lower than the force needed to compress it into itself.

The structural parameters used are shown in Figure 29. The wall lengths in Freeze-cast monoliths are irregular (see for instance Figure 28 a), as shown earlier in equation 9 the conditions for buckling are easily satisfied for the walls in freeze-cast structures. Buckling is therefore a very possible
mechanism of failure for freeze-cast monoliths which have a distinctly lamellar structure.

Figure 29: A representation of a section of a freeze-cast monolith, with highlights at the various important parameters.

The compressive strengths versus the average pore cross-sectional aspect ratio have been plotted in Figure 30. The a model for the compressive strength was fitted by varying an empirical factor, \( q \), in a modified expression for the Euler buckling mechanism (10), which accounts for the bulk porosity and pore shape, and where the moment of inertia has been replaced by the area moment of inertia:\(^{100}\):

\[
\sigma^* = \frac{\pi^2 q^2 E}{(k'L)^2} \left( \frac{A_w^2}{3b^2} \left( \frac{1}{\chi} \right)^2 + \frac{A_w}{2} \left( \frac{1}{\chi} \right) + \frac{b^2}{4} \right)
\] (10)

In this formula, \( q \) is an empirical factor relating to the surface roughness of the lamella, \( k' \) is a constraint factor that was set to 0.5, \( L \), the lamellar wall height, that was set to an approximated minimum value of 500 \( \mu \)m, \( A_w \) is the wall cross-sectional area (calculated from pore length and wall thickness) and \( b \) is the pore minor axis. Very notably, the fitted value for \( q \) was 1.00, which means that the formula already contains all significant parameters and \( q \) may be omitted.
Figure 30: The compressive mechanical strength $\sigma$ versus the average cross-sectional aspect ratio of the pores of the freeze-cast monoliths, same ones as shown in Figure 25. The open symbols denote low-density monoliths, cast from the A18 suspension, and the closed symbols denote high-density monoliths out of A29. Squares indicate a cooling rate of 10 °C/min and diamonds 1.5 °C/min. The violet crosses and dotted lines show the predicted strength according to equation 14. Figure adapted from Paper 2.

The modified Euler buckling model was found to predict the strengths very accurately, even for the 10.0 °C/min –monoliths, which for all purposes resembles a honeycomb monolith with little or no buckling. From the shape of the model curve it also seems obvious that there is no call for slow cooling rates, unless we also apply a method to disturb the lamellar structure and make the pores more round and strong. It should also be noted that, even if the strongest monolith has an aspect ratio which is only 2.27, the compressive strength is not expected to increase much further even if the aspect ratio would become close to 1. The maximum strength prediction for a bulk composite is still 1110 kPa from combining equations 4 and 5, and one should interpret the buckling model values carefully when out of the buckling domain.

**Weibull Analysis**

The data from the third compressive test series (Figure 25 and Figure 30) were combined and analyzed by Weibull statistics, which gives the probability of survival $P_S$ of an object under an applied force $\sigma$.
\[ P_S = \exp \left[ -\left( \frac{\sigma}{\sigma_0} \right)^m \right] \]  

(11)

In where \( \sigma_0 \) is the characteristic strength for which the survival probability is \( 1/e \) (0.37) and \( m \) is the Weibull modulus. The Weibull modulus is obtained by first ranking the measurements in the order of increasing failure strength and then individually assigning them the \( P_S \), so that the \( j \)th specimen in a series of \( N \) measurements has:

\[ P_S = 1 - \left( \frac{j - 0.3}{N + 0.4} \right) \]  

(12)

Then a plot of \( \ln \ln (1/P_S) \) versus \( \ln \sigma \) is constructed, which will make up a straight line with the slope \( m \), shown in Figure 31 (a). A high value of \( m \) means that the measured samples all failed in a narrow strength region, and the fracture prediction reliability is high. In contrast, a low \( m \) is a sign of a considerable susceptibility to flaws and an indication of a low reliability.

The compressive data were collected from a number of monoliths (up to ten each) belonging to one the four investigated monolith types, A18 and A29 at 1.5 and 10.0 °C/min. According to the procedure, the data were arranged in order from weakest to strongest, plotted as in Figure 31 (a), and then a probability of survival \( P_S \) was calculated for each monolith, as shown in Figure 31 (b).

*Figure 31: Weibull statistic plots from freeze-cast 4A monoliths, the closed symbols denote A32 monoliths and the open symbols are A20 monoliths. Squares indicate a cooling rate of 10 K/min and diamonds 1.5 K. In (a) is the plot used to calculate the Weibull modulus from the slope of the regression line, and in (b) is the survival probability of the four series based on the average crushing strength and Weibull modulus. Figure taken from Paper 2.*
The Weibull analysis divided the monoliths into two categories: monoliths from A18 frozen at 1.5 and 10.0 °C/min, displaying relatively high Weibull moduli of 6.9 and 7.1, respectively, and monoliths from A29 frozen at 1.5 and 10.0 °C/min, which resulted in relatively low Weibull moduli of 2.6 and 3.4, respectively. The low moduli are likely a result of the highly fragile interconnections present in the columnar structure, which suffers somewhat from the anisotropy and randomness during the freezing. Figure 32 shows how the monoliths break under compression, the monolith with a low pore aspect ratio (A29) fails essentially into distinct sections; one vertical crack at a time propagates across the entire monolith. The schematic shows how the lamellar interconnections break under gliding and tensile stresses, and the probability of finding the first, critically flawed section, varies across the monolith and possibly between the monoliths as well.

The monoliths exhibiting the high moduli have fewer interconnections and they meet the compressive stress largely unsupported, except for the neighboring domains with a different pore orientation. The buckling failure occurs at a set strength, and since the lamella are very uniform in size, the compressive strength does not show much variation. The snapshot image during compression indicates an early failure of the individual lamella; they are broken into small pieces, and enter the structure during compression, causing sideways expansion at the top of the monolith, which makes it open up in a conical shape.

![Figure 32: Snapshots taken during the compressive tests show the failure difference between columnar (A29 at 1.5 °C) and lamellar (A18 at 1.5 °C) structures, where the former one is broken in distinct splinters along the main pore direction, and the latter is essentially crumbling apart, as illustrated by the graphical addition. The surface of the monoliths is normally white, but has for these shots been painted with small black dots in order to follow the deformation of the surface. Figure adapted from paper 2.](image-url)
Gas separation by freeze-cast porous monoliths

We used gravimetric methods to characterize the time-dependent gas uptake of our freeze-cast zeolite 13X monoliths. A magnetic suspension balance monitored the mass of the monolith inside a closed vessel, both of which had been degassed by heating them under vacuum. At the beginning of the measurement carbon dioxide gas at a certain pressure is let into the chamber, where it immediately begins to adsorb and diffuse into the monolith and increase its mass until the monolith is saturated. Monitoring the time-dependent uptake will then give us information both about the rate of adsorption (kinetics) and about the total uptake capacity of the monolith.

Diffusion and uptake of CO₂

The main purpose of freeze-casting the adsorbent into highly porous monoliths is to optimize its uptake, and therefore the most important property to measure is the uptake kinetics. For this purpose we measured the uptake of carbon dioxide in a gravimetric unit that determined the uptake as a function of time. An example of the results is shown in Figure 33, where a freeze-cast zeolite 13X monolith, and a reference monolith prepared by isostatic compression, has been through three successive cycles of adsorption/desorption. The experiment was run over a long time period to ensure complete saturation so the time resolution is poor (the ultra-rapid adsorption cycle should be below 30 seconds), but it is still evident from comparing the curves how the monolith structured by freeze-casting outperforms the reference monolith with respect to the uptake kinetics.

The gravimetric uptake measurements were done for monoliths in a hanging mesh holder, inside a closed chamber where the temperature and pressure could be adjusted. The monolith had been degassed during several hours at an elevated temperature, and at time zero it was subjected to pure carbon dioxide at 140 kPa. The gas is immediately adsorbed into the monolith through its macroporous channels, and when the adsorption reached equilibrium, the pressure is lowered to a low vacuum (6 kPa) in order to empty the monolith, in accordance with the pressure swing adsorption (PSA) process.
Figure 33: The gravimetric time-dependent uptake of carbon dioxide at 303 K and 140 kPa in a macroporous monolith frozen from X26 suspension at 5.0 °C/min (blue line), and a reference monolith prepared by isostatic compression from the same starting mixture as X26.

Not nearly all gas molecules are released during vacuum treatment, complete desorption normally requires heating the monoliths. However, the uptake equilibrium values reached during high and low pressure for the second and subsequent cycles should always be the same, otherwise the adsorbent may be deteriorating or changing composition during runs. The maximum and minimum equilibrium uptake limits also gives the maximum working capacity of the adsorbent.

The high affinity of the carbon dioxide to the zeolite is linked to the incorporation of Al(+III) into the network of tetrahedral Si-O–building units, which leads to large electrostatic interactions (acid sites) and in some cases even chemical bonding through carbonate formation (CO$_3^{2-}$). The rearrangement of chemical bonds is known as chemisorption, as opposed to physisorption, which refers to attraction by weaker physical interaction, such as electrostatic or Van der Waals forces. It is assumed that most of the gas which is reversibly adsorbed during the pressure swing cycles is physisorbed, and the gas remaining even during low vacuum is mainly chemisorbed.
The diffusion in a spherical crystal $D_c$

The rate of the uptake depends on how fast the gas can diffuse into the available adsorption sites in the micropores throughout the monolith. Thus, the macropore size and shape, and even the voids between the zeolite crystals (~1 µm), should offer negligible resistance for the gas molecules. The rate limiting factor is the maximum length of the micropores, which is related to the radius of the zeolite crystals.

Figure 34: The carbon dioxide uptake to 140 kPa of pre-cycled (i.e., 2nd or 3rd uptake cycle) freeze-cast zeolite 13X monoliths compared with a compressed reference monolith. The individual lines correspond to different solids loadings (X22-X26), and the content of the inorganic binder bentonite is varied between graphs: (a) contains 9.1 wt% bentonite, and (b) contains 16.7 wt% bentonite. Figure is adapted from Paper 1.

Figure 34 shows how the binder content affects the uptake, by plotting the time-dependent uptake of carbon dioxide of monoliths with the binder amount kept small (a; 9.1 wt%) and moderate (b; 16.7 wt%). The uptake into the former is indeed independent of the density, and the only significant resistance comes from the diffusion into the micropores of the spherical crystals, which are similar between the monoliths. However, the increased bentonite content affects the uptake rate and equilibrium significantly, assumedly blocking the micropores in the crystals and the macropores in the walls, slowing and scattering the uptake.

For comparison and calculation of the diffusion, we calculated the diffusion coefficient $D_c$ for a spherical particle with radius $r$, for uptake $m$ at time $t$, from an isothermal expression\textsuperscript{102,103}:

$$\frac{m_t}{m_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( -\frac{n^2 \pi^2 D_c t}{r^2} \right)$$  \hspace{1cm} (13)
The long time asymptote at $m_t/m_\infty > 0.75$ should converge to the first $n$, simplifying equation 13 and giving:

$$\ln \left( 1 - \frac{m_t}{m_\infty} \right) = \ln \left( \frac{6}{\pi^2} \right) - \left( \frac{\pi^2 D_c t}{r^2} \right)$$

Therefore, a plot of $\ln(1 - m_t/m_\infty)$ versus $t$ should be linear with an intercept of $\ln(6/\pi^2)$ and a slope $x = -\pi^2 D_c/r^2$. Such a plot is shown in Figure 35, with the uptake data (a) and corresponding plot for obtaining the diffusion coefficient (b). The calculated $D_c$ for the last two cycles, which are the relevant cycles during a pressure swing adsorption process, was $7 \times 10^{-16}$ m$^2$/s. The reported values for a large single crystal using solid-state nuclear magnetic resonance is significantly higher, $9 \times 10^{-8}$ m$^2$/s, however it is entirely in line with reported values for binderless zeolite 13X beads, $10.9 \times 10^{-16}$.

Figure 35: The (a) time-dependent CO$_2$ uptake and (b) a plot of $\ln(1-m_t/m_\infty)$ at 303 K to 140 kPa for the first (black), second (blue) and third (green) cycles into a freeze-cast 13X monolith prepared from a suspension with a solids loading of 30.2 wt% dwb and frozen at 1 K/min.

However, equation 13 is strictly valid only at constant diffusivity under isothermal conditions. As is seen from the first uptake curve (black) in Figure 35, the ln plot shows a clear deviation from the linear prediction. This is a strong indication that there is another parameter that influences the uptake kinetics. It is possible and in fact high likely that the strong and rapid adsorption of 5 mmol/g of CO$_2$ will increase the local temperature, which will slow down further adsorption. During cycles two and three, the amount of CO$_2$ adsorbing is halved, and, which is probably more important, the chemisorption and the strongly bonding sites are not active anymore.
Gas breakthrough in zeolite 4A monoliths

The freeze-cast zeolite 4A monoliths could not be analyzed by uptake measurements of pure carbon dioxide, in the same way as 13X, due to its very narrow pore size. It is actually so narrow that just by increasing the size of the framework cation (for example from Na\(^+\) into K\(^+\)) will cause large differences in the uptake of carbon dioxide, and by adjusting the ion-exchange ratio, the selectivity between carbon dioxide over nitrogen can be greatly improved at the same time as keeping the uptake capacity high.\(^{108}\) On the other hand, the narrow pores of 4A prevent nitrogen uptake at -196 °C which is the normal analysis condition,\(^{78}\) and even our attempts to measure the uptake of pure carbon dioxide in 4A monoliths were met with prohibiting mass transfer resistances, which were likely induced by the generation of heat.

Instead, we applied a gas breakthrough method to determine the diffusion into freeze-cast zeolite 4A monoliths, and also studied the difference between two different ion-exchange ratios. First, pure nitrogen was flowed through a regenerated bed of 4A monoliths at 150 ml/minute, and then, at time zero, the flow was changed into a 1:9 mixture of carbon dioxide and nitrogen, which is representative of composition of a flue gas. A detector on the other end of the bed monitored the concentration of carbon dioxide in real time to determine how quickly the gas broke through and how quickly the bed was saturated.

![Figure 36](image)

*Figure 36: The carbon dioxide (10% in nitrogen) breakthrough for freeze-cast monoliths frozen at 10.0 °C/min from the A18 suspension of zeolite NaA (black squares), 10.2% K-exchanged NaKA (green circle) and 17.6% K-exchanged NaKA (blue triangle). Image taken from Paper 2.*

The resulting breakthrough curves can be seen in Figure 36. Initially, all carbon dioxide is being adsorbed inside the bed and nothing is coming through. The breakthrough occurred after 30 seconds for the ion-exchanged monoliths and 50 seconds for the unexchanged one. The following steep and
steady increase in the concentration after the initial breakthrough and until saturation of the ion-exchanged monoliths is a sign of a sharp front where the gas propagates, also known as the mass transfer zone (MTZ). In a bed with tortuous flow channels, the forward flow of the gas quickly dissipates to all sides, and the adsorption front assumes a parabolic shape which expands the MTZ, in effect leaving unused volume in the bed since the flow is normally stopped right before the separated gas breaks through. If the channels are straight, the forward flow will continue unhindered (plug flow) and thus utilize the entire volume more efficiently, as appears to be the case with the freeze-cast monoliths.

The small differences in the breakthrough curves stem from the varying degree of cation exchange. The unexchanged zeolite 4A (black squares) has the largest pores and surface area, which leads to a fast uptake and highest capacity for a single uptake of the three monoliths. The 10.2% potassium-exchanged monolith has smaller capacity (earlier breakthrough), but since the uptake is equally rapid with 4A, it can probably also be regenerated faster, meaning that during continuous use over several hours both will process equally much gas. Having a better selectivity for carbon dioxide than 4A makes this material very interesting. Finally, the 17.6% potassium-exchanged monolith showed the poorest performance, with both a smaller uptake capacity and a slow uptake with an increased MTZ.

The effective diffusivities in the beds could be calculated from the breakthrough curves to $2.3 \times 10^{-7}$, $2.2 \times 10^{-7}$ and $1.3 \times 10^{-7}$ m$^2$/s, for the unexchanged 4A, 10.2% exchanged NaKA, and 17.6% exchanged NaKA, respectively. These diffusion coefficients are very fast, especially compared to the freeze-cast monoliths of 13X with gravimetrically determined diffusion in the order of $10^{-17}$ m$^2$/s. The difference may largely be explained in terms of heat effects by the lower carbon dioxide concentration in the breakthrough measurements compared to the gravimetric measurements (10% instead of 100%), and that the flow of the carrier gas (nitrogen) in the breakthrough experiments may transport away some of the heat evolved during uptake.

Crystallinity and crystalline strain in pulsed current processed zeolite monoliths

In paper 3, *The effect of temperature on the pulsed current processing behaviour and structural characteristics of porous ZSM-5 and zeolite Y monoliths*, we prepared strong, pressed monoliths out of single-component zeolite precursor powders. Zeolite powders are metastable and quickly lose their surface area and crystal structure upon heating above a certain temperature, so therefore zeolites are conventionally mixed with a binder which activates before the zeolite is affected. However, pulsed current processing (PCP) is a novel technique where the powder is loaded in a graphite die and subjected
to rapid pulses of a high direct current, which heats up the die at very fast rates. A heating rate of 100 °C/minute was used under a pressure of 20 MPa to a designated target temperature, with a holding time for 3 minutes. During such short times the zeolite crystals did not lose activity, but they did start to form bonds via amorphous contact points to other crystals. This formed a strong consolidated network of active zeolite without any additional binder.

We used two commercial zeolite ZSM-5 powders with SiO$_2$/Al$_2$O$_3$–ratios of 30 and 50, and two zeolite Y powders with SiO$_2$/Al$_2$O$_3$–ratios of 30 and 60.

The effect of the holding temperature to the zeolites was investigated by direct surface area measurements, as shown in Figure 37. The measurements confirmed that the zeolites had indeed retained their surface area also at relatively high temperatures, at which the zeolites would turn amorphous in a conventional furnace. The crystallinities were assessed by internal standard method, by mixing a known amount of quartz with the zeolite. The changes in the monoliths were then assessed by comparing the calculated crystallinities of all other monoliths to the crystallinity of the monolith prepared at the lowest temperature in the series. Figure 38 shows that the increase in amorphous content goes hand in hand with a decrease in the surface area.

Figure 37: The effect of the PCP holding temperature to the surface area of zeolite monoliths. Image adapted from Paper 3

Figure 38: The effect of the PCP holding temperature to the amorphous content of the zeolite monoliths.
For each zeolite there was a certain temperature under which they retained their surface area with only a little loss: for ZSM-5 (30) and (50) it was determined to be 850-900 and 900-950 °C, respectively, and for zeolite Y (30) and (60) it was 700-750 and 800-850 °C, respectively. It is notable that these temperatures increased by 100 °C if the respective silica to alumina contents are doubled. The thermally stabilizing effect of increasing the silicon amount in the network is well known, however such well-defined processing temperature ranges as these are valuable for future work with these zeolites.

Thermal expansion behavior of zeolites and membrane supports

In paper 4, *Hierarchically porous binder-free silicalite-1 discs: a novel support for all-zeolite membranes*, the thermal expansion coefficient of an all-zeolite membrane support, prepared by the pulsed current processing (PCP) route, was compared to a commercially available alumina support and a typical zeolite membrane material. Investigations into the thermal expansion of common zeolites show that it is possible to do advanced thermal behavior analysis using in-house powder x-ray diffractometer equipped with a reaction chamber.

A ceramic membrane is a sheet which controls the passage of molecules, and is ideally as thin as possible; the theoretical limit is the unit cell of the membrane material. An illustration in Figure 39 shows a schematic support coated with a zeolite membrane which has been grown on the substrate in order to get full coverage over the support. The membrane is sieving the gas; the support itself should contain large pores which are not offering any added resistance. Membrane separation is a promising alternative for gas separation, since it works in a continuous flow rather than in cycles as adsorbents do, and zeolites are especially suitable candidates for gas membranes due to their have a very targeted molecular sieving effect.
Figure 39: A schematic illustration of a ceramic membrane, which selectively lets through only the red species from a mixture of red and green. The membrane itself (orange layer at the top) is very thin and weak, so it has been grown on a coarse and mechanically strong support material. The picture is not drawn on scale; the membranes are usually 100–1000 times thinner than the supports. The photograph, which is taken from Paper 4, shows PCP-consolidated silicalite-1 membrane supports.

The main drawback of a membrane is their high susceptibility to faults. A single crack in the membrane layer will significantly reduce the separation capability of the membrane, and ceramics, known to have a low damage resistance, are problematic. Great care must therefore be taken with the placement and protection of membranes; if the membrane is subjected to large variations in heat, either during calcination of the grown crystals or repeated thermal variations, such as when filtering a hot gas, there will be thermally induced stresses which may cause cracking if the thermal expansion coefficients of the support and the membrane do not match well.

Alumina (Al₂O₃) and sometimes steel are frequently used support materials. Although some exceptions exist, dense materials usually always expand during heating:¹¹⁴ the added energy goes into the chemical bonds, increasing their longitudinal vibration amplitude and thus extending the bond. Zeolites, however, are not dense; they are basically built up from rigid tetrahedra which form themselves into secondary building units (SBU), such as the double-4-ring (D4R) in Figure 40. The available space in the adjacent zeolite cavity enables new vibrational modes, so the increase in the available thermal energy, which normally would increase the bond length, instead goes to increasing transverse or rotational vibrations between the tetrahedra.¹¹⁵⁻¹¹⁷ This leads to torsion in the SBU, which in turn leads to reduction in the size of the SBU and eventually the entire structure.¹¹⁸⁻¹²⁰ However, in many zeolithic materials, especially those containing aluminium and large cations, the rotations are hindered and vibrational amplitudes may be increased instead, resulting in a non-uniform and negative thermal expansion.¹¹⁷,¹²¹⁻¹²³
Figure 40: Representation of the LTA framework (zeolite 4A) around its unit cell, with only the tetrahedral central atoms (Si or Al) shown. The smallest SBU that the structure can be built out of is the D4R, which is shown in detail and with included oxygen atoms in the inset. The oxygen-cornering tetrahedra are rigid compared to their connections via the corner oxygen atoms, allowing the tetrahedra in the SBU to rotate.

Figure 41 shows temperature dependent PXRD measurements on silicalite-1 and alumina. The most obvious feature is that silicalite-1 is actually shrinking while heated, whereas alumina is expanding. The large thermal mismatch between the zeolite membrane and alumina support will lead to high stresses if the temperature is varied. Since the zeolite is shrinking while the alumina is expanding, they may crack or delaminate, which is deleterious to the functionality of the membrane.

Figure 41: The unit cell volume of (a) silicalite-1 and (b) alumina, determined by in situ x-ray powder diffraction. Figure taken from Paper 4.

The linear thermal expansion coefficient $\alpha$ is traditionally measured using a dilatometer, which measures the expansion of the sample material in one direction. However, some zeolites, such as the MFI framework (Silicalite, ZSM-5), have different directions in the crystal, depending on how the pores and framework are oriented, and they will show different behavior into dif-
ferent directions. In-situ diffraction techniques (PXRD and other radiation sources) are able to resolve all directions by showing how the crystal structure changes at different temperatures. This has been done before using synchrotron radiation and setup, but we have been able to produce comparable results conveniently with an in-house PXRD instrument, fitted with a reaction chamber.

Figure 42: The thermal expansion of dehydrated zeolite 4A from 30 to 500 °C. The grey area shows the standard deviation from several measurements (6-8) pooled together. The three black lines are the linear fits for different regions of thermal expansion. The blue symbols are a comparison with reported data of hydrated (filled symbols) and dehydrated (hollow symbols) zeolite AgA, from Carey et al. The measurements and data analysis have been done by ms Niina Merilaita and reported in her project work.

The thermal expansion behavior of the investigated dehydrated zeolite 4A in vacuum, Figure 42, varied significantly in the measured range. The thermal expansion of the dehydrated zeolite was initially strongly positive, \(58.6 \times 10^{-6} \text{ K}^{-1}\), from 30 to 100 °C, after which it became strongly negative, \(-26.7 \times 10^{-6} \text{ K}^{-1}\) until 573 K, and then slightly negative, \(-8.57 \times 10^{-6} \text{ K}^{-1}\), until 500 °C, which was the highest temperature measured. Upon cooling the zeolite showed reversible expansion. Figure 42 also includes comparison to reported results from Carey et al. on silver-exchanged zeolite A, in both its hydrated and dehydrated forms, measured with synchrotron X-ray radiation. The relatively large difference in the hydrated and dehydrated forms reveals the significant role that water has in acidic zeolites, bridging and pulling the
zeolite framework together. Besides that the shapes of the curves do not really seem to coincide, there is at least a 150 °C shift in the maxima of our 4A and Carey’s hydrated AgA, but there might in fact exist two maxima or, more likely, the expansion is influenced by the difference between having different cations.¹²⁰,¹²⁸

Figure 43: The thermal expansion of dehydrated zeolite 13X from 30 to 600 °C. The grey area shows the standard deviation from several measurements (6-8) pooled together. The two black lines are the linear fits for different regions of thermal expansion. The green and red symbols are comparative results of 13X published by Couves et al.¹²⁴ and Krokidas et al.¹²³, respectively, and the blue symbols are results on siliceous Faujasite by Attfield et al.¹²⁹ The measurements and data analysis have been done by ms Niina Merilaita and reported in her project work.¹²⁷

Figure 43 shows the thermal behavior of 13X, together with three comparative works.¹²³,¹²⁴,¹²⁹ Comparatively the change in the unit cell length is of the same order of magnitude as for zeolite 4A, however there is not enough deviation in the high temperature data to warrant three different regions of thermal expansion. Otherwise 13X and 4A, which are much alike, perform rather similarly even in thermal expansion. However, when compared with other studies, the variation to the comparative studies of 13X is much larger than for 4A. The discrepancy is easiest to explain for the high-silica Faujasite of Attfield,¹²⁹ which, due to lack of aluminium atoms and charge-compensating cations, has a large region of uniform negative thermal expansion. The two other studies are close enough to ours so that experimental parameters might have affected the results. However, the most important feature we found was the change from strongly positive (83.7 *10⁻⁶ K⁻¹) to
slightly positive \((2.30 \times 10^{-6} \text{ K}^{-1})\) thermal expansion at 100 °C, very similar to that of 4A, and, given the similarity of the two zeolites, possibly originating from a similar deformation mechanism.

**Figure 44:** The thermal expansion of dehydrated ZSM-5 from 30 to 800 °C. The grey area shows the standard deviation from several measurements (6-8) pooled together. The two black lines are the linear fits for different regions of thermal expansion. The green symbols are comparative results of hydrated ZSM-5 published by Marinkovic et al.\(^{125}\), and the red and blue symbols are results from Silicalite-1 by Bhanage et al.\(^{130}\) and Krokidas et al.\(^{119}\). The measurements and data analysis have been done by Ms Niina Merilaita and reported in her project work.\(^{127}\)

Figure 44 shows the thermal behavior of ZSM-5, which is isostructural to Silicalite-1 but contains more aluminium. The unit cell symmetry is slightly monoclinic, with the unique angle being at 90.5°, until it is heated a few hundred degrees and it becomes orthorhombic. There were thus many parameters to report, but the most general one is the unit cell volume, which is also shown in the graph. ZSM-5 doesn’t have any distinct unit cell maxi-
mum, rather its thermal expansion coefficient changes from the initial $27.5 \times 10^{-6} \text{ K}^{-1}$ between 30 and 300 °C to $-17.3 \times 10^{-6} \text{ K}^{-1}$ between 500 and 700 °C.

There is one comparative study of an identical material, ZSM-5 by Marinkovic et al., shown in the graph. The data do not quite coincide, but it is likely an experimental factor: Marinkovic used hydrated ZSM-5 in air, which loses its last trace of water around 400-500 °C, while our zeolite was already dehydrated and in vacuum. The two studies on silicalite-1 have found similar values, and they only differ from ZSM-5 by having no aluminium in the framework.

In summary, in-situ powder x-ray diffraction is a handy and accessible tool for the examination of thermal behavior. We used a robust method which consisted of adding a small amount of silicon powder to the sample, and then using it as an internal standard to correct the pattern for sample displacements and thermal movement of the sample holder. The Rietveld full-profile analysis is also highly useful to analyze all data, and it gives very minute details of the changes in the unit cell when needed.

Characterization of synthesized nanozeolites

In paper 5, *Methylcellulose-directed synthesis of nanocrystalline zeolite NaA with high CO$_2$ uptake*, nanocrystalline zeolite 4A was synthesized and characterized. The reduction of size in zeolite crystals is of great interest for high activity and fast uptake kinetics, and viable pathways to reliably synthesize nano-sized crystals are crucial to their utilization.

The challenges in synthesizing nano-sized zeolites lie in cost and product quality. The reaction pathways regularly need high temperatures, structure-directing agents and synthesis times in the order of days, and might yield crystals with a broad size distribution. Confined space synthesis is an alternative approach to the regular hydrothermal synthesis; the synthesis is done in, for example, a porous medium or gel, which restricts the crystal growth in a narrow range. It has been successfully used for template-free preparation of zeolite 4A nanocrystals together with methylcellulose before, and has now been optimized for low-temperature synthesis of nano-sized zeolites with a short reaction time by adjusting the concentration of the methylcellulose, reaction temperature and reaction time.

The optimized conditions were found at 50 °C and 8h of reaction time, for a methylcellulose concentration of 3.5-6.8% of the precursor solution. This yielded zeolite A nanocrystals with a particle size of 100-150 nm and particle size distribution within 20 %. The crystallinity was determined by powder x-ray diffraction (PXRD) using the quantitative phase analysis (QPA) method, and was found to be very high (>95%) for the 100-150 nm particles (Figure 45).
Figure 45: Powder x-ray diffraction patterns of nano-sized zeolite 4A crystals synthesized in different amounts of methylcellulose. From (a) to (j), the amounts of methylcellulose are: 0.9%, 1.8%, 3.5%, 5.2%, 6.8%, 8.3%, and 0%. Taken from Paper 5.

The nano-sized 4A crystals were found to be good adsorbents; the best particles, prepared from a 5.2% methylcellulose solution, had a $D_c$ of $3.64\times10^{-10}$ m$^2$/s calculated by manometric methods. It should have been even better due to its small particle size, but the issue of the diffusion coefficient being smaller than expected has been noted by us and other studies in the field where large amounts of adsorbent has been used, and possible explanations involve the increased heat from rapid simultaneous uptake in the adsorbent$^{138,139}$ and a the effect of a disordered surface layer especially in small crystals with a high surface curvature.$^{140}$

This study demonstrated the preparation of nano-sized particles of zeolite A with a small particle size distribution and a high crystallinity, using a fast and economically viable synthesis route. The gas uptake of the crystals was high, but lower than expected from small particles.
Conclusions

We have successfully utilized freeze-casting, a cheap, economic and versatile templating method, in making large adsorbent monoliths for carbon dioxide capture. The ice-templated lamellar structure demonstrated excellent kinetic properties, and we have shown that it is indeed a very strong candidate for adsorbent structuring. We have investigated both the structure-property relationship between the adsorbent gas and the adsorbent monolith, but also the process-structure dependency when forming the monolith by identifying and varying some crucial properties, such as the suspension concentration and cooling rate.

We found that viscosity measurements and compressive tests are ample tools to probe the concentration domain of the formed freeze-cast monoliths, and also that their mechanical stability is greatly enhanced if the typically lamellar structure is perturbed into one resembling a honeycomb, for example by cooling the monolith fast. A buckling mechanism was also found to describe the mechanical failure upon compression.

Our kinetic experiments revealed that the main property to control is the wall thickness. Since the bottleneck of the uptake is diffusion into micropores, this diffusion distance in the walls, which contain the micropores, has to be minimized. We also measured and modelled gas breakthrough curves on monoliths of zeolite 4A with adjusted selectivity by ion-exchange, and found that while the uptake capacity is decreased in a breakthrough experiment, it still goes hand in hand with reduction in the uptake time. Freeze-cast monoliths displayed desirable properties for gas separation by pressure swing adsorption.

Powder x-ray diffraction has also been utilized as an effective tool by in both quantitative phase analysis (QPA) and thermal expansion studies. The QPA was optimized for a system consisting of either zeolite 13X or 4A, and using the other zeolite as an internal standard in a full-profile refinement. Silicon as the internal standard was also used in following the thermal changes in ceramic materials in order to correct for sample displacement by thermal effects.
Outlook

Although we have identified freeze-casting as a feasible and robust route to structure tailored monoliths for gas adsorption, only the first steps have been taken. The research so far has necessarily only been focused on simple geometries which have been frozen from one side. In order to start tapping the true available potential, several routes lie now open:

1. Understanding the role of additives in tailoring the ultimate monolith. The freeze-casting structure is actually controlled by particle mobility close to the growing ice front. By adjusting the viscosity – either by viscous additives or anti-freeze agents – one can establish a new tool in the freeze-casting box.

2. Improving the bulk mechanical properties of the freeze-cast monoliths. We have been using bentonite, the first material on hand, suitable for making pellets and granules, but sometimes lacking in the small amounts and dimensions inherent in freeze-casting. Chemical routes, involving polymers or silicate polymerization or geopolymers, are still largely untapped and have the potential to give these materials a giant leap forward.

3. Improving the geometry. The boring bottom-to-top cylinder is only useful in exploring the effects on different variations in the pore structure, but truly useful materials have to be able to scale up. How to control the freezing in order to make a meter wide monolith instead of 2 cm, or how to deal with the heat flow in order to freeze a meter tall monolith sound more like engineering problems, but how will different mold geometries affect the structure? Patterns on the mold? Freezing directions? As some fuel for imagination, attached is a concept art and actual photograph of a radially freeze-cast doughnut. It is both a way to freeze much taller monoliths than we have been doing so far, and to improve the mechanical and uptake properties since the radially aligned walls always have their strong side outwards, and the pores are there as well!
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References


