Straightforward Processing Route for the Fabrication of Robust Hierarchical Zeolite Structures

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ABSTRACT: Strong hierarchical porous zeolite structures are prepared by a sol−gel method using freeze gelation. Instead of conventional binders in powder form, such as bentonite or kaolin, it has been proven that using a freeze gelation method based on a colloidal silica sol is a more straightforward and easier-to-use-approach in fabricating highly mechanically stable zeolite monoliths. The resulting zeolite slurries possess superior rheological properties (not being pseudoplastic) and show low viscosities. This low viscosity of the slurry enables an increase in the solid content without compromising the extraordinary good flow behavior for casting applications. Additionally, in comparison to conventional powdery binders, zeolite samples prepared by using a colloidal silica sol exhibit a significantly higher mechanical strength. This mechanical strength can be further improved by either increasing the zeolite content or increasing the silica to zeolite ratio. Increasing the zeolite content leads to an increased volumetric adsorption capacity for CO2 as the test gas, resulting from the increased amount of zeolite particles per unit volume. In addition, a higher solid content of the zeolite monoliths leads to higher compression strengths, while showing the same elastic deformation and brittle failure characteristics. In turn, increasing the silica to zeolite ratio does not affect the volumetric adsorption capacity for CO2. Nevertheless, higher silica contents lead to a significant increase in the elastic deformation and absorbed work until failure. Therefore, the proposed processing route based on freeze gelation presents an easy and unique tool to tune the mechanical and gas adsorptive properties of hierarchically structured zeolite monoliths, according to the application requirements.

1. INTRODUCTION

Hierarchically ordered structures offer superior properties to overcome mass-transfer limitations.1,2 Therefore, hierarchy in material systems is intensively investigated for processes that are limited or characterized by mass-transfer, for example, in catalytic or cyclic swing adsorption applications. In particular, to increase the efficiency of swing adsorption processes, zeolite powders are colloidal-processed to form monoliths with a hierarchical porosity.3−5 Porous-structured monoliths feature superior heat-transfer properties for nonadiabatic processes and fast mass-transfer kinetics because diffusion on small scales is reduced to small path lengths.10−13

Hierarchical porous zeolite 13X monoliths are often fabricated by casting techniques, using sacrificial templates as pore creators or by freeze-casting methods. For example, Akhtar et al. added carbon spheres and whiskers with dimensions between 5 and 40 μm to a colloidal zeolite 13X slurry serving as a sacrificial template.4 This results in porous monoliths with a highly hierarchical pore structure after the burnout of the template. The different levels of hierarchy are created by (i) the pores generated by the burnout of the templates, (ii) the interparticle pores between the zeolite primary particles, and (iii) the micropores derived from the zeolite material itself. Furthermore, Ojulu et al. used the freeze-casting technique to fabricate porous zeolite 13X monoliths.5 In this case, the hierarchical structure is formed by the ice-crystal-like freeze-cast lamellas (∼10 μm), the interparticular pores between the zeolite primary particles (∼1 μm), and the micropores of the zeolite (∼0.7 nm). They showed that this pore system features high mass-transfer kinetics and that the prepared monoliths show a rapid uptake of carbon dioxide (CO2) in cyclic adsorption processes. Our previous study on hierarchical porous zeolite structures for pressure swing adsorption applications presents a combination of freeze casting with the sacrificial template technique.6 In addition to the lamellar pore channels generated by freeze casting, a polymeric foam is used as a sacrificial template providing a highly interconnected network of pores between 100 and 200 μm, depending on the type of polymeric foam (i.e., polyurethane foams with varying pore sizes from 10 to 35 pores per inch). This results in superior mass-transfer kinetics with a very high and rapid volumetric uptake of CO2.

Besides a rapid CO2 uptake, a high volumetric adsorption capacity, and good heat-transfer properties, one of the key...
challenges for monolithic adsorbents is their mechanical stability, especially when developing real applications. In practice, reactors for catalytic applications are filled by pouring the adsorbent monoliths into the reactor columns, which requires a sufficient mechanical strength. Even when the superior properties of large monoliths may enforce a change in the reactor design from a "top-down" filling of the reactor column to a more "bottom-up" stacking of monolithic elements, high pressure differences, for example, in pressure swing adsorption applications of 1000 kPa (10 bar) and more, still require an appropriate level of mechanical stability.

In general, there are three different ways for the fabrication of mechanically stable zeolite monoliths: (i) binderless sintering, (ii) binder conversion and (iii) conventional sintering. Binderless sintering is a relatively new approach, where the zeolite monolith is prepared without an inorganic binder. The final mechanical stability is obtained by material consolidation using spark plasma sintering, induced by an alternating electrical current. Another possibility is related to binder conversion. This process is based on the hydrothermal transformation of an inorganic binder, usually clays such as kaolin, metakaolin, or silica. Because of the hydrothermal treatment, the binder material is transformed into the zeolite matter, which intergrows with the primary zeolite particles to form a stable bond. Compared to the other two fabrication techniques, this processing route usually requires a comparably high amount of chemicals and produces a notable amount of waste water, which is not environmentally friendly. The most simple and straightforward approach to fabricate mechanically stable zeolite monoliths is conventional sintering. Here, typical zeolite slurries for casting processes consist of the zeolite powder as the matrix, water as the solvent, and organic as well as inorganic binder additives. Organic additives are usually added to increase the green body strength, whereas inorganic binders, for example, bentonite or kaolin, are added to provide mechanical stability after heat treatment.

In application, the mechanical requirements and specifications for zeolite monoliths are very complex and depend on different processing parameters. For instance, pouring monoliths into a reactor column highly depends on the column height and usually requires a high amount of mechanical stability in all directions. When the adsorbents are not poured, the requirements for mechanical strength are different, where high mechanical strength is only required at regions with high mass-transfer, thereby highly depending on the pressure drop and pore structure. However, even though inorganic binders are added, most zeolite monoliths prepared by conventional sintering lack the sufficient mechanical stability needed for application. In practice, the prepared monoliths are usually mechanically stable enough for careful sample handling and standard analyses for characterization. For instance, zeolite monoliths with graded pore size prepared in our previous study (mechanical properties comparable to those in refs 5 and 8) show sufficient mechanical stability for sample handling and withstand stresses of gas permeation and cyclic adsorption/desorption measurements with pressure differences of around 140 kPa (1.4 bar), but the obtained mechanical stability of around 0.05–0.15 MPa is not high enough to maintain shape when, for example, the sample is dropped from a table.

For this reason, we propose a straightforward processing route based on a sol–gel transition during freeze casting as a promising alternative for the preparation of highly stable, hierarchically structured zeolite monoliths, opening up the door to get closer to real applications. Different binder types are compared, and their influence on the rheological properties of the zeolite slurry as well as the mechanical stability of the adsorbent is studied. Figure 1 shows a schematic overview of the processing routes using powdery binders (A) and colloidal silica sol (B) as representatives for inorganic binders. Processing steps involve dispersing of the zeolite particles, ball-milling or rather pH-shift, molding, a freezing step, freeze drying, and final heat treatment mediated by sintering at 780 °C under air (A) and nitrogen atmospheres (B). Parts of this figure are adapted from ref 9.
prepared samples is investigated. Comparing the influence of sintering at 780 °C under air and nitrogen, the sintered zeolite monoliths are characterized by scanning electron microscopy (SEM), mercury intrusion porosimetry, standardized compression tests, and finally volumetric CO₂ adsorption. In this case, volumetric CO₂ adsorption is used as a measurement technique to evaluate the monolith performance with regard to the amount of active sites available. Although our previous study to evaluate the monolith performance with regard to the bodies are required.

Volumetric CO₂ adsorption is used as a measurement technique prepared samples is investigated. Comparing the in ACS Omega sintering at 780 °C (Sanyo Ultra Freezer, MDF-1155, Sanyo, Japan). After demolding, the samples are subsequently placed in a freeze dryer (P8K-E-80, Dieter Piatkowski—Forschungsgeräte, Germany) and dried at −30 °C at a reduced pressure of around 50 μbar for at least 4 d. The dried monoliths are cut to their final height of 40 mm before the heat treatment, using a disc cutter (CUTO 1, Jean Wirtz, Germany). To ensure a homogeneous pore structure throughout the monoliths and to avoid boundary effects, both the top and bottom of the cylindrical samples are cut, each about 10 mm. Afterward, the zeolite monoliths are heat-treated up to 780 °C, following a temperature profile similar to our previous study, operating in air as well as under a nitrogen atmosphere. The conventional heat treatment in air is performed in a furnace from the company Nabtherm, model HT 04/17 (Nabtherm GmbH, Germany). By contrast, the heat treatment under the nitrogen atmosphere is carried out in another furnace from the company Thermal Technology (model 1000, Thermal Technology LLC, USA). To ensure high purity of nitrogen in the sintering atmosphere, the furnace is evacuated three times and refilled with nitrogen. During heat treatment, the whole furnace is constantly streamed with nitrogen.

2. EXPERIMENTAL SECTION

2.1. Materials. To prepare a zeolite slurry for freeze casting, zeolite 13X powder with a primary particle size of around 2 μm was used as the ceramic material (molecular sieves 13X, Lot. MKBV6417V, Sigma-Aldrich Chemie GmbH, Germany), and deionized water (Seradest SD 2000, USF SERAL, Austria) was used as the solvent. Two different inorganic binders available in powder form, namely bentonite (nonaoyl, hydrophilic bentonite, Lot. MKBR9459V) and kaolin (halloysite nanoclay, Lot. MKBW6030V), as well as poly(ethylene glycol) (PEG) used as a dispersant and an organic temporary binder (BioUltra 8000, Lot. BCBP8378V) were purchased from Sigma-Aldrich Chemie GmbH (Germany). In addition, a colloidal silica sol with a primary particle size ranging from 5 to 10 nm (BegoSol K, Lot. 0116K 0216, BEGO GmbH & Co. KG, Germany) served as the inorganic binder and freezing agent. To initiate the sol–gel transition before molding, poly(acrylic acid) (PAA, Syntran 8220, batch number 101021W41, Interpolymer GmbH, Germany) was used to shift the pH value and served as a temporary binder to enhance the green body strength.

2.2. Processing Route. The slurries used for the fabrication of zeolite monoliths are prepared in two different ways, depending on the binder type. The additional amount of binder is always chosen depending on the amount of zeolite and presented in dry weight basis (dw %). For the powdered binders, namely bentonite and kaolin, the processing route based on our previous study is used, as schematically shown in Figure 1A. First, PAA serving as the dispersant and organic temporary binder is dissolved in deionized water. Then, the zeolite as well as the powdery binder type are coarsely dispersed in deionized water using a mechanical stirrer (RW20DZM, IKA LABORTECHNIK, Germany) for 30 min. The hydrophilic zeolite particles can be easily dispersed in water, but the used binder additives in powder form, especially bentonite, form agglomerates and disperse poorly. Therefore, the mixture is milled for 6 h in a ball mill to achieve a homogeneous slurry. By contrast, when using the colloidal silica sol as a representative for an inorganic binder, this ball-milling step is not necessary because the binder particles are already dispersed, as schematically shown in Figure 1B. Here, the zeolite powder is dispersed in deionized water using a magnetic stirrer, followed by addition of the silica sol. It is important to note that the amount of silica given in dwb % represents the dry amount of silica particles within the silica sol (~30 wt %) related to the dry amount of zeolite powder. The mixture is stirred for 1 h to cool down until it reaches room temperature because dispersing the zeolite particles generates heat. Prior to molding, pH is shifted from around 10 to 7 using PAA to initiate the sol–gel transition. After successful preparation of the zeolite slurries, they are poured into aluminum molds with an inner diameter of 20 mm and a height of 60 mm. The bottom plates of the molds are made of a plastic material (polyvinyl chloride) with a low thermal conductivity to enforce the freezing of the ice crystals in the radial direction. As already indicated in Figure 1, the two different processes are referred to as freeze casting (A) and freeze gelation (B), when using powder binders or colloidal sol, respectively. Both freeze casting as well as freeze gelation are carried out at −150 °C for at least 30 min (Sanyo Ultra Freezer, MDF-1155, Sanyo, Japan). After demolding, the samples are subsequently placed in a freeze dryer (P8K-E-80, Dieter Piatkowski—Forschungsgeräte, Germany) and dried at −30 °C at a reduced pressure of around 50 μbar for at least 4 d. The dried monoliths are cut to their final height of 40 mm before the heat treatment, using a disc cutter (CUTO 1, Jean Wirtz, Germany). To ensure a homogeneous pore structure throughout the monoliths and to avoid boundary effects, both the top and bottom of the cylindrical samples are cut, each about 10 mm. Afterward, the zeolite monoliths are heat-treated up to 780 °C, following a temperature profile similar to our previous study, operating in air as well as under a nitrogen atmosphere. The conventional heat treatment in air is performed in a furnace from the company Nabtherm, model HT 04/17 (Nabtherm GmbH, Germany). By contrast, the heat treatment under the nitrogen atmosphere is carried out in another furnace from the company Thermal Technology (model 1000, Thermal Technology LLC, USA). To ensure high purity of nitrogen in the sintering atmosphere, the furnace is evacuated three times and refilled with nitrogen. During heat treatment, the whole furnace is constantly streamed with nitrogen.

2.3. Characterization Methods. To investigate the slurry behavior, rheological measurements were performed using a Kinexus pro+ rotational rheometer (Malvern Instruments, Germany). For this, viscometry shear rate ramp measurements were carried out from 0.01 to 1000 s⁻¹, with a cone-plate setup (50 mm in diameter).

The heat-treated zeolite monoliths were finally characterized by determining the bulk density, total porosity, pore size distribution, compressive strength, as well as their adsorption capacity for CO₂. For the determination of the bulk density and total porosity, the geometrical method is applied. During our studies, we revealed that conventionally sintered samples (in air) are exposed to humid-rich air of the environment during the final cool-down step, which immediately results in water adsorption, compromising the total sample weight that leads to higher bulk densities (i.e., overestimation). Until now, we have not been able to dry the relatively large samples after sintering in an adequate way (e.g. at 350 °C and vacuum) without destroying them or risking a sample damage and hence affecting their structural properties. Thus, the only results of samples sintered under nitrogen are presented. Here, the cool-down phase is performed under an inert atmosphere, inhibiting water adsorption. To allow the measurement of the sample weight in their completely dry stage, the samples are directly transferred from the furnace into a desiccator after heat treatment for transportation and storage. The geometrical density and total porosity are determined by subsequently measuring the sample weight and dimensions (six times height and six times diameter at the top and bottom). To ensure high reproducibility, the measurements are performed on 12 different samples derived from 3 individual processing batches. For the visualization of
the pore structure and morphology, SEM is performed using a field emission SEM SUPRA 40 (Zeiss, Germany). The pore size distribution is determined by mercury (Hg) intrusion porosimetry using a Pascal 140 and 440 mercury porosimeter (Porotec GmbH, Germany). For this, the cylindrical zeolite samples are broken into pieces to fit into the measurement cell.

A reliable determination of the mechanical stability of the prepared zeolite monoliths is very important for accurate evaluation. Therefore, compression tests are carried out following the ASTM C773-88 using a ProLine table-top Z005 testing machine (Zwick/Roell, Germany). Following the standard testing procedure, $n = 10$ samples are tested for each formula to obtain reliable results. The 10 samples are obtained from 3 individual processing batches. The cylindrical samples have a height to diameter ratio of 2 (40 mm height, 20 mm diameter), and the testing speed is set to 0.5 mm min$^{-1}$ to ensure monolith failure within the first 30 s, preventing subcritical crack growth.

To evaluate the gas adsorption performance of the zeolite monoliths, volumetric CO$_2$ adsorption measurements are carried out at 30 °C using a BELSORP-Max instrument (BEL Japan Inc., Japan). For this, the samples are broken into pieces to fit into the measurement cell. Three samples derived from three individual processing batches are tested for each formula. Prior to adsorption measurements, the samples are thermally activated at 350 °C under vacuum ($\leq2$ Pa) for 16 h. Different slurry compositions, for example, different zeolite to binder ratios, will affect the adsorption capacity, when relating the adsorbed amount of CO$_2$ to the sample mass. To ensure comparable results, the volumetric adsorption capacity is presented instead. For this, the measurement data are recalculated to mmol cm$^{-3}$ using the bulk density. Please note that in this case, the (volumetric) adsorption capacity is defined as the maximum adsorbed amount of CO$_2$ at 100 kPa (1 bar) on a thermally activated sample.

3. RESULTS AND DISCUSSION

3.1. Freeze Casting versus Freeze Gelation: The Right Choice of Inorganic Binder. One of the biggest challenges for casting processes is related to the handling of the rheological behavior of the slurry. In our last study, the rheological properties of the slurry were the limiting factor in increasing the zeolite content aiming at high volumetric CO$_2$ capacities of zeolite monoliths.$^9$ In fact, the highly viscous slurries could only be processed by applying a degassing step to remove air bubbles before molding, and the molding step itself could only be achieved by pushing the slurries through a small syringe (needle diameter 120 $\mu$m, injection speed $1.35 \pm 0.17$ mL s$^{-1}$), utilizing the effects of shear-thinning and thixotropy and leading to lower viscosities for a short period of time. Figure 2 shows the representative results of the shear rate ramp measurements with zeolite slurries containing 35 wt % zeolite and different inorganic binder types as additives (each 10 dwb %), referring to bentonite, kaolin, and silica.

The zeolite slurry with bentonite as the binder has the same composition, compared to the “optimum” slurry used in our previous work, and serves as the reference.$^9$ Clearly, the slurry consisting of 35 wt % zeolite and 10 dwb % of bentonite shows a high viscosity and shear-thinning behavior (pseudoplastic) compared to slurries containing kaolin or silica as inorganic additives. Here, the viscosity can be as high as 100 Pa s for small shear rates, which decreases to 0.1–0.2 Pa s for high shear rates. For comparison, honey usually has viscosities between 10 and 20 Pa s$^{15,17}$ and water at 20 °C has a viscosity of around 0.001 Pa s.$^{18,19}$ Kaolin when used as the inorganic binder reduces the overall viscosity to around 0.01–0.05 Pa s, and the slurry does not show shear-thinning behavior. Because of this rheological behavior, the filling of the mold does not require an additional syringe, and the slurry can easily be poured into the molds. However, a degassing step before the molding is still necessary to remove existing air bubbles. In contrast to bentonite and kaolin, using silica as the inorganic binder results in slurries with a very low viscosity, usually between 0.003 and 0.01 Pa s. The silica particles are already dispersed and available as a colloidal sol, stabilized at an elevated pH of around 10. At this pH, the silica particles show a negative zeta potential because of the isoelectric point (IEP) of SiO$_2$ being at a pH of around 2.$^{19,20}$ Our measurements show that the zeolite particles also have a negative zeta potential at this pH value (IEP of $\sim$5, see Figure S1 in the Supporting Information). Furthermore, when dispersing zeolite 13X particles in water, pH shifts drastically to around 10 because of their strong surface charges. Therefore, when mixing the colloidal silica solution with zeolite particles dispersed in water, two very well-dispersed and highly stable solutions with identical pH and negatively charged particles are homogenized. This results in a stable slurry system with very low viscosities.

Because of the very fast and easy way of slurry preparation when using the silica sol, the processing route can be significantly shortened, as already indicated in Figure 1. Zeolite 13X is highly hydrophilic and can easily be dispersed in water. In practice, dispersing the zeolite powder and adding the silica sol to obtain a homogeneous slurry take merely about 5–10 min. Here, the applied total time of 1 h for dispersion is used only for the slurry to cool down to room temperature. This step can be speeded up by actively cooling the slurry during dispersion, which reduces the preparation time to about 15 min (data not shown). In this study, the slurry is not actively cooled for the sake of simplicity, but it demonstrates the potential of using colloidal sols as the binder. In addition, the homogenization step (also for solid loadings as high as 40 wt %) can be performed by using a magnetic stirrer instead of a mechanical stirrer, which is needed for binders in powder form. In summary, using a colloidal silica sol as the inorganic binder significantly simplifies the processing route and reduces the...
processing time from about 6−7 h to around 1 h, while obtaining comparably low slurry viscosities.

To evaluate the performance of the different binder types, hierarchical zeolite monoliths are prepared by freeze casting and freeze gelation. Aiming at a straightforward processing route, a common heat treatment is used similar to other working groups without further treatment steps, for example, binder transformation. In general, structures prepared by freeze-casting techniques are near-net shaped, showing a very high shape accuracy combined with a low shrinkage of 20%. For the freeze-casted zeolite samples, a very high shape accuracy with relative standard deviations of height and diameter <0.2% and low total shrinkage of <1% are achieved.

Figure 3A presents the results of compression tests performed on zeolite monoliths with a height to diameter ratio of 2, containing different binder types, finally heat-treated at 780 °C in air or nitrogen (N2). Figure 3B shows the representative stress−strain curves for samples treated in N2. All monoliths are prepared from slurries with 35 wt % zeolite, equivalent to 30 wt % zeolite with 10 dwb % of bentonite as the binder.5 For the explanation of the differences in the compression strength, two reasons can be indicated: (i) the geometrical sample size dimensions and (ii) the orientation of the freeze-cast lamellas. In contrast to our studies, Ojuva et al. as well as other literature dealing with compression tests of zeolite monoliths used samples with height to diameter ratios (h/D) of 1 or even less.5,8,14 It is commonly known that the height to diameter ratio of the samples used in compression tests significantly influences the obtained compression strength, showing higher strength values for smaller h/D ratios, which asymptotically decrease with increasing h/D ratio.21,22 This seems to be even more present for freeze-casting structures, and within our studies, we found around 3 times higher compression strength (0.49 ± 0.05 MPa) for zeolite samples with a ratio of h/D = 1 (35 wt % zeolite, 10 dwb % bentonite, heat-treated in air, data not shown). For this reason, the samples are prepared according to the suggestions from the ASTM C773-88, which recommends a ratio of h/D between 1.9 and 2.1. According to our findings, this ratio is highly recommended for all studies dealing with applicability. Furthermore, in most studies dealing with zeolite monoliths prepared by freeze casting, the freezing direction is usually chosen from the bottom to the top of the sample.5,8,23 This leads to significantly higher compression strengths because of the orientation of the freeze-cast lamellas parallel to the direction of the applied force, with the usual mode of failure being buckling.23 Referring to our studies, we found that the compression strength is 4−5 times higher for samples with freeze-cast lamellas oriented in parallel to the applied force vector (axial freezing) in comparison to samples with lamellas oriented in the perpendicular direction (radial freezing); data not shown. In this study, the chosen freezing direction is radial instead of axial (Figure 1) because we determined an anisotropic pore structure with lamellar pore channels of increasing diameter from the bottom to the top, when the sample height is as large as 40 mm. Presumably, this derived from the lower thermal conductivity of the formed ice crystals compared to the metal material of the used mold, limiting heat-transfer with increasing height of the freezing front. Therefore, aiming at high reproducibility and reliability of the results, radial freezing is chosen to prepare the zeolite samples, ensuring a highly homogeneous pore structure throughout the samples. Accordingly, the usual modes of failure observed within this study are shearing (Figure 3) and splitting.

In accordance with our previous work using bentonite as an inorganic binder,1 the zeolite monoliths possess a compression strength of 0.15 ± 0.01 MPa, suitable for careful sample handling. The compression strength increases to 0.2 ± 0.02 MPa (factor of 1.3) when sintering under a N2 atmosphere. By contrast, the samples are significantly weaker on using kaolin as the binder, independent of the sintering atmosphere (<0.03 MPa). The mechanical stability of such zeolite monoliths with kaolin as the binder is not suitable for sample handling and hence not recommended for real applications. Please note that
although operating with extreme care, only 9 out of 12 samples could be tested because of sample destruction while handling. Besides simplifying the processing route, the colloidal silica sol used as the binder significantly increases the compression strength of the zeolite monoliths to values of around 0.36 ± 0.06 MPa. Furthermore, changing the sintering atmosphere from air to N\textsubscript{2} leads to an additional increase in the compression strength (0.42 ± 0.04 MPa), showing smaller standard deviations (significance confirmed with a student’s t test, data not shown). The silica particles used as the binder are comparably small ranging from ∼5 to 10 nm, according to the manufacturer. These small nanoscaled particles have a high surface area to volume ratio and in turn offer a high surface energy. The thermodynamic driving force of “sintering” is the reduction in the Gibbs free energy of the system.\textsuperscript{24} Accordingly, this driving force is much higher for small particles compared to large particles, and neck formation due to surface diffusion can start at lower temperatures. In addition, the sol–gel transition of the slurry system is initiated before freezing by adding PAA for shifting the pH value to 7. The silica particle distribution in the slurry will then be transformed from a random distribution to a short-order distribution by agglomeration and formation of silica chains (gelation). Therefore, the silica particles are already arranged in a closed order, providing a high interconnectivity when the slurry is subsequently frozen. Both the high surface energy of the small particles as well as the high interconnectivity due to gelation are possible explanations for the determined higher mechanical stability in comparison to monoliths prepared with conventional binders in powder form.

3.2. Robust Hierarchical Zeolite Monoliths by Freeze Gelation: Increasing the Solid Content. On the basis of the rheological behavior of the slurry system, combined with simple and fast processing as well as the obtained superior mechanical stability, the freeze-gelation process based on the colloidal silica sol and heat treatment under a N\textsubscript{2} atmosphere is further used for all experiments. In the context of fabricating robust zeolite monoliths, the influence of the zeolite and the binder (silica) amount is investigated by independently varying the zeolite content and the silica to zeolite ratio, where corresponding results are marked for better visualization by a color code using green and purple, respectively. The resulting monolithic structures are characterized in terms of structural properties in relation to the bulk density, total porosity, pore morphology, and pore size as well as their performance regarding mechanical strength and CO\textsubscript{2} adsorption capacity. Figure 4 shows the SEM micrographs of the fractured surfaces of hierarchical-structured zeolite monoliths with increasing zeolite content from 35 to 40 wt % (part A) and increasing silica to zeolite ratio from 10 to 50 dwb % silica, using a constant zeolite amount of 35 wt % (part B). In contrast to our previous study,\textsuperscript{9} it is possible to increase the zeolite content up to 40 wt % because of the low viscosity of the slurry, when using colloidal silica sol as the binder. Consequently, the micrographs presented in Figure 4A show an increasing strut thickness and a decreasing amount of freeze-casting pores with increasing zeolite content.

These tendencies can also be confirmed by the increasing bulk density and decreasing total porosity presented in Table 1. Increasing the silica to zeolite ratio for a constant amount of

| zeolite content in wt % | silica content in dwb % | bulk density in g cm\textsuperscript{-3} | total porosity in % |
|------------------------|-------------------------|------------------------------------------|---------------------|
| 35                     | 10                      | 0.475 ± 0.002                           | 79.73 ± 0.10        |
| 37.5                   | 10                      | 0.514 ± 0.002                           | 77.92 ± 0.08        |
| 40                     | 10                      | 0.570 ± 0.003                           | 75.52 ± 0.12        |
| 35                     | 25                      | 0.513 ± 0.002                           | 79.90 ± 0.10        |
| 35                     | 50                      | 0.590 ± 0.004                           | 73.95 ± 0.18        |
zeolite also increases the bulk density and reduces the total porosity. In contrast to increasing the zeolite content, increasing the amount of silica results in neither increasing the strut size nor decreasing the amount of freeze-casting pores. Instead, the silica nanoparticles predominantly arrange between the zeolite particles to fill up the interparticular pore space between them (Figure 4B). For moderate amounts of silica (10 dwb %), the porous structure is characterized by the zeolite primary particles, which are interconnected and held together by the silica acting as the inorganic binder. By contrast, for high amounts of silica (≥25 dwb %), the microstructure is different, and the silica content seems to serve as a matrix incorporating the zeolite particles.

Figure 5 shows the results of exemplary mercury intrusion porosimetry measurements performed on hierarchical porous zeolite monoliths with varying zeolite contents (A) and varying silica to zeolite ratios (B). Analyzing all measurements performed within this study, considerable differences regarding the open porosities for samples with identical composition and even for measurements performed twice on a single sample are obtained. Two examples for such measurement outliers are "37.5 wt % zeolite, 10 dwb % silica" in Figure 5A and "35 wt % zeolite 50, dwb % silica" in Figure 5B. These outliers always show a high deviation beginning from large pore diameters (20–100 μm). One possible explanation can be related to artifacts when Hg starts to penetrate into the sample, maybe due to surface effects caused by the sample preparation (the samples are crushed to fit into the measurement cell). Therefore, the mercury porosimetry measurements are only used for qualitative analysis.

For all measured samples, trimodal pore size distributions are obtained, and the individual peaks can be clearly identified. The first peak with the highest pore volume is obtained at pore diameters of around 10–20 μm and belongs to the lamellas derived from the ice crystals during freezing, which can also be confirmed by the corresponding SEM micrographs (Figure 4A). The next peak is attributed to pore diameters that are 1 order of magnitude smaller, showing values of around 1–2 μm. Such pores can be assigned to the interparticular pore volume between the zeolite primary particles, which is in accordance with the SEM results (Figure 4B). The third increase in the relative pore volume can be addressed to very small pores <10 nm belonging to the interparticular pore volume between the silica nanoparticles.

In general, mercury porosimetry measurements confirm the relation between the solid content and pore structure, as...
expected from the SEM analysis shown in Figure 4. When increasing the zeolite content, the pore structure mostly remains the same, showing that the amount of freeze-cast lamellas is decreased and that the amount of interparticular pores between the zeolite particles is increased. These tendencies are confirmed by the mercury intrusion porosimetry measurements presented in Figure 5A, showing similar pore structures. Bearing in mind the deviations of open porosities at relatively large pores (20−100 μm), the relative pore volume of interparticular pores is subsequently increased with increasing zeolite content. Figure 4 further shows that the silica nanoparticles are predominately arranged between the zeolite particles in the interparticular pore volume, subsequently filling it when the amount of silica is increased. This trend can be confirmed by the mercury porosimetry measurements presented in Figure 5B. Here, the relative pore volume between 1 and 2 μm is significantly decreased when increasing the silica to zeolite ratio, while the relative pore volume below 10 nm is increased. In addition, the peak in relation to pore diameters between 10 and 20 μm (freeze-casting pores) is independent of the amount of silica, giving the proof that the silica nanoparticles mostly arrange in between the zeolite particles without affecting the channel-like pore structure created by freeze casting. However, the higher amount of silica particles significantly decreases the interparticular pore volume in between the zeolite particles, limiting one level of hierarchy, as shown in Figure 5B. A high level of hierarchy is a key requirement for zeolite monoliths, when aiming at a rapid uptake of gaseous species. Therefore, this “pore-filling effect” by the silica binder may compromise a fast uptake of gas because of limiting the gas diffusion from the freeze-casting pores to primary zeolite particles. However, when using commercially available zeolite powders, the limiting step of mass-transfer is the gas diffusion into the primary particles. It is assumed that only when the primary zeolite particles feature a very rapid gas uptake, for example, due to a hierarchical porosity, the pore-filling by the silica particles will result in a diffusion limitation.

To evaluate the influence of the zeolite content and the silica to zeolite ratio on the mechanical stability, compression tests are carried out. Figure 6 shows the results of compression tests performed on hierarchical zeolite monoliths with various zeolite amounts from 35 to 40 wt % (A) and different silica amounts from 10 to 50 dwb % (B). The compression strength values are presented in mean values with standard deviations (Figure 6A1,B1) and representative stress strain curves are shown (Figure 6A2,B2).

The results show that increasing the zeolite content as well as increasing the amount of silica result in an increase in the compression strength from 0.42 ± 0.04 to 1.06 ± 0.33 and 1.38 ± 0.2 MPa, respectively (Figure 6A1,B1). Both increasing the amount of zeolite as well as increasing the silica to zeolite ratio for a constant amount of zeolite lead to an increase in the “total” solid content of the slurry from 37.45 wt % to 44 (A1)
Increasing the silica content leads to a transition in the material behavior when a load is applied. Increasing the silica content leads to an increase in the mechanical strength, which is confirmed by the determined compressive strength values in this study. Because of the increase in the zeolite as well as silica content, the compression strength is increased to values of 1.06 ± 0.33 and 1.38 ± 0.2 MPa, respectively. The samples consisting of 40 wt % zeolite showed signs of crack formation after sintering, resulting in comparably high standard deviations. Presumably, the cracks were derived from desorption of a relatively large amount of water adsorbed within the samples during the heat treatment between 100 and 200 °C. A possible strategy to avoid these cracks for samples with high solid contents is related to the introduction of additional dwell times at, for example, 100 and 200 °C, guaranteeing more sensitive removal of residual water.

Figure 6A2,B2 shows the representative stress–strain curves obtained from compression tests performed on samples with varying zeolite and silica contents, respectively. For a higher amount of zeolite, at a constant silica to zeolite ratio, the stress–strain curves feature a steeper increase (i.e., higher Young’s modulus for compression) until the samples finally crack leading to a higher compressive strength. The maximum strain at the time of fracture is between 0.5 and 1% and independent of the amount of silica particles within this matrix. But, a higher amount of silica particles will result in a higher modulus for compression will be decreased porosity (and thereby increased bulk density) leads to an increase in the mechanical strength, which is confirmed by the corresponding SEM micrographs in Figure 4. This matrix consists of a highly interconnected network of silica particles formed by the silica gel, which is only partially sintered, leading to a porous matrix (Figure 5). The decrease in the Young’s modulus for compression for samples with 25 dwb % of silica represents this transition from an interconnected zeolite particle system to a system where zeolite particles are embedded into a porous silica matrix. Accordingly, the Young’s modulus for compression will be defined by the silica matrix, independent of the amount of silica particles within this matrix. But, a higher amount of silica particles will result in a higher degree of interconnection and a larger quantity of bonds, leading to a material system capable of elastically storing more energy.

For a better comparison, Figure 7 shows the compressive strength (part A) and the work until failure (part B) depending on the bulk density of the samples. In this case, the work until failure represents the area under the stress–strain curve until the maximum force is reached. When comparing the compression strength with the geometrical density for samples with varying zeolite and silica contents, both variations show a clear dependency with a similar trend. In turn, the work until failure presents a different behavior. The average area under the stress–strain curves increases linearly with increasing zeolite content. Samples with 37.5 wt % zeolite and 10 dwb % of silica show a very similar bulk density than samples with 35 wt % zeolite and 25 dwb % of silica, and also the work until failure is very similar. By contrast, samples with 50 dwb % of silica show a significantly increased work until failure behavior.

In summary, both increasing the zeolite as well as the silica contents of the slurry lead to an increase in the bulk density as well as the compression strength of the zeolite monoliths. The increase in the final compression strength is independent of this variation, but the overall mechanical behavior against an external load shows differences. Increasing the zeolite content leads to an increase in the Young’s modulus for compression,
and increasing the silica content leads to a compression behavior characterized by a significantly larger work until failure. In swing adsorption processes using solid sorbents, the adsorption capacity for gases is one of the most important material properties. For this reason, CO₂ is used as a representative for gas adsorption studies to investigate the influence of the zeolite as well as silica content on the adsorption capacity of the prepared zeolite monoliths.

It is worth pointing out that the adsorption capacity is mainly influenced by the zeolite primary particles and is not influenced by the binder type (see Figure S2 in the Supporting Information). Although the adsorption capacity related to the sample mass may change depending on the density and relative amount of the binder, the volumetric adsorption capacity is completely independent of the binder type and amount (see also Figure 8). Figure 8 shows the results of CO₂ adsorption measurements performed on monoliths with varying zeolite (A) and silica (B) contents. The adsorbed amount of CO₂ is presented with respect to the sample mass (mmol g⁻¹) as well as volume (mmol cm⁻³). Keeping the amount of silica constant (10 dwb %), increased zeolite contents result in a similar material composition of the monoliths. Therefore, when relating the adsorbed amount of CO₂ to the sample mass, it remains constant at around 5 mmol g⁻¹ (Figure 8A1), which is in agreement with the results of our previous study using bentonite as the binder. Relating the amount of CO₂ per unit volume, the increase in the zeolite content of the slurry directly leads to an increase in the volumetric adsorption capacity (Figure 8A2) because of the higher amount of zeolite primary particles per unit volume of monoliths. By contrast, when increasing the silica to zeolite ratio, the material composition of the monoliths is changed, more precisely, a higher amount of material with a significantly smaller adsorption capacity is added. This leads to a decrease in the CO₂ adsorption, when related to the sample mass (Figure 8B1). In turn, when the zeolite content is kept constant at the same time, the amount of zeolite particles per sample volume remains the same, and therefore, the CO₂ adsorption per unit volume almost remains constant at nearly 2.5 mmol cm⁻³ (Figure 8B2). There seems to be a slight decrease in the adsorption capacity for higher silica to zeolite ratios, but the differences in the mean values are within the standard deviations, and therefore no statistical significance is present. Nevertheless, a slight decrease in the adsorption capacity is plausible, when assuming that the amount of silica particles forming sintering necks on the surface of the zeolite particles is significantly increased. However, no significant effect can be statistically shown, and therefore it is assumed that the volumetric adsorption capacity is mainly independent of the amount of silica.

In summary, preparing hierarchically structured zeolite monoliths by freeze gelation using silica sol as the binder results in a straightforward and fast processing route. The slurry
is highly stable, and the rheological properties outrun the performance of conventionally used compositions for the application in a casting or molding process. Because of the low viscosity of the slurry, it is possible to prepare slurries with a significantly higher amount of solid content. Both the increase in the zeolite content and the increase in the silica content result in an increase in the mechanical stability of the zeolite monoliths. In turn, while leading to comparable compression strengths, the increase in the zeolite content further results in an increase in the volumetric working capacity, and the increase in the silica content leads to an increase in the absorbed work until failure.

4. CONCLUSIONS
Hierarchically structured zeolite monoliths are prepared by a straightforward processing route based on a commercially available zeolite 13X powder. Different, commonly used binder types are applied to investigate their influence on the rheological behavior of the slurry and the final properties of the zeolite monoliths, focusing especially on the mechanical strength and the adsorption capacity for CO2. The results show that a processing route based on freeze gelation using silica sol as the binder significantly decreases the effective processing time from around 7 to 1 h. This leads to the conclusion that a sol–gel based preparation route offers unique possibilities for a time- and cost-effective processing. At the same time, such prepared zeolite monoliths present superior mechanical stability, possessing a compressive strength level that is 3 times higher than the reference structures using bentonite as the binder, making the silica sol route an easier to use and a better suitable alternative when aiming at a higher mechanical stability.

Additionally, the rheological properties of the resulting slurry allowed easy handling and a further increase in the solid content of the slurry. Both the zeolite (40 wt % zeolite, 10 dwb % silica) and the silica contents (35 wt % zeolite, 50 dwb % silica) could be increased leading to significantly higher compression strength values above 1 MPa in both cases. In practice, the prepared samples featured mechanical stability, which allowed them to withstand a drop from a table without breaking or falling apart. While showing a similar relation between the bulk density and compression strength, both sample types show differences regarding other properties. With an increase in the zeolite content, a significant increase in the volumetric adsorption capacity for CO2 can be achieved. In turn, increasing the silica content does not lead to an increase in the adsorption capacity, but the absorbed work until failure is significantly increased, making the monoliths more resistant against applied mechanical forces. Of course, there will always be a tradeoff between the desired material properties and what can be achieved in practice. For example, for casting processes, the slurry viscosity is one major limiting factor. As shown in this particular case, the large difference in the particle size between the binder and primary zeolite particles allows comparably high solid contents, but both cannot be increased without limits. In the end, the choice of the “total” solid content and the silica to zeolite ratio will depend on the requirements of the envisaged application and is a part of optimization, but the results presented in this work can be used as general guidelines. For instance, in the particular case of swing adsorption processes, the volumetric adsorption capacity for gases is very important, and therefore, high zeolite contents are often desired. High zeolite contents with a comparable low amount of binder provide an appropriate amount of mechanical stability for temperature swing adsorption processes, whereas a higher amount of binder may be needed to provide higher mechanical strength levels for pressure swing adsorption where pressure drops can be as high as 1000 kPa (10 bar) or when the adsorbents need to be poured into a column. Here, the proposed processing route provides an easy way to adjust the monoliths’ properties according to the requirements of the envisaged application. Furthermore, the processing route is transferable to other materials, which can be processed in aqueous solutions and can withstand a heat treatment up to 780 °C in the nitrogen atmosphere to fabricate stable and hierarchically structured monoliths.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00972.

Zeta-potential measurement for zeolite 13X and CO2 adsorption isotherms of zeolite 13X monoliths (PDF)

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Notes
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