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Bio-based Micro-/Meso-/Macroporous Hybrid Foams with Ultrahigh Zeolite Loadings for Selective Capture of Carbon Dioxide

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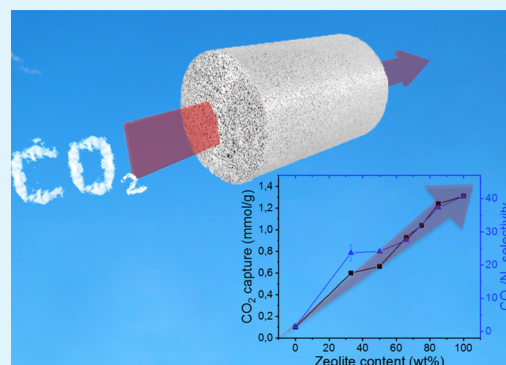
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Supporting Information

ABSTRACT: Microporous (<2 nm) crystalline aluminosilicates in the form of zeolites offer a great potential as efficient adsorbents for atmospheric CO₂ in the eminent battle against global warming and climate change. The processability of conventional zeolite powders is, however, poor, which limits their implementation in many applications, such as in gas filtration industrial systems. In this work, we overcome this issue through the preparation of hybrid foams using mesoporous/macroporous supporting materials based on the strong network properties of gelatin/nanocellulose, which can support ultrahigh loadings of silicalite-1, used as a model sorbent nanomaterial. We achieved up to 90 wt % of zeolite content and a microporous/mesoporous/macroporous hybrid material. The application of hybrid foams for selective CO₂ sorption exhibits a linear relationship between the zeolite content and CO₂ adsorption capacity and high selectivity over N₂, where the gelatin/nanocellulose foam efficiently supports the zeolite crystals without apparently blocking their pores.

KEYWORDS: hybrid foams, nanocellulose, gelatin, zeolites, selective capture, CO₂ adsorption



INTRODUCTION

The pressing need to abate the increasing concentration of CO₂ in the atmosphere, which is strongly linked to global climate change,¹ requires the development of new technologies to reduce CO₂ emissions. These technologies must be inexpensive and highly selective to CO₂. In this context, porous materials with high CO₂ adsorption capacity, such as zeolites,² activated carbons,³ and metal organic frameworks,⁴ have been proposed during the last decades. In particular, zeolites are crystalline microporous aluminosilicates consisting of a 3D network of tetrahedral AlO₄ and SiO₄ quadri-connected via oxygen bridges, resulting in a system of cavities or pores that forms channels through the material, allowing the capture of smaller molecules inside the framework.⁵ Zeolites have been widely studied in applications such as gas separation,⁶ ion exchange,⁷ and catalysis⁸ because of their superior chemical and thermal stability, as well as their great potential to separate mixtures of molecules based on preferential adsorption. Moreover, zeolites exhibit shape-selective molecular sieving because of their narrow and adjustable microporosity.^{9,10}

However, the key challenge for zeolites in most applications is their poor processability into structural materials because of their crystalline powdered form, which limits their implementation in many large-scale applications, such as in gas

separation for industrial processes. Moreover, the employment of adhesives and inorganic binders to prepare zeolite-based materials typically leads to pore blockage and reduced gas adsorption capacity.¹¹ A way to overcome these limitations is through the preparation of zeolitic hybrid foams using porous supporting materials that can uptake high quantities of zeolites while preserving their efficiency and selectivity.

Bio-based foams represent an attractive alternative as supporting materials of sorbent nanomaterials from an environmental point of view not only because of their biodegradability but also because of their low cost and extremely low densities.¹² Foams have been widely investigated for several applications including heat-insulating materials,¹³ supercapacitors,¹⁴ and as superabsorbents.¹⁵ Moreover, recently, foams have also received increased attention for CO₂ capture^{16–18} because of their hierarchical meso-/macroporosity, which can enhance the diffusion of molecules and limit the pressure drop over the adsorbent, allowing for high gas flow rates. Foams are attractive also for their ease of processing and their scalability. Hybrid aerogels of zeolites with nanocellulose have been previously reported by the

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deposition of zeolite particles onto the cellulosic structure,⁵ where they proved to decrease the thermal conductivity upon addition of zeolites (up to 10 wt % of nanozeolite), and their potential use as super-insulating materials. However, the preparation of bio-based freestanding foams with ultrahigh loadings of zeolite has never been reported as adsorbents for selective CO₂ capture. In this work, we take advantage of the strong network properties of gelatin/nanocellulose-based foams to support ultrahigh loadings of colloidal zeolite silicalite-1, withstanding up to 90 wt % of zeolite content, which appears to be the highest loading of adsorbent in a foam ever reported.

■ EXPERIMENTAL SECTION

Chemicals and Materials. Sodium bromide (NaBr), sodium hypochlorite (NaClO), gelatin, and 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) were purchased from Sigma-Aldrich (Germany). High-purity cellulose from softwood fibers (Norwegian spruce) with a high cellulose content (95% cellulose, 4.5% hemicellulose, and 0.1% lignin content as provided by Domsjö Fabriker AB, Sweden) was used as a starting material to produce TEMPO-oxidized cellulose nanofibers (TOCNFs). The silica source used for the silicalite-1 synthesis was tetraethylorthosilicate (TEOS, >98%, Sigma-Aldrich), and the alkali was tetrapropylammonium hydroxide (TPAOH, 1.0 M aqueous solution in water, Sigma-Aldrich). Deionized water was used for the preparation of all solutions.

Preparation of TOCNF. TOCNFs were obtained from a defibrillation process of soft wood pulp, following the reported procedures from Isogai et al.¹⁹ In brief, an aqueous suspension of cellulose pulp from Norwegian spruce was subjected to TEMPO-mediated oxidation steps using TEMPO, NaClO, and NaBr. The obtained carboxylated fibers were subjected to mechanical disintegration using a high-pressure homogenizer to yield fully defibrillated oxidized cellulose nanofibrils with a carboxyl group content of 1.5 mmol·g⁻¹.

Preparation of Silicalite-1. The colloidal suspension of silicalite-1 particles was prepared, following the procedure developed by Persson (now Palmqvist) et al.²⁰ In short, 4.5 g of TEOS was added to 7.2 g of tetrapropylammonium hydroxide (1 M TPAOH) solution with magnetic stirring in a polypropylene bottle for 24 h at room temperature. The clear solution was then heated at 98 °C for 24 h. The colloidal zeolite particles were separated by centrifuging the sols in a Labofuge 200 (Heraeus Sepatech) at 5600 rpm for 2 h. The supernatant was carefully decanted, and the residue was redispersed in water by sonication for 1 h, after which the sample was once more centrifuged. These cleaning process steps were repeated four times to ensure the complete removal of unreacted silicates and TPAOH. The solid product was dried at 100 °C overnight. The white dry powder was then transferred to a calcination oven at 600 °C for 4 h to remove the template. The size of the nanoparticle was estimated to 120 nm by scanning electron microscopy (SEM, see Figure S1).

Fabrication of Hybrid Foams. The hybrid foams were prepared based on our previously reported procedure,²¹ by first mixing different loadings of silicalite-1 with TOCNF (15 g, 0.5 wt %) and 5 g (4 wt %) of gelatin, and stirring thoroughly for 2 min using a high-speed disperser (Ultra-Turrax, IKA) and pouring into Teflon molds and leaving them for cooling at 4 °C for 1 h. Then, the suspension was degassed, and the molds were placed on a copper plate in contact with dry ice to initiate the directional freeze-casting, following previous reports from Bergström et al.,²² (cooling rate is estimated as 15 K·min⁻¹) followed by freeze-drying. Foams of TOCNF/gelatin without silicalite-1 were also prepared as controls (and denoted Ref.).

Characterization. Zeta potential measurements of 0.1 wt % suspensions were carried out using a Zeta sizer Nano ZS Malvern Instruments, using NaOH (0.1 M) and HCl (0.1 M) to adjust the pH, with results, as shown in Figure S2.

The apparent densities of the foams were calculated by weighing the samples and measuring their volumes. The specific surface area and the average pore size distribution in dry state were determined from nitrogen adsorption–desorption measurements at 77 K using the Brunauer–Emmett–Teller (BET) and Barrett, Joyner, and Halenda methods, respectively. The measurements were performed using a Micromeritics ASAP 2020 instrument, and the samples were degassed at 100 °C for 10 h in dry N₂, prior to measurements.

The morphology of the samples and energy-dispersive spectroscopy (EDS) elemental analyses were determined by SEM conducted on a JEOL 7000 with an acceleration voltage of 2 kV. The specimens were coated with a thin gold layer prior to visualization for 30 s.

The mechanical properties of the foams were characterized using an Instron 5966 Dual Column Tabletop Testing System equipped with a load cell of 100 N. The average sample diameter was measured and taken into account while performing the test. Prior to the compression test, the samples were conditioned during 40 h at 50 ± 5% relative humidity and 23 ± 2 °C. The compression test was performed at a speed of 1 mm/min until the sample was compressed to 80% of its original height or when 95 N of force was applied.

N₂ and CO₂ Adsorption by Volumetric Analysis. Volumetric CO₂ and N₂ adsorption–desorption isotherms were recorded at 35 °C using ASAP2020 adsorption analyzer. Sample tubes with approximately 120 mg of sample, sealed using a frit seal, were loaded. All of the samples were evacuated to ultrahigh vacuum at 100 °C for 10 h before the measurements. The dehydrated samples were weighed and then transferred back to the analyzer with the frit seal preventing sample exposure to air.

Gravimetric Gas Adsorption of Foams. Gravimetric gas sorption was performed with a TA Instruments Discovery thermobalance using LABLINE 5.5 CO₂ and 5.0 N₂ gases. The samples were weighed in 100 μL Pt pans. The CO₂ adsorption and apparent selectivity at 25 °C were determined by the weight increase upon switching from N₂ to CO₂ atmosphere.

■ RESULTS AND DISCUSSION

The aim of this study was to develop a method to support zeolite powders on a meso-/macroporous support with the highest possible amount of zeolite and thereby form a hierarchical pore structure of the material while also improving the processability of zeolites. This is of importance for the scaled-up implementation of zeolites as gas sorbents and requires, in addition, to be done without reducing the sorption capacity of the zeolites by avoiding the use of binders/adhesives that would otherwise block the pore entrances of the zeolite. Herein, we report the successful development of hybrid biofoams, which can support ultrahigh loadings of colloidal silicalite-1 that provides selective adsorption capacity of carbon dioxide without detrimentally affecting the mechanical robustness of the foams. The foams are prepared by unidirectional freeze-casting technique, resulting in the formation of a hierarchical anisotropic three-dimensional porous network. The use of unidirectional freeze-casting as foaming method offers two main advantages: (i) high degree of reproducibility among samples prepared using similar operating conditions (cooling rate and temperature), and (ii) the unidirectional alignment of the nanofibers in the foam provides high uniaxial mechanical strength, which is essential for the durability of the foam structure, as will be discussed later in the article.

The preparation of these foams allows the combination of highly CO₂ adsorbing microporous zeolites, with less mass transport-restricted meso-/macroporosity of the biopolymer substrate, providing a hierarchical pore structure with excellent diffusion of the adsorbate gas molecules into and out of the structure.^{23,24} A conceptual schematic diagram of the hybrid

foam composed of a strong network of gelatin/TOCNF with silicalite-1 embedded in the network is presented in Figure 1.

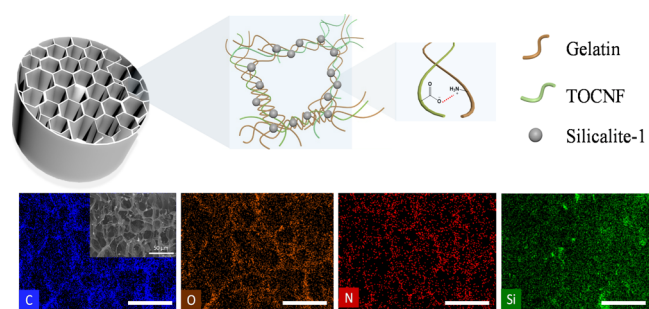


Figure 1. Conceptual schematic diagram of the network formed among gelatin/TOCNF and silicalite-1 conforming the hybrid foams. The EDS mapping images prove the distribution of different components in the hybrid foam (Scale bar = 50 μm).

Gelatin, a protein obtained through denaturation of the triple-helix structure of collagen, was selected as the main component for the preparation of foams. TOCNFs were used as the secondary component in the foams and interact electrostatically with gelatin because of their opposite surface charge (see Figure S2). For the preparation of foams, a gelatin suspension is mixed with the suspension containing TOCNF and silicalite-1. Then, the mixture is homogenized and cooled for 1 h because it is known that gelatin undergoes a first-order thermoreversible gelation transition at low temperatures, during which gelatin molecules experience an association-mediated conformational transition from random coil to triple helix, recovering partially the collagen triple-helix structure by disorder–order rearrangements.^{25,26} At this stage, a three-dimensional interconnected network between gelatin chains is formed in the presence of TOCNF, which are embedded in the gelatin matrix, forming a strong interpenetrating network, which is further reinforced by the electrostatic interactions among both components. The aforementioned interaction between gelatin and TOCNF leads to an increase in the storage modulus (G'), loss modulus (G''), and viscosity (η) upon cooling the suspension (see Figure S3). Furthermore, after freeze-casting, the gelatin/TOCNF matrix can provide an excellent support for an ultrahigh loading of sorbent nanomaterials into foams. Our developed foams indeed exhibit the highest loading capacity ever reported (up to 90 wt % content), as observed in Table 1 a comparison of previous works relating foams/aerogels with loaded sorbent nanomaterials. In addition, the loading of colloidal zeolite does not alter significantly the mechanical robustness and anisotropic behavior of the foams because it will be systematically shown in the following parts of the article.

Microstructure of the Hybrid Foams. Effects of the zeolite content on the morphology and structural characteristics of the hybrid foams were evaluated using SEM, and the micrographs are shown in Figure 2. The pure zeolite sample is furthermore displayed in the Supporting Information (see Figure S1).

The foams display a conventional honeycomb pore structure composed of macropores of approximately 40 μm (observed in the SEM micrographs at low magnifications), where the unidirectional ice-templating process forms an anisotropic tubular pore structure because the pores run parallel to the freezing direction throughout the material.²² The cell walls of

Table 1. Comparison of Loading Capacity for Various Foams/Aerogels Loaded with Sorbent Nanomaterials

material	sorbent	loading capacity [wt %]	reference
TOCNF/gelatin	silicalite-1	90	here
TOCNF	nanozeolite	10	Bendahou et al. ⁵
chemically cross-linked cellulose nanocrystals	ZIF-8, UiO-66 and MIL-100	50	Zhu et al. ²⁷
TOCNF	ZIF-8	81	Zhu et al. ²⁸
cellulose	ZIF-8	30	Bo et al. ²⁹
graphene	MIL-101	70	Zhang et al. ³⁰
silica	Cu-BTC	30.5	Ulker et al. ³¹
chitin	Cu-BTC	53	Wisser et al. ³²
graphene	ZIF-8	86.7	Jiang et al. ³³

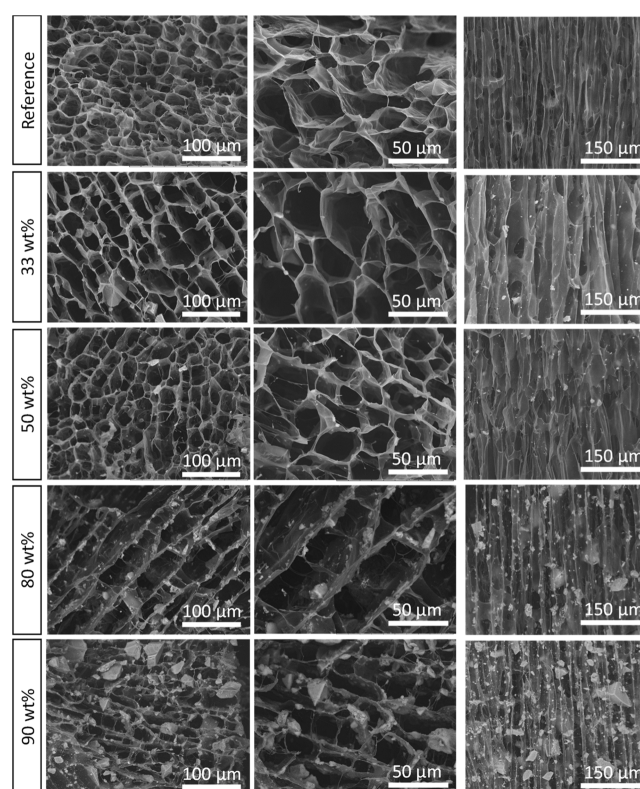


Figure 2. SEM micrographs (contrast enhanced) at different magnifications of the hybrid foams with different mass fractions of silicalite-1. Right column corresponds to cross-sectional micrographs of the foams displaying their anisotropic structure.

the foams are known to be interconnected with each other by mesopores³⁴ (although not observable in SEM images), which is believed to improve the gas diffusion through the foam, as well as the zeolite exposure to CO_2 , thus leading to an efficient adsorption. The zeolites were found to be homogeneously embedded in the foam walls, which is also corroborated by EDS mapping in Figure 1. It is also noteworthy that the anisotropy of the foams was preserved even at high loadings of zeolite content, as can be observed in the cross-sectional micrographs in Figure 2.

The influence of the silicalite-1 content on the pore structure of the hybrid foams was studied by N_2 adsorption/desorption isotherms (see Figure S4), and the corresponding specific

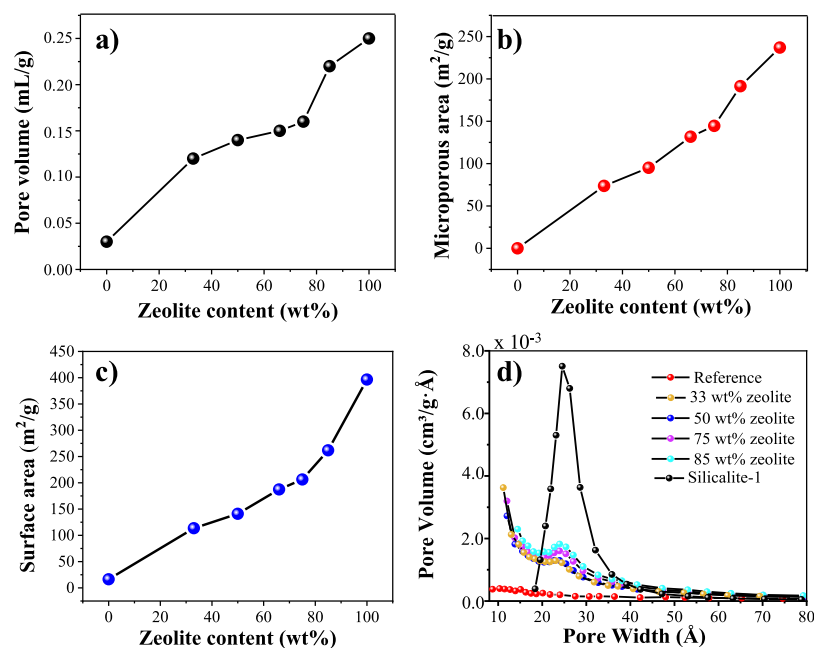


Figure 3. Influence of zeolite content on the specific pore volume (a); specific microporous surface area (b); specific surface area (c); and pore size distribution (d) in the hybrid foams.

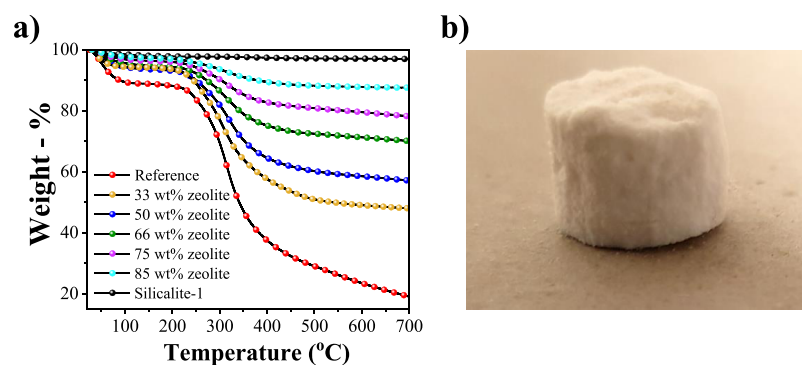


Figure 4. (a) TGA thermogram of hybrid foams and (b) picture of a hybrid foam with an initial content of 85 wt % zeolite imaged after calcination at 600 °C.

surface areas, pore volumes, and size distributions are presented in Figure 3. All samples show distorted type-IV-like isotherms, exhibiting a steep uptake at very low pressures corresponding to the microporosity given by the presence of silicalite-1. The latter can be confirmed with pore size distributions (see Figure 3d), where a steep increase and a peak are found below 10 Å and at 25 Å, respectively. Moreover, the observed hysteresis loop can be attributed to the gelatin/cellulose matrix, which upon freeze-drying forms a mesoporous structure by itself. This can also be observed in the pore size distribution, which exhibits pore sizes between 300 and 500 Å (see Figure S5).

The presence of silicalite-1 lead to a significant increase of the porosity and a specific surface area of the foams (see Figure 3a–c), exhibiting a quasi-linear relationship between the specific surface area and the zeolite content. The deviation from perfect linearity suggests that there is some loss of meso-/macroporosity for the samples with intermediate silicalite-1 loadings. Most importantly, the results confirm that colloidal zeolite particles can be accommodated within the foam walls without significantly suffering from pore blockage, and therefore the exposed specific surface area increases as

expected by the increased amount of silicalite-1 in the hybrids. The corresponding linear adsorption relationship will be shown later to be valid also for CO₂ adsorption.

Thermogravimetric analysis (TGA), as shown in Figure 4a, was conducted to illustrate the content of zeolite comprising the hybrid foams and to evaluate the effect on the thermal stability of foams. The analyses were carried out in a thermobalance from 30 to 700 °C under N₂ atmosphere, passing over the temperature at which the gelatin/nano-cellulose matrix decomposes. Overall, it can be observed that the sample's weight increasingly stabilized above 300 °C, which is attributed to the superior thermal properties of zeolites that remain intact up to 700 °C, in contrast to both biopolymers, which start decomposing around 280 °C. To further illustrate this, in Figure 4b, a photograph of the hybrid foam with 85 wt % zeolite content is exhibited after calcination at 600 °C, demonstrating the homogenous distribution of zeolites throughout the nanocellulose/gelatin matrix.

Mechanical Properties of the Hybrid Foams. The hybrid foams were subjected to uniaxial compression tests to determine the effect of the zeolite content on their mechanical properties, and the typical stress–strain curves are presented in

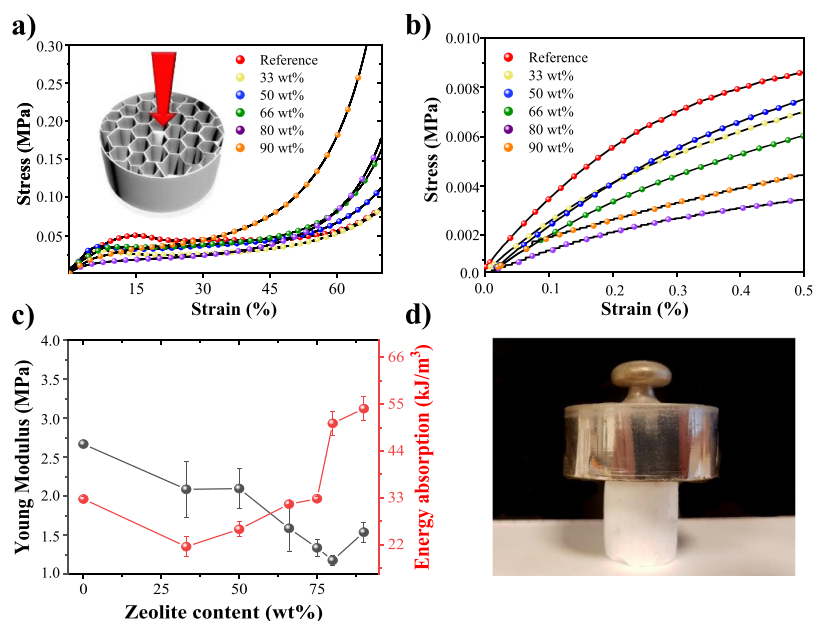


Figure 5. Stress–strain plots showing the compressive mechanical properties of foams with different zeolite content (a,b); compressive modulus and energy absorption of foams with different zeolite content (c); photograph of hybrid foam comprising 50 wt % content of silicalite-1 withstanding 100 g of weight (d).

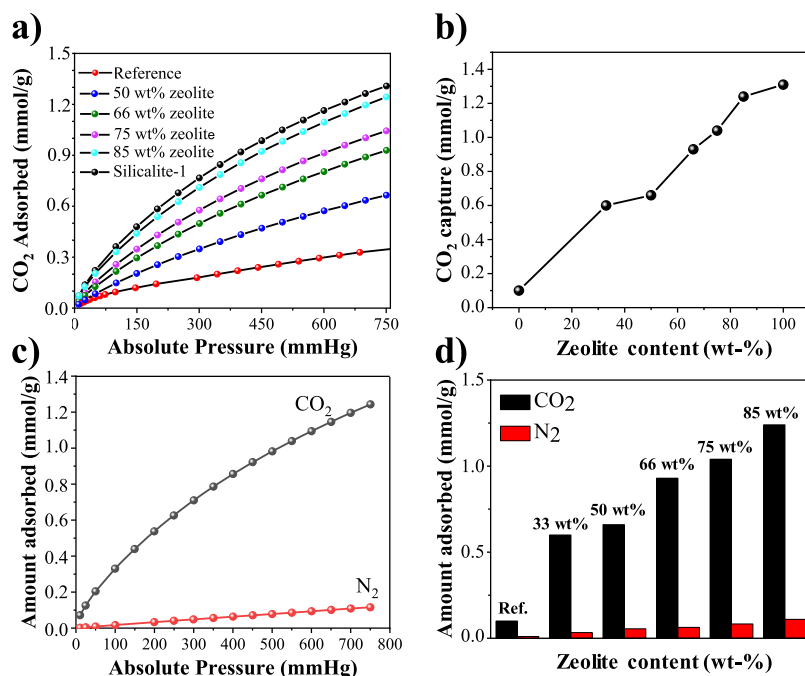


Figure 6. CO₂ adsorptive properties of hybrid foams. (a) CO₂ adsorption isotherm of hybrid foams; (b) CO₂ capture capacity of hybrid foams as a function of zeolite content; (c) comparison between adsorption of CO₂ and N₂ showing the high selectivity for CO₂ in the foam consisting of 85 wt % silicalite-1; and (d) final amount of CO₂ and N₂ adsorbed at 1 bar absolute pressure for different foams.

Figure 5a. All foams went through three stages of compressive deformation, characteristic of all foams. The first section of the curves shown in **Figure 5b**, from which the apparent Young's modulus (E) is calculated, shows a linear elastic behavior in all cases, corresponding to the bending of the honeycomb structure walls owing to the applied compressive force. The elastic modulus of the foams exhibits a detrimental decrease as a function of the zeolite content (see **Figure 5c**), suggesting that the stiffness of the foam walls is significantly affected by the incorporation of zeolites, presumably because of the

formation of zeolite aggregates at high loading (visible in **Figure 2**), which affects the immediate deformation of the foams.

Nevertheless, for the desired application, it is indeed the energy absorption (also known as work to failure, calculated from the stress vs strain curve, considering the area under the curve up to 70% strain) of the samples the most crucial parameter in terms of mechanical properties. As can be observed in **Figure 5c**, first, upon the initial addition of low amount of zeolite (i.e., 33 and 50 wt %), the energy absorption

of the foam was reduced compared to the reference sample, presumably because of the disruption of the original structure of the foam by the zeolites. However, upon incorporation of a higher amount of zeolite, the energy absorption gradually increased, reaching a value up to 53.8 kJ m^{-3} , corresponding to the foam with 90 wt % zeolite and is 64% higher than the reference foam (32.7 kJ m^{-3}). This behavior is suggested to be because of the large increase in wall density of the foams (see Figure S6), which after certain zeolite loading plays a more important role during compression than the partial disruption of the honeycomb structure by the zeolite. As a direct proof of the mechanical robustness of the hybrid foams, the ability of the hybrid with 85 wt % zeolite to withstand 100 g of weight placed on the top of it is shown in Figure 5d. It is worth mentioning that small changes in the foam-preparation conditions can significantly alter the mechanical properties of the resultant foams, for instance, because of the generation of bubbles which later act as defects in the resulting foams or incomplete gelation of gelatin, among other possible factors. The good mechanical properties of our hybrid foams suggest their potential long-term use at large-scale applications, as well as their structural resistance to withstand multiple adsorption cycles even at high gas fluxes.

Evaluation of Hybrid Foams for CO₂ Capture. The application of hybrid foams for the selective capture of carbon dioxide was investigated, and the results are shown in Figure 6a. Overall, the presence of silicalite-1 significantly increased the specific CO₂ adsorption capacity compared to the reference foam containing solely gelatin/TOCNF, increasing linearly as a function of zeolite content (see Figure 6b), and reaching almost the value of pure silicalite-1 (1.3 mmol/g). Commonly, the driving force for the adsorption of CO₂ in zeolites arises from electrostatic interactions between the gas molecules and the strong electrical field of the zeolite owing to the negatively charged framework that interacts with the CO₂ molecules, which has a quadrupole moment leading to uneven charge distribution for a short period.³⁵ When one side is slightly positive, an attraction between the positive charge of the gas molecule and the electrical field gradient of the zeolite occurs. Although, silicalite-1 is a pure-silica zeolite with the MFI zeolite structure, which in principle, does not have exchangeable cations, negative charges exist as deprotonated silanol groups are located at the external surface terminating the crystal structure, as well as at the internal surface as silanol nests caused by silica tetrahedron vacancy defects. As a comparative study, we also evaluated the CO₂ sorption of amorphous nonporous silica materials with a similar surface area to silicalite-1. These exhibited much lower CO₂ sorption capacity, compared to silicalite-1 (see Figure S7), demonstrating that despite the absence of aluminum sites in silicalite-1, its structure is better suited for efficient capturing of CO₂ likely because of van der Waals interactions between the molecule and the framework.³⁶ Moreover, a comparative test was also carried out using a hybrid foam comprising 50 wt % colloidal ZSM-5 particles (Al/Si = 38) instead of silicalite-1, which, as expected, exhibited a higher CO₂ sorption capacity compared to silicalite-1 (see Figure S7), proving that both the microporous crystalline structure and the negatively charged framework play a crucial role in the CO₂ adsorption process. It also demonstrates the versatility of our system in which CO₂ adsorption capacity could be fine-tuned by varying the type of zeolite and its alumina content.

As previously mentioned, the incorporation of zeolites led to a significant increase of the porosity and specific surface area of the foams (see Figure 3c), which has a strong effect on the number of CO₂ molecules that can be adsorbed within the framework, as shown in Figure 6a. Thus, a linear relationship between the silicalite-1 content and the CO₂ adsorption capacity was observed (see Figure 6b), confirming that the porous support composed of gelatin/nanocellulose apparently does not block significantly the pores of the zeolites or limit the diffusion of gas molecules to the zeolite particles. The excellent accessibility of gas molecules to zeolite pores can be attributed to the overall foam porosity, pore interconnectivity, and the porosity of the gelatin/nanocellulose network. The adsorption of N₂, also measured by volumetric gas adsorption (see Figure 6c,d), was significantly lower than CO₂ adsorption, suggesting the possible application of the foams for gas separation, owing to the fact that CO₂ is a major contaminant of methane-rich gases and hydrogen fuels. The low degree of N₂ adsorption is likely a result of the low polarizability of the nitrogen molecule.³⁷

Reusability and Stability of the Hybrid Foams for CO₂ Capture. The reusability and long-term stability for CO₂ capture of the hybrid foams were studied by gravimetric adsorption measurement in a TGA instrument, by subjecting the foams to repeated CO₂/N₂ adsorption/desorption cycles at room temperature, monitoring the weight % variation, as shown in Figure 7a. The relevance of these types of

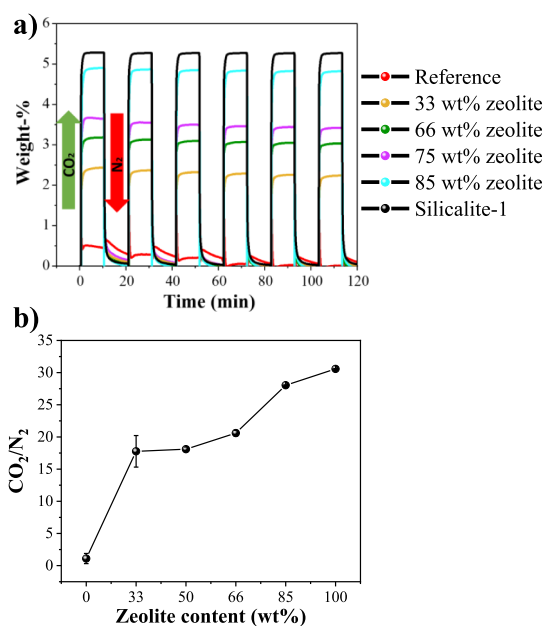


Figure 7. Gravimetric gas adsorption measurements of the hybrid foams: (a) cycles of CO₂/N₂ adsorption of hybrid foams measured by TGA and (b) apparent selectivity of foams as a function of zeolite content in the foams.

measurements arises from the fact that for practical applications, an adsorbent should not only exhibit high adsorption capacity and selectivity, but also provide long-term stability in their performance over multiple cycles.³⁸ Overall, the adsorption capacity presented in Figure 7a shows only a very small change with the cycle number measured as the weight increases upon CO₂ exposure and thus an excellent reproducibility. The apparent CO₂/N₂ selectivity in CO₂

capture of the foams was furthermore studied by comparing the gravimetric response of CO₂ and N₂ adsorption, respectively (see Figure 7b), considering the ratio of gained weight % upon CO₂/N₂ atmosphere, multiplied by the density ratio of both gases (ρ_{N_2}/ρ_{CO_2}). Overall, the selectivity linearly increased as a function of zeolite content, as expected, is attributed to the higher affinity of silicalite-1 for CO₂ molecules compared to N₂.

CONCLUSIONS

We successfully developed a highly mechanically stable hybrid foam consisting solely of gelatin/nanocellulose and different loadings of colloidal zeolite particles of up to 90 wt %, without the need for using any chemical cross-linkers. The CO₂ sorption capacity and selectivity of these foams showed a linear relationship with respect to the zeolite content, demonstrating that the gelatin/nanocellulose matrix does not block the pores of the zeolites and only acts as a support for the zeolites. We also evaluated the reusability of the foams by exposing them to repeated CO₂/N₂ cycles, showing only a minor decrease in the adsorption capacity. Moreover, the mechanical properties of the foams exhibit a nonlinear behavior in terms of the energy absorption of the foam that decreased upon addition of low amounts of zeolite compared to the zeolite-free sample, presumably because of the disruption of the original structure of the foam by the zeolites. Upon incorporation of higher amounts of zeolite, the energy absorption gradually increased with increasing zeolite content, providing the best overall combination of mechanical and adsorption properties for the highest loaded samples studied (90% zeolite loading). The approach reported here is not only expected to have great implications in the development of bio-based materials with ultrahigh loadings of adsorbents, but could also be expanded to support other functional subcomponents, such as catalytically active materials, to incorporate different functionalities and target other applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b11399.

SEM micrograph of silicalite-1; zeta potential of all building blocks for hybrid foams; rheological properties of gelatin and gelatin/TOCNF suspensions; BET isotherms of all hybrid foams and pore-size distributions; density of hybrid foams as a function of zeolite content; and CO₂ adsorption isotherm of a hybrid foam with ZSM-5 and amorphous silica nanoparticles (PDF)

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L.V. and W.R. authors contributed equally to this work. The manuscript was written through contributions of all authors.

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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