Reticulated Alumina Replica Foams with Additional Sub-Micrometer Strut Porosity

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Ceramic alumina foams are suitable catalyst supports with high temperature stability used, for example, in catalytic cracking processes or combined heat and power units. Herein, such replica foams are generated from macroporous α-Al₂O₃ powder synthesized by a sol–gel process. The foam windows, constituting intrinsic (macroscopic) foam porosity, are supplemented by an additional porosity within the struts of the foams. These pores, originating from the sol–gel process, are preserved during sintering at 1350 °C. This results in less dense foams compared with foams from conventional alumina powders. Foams sintered at 1350 °C exhibit an increased strut porosity of approximately 62%, of which approximately 84% are open, with pore diameters in the range of 200–500 nm and a compressive strength of 0.2 MPa. Foams sintered at 1600 °C or higher possess an almost tenfold compressive strength but no additional strut porosity. Due to the use of carboxylic acids as porogens in the sol–gel process, all samples generated from sol–gel-derived alumina powder exhibit significantly higher porosity values than the respective reference foams made from commercial alumina powder. Although specific surface areas of 3 m²g⁻¹ are still small, this value is significantly improved by additional strut porosity.

1. Introduction

Ceramic foams can be encountered in a wide range of applications, such as lightweight design,[1] separation processes for gases and liquids,[2] fluidic applications,[3] both electrical and thermal insulation,[1] catalyst supports in heterogeneous catalysis,[4–6] and several more.[2,7] Due to their cellular structure, formed by a 3D network of struts, they combine such interesting properties as small deadweight and low pressure drop (in fluidic applications) with reasonable mechanical stability[8–11] and refractoriness, which implies both a low thermal conductivity and a high temperature resistance.[12]

The motivation of our work was to fabricate ceramic foams with enhanced specific surface area that can be used as a high temperature stable catalyst support, intended for implementation in high temperature applications such as petroleum refining processes, for example, catalytic cracking and steam reforming,[6,13] or combined heat and power units (CHP). γ-alumina is a suitable material for most catalytic applications, as it is inexpensive, readily moldable, and has easily controllable[14,15] However, it does not comply with the requirements of catalytic postcombustion in certain applications, where temperatures above 1000 °C are often encountered.[14]

Under these conditions, γ-alumina is subjected to a phase transition to the thermodynamically stable α-modification.[15,16] This, in turn, entails several problems. Due to the fundamental change in crystal structure from γ- to α-Al₂O₃, the porosity of the catalyst material drastically decreases. Active sites thus become inaccessible, resulting in the loss of most, if not all, catalytic activity.[17] In fact, even at temperatures below the γ → α-transition, sintering[18,19] can lead to inaccessible pores and hence deactivation. This thermal instability of γ-Al₂O₃ effectively represents the main cause for activity loss in wood log stove catalysts.[20] An adequate and well-known measure to stabilize γ-Al₂O₃ at temperatures above 1000 °C consists of doping with oxides of rare earths, such as La or Ce.[21,22] However, these dopants can also cause a decrease in catalytic activity.[21–24]

In the case of washcoated catalysts, thermomechanical stress may also lead to spalling of the washcoat at elevated temperatures.[14,25] As it bears the catalytically active sites, usually metals of the Pt group,[26–30] this also results in a drastic activity drop. All these difficulties could be circumvented by a ceramic foam catalyst support consisting of corundum, the thermodynamically stable α-modification of Al₂O₃. The fact that it has not been reported yet to exhibit stable mesopores does not pose a problem for the envisaged applications: diffusion within small pores is limited once the mean free path of the reactants reaches the dimension of the pore diameter.[31] At reaction temperatures of 400–800 °C (or even higher), this is the case, and Fick’s laws...
do not apply anymore, as Thiele already assessed in 1939.\textsuperscript{[32]} A hierarchically structured pore system can help avoid diffusion limitation.\textsuperscript{[13]} Moreover, introducing smaller primary pores into the struts of a ceramic foam would also result in an increased specific surface area. The thermal stability of corundum has one major drawback: its surface area is typically below 1 m\(^2\) g\(^{-1}\).\textsuperscript{[14]} For these two reasons, we sought to introduce additional porosity into the struts of our ceramic alumina foams—referred to as “strut porosity” in the following—to obtain a temperature stable catalyst support with an enhanced specific surface area.

Different well-established techniques are commonly applied for the manufacturing of ceramic foams. The most prominent ones include the direct foaming method, replication techniques, use of sacrificial templates, gel casting, and freeze casting, as reviewed by Studart et al.\textsuperscript{[2]} and Deville.\textsuperscript{[15]} For example:

In direct foaming methods, foam structures are created in situ by the formation of gas during a chemical reaction, accompanied by a liquid–solid transformation process, e.g., a polymerization.\textsuperscript{[36–40]} Burnout of sacrificial filler materials can also create foamed structures in originally dense solids.\textsuperscript{[41,42]} A similar effect can be obtained by freeze casting or a combination of foam replication and freeze drying.\textsuperscript{[49]}

The most common approach to generate ceramic foam structures is found in the replica technique.\textsuperscript{[2,4,50–56]} In this process, an open cell template, which is often a polyurethane (PU) foam, is coated with a ceramic slurry and then dried. The PU template is burned out afterward, and the remaining green body undergoes sintering for consolidation and formation of a ceramic material.

Alumina is frequently used as a raw material in such replica processes to fabricate ceramic foam structures.\textsuperscript{[57]} As mentioned earlier, a major challenge is the introduction of porosity into the struts of such foams. Different studies on manufacturing bulk ceramics with tailorable porosity have been published over the past decade.\textsuperscript{[42,43,58]} However, none of these studies deal with ceramic foams, and the issue of introducing strut porosity in ceramic foam structures remains a challenging one, although it has been addressed more broadly and discussed more thoroughly in the literature recently.\textsuperscript{[13]} Our work is the first report on the combination of a replica technique with porous alumina from a sol–gel process as raw material that results in a ceramic foam structure with additional strut porosity. This additional porosity goes far beyond what can be achieved by burning out PU templates to simply create hollow struts with nonporous walls. Porosity values of our sol–gel-derived ceramic foams are significantly higher than the ones of foams obtained with nonporous commercial alumina powder. Although weakening of the foam structure would be expected due to additional strut porosity, the sol–gel-derived foams attain compressive strength values equal to the ones of foams without additional strut porosity. We can hence report that despite the enhanced porosity, there is no loss of mechanical stability.

2. Results and Discussion

2.1. Preconditioning of Macroporous Alumina from the Sol–Gel Process

Macroporous α-alumina powder samples were prepared as described in Section 4.\textsuperscript{[19]} Particle size distributions of different samples are shown in Figure 1. Interestingly, the untreated powders (○ and △), that is, before grinding and milling, already possess a bimodal particle size distribution. This can be attributed to the chalk-like habitus of the macroporous α-Al\(_2\)O\(_3\) from the sol–gel process, so the product not only contains some larger granules but also fine powder.

Manual grinding (pestling) reduces the overall particle size (▲ and ●). However, particle sizes with \(d_{50}\) values of 560 μm were still too large to permit slurry preparation, adequate template impregnation, and sintering. Our attempts to manufacture ceramic foams made from nonsieved ground powder slurries (SL-grp, cf. Section 4) resulted in highly unstable and hardly manageable structures. We hence continued by ball milling the powders. After sieving through a mesh of 112 μm, the \(d_{50}\) value was reduced to 48 μm. This particle size is still large enough to preserve a reasonable part of the initial sol–gel macropores. At the same time, particles are now sufficiently small for effective coating of PU templates with slurry, and to enable sintering, which, in turn, is essential for the stability of ceramic foams.

Mercury intrusion histograms and scanning electron microscopy (SEM) images of nonground sol–gel granulate materials, ground powder, and powder after ball milling and sieving (mesh 112 μm) are shown in Figure 2. Evidently, particle sizes diminish with grinding and milling. At the same time, the pore volume of the initial sol–gel macropores decreases with each grinding step, i.e., from granules over manually ground powder to ball-milled powder, whereas the modal pore diameter remains fundamentally unchanged. (The apparent increase in pore volume from ground powder to ball-milled and sieved powder in Figure 2 is due to diminished particle size, with interparticular voids being falsely detected as “pores” by the intrusion measurement.) Broadening of the pore size distribution is likely due to the reduction of pore length in small particles after grinding. However,
this does not imply a problem in terms of preservation of porosity in the sintered ceramic foams.

Another important aspect regarding the stability of sintered ceramic foams is the solid fraction in the slurry. During preliminary coating tests, the powder fraction was not sufficiently high, which resulted in dripping of the slurry before drying. We hence sought to keep solid fractions as high as possible (cf. Section 4) to obtain evenly and fully coated PU foams.

2.2. Influence of the Sintering Temperature on the Porosity

While the program steps for drying, PU template burnout, and binder removal were kept unchanged for all ceramic foams, the decisive sintering plateau temperature was varied in the range of 1350–1650 °C. Evidently, there is a significant effect on both porosity and stability of the foams. As these two characteristics are natural antagonists, we prioritized the preservation of porosity over mechanical stability when investigating the optimum sintering conditions.

An overview of attainable foam porosities for two different sintering temperatures (1350 and 1650 °C, respectively), as determined by the Archimedes method, is shown in Figure 3.

In this graph, we differentiate between open strut porosity and closed strut porosity, as derived from the immersion measurements. The total foam porosity, including also open cells and windows, cannot be determined directly by immersion but is calculated using the ratio of bulk density over material density. The closed porosity is then the difference of total and open porosity. Total foam porosities lie within a range from 88% to 95% for all obtained ceramic foams. Ceramic foams derived from the sol–gel powder (SL67a and SL67b are shown exemplarily) possess open strut porosities of ≥50%, giving total strut porosities of ≥62% (including a closed strut porosity of ≈11%) at lower sintering temperatures (1350 °C). These values are considerably higher than those for SL-cap foams obtained from commercial alumina powder, containing total strut porosities of 39% (comprising 28% open and 11% closed strut porosity), which is in accordance with our expectations. The preservation of open sol–gel macropores as enhanced strut porosity in ceramic alumina foams is demonstrated for the first time in this study. Modal pore diameters and cumulative pore volumes calculated from mercury intrusion in Table 1 confirm our findings from immersion measurements.

Figure 2. Mercury intrusion histograms and SEM images of as-synthesized granular sol–gel α-alumina (top), manually ground powder (middle), and powder after ball milling and sieving (mesh 112 μm; bottom). Two different magnifications are shown to illustrate preservation of microstructure with simultaneous reduction of particle size.
While at 1350°C, the open porosity of the foam decreases with increasing sintering temperature (cf. also SEM images in Figure S1, Supporting Information). There is hence no porosity left in the struts except for the hollow strut core previously occupied by the PU template foam. For sol–gel-derived foams, Table 1 shows a loss of strut pore volume of about 65% after sintering at 1350°C. After sintering at 1550°C, the pore volume decreased by 82% for large macropores (≥1 μm), and by about 95% after sintering at 1650°C, which is a result of particle densification in the sintering process. For the sol–gel-derived foams, for example, SL67a-1650, this effect is even more important, again due to greater initial porosity, which brings about a higher potential of densification.

### 2.3. Microstructure and Mechanical Properties

When discussing porous materials, a closer look at their microstructure is always worthwhile. SEM images of the sol–gel-derived

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**Table 1.** Modal pore diameters of the strut pores ($d_p$) and cumulative pore volumes ($V_p$) of selected foams as calculated from mercury intrusion measurements before (bef) and after (aft) sintering at different temperatures.

| Foam sample | $d_p, \text{bef}$ [nm] | $d_p, \text{aft}$ [nm] | $V_p, \text{bef}$ [cm$^3$ g$^{-1}$] | $V_p, \text{aft}$ [cm$^3$ g$^{-1}$] | $\Delta V_p$ [%] |
|-------------|------------------------|------------------------|---------------------------------|---------------------------------|----------------|
| SL55-1350   | 1078                   | 479                    | 1.43                            | 0.49                            | –66            |
| SL55-1550   | 1078                   | 511                    | 1.43                            | 0.26                            | –82            |
| SL67a-1350  | 292                    | 213                    | 0.69                            | 0.25                            | –64            |
| SL67a-1650  | 292                    | n/a                    | 0.69                            | 0.02                            | –97            |
| SL-cap-1350 | 208                    | 127                    | 0.34                            | 0.07                            | –79            |
| SL-cap-1650 | 208                    | n/a                    | 0.34                            | 0.02                            | –94            |

Although the decrease in pore volume ($\Delta V_p$) is evident, the final product still exhibits a remarkable strut porosity with relatively well-defined pore diameters ($d_p$) in the range of 200–500 nm. Further results are shown in Section 2.3.

When raising the sintering temperature, porosities decrease. The critical sintering temperature at which preintroduced pores collapse appears to be in the range of 1550–1600°C for sol–gel-derived ceramic foams. The open porosity of the foam decreases with increasing sintering temperature (cf. also SEM images in Section 2.3). While at 1350°C, preservation of sol–gel macropores is observed, they vanish due to sintering effects at 1650°C. The strut porosity also decreases to ≥30% (comprising ≥20% open and ≤10% closed strut porosity) after sintering at 1650°C. This holds equally true for ceramic foams from commercial alumina powder. In both cases, this porosity is mainly due to hollow struts, as mercury intrusion and SEM images show little-to-no significant remaining porosity within the strut walls.

However, when initially introducing larger pores via the sol–gel powder, as in slurry SL55, for example, a pore volume of 0.26 cm$^3$ g$^{-1}$ can be preserved even after sintering at 1550°C (cf. Table 1). The modal pore diameter diminishes to half the original size due to sintering effects, but pores remain open and accessible, as mercury intrusion data show. Corresponding mercury intrusion curves and histograms are depicted in Figure S1, Supporting Information.

The volumetric shrinkage is significantly lower for reference foams from commercial alumina powder (SL-cap) than for sol–gel-derived ones, as shown in Figure 4. SL-cap foams initially exhibit no strut wall porosity, their strut porosity entirely arises from hollow strut cores, and hence they are already considerably denser. During sintering at the relatively low plateau temperature of 1350°C, they densify further, with resulting relative densities of ≥0.075 (cf. also Table S1, Supporting Information).[60,61] Meanwhile, sol–gel-derived foams do not compact as much, restrained by their greater initial porosity due to porous strut walls, attaining relative densities of ≤0.06.

After sintering at 1650°C, however, none of the ceramic foams exhibited a strut pore volume of more than 0.02 cm$^3$ g$^{-1}$ (as determined by mercury intrusion). There is hence no porosity left in the struts except for the hollow strut core previously occupied by the PU template foam. For sol–gel-derived foams, Table 1 shows a loss of strut pore volume of about 65% after sintering at 1350°C. After sintering at 1550°C, the pore volume decreased by 82% for large macropores (≥1 μm), and by about 95% after sintering at 1650°C, which is a result of particle densification in the sintering process. For the sol–gel-derived foams, for example, SL67a-1650, this effect is even more important, again due to greater initial porosity, which brings about a higher potential of densification.

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**Figure 4.** Photographs of SL67a (top) and SL-cap (bottom) at different stages: coated PU templates (left), sintered at 1350°C (center), and sintered at 1650°C (right), respectively.
ceramic foam SL67a-1350 (sintered at 1350 °C) in Figure 5 clearly show that struts are hollow. The inner part of the strut is occupied by the PU template foam before sintering; after pyrolysis of the template, a ceramic foam with hollow struts is obtained. Characteristic values for strut thicknesses from computer tomography (μ-CT) scans for sol–gel-derived ceramic foams are ≈530 μm when sintered at 1350 °C, or ≈425 μm after sintering at 1650 °C, with hollow struts being considered as one solid strut. These values are averaged over entire foams and in all three dimensions. (The strut in the top left image in Figure 5, for instance, is much smaller in the front view but larger in the z direction.) In comparison with the foam made from commercial α-alumina powder (SL-cap-1350, Figure 5 on the right), SL67a-1350 exhibits a microstructure with smaller grains, clearly showing a more complex porosity within the strut walls. While a similar morphology was observed for SL-cap-1350, it exhibits a less pronounced porosity and already further progressed grain growth due to onsetting sintering.

This work is the first to have preserved such strut wall porosity for α-alumina foams sintered at temperatures of 1350 °C and higher. The greatest magnification in Figure 5 reveals an interconnected porosity accessible from all faces. The modal pore diameter decreased by 71 nm (from 292 to 231 nm) compared with the original sol–gel-derived powder, and pore volume by 64%, as revealed by mercury intrusion. For the reference foams from commercial α-alumina powder, modal pore diameters also decreased by 81 nm (from 208 to 127 nm) upon sintering at 1350 °C. Regarding the pore volume, however, a considerably more important loss of porosity of 79% is observed (cf. also Table 1).

Both features (hollow struts and porous strut walls) give rise to additional porosity and, consequently, an enhanced specific surface area. For SL67a-1350, a value of 3 m² g⁻¹ for \( A_{\text{BET}} \) was determined by nitrogen sorption, which is remarkable for alumina treated at 1350 °C. Corundum usually has a surface area far below 1 m² g⁻¹[34] and for SL-cap–1350, the value could not be reliably determined by nitrogen sorption, as it is below 0.1 m² g⁻¹.

At an elevated sintering temperature of 1650 °C, the strut surfaces become almost nonporous, as mercury intrusion data

![Figure 5](image_url)

**Figure 5.** SEM images of sol–gel-derived foam SL67a-1350 (left) and SL-cap-1350 from commercial alumina powder (right) at different magnifications. Pore size distributions (as determined by mercury intrusion) are included as thumbnails.
already suggested (Table 1). Figure 6 shows the corresponding SEM images, revealing a more progressed grain growth for the SL-cap foams, despite originally even smaller particles for the commercial α-alumina powder (Figure 1). Grain growth can onset earlier in the nonporous commercial alumina powder, whereas macropores tend to collapse in the sol–gel-derived foams before grain growth can commence.

As for the foams obtained from ground but not milled sol–gel powders, SEM images (not shown) reveal a microstructure similar to the one observed for milled powders (cf. Figure 5). However, they exhibit defects (nonporous or blurred areas), most likely due to imperfect coating of the PU template, originating in large particles left in the ceramic powder used for the SL-grp slurry. This promotes crack formation in the structure of the foams. Ball milling of the sol–gel alumina powder is hence indispensable to obtain crack-free, stable ceramic foams with additional strut wall porosity.

Compressive strength tests were conducted on the sintered foams to determine their mechanical stability. In general, the compressive strengths of ceramic foams sintered at 1350 °C do not exceed 0.3 MPa, both for sol–gel-derived foams and foams made from commercial alumina powder. Yet, these values still lie within an expectable range for foamed ceramics, spanning approximately from 0.1 to 10 MPa, as compiled by Gibson and Ashby.[63]

The individual measurements result in quite divergent compressive strength values, which is primarily due to the intrinsically fragile foam macrostructure. When compressed, only a small number of struts or possibly even only a single strut has to support the entire weight force applied to the foam. As the loading of individual struts is not necessarily perfectly homogeneous within a batch of foam samples, breakage may occur at varying values.

Gibson and Ashby postulated a mathematical model for the analysis of compressive strength datasets, applicable to cellular materials.[63] This calculation operates among others with the relative density, which is an important property of cellular materials. It is defined as the density of the cellular material \( \rho^* \) divided by the bulk density of the strut material \( \rho_s \), which we assume to equal the theoretical density of 3.94 g cm\(^{-3}\).[64]

\[
\text{Relative density} = \frac{\rho^*}{\rho_s},
\]

with the density of the cellular material \( \rho^* \) being calculated from the dry weight \( m_t \) of the cellular material divided by its volume \( V_t \).

\[
\rho^* = \frac{m_t}{V_t}
\]

The relative density increases with increasing strut thickness and/or decreasing foam volume. The mathematical model shows a correlation between compressive strength \( \sigma_{cr} \), bending strength \( \sigma_{fs} \), and relative density. \( C \) is a geometric parameter, which in our case equal to 0.2.[63]

\[
\frac{\sigma_{cr}}{\sigma_{fs}} = C \left( \frac{\rho_s}{\rho^*} \right)^n
\]

For \( \sigma_{fs} \), a value of 244 MPa was determined by three-point bending tests of separately fabricated SL-cap-1650 rods, which leads to the following equation for \( \sigma_{cr} \)

\[
\sigma_{cr} = \sigma_{fs} C \left( \frac{\rho_s}{\rho^*} \right)^n
\]

By letting the exponential parameter \( n \) converge numerically, Equation (3) leads to so-called Gibson–Ashby fits, which give a measure of how strongly the porosity of a foam degrades its mechanical stability, as shown in Figure 7.

It becomes apparent that relative density values vary for foams sintered at the same temperature. For better comparability, the parameter \( n \) was determined after linearization of Equation (3) for a series of foams and the relative densities were normalized for both sintering temperatures. (Corresponding values of \( n \) and \( \sigma_{cr}^* \) can be found in Table S1, Supporting Information.) The resulting compressive strengths of the foams with respect to their relative densities can now be compared. Although the absolute compressive strength values of SL67a-1350 foams are lower than the ones of the reference SL-cap foams, their mechanical stability with respect to their porosity, that is, their relative density, is almost as high. At higher sintering temperatures, in our case 1650 °C, the compressive strengths of the sol–gel-derived foams even exceed those of the SL-cap foams. Absolute values (not shown) for SL67a-1650 go up to 1.8 MPa for one extreme case, whereas most of them lie around 0.9 MPa. For SL-cap-1650, absolute values of only half these magnitudes are obtained, around 0.4 MPa, with an outlier at 0.8 MPa (not shown).
When fitted to include the relative density, this results in a somewhat higher mechanical stability (calculated $\sigma^{*} \text{cr}$ of 0.7350 MPa) for sol–gel-derived foams at an almost identical strut porosity of $\approx 30\%$, according to the Archimedes method (cf. solid curves in Figure 3), corresponding to a pore volume of 0.02 cm$^3$ g$^{-1}$, as determined by mercury intrusion (cf. Table 1). At this elevated sintering temperature, this effect is likely due to the more important volumetric shrinkage in the sol–gel-derived foams, as demonstrated in Section 2 (cf. Figure 4). To attain a similar microstructure, sol–gel-derived foams undergo a more pronounced densification process, leading to a more densely sintered structure and hence better coherence, which manifests in increased mechanical stability.

A way to further raise the mechanical stability of $\alpha$-alumina replica foams would obviously lie in the prolongation of sintering durations. However, longer sintering plateau times will not only lead to grain growth but also simultaneous loss of porosity.\[^{[65]}\]

### 3. Conclusion and Outlook

Macroscopically stable foams with additional open pores in the struts were generated from macroporous $\alpha$-Al$_2$O$_3$ powders obtained from a sol–gel process. In addition to the intrinsic foam porosity, consisting of macroscopic foam windows, a supplemental porosity (on the nanoscale) was introduced into the walls of the foam struts, with pore diameters ranging from 200 to 500 nm. Sintering temperatures were varied in the range from 1350 to 1650 °C. By increasing the sintering temperature, the additional strut wall porosity degraded, resulting in denser and hence mechanically more stable foams. To preserve the porosity from the sol–gel process, sintering temperatures should not exceed 1550 °C.

Sol–gel-derived ceramic foams were compared with ceramic foams obtained by the same replication route but from commercial $\alpha$-alumina powder with high sintering activity. The sol–gel-derived foams were found to exhibit a significantly higher porosity, having strut porosities of up to 65%, comprising $\geq 50\%$ open (accessible) porosity and 11% closed porosity.

In the resulting ceramic foams, porosity increases both with decreasing powder particle size and with decreasing sintering temperature. However, the latter also brings about a decrease in the compressive strength of the obtained replica foams. The additional strut wall porosity with relatively narrow pore size distributions and an interconnected pore system results in specific surface areas of up to 3 m$^2$ g$^{-1}$. Further stabilization of replica foams will be the main focus of our continued effort on this topic.

### 4. Experimental Section

**General Approach:** A brief overview of the general manufacturing route of reticulated aluminum oxide ceramic foam manufacturing is shown in Figure 8. All steps are explicated in detail in the following sections.

**Materials:** All starting materials were used as received, without further purification or treatment. Solvents (ethanol and distilled water) were taken from domestic lines. The deflocculant Dolapix CE, binder Optapix PA 4G, and antifoaming agent Contraspum for slurry preparation were delivered by Zschimmer & Schwarz GmbH & Co. KG. Precast polyurethane foam templates (20 ppi) were purchased from Koepp Schaum GmbH, Aachen, Germany.

**Figure 7.** Values of compressive strength measurements plotted versus the relative density of the investigated foams. Sintering duration was 3 h for all samples.

**Figure 8.** General route toward reticulated aluminum oxide ceramic foams.
Preparation of Macroporous \( \alpha \)-Al\(_2\)O\(_3\) Powder. Macroporous materials were prepared by a sol–gel process using dicarboxylic acids or citric acid as structure directing agents, as reported recently.\(^{59,66}\) For a standard synthesis, 7.80 g of AlCl\(_3\)·6H\(_2\)O and 6.98 g of distilled water were placed in the reaction vessel and dissolved in 7.90 g of ethanol, resulting in a ratio of H\(_2\)O/Al(III)-ions of 18. An organic carboxylic acid was added to the mixture immediately before the reaction. The solution was placed in an ice bath and cooled down to 4 °C while stirring. Afterward, propylene oxide (7 mL) was added with a syringe under vigorous stirring. The ice bath was removed after 3 min. After a total reaction time of 10 min, the stirring bar was removed from the reaction vessel, which was then placed in a 40 °C water bath for 2 h for gelation and gel aging. Subsequently, solvent exchange took place in an ethanol bath for 3 days. After drying at 70 °C for 7 days, calcination followed at 1200 °C for 6 h to obtain pure porous \( \alpha \)-Al\(_2\)O\(_3\). As different additives were used, pore diameters and pore volumes varied. Raw materials were hence characterized individually by mercury intrusion to allow a comparison of each starting material with the corresponding ceramic foams.

Granular \( \alpha \)-Al\(_2\)O\(_3\) samples were ground manually (referred to as “pestled”) prior to grinding in a planetary ball mill (PM 400, Retsch GmbH, Haan, Germany). Pested powders were milled for 30 min with distilled water and 60–70 alumina grinding balls with a diameter of 10 mm; the grinding container accommodates a total volume of 150 mL. Milled powders were placed in a drying chamber at 110 °C while stirring. Afterward, the powder was sieved to obtain a particle size fraction of <112 μm for slurry preparation. Sieved powder fractions were characterized with respect to their particle size distribution, and the remaining porosity was monitored by mercury intrusion.

For comparison, we also prepared foams from a ground powder without milling, designated as SL-grp, and from commercial \( \alpha \)-alumina powder (SL-cap, from CT30005G by Almatis GmbH), following the same procedure.

Slurry Preparation and Impregnation of Template Foams: Slurries were designated according to the \( \alpha \)-Al\(_2\)O\(_3\) powder fraction for sol–gel powders. SL-grp was made from (not milled) ground powder. The reference SL-cap contains nonporous commercial \( \alpha \)-alumina powder.

Slurry preparation for all sample series started from the following standard composition: powder and distilled water were mixed in a weight ratio of 4:1, giving a solid fraction of 8.0 wt% (50.4 vol%). They were mixed with the aid of a deflocculant (Dolapix CE), of which a supplementary amount of 1.5 wt% (4.7 vol%) of the solid fraction was added. Afterward, the slurry was homogenized in a centrifugal blender (2000 rpm for 15 min). Subsequently, the binder Optapix PA 4G and the antifoaming agent Contrasperm were added, with respective amounts of 1.5 wt% (4.7 vol%) and 0.1 wt% (0.4 vol%), with respect to the solid fraction. If required, distilled water was added to ensure a complete dispersion of the powder, followed by a second homogenization step in the centrifugal blender. All slurry compositions are listed in Table 2.

Polyurethane foam templates (20 pp) with a size of \( 15 \times 15 \times 20 \) mm\(^3\) were subsequently impregnated with these slurries. Each foam template was immersed separately in the slurry and manually rid of excess impregnant by careful squeezing. Impregnated PU foams were weighed to monitor and ensure comparable loading of all templates. All impregnated foam samples were air dried under ambient conditions (\( T = 20^\circ\)C, ambient pressure) for 24 h.

Thermal Processing: All impregnated foams underwent the following temperature program: they were dried at 120 °C, debindered in a two-step process at 250 and 400 °C, and the remaining template PU foam was removed at 600 °C. All plateau temperatures were approached at a heating rate of 3 K min\(^{-1}\), and all plateaus were held for 3 h. Sintering was conducted at different temperatures ranging from 1350 up to 1650 °C. The cooling rate was also set to 3 K min\(^{-1}\) from the sintering plateau down to 800 °C to prevent breakage from thermal shock and then accelerated to 10 K min\(^{-1}\). All thermal steps were conducted in air.

Sintered foam samples were designated according to the slurry they were derived from, extended by the maximum sintering temperature they were exposed to. For example, foams SL67a-1350 and SL67a-1650 were both made from slurry SL67a but underwent sintering at maximum temperatures of 1350 or 1650 °C, respectively.

Characterization: Microstructural characterization of the initial macroporous \( \alpha \)-Al\(_2\)O\(_3\) granulate materials and powders was conducted by mercury intrusion, particle size analysis, and SEM. Complete conversion to \( \alpha \)-Al\(_2\)O\(_3\) was confirmed by X-ray diffraction (XRD) beforehand (not shown).

The reticulated foams were also characterized by mercury intrusion and SEM. Furthermore, nitrogen sorption, microcomputed tomography, determination of the compressive strength, and porosity measurements via the Archimedes method were used. Weight loss and volume change were measured with a caliper and a balance (Cubis, Sartorius, Göttingen, Germany).

Mercury intrusion was performed with a PASCAL 440 porosimeter by ThermoScientific/ POROTEC (Hofheim am Taunus, Germany) with pressures ranging from 0.2 to 4000 bar. The mercury surface tension was assumed to be 0.484 N m\(^{-1}\).\(^{61}\) Its contact angle was set to the standard value of 141.3°. Samples were outgassed at 0.2 mbar for 10 min at ambient temperature prior to filling the sample cell with mercury.

Particle size analysis was conducted by laser diffraction with a Mastersizer 2000 (Malvern Instruments Ltd., Malvern, UK) with a nominal detection range of 20–2 mm. Approximately 300 mg of the powder sample was measured three times and averaged by the manufacturer’s software (Mastersizer 2000, Malvern Instruments, Ver. 5.60, UK). The Fraunhofer model for particles >1 μm was applied to calculate particle sizes.\(^{62}\) All measurements were performed in water.

SEM images were obtained using two different devices. Powder samples characterized with a Leo Gemini 1530 by Zeiss, Oberkochen, Germany, were mounted on a carbon foil and vapor coated with a gold film. An accelerating voltage of 10 kV was used. Secondary electrons were collected by an Everhart–Thornley detector. Foam samples characterized on a XL30 ESEM-FEG by FEI/Philips were collated onto the probe heads with an adhesive, electrically conducting carbon paste (PLAN0 Leit-C, Plano GmbH, Wetzlar, Germany), and also vapor coated with a gold film. The accelerating voltage was 25 kV.

Nitrogen sorption was conducted on an ASAP 2000, Micromeritics, Unterschleißheim, Germany. Prior to examination, samples were dried.

| Designation of slurry\(^{a}\) | SL-cap\(^{b}\) | SL67a,b\(^{c}\) | SL64 | SL57 | SL55 | SL-grp\(^{d}\) |
|-----------------------------|------------|-------------|------|------|------|------------|
| \( \alpha \)-Al\(_2\)O\(_3\) powder [wt%] | 80.0 | 66.9 | 64.0 | 57.3 | 55.2 | 58.0 |
| \( \alpha \)-Al\(_2\)O\(_3\) powder [vol%] | 50.4 | 33.9 | 31.1 | 32.8 | 23.8 | 26.0 |
| Distilled water [wt%] | 20.0 | 33.1 | 36.0 | 42.7 | 44.8 | 42.0 |
| Distilled water [vol%] | 49.6 | 66.1 | 68.9 | 67.2 | 76.2 | 74.0 |

\(^{a}\)Slurries are designated according to the \( \alpha \)-Al\(_2\)O\(_3\) powder fraction for sol–gel powders. \(^{b}\)The reference slurry SL-cap is made from commercial \( \alpha \)-alumina powder. \(^{c}\)Two different slurries containing the same solid fraction were mixed from different sol–gel powders as starting materials. \(^{d}\)SL-grp is made from (not milled) ground powder.
outgassed, and activated at 300 °C under vacuum. Determination of the specific surface area \( \left( A_{\text{BET}} \right) \) was conducted using the linearized form of the BET equation in the range of 0.05 < \( p/p_0 \) < 0.30. [69]

Complete transformation to \( \alpha-Al_2O_3 \) and phase purity were confirmed by XRD on a D8 Discover by Bruker with a VANTEC500-2D GADDS detector, using CuK\( \alpha \) at 40 kV and 40 mA. Phase identification was conducted using Match! Software by Crystal Impact, Bonn, Germany.

For scanning in an X-ray computer tomograph, reticulated foams were fixed separately on the sample holder of the X-ray computer tomograph Nanotom S (GE Sensing & Inspection Technologies, Wunstorf, Germany). The adjusted voltage was 60 kV, the tube current was set to 160 \( \mu \)A, and the distance of sample holder to X-ray tube and detector was defined to obtain a voxel size of 7.5 \( \mu \)m for scanning all foams. Reconstruction of datasets was performed with the software package phoenix dataX 2.0 (GE Sensing & Inspection Technologies, Wunstorf, Germany). With the software CT Analyzer 1.17.7.2 (Skyscan/Bruker microCT, Kontich, Belgium), a 3D model was calculated from the collected data, revealing windows, hollow struts, and strut thicknesses. For more details of the calculation procedure please refer to the study by Betke et al. [70]

The mechanical strength of the foams was quantified with the compressive strength measuring device TIRATEST 2825 (TIRA GmbH, Schalkau, Germany). The strain-controlled testing was conducted as follows: the traverse speed was adjusted to a constant value (2 mm min\(^{-1}\)). Underneath and above the sample, a cardboard sheet was placed between sample and pressure disk to ensure a proper force transfer onto the entire foam area. The area of the foam samples was determined prior to the measurement using an electronic caliper. Monitoring of the required force up to collapse of each foam was executed by TIRATEST 2825, and data files were recorded. To determine the compressive strength \( \sigma \), the first maximum value of compressive force was divided by the area of the foam. [71]

Porosities were determined by the Archimedes principle according to DIN EN ISO 1183. [72] Archimedes principle indicates that there is an equal weight of the submerged liquid, which can be determined with the aid of an electronic caliper. Monitoring of the required force up to collapse of each foam was executed by TIRATEST 2825, and data files were recorded. To determine the compressive strength \( \sigma \), the first maximum value of compressive force was divided by the area of the foam. [71]

Supporting Information
 Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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