



Impact of sodium and synthesis parameters on silica aerogel from waterglass

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ARTICLE INFO

Keywords:

Silica aerogel
Thermal conductivity
Insulation material
Sodium silicate
Gelation mechanism

ABSTRACT

This study explores the optimization of acid-catalyzed sol-gel processes for sodium silicate-derived aerogels prepared via the ambient pressure drying (APD) method. Removal of sodium remains a challenge in waterglass-based aerogels, as ion exchange resin adds complexity to the protocol, and the use of acidic gelation agents requires additional purification steps. This work presents an alternative approach to Na^+ removal by incorporating it into the solvent exchange steps. Additionally, four sodium removal methods are compared, and the influence of sol-gel conditions on sodium removal and aerogel properties is analyzed. Three catalysts - tartaric, acetic, and hydrochloric acids - are evaluated, with synthesis parameters optimized for each. The findings aim to provide a framework for selecting synthesis protocols tailored to desired aerogel properties and production requirements. Tartaric acid was found to promote sodium removal during the solvent exchange step more efficiently than other acids. Washing aerogels post-drying was successful in removing sodium but led to changes in the silica network. Washing hydrogels was efficient in reducing Na^+ contents in the aerogels by up to 80%, but also led to a decrease in quality. Depending on the synthesis conditions, the aerogels produced had low thermal conductivity and bulk density, high specific surface area, and were hydrophobic.

1. Introduction

Silica aerogel is an outstanding insulation material due to its low density and thermal conductivity, as well as high porosity and specific surface area. [1,2] Traditionally synthesized via hydrolysis and condensation of organic silicates, these gels are often dried through the supercritical drying (SCD) method. [3] However, their large-scale application is limited due to the high production costs and embodied energy. [4] To address these challenges, the ambient pressure drying (APD) method is commonly used to decrease energy and equipment demands while producing high-quality aerogel. [5–8] Furthermore, sodium silicate is a cheaper and more sustainable precursor option, which can be used instead of the conventional tetraethyl orthosilicate (TEOS). [7,9,10]

Hydrogel preparation from sodium silicate involves lowering the pH of the sol to promote hydrolysis and condensation. This is commonly done either by using ion exchange resin, which replaces sodium ions with H^+ , or by adding acidic catalysts. Prior research explored various acid types as gelation catalysts, such as tartaric [11], sulfuric [12], nitric [13], acetic [14], and hydrochloric [15]. Gelation conditions such as

time of gelation and aging, sol pH, and silica concentration in the sol have a strong influence on the physical properties of the resulting aerogel. However, U. Bangi et al. found that acid type also influences the aerogels, reporting that stronger acidic catalysts led to significantly higher shrinkage than weaker acids. [15] While the sol parameters for hydrolysis and condensation have been extensively studied in the literature, there is still little work focused on the effect of acidic catalysts in aerogel synthesis from sodium silicate.

Protocols involving waterglass include some way of sodium removal as it was shown to negatively affect gelation and the properties of a resulting aerogel. [7] Ion exchange resin is widely used to remove sodium ions and obtain silicic acid $\text{Si}(\text{OH})_4$, which can undergo gelation at specific pH, silica concentration in the solution, and temperature. [16–18] The pH of the sol is one of the key factors in gel preparation, as it influences the properties of the resulting aerogel. [7,10] It is usually adjusted using a basic catalyst, as the solution becomes acidic after passing through the resin. However, this step is time-consuming, and the ion exchange resin needs to be recovered by passing an acidic solution through it once it reaches saturation. [5] In practice, sodium silicate often remains in the resin and gels upon interaction with the acid,

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<https://doi.org/10.1016/j.mtcomm.2026.115944>

Received 1 July 2025; Received in revised form 23 July 2026; Accepted 18 August 2026

Available online 19 August 2026

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leading to resin clustering and difficulties with reuse. Therefore, prior research developed several protocols that remove sodium ions by other means, such as solution-crystallization, [12,19] passing water vapor through the gel, [11] or implementing a solvent exchange sequence to displace pore water. [20] These aerogels were reported to perform similarly to those synthesized using the ion exchange resin. In 2008, Bangi et al. showed that washing the hydrogel with water to remove Na^+ leads to a decrease in aerogel density and an increase in its optical transmission. [5] Naturally, the higher purity of aerogel is likely to lead to better quality since the presence of sodium within the pore network decreases the surface area and increases the bulk density and thermal conductivity. [21]

Prior research investigated the influence of the sodium ions during the gelation step, which is the case when using most acid-catalyzed protocols. Luo et al. looked into the effect of Na^+ on the properties of silica aerogels, although the sodium was added manually as NaCl after the ion exchange resin step. [21] They found that with the increasing amount of sodium added, the quality of the aerogel decreased in part due to Na^+ interference with the hydrophobization of the aerogel. At the same time, the chemical structure and composition of the silica network were not affected by the Na^+ . However, sodium was shown to cause alkaline dissolution, which can lead to a weaker silica network and a subsequent decrease in quality. [22] As such, sodium ions residing in silica networks disrupt structural stability by introducing non-bridging oxygen defects to the Si-O-Si bonds, accelerating the collapse of aerogel under stress. [23]

While it was shown that sodium negatively affects the aerogel quality, it is unavoidable when using sodium silicate as a precursor, because some Na^+ remains even when using an ion exchange resin. [12] It is possible to minimize its amount by various removal techniques or by adjusting the synthesis recipe. However, there is little research on the effect of the sol-gel conditions on the sodium contents and removal efficiency. The APD method is flexible to modifications of parameters, such as aging time, solvent exchange species and sequence, surface modification agents, and drying conditions. This leads to difficulty in comparing literature protocols, as these variations impact the resulting silica aerogel. Therefore, attributing the quality of aerogel to one parameter, in this case, the sodium removal method, would be inaccurate. This study addresses these gaps by investigating the effect of sodium and synthesis parameters on silica aerogel qualities while maintaining consistent baseline processes. The aim is to determine which protocol results in a higher quality aerogel while considering the potential for industrial upscaling and optimization of time and resources. To achieve this, the current work systematically compares previously reported and novel protocols for aerogel synthesis and sodium removal.

Tartaric, acetic, and hydrochloric acids were evaluated to assess the effect of acid strength and the difference between monoprotic and diprotic catalysts. Parameters such as silica contents (wt%), silica-to-acid molar ratio, and pH of gelation were optimized for each gelation agent. Removal of Na^+ ions was investigated by evaluating the sodium contents in four different cases. Ion-exchanged sol was used as a control, and removal of Na^+ during the solvent exchange sequence, washing of hydrogels with water, and similarly washing the dried aerogels with water were assessed for efficiency for the three acidic catalysts. This work investigates the link between sol-gel conditions and sodium removal efficiency, proposing a novel pathway to cost-effective silica aerogel synthesis.

2. Methods

2.1. Raw materials

Sodium silicate was purchased from LabShop (Netherlands) and used as a raw material for all samples. For the control sample, Amberlyst 15 hydrogen form (cation exchange resin, Sigma-Aldrich) was used to

remove sodium ions and ammonia (NH_4OH , VWR) was added as a basic catalyst. For the acid-catalyzed samples, L(+)-Tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$, 99%, VWR), glacial acetic acid ($\text{C}_2\text{H}_4\text{O}_2$, 100%, VWR), and hydrochloric acid (HCl, 35%, VWR) were used. The solvent exchange was conducted using DI water, ethanol (VWR), and n-heptane (Biosolve). All aerogels were modified using trimethylchlorosilane (TMCS, 98%, Thermo Fisher Scientific).

2.2. Experimental procedure

2.2.1. Silica aerogel synthesis

Sodium silicate (Na_2SiO_3) 37 wt% solution (Na:Si ratio of 2:1) was diluted with deionized water to obtain various silica concentrations, ranging from 3.0 to 8.0 wt%. Different catalysts, tartaric, acetic, or hydrochloric acids, were used, as detailed in Table 1. The choice was made to compare three gelation agents: tartaric acid, a diprotic organic acid; acetic acid, a weak monoprotic organic acid; and hydrochloric acid, a strong monoprotic inorganic acid. The parameters were selected based on the literature; Si wt% was minimized to reduce the density of the resulting aerogel, and Si:acid molar ratios were varied to obtain different pH of the sol. For gels catalyzed with HCl, the additional factor limiting the Si:acid molar ratio was rapid gelation, which occurred once the pH reached 9–10 for higher Si wt%.

The acid was added to the diluted sodium silicate solution, and the mixture was stirred for one minute. The synthesis parameters were selected based on literature-reported ranges, and then optimized based on the preliminary results of aerogel quality. The pH of the resulting sol and the gelation time were recorded. The Si:acid molar ratio varied from 1.1 to 4.3, depending on the catalyst used. A two-step gelation process was employed for the control sample. The diluted sodium silicate solution was initially passed through an ion exchange column to yield silicic acid (pH~2). Subsequently, the pH was adjusted to 5–6 by adding 1 M aqueous NH_3 under vigorous stirring, leading to gelation.

After gelation, the hydrogels were aged at room temperature for one hour. They were then cut into pieces and subjected to a gradual solvent exchange sequence involving EtOH/water, EtOH, EtOH/n-heptane, and finally, n-heptane for 12 h each at 60 °C. After the solvent exchange, the gels were treated with a silylating mixture of TMCS:n-heptane in a 1:3 ratio. The mixture was left at 60 °C overnight to allow for surface modification. Unreacted TMCS and the by-product HCl were carefully removed with a pipette, and the gel was washed with n-heptane. The organogel was thoroughly dried stepwise: first at 60 °C, followed by 80 °C, and finally at 150 °C, for 2 h each to achieve a complete spring-back effect. [5]

Table 1

Summary of parameters used for preparation of various silica aerogel samples. Some samples gelled in under one minute during stirring, in which case the pH measured is approximate.

Name	Catalyst	Si wt%	Si:acid mol	pH	Time of gelation, min
AG-T-a	Tartaric	5.5	1.1	3.0	90
AG-T-b	Tartaric	7.0	1.1	~3.0	< 1
AG-T-c	Tartaric	3.0	3.0	5.0	90
AG-T-d	Tartaric	5.5	3.0	~8.0	< 1
AG-T-e	Tartaric	3.0	1.5	3.7	30
AG-T-g	Tartaric	4.5	3.0	~8.0	< 1
AG-A-a	Acetic	3.0	3.0	10.0	90
AG-A-b	Acetic	3.0	1.5	6.0	30
AG-A-c	Acetic	4.5	3.0	9.0	15
AG-A-d	Acetic	4.5	1.5	5.5	15
AG-A-e	Acetic	5.3	2.4	10.0	?
AG-H-a	HCl	5.6	4.3	10.0	20
AG-H-b	HCl	4.2	3.2	10.5	90
AG-H-c	HCl	2.8	2.2	10.0	Did not gel
AG-H-d	HCl	3.3	1.7	~5.0	< 1
AG-H-e	HCl	4.4	2.4	~9.0	< 1
AG-H-f	HCl	3.0	1.8	~7.0	< 1
Control	NH_3	8.0	-	5.5	30

2.2.2. Sodium removal techniques

Three variations of sodium removal were implemented (Fig. 1). At first, aerogels were made with no additional measures (0) to investigate the effects of sodium on the gel and quantify the efficiency of unintentional sodium removal during the solvent exchange. [20] The first sodium removal (1) approach included washing the aerogels with water to remove residual sodium and investigate the effect of water on the aerogel structure. The second (2) method included washing the hydrogels in DI water by placing them in a shaker, similar to the procedure reported by Bangi et al. [5] The third (3) way of removing sodium was done by using a traditional ion exchange resin approach and is included as a control sample. The numbers in the sample names in this study correlate with the sodium removal method (e.g., AG-acid name-sample index + number).

2.3. Characterization

All aerogels were analyzed with several techniques. Their specific surface area was evaluated using BET theory, and the pore size distributions were calculated with BJH theory using the nitrogen physisorption device (Tristar II) at 77 K. The insulating properties were determined by measuring the thermal conductivity at room temperature (21 °C) with a Hot Disk Thermal Constants Analyser (TPS 2500 S) and a 7577F1 sensor with the transient plane source method. A reference

sample with $\lambda = 25.3 \text{ mW/m}\cdot\text{K}$ was used to calibrate each measurement by determining the correct calibration constant. Additionally, a commercial aerogel (Cabot p100) with known thermal conductivity was measured to validate the results for particle-form samples. The bulk density was calculated by compressing the sample in a 2 ml syringe and recording the mass, and the skeletal density was quantified with a Helium pycnometer (AccuPyc II 1340 Micromeritics). The hydrophobicity was recorded with a Dataphysics Contact Angle System by distributing fine aerogel particles on a glass slide and placing a 10 μl droplet from Milli-Q. Silica aerogels were analyzed with Scanning Electron Microscopy (SEM) Quanta 3D FEG at 10 kV. The samples were coated with platinum (Q150T Plus, Quorum) for 30 s with a sputter current of 30 mA.

Ion Chromatography (IC), performed with an external standard method, was used to quantify the amount of sodium in the aerogels and hydrogels by analyzing the water from washing the samples (Table S1). For cation chromatography, a Thermo Fisher / Dionex 1100 with an ion exchange column CS12A (2 x 250 mm) with an eluent of 30 mM Methanesulfonic acid and an isocratic flow of 0.25 ml/min was used. The detection of ions was done by suppressed conductivity (CSRS 500 2 mm). For anion chromatography, a Thermo Fisher / Dionex 1100 with an ion exchange column AS9-HS (2 x 250 mm) with eluent 9 mM sodium carbonate (Na_2CO_3) with an isocratic flow of 0.25 ml/min has been used. Detection of ions was done by suppressed conductivity (AERS 500

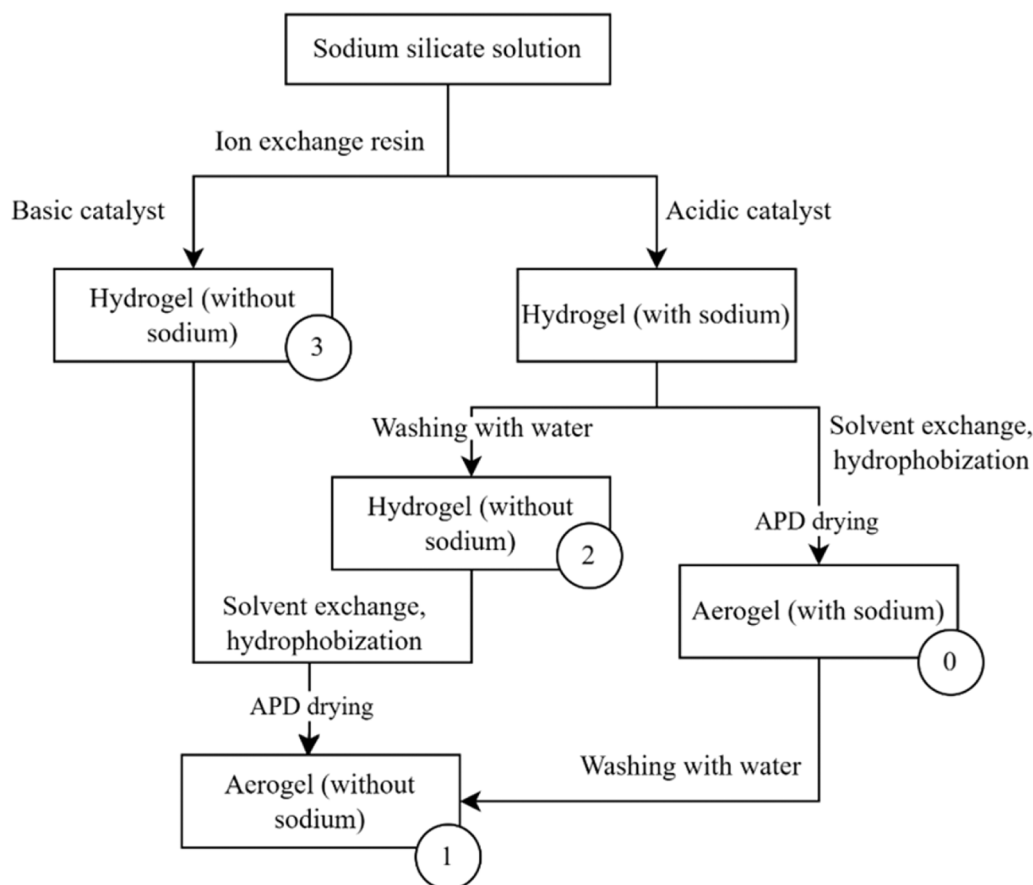


Fig. 1. Schematic summary of the three methods of sodium removal investigated in this study. Acid-catalyzed aerogels (0) were washed with water after drying (1) by placing 0.5 g of aerogel with 50 ml of DI water in a shaker at 200 strokes/minute for an hour. Selected hydrogels (2) were also washed with water, using 100 ml of DI water per 75 ml of hydrogel. They were placed in a shaker at 125 strokes/minute to avoid damage to the hydrogel, and the procedure was done twice for 30 min each. The washing duration was selected as a representative condition to evaluate the overall effect of washing on sodium removal. Hence, it is possible that a shorter or longer washing would be optimal. All solutions were then filtered, and the solid phase was dried at 150 °C for an hour to remove any residual water from washed aerogels. Washed hydrogels were subjected to a solvent exchange procedure according to the described methodology. The collected liquid phase was analyzed with IC to quantify the salt. Apart from small amounts (2 – 9 mg/l) of ions such as potassium and calcium that are likely originating from the glassware or other contamination, the only ions detected in high concentrations (>180 mg/l) were sodium and chloride.

2 mm).

3. Results and discussion

3.1. Parameter optimization

First, several gelation agents were investigated – tartaric acid, acetic acid, hydrochloric acid, and ammonia, used together with ion exchange resin serving as a control. The Si wt% and acid-to-silica ratios were varied to determine the optimal ones for each, as optimal parameters largely depend on the strength of the acid. Fig. 2 shows a photo of aerogels produced with different gelation catalysts, and an overview of their properties is presented in Table 2. No intentional sodium removal was implemented in this section, but the addition of acids and further solvent exchange was expected to remove some Na^+ from the gels. That is because acids, upon interaction with Na^+ in sodium silicate, form respective salts (di-sodium tartrate, sodium acetate, and sodium chloride).

Overall, tartaric acid-catalyzed aerogels showed better performance across all properties compared to the other two acids. Among the acetic acid-catalyzed samples, some properties, such as thermal conductivity, surpassed the tartaric acid-catalyzed samples (AG-A-b). Lastly, several hydrochloric acid-catalyzed aerogels presented with low quality based on their comparatively high thermal conductivity ($>42.6 \text{ mW/m}\cdot\text{K}$) and bulk density ($>249 \text{ kg/m}^3$), among other properties. However, two aerogels made with optimized parameters (AG-H-d and -f) showed comparable properties with the abovementioned samples. The effects of the gelation agent, Si wt%, Si:acid ratio, and pH of the sol before gelation on the performance of aerogels were analyzed to determine the best parameters.

3.1.1. Tartaric acid

Unlike the traditional ion exchange method (Control), which was shown to yield aerogel with lower thermal conductivity at 8 wt% of silica, tartaric acid-catalyzed samples exhibited the best performance at a lower Si wt% of 3 (AG-T-c). [8,17] Prior research also found 3–5 Si wt % to be optimal, with $< 3 \text{ wt\%}$ resulting in a weak silica network prone to pore collapse upon drying and $> 5 \text{ wt\%}$ resulting in higher-density aerogels. [5] At the same time, for APD aerogels, there is a balance between the solid content of the gel and the efficiency of the spring-back effect during drying. [24] The spring-back effect describes the re-expansion of aerogel pores after some shrinkage has occurred during APD. It is enabled by surface modification (for example, with TMCS), which prevents irreversible shrinkage, further condensation, and pore collapse. [25] In this study, varying the Si wt% from 3.0, 5.5, and 7.0 (AG-T- c, a, and b, respectively) while maintaining the pH in the acidic range confirmed that lower silica wt% performed better. However, changes in Si wt% led to variations in pH and gelation times, making it difficult to isolate the effect of a single parameter.

As shown by prior research, aerogels that undergo gelation at pH 5–7 show better properties due to condensation being favored. [7,10,26] In this work, among the aerogels gelled at $\text{pH} < 7$ (AG-T-a, b, c, and e),

sample AG-T-c exhibited the highest performance, suggesting that a pH of 5 results in a stronger network than a pH of ~ 3 . This is because at $\text{pH} < 4$, the positive charges on the silica species lead to repulsion, making condensation kinetically unfavorable. [16] Apart from the degree of dilution (Si wt%), the pH is influenced by the relative amount of the gelation agent added. Prior research by J. Gurav et al. varied the Si: tartaric acid ratio from 0.5 to 3.3 and found that the lowest bulk density was achieved for aerogels with a ratio of 0.8 – 1.3. [11] Additionally, U. Bangi et al. found that in the range of 0.8–3.7 silica-to-acid molar ratios, the bulk density is bimodal, with the lowest density achieved at a ratio of 3.7 and around 0.9–1.4. [5] Since tartaric acid can form di-sodium tartrate and has two binding sites for the Na^+ ion, a Si:acid ratio of around one (or Na:acid ratio of 2) was expected to remove the sodium more efficiently and result in a more uniform silica network formation. However, such a low ratio resulted in highly acidic sols for AG-T-a, -b, and -e, which led to hydrolysis being favored. This explains why AG-T-c, with Si:acid ratio of 3 but a higher pH, outperformed other samples gelled in acidic conditions. Moreover, samples with a low Si-to-tartaric acid ratio (AG-T-a and -b) produced a layer of salt precipitate during gelation, which was likely caused by an excess acid addition (Figure S1).

To further investigate whether a higher silica-to-acid ratio of 3 results in better properties, two samples were produced with this ratio but a higher pH of 8 (AG-T-d and -g). In acidic conditions, where only minor silanol groups are ionized, water glass mainly exists as silicic acid, and sodium cations do not significantly influence aggregation. [27] In contrast, at basic pH (7–10), colloidal silica-water systems gel significantly faster in the presence of salt, which stabilizes the negative charge on non-bridging oxygen. [10,28,29] Since the initial synthesis did not include any intentional sodium removal techniques, the Na was present as NaCl in most gels, as detected by EDX (Figure S2). It is possible that other sodium salts remained as well, but they were not observed during the SEM-EDX or IC analysis. Remarkably, while AG-T-d showed a lower surface area than most samples, it also had the lowest thermal conductivity. The average pore width was also higher than that of other aerogels (16.55 nm), likely due to the different mechanisms of network formation under the basic conditions.

The desired aerogel properties can be obtained by varying the gelation conditions. The results showed that sol $\text{pH} \sim 3$ led to worse performance regardless of other parameters. The sol $\text{pH} \sim 5$ yielded a low thermal conductivity aerogel with Si wt% of 3.0 (AG-T-c), but if silica concentration was increased, the thermal conductivity would increase as well. This was not the case under basic conditions, as, given the presence of salt, sol $\text{pH} \sim 8$ produced high-performance aerogels as well, with Si wt% of 5.5 (AG-T-d). This aerogel had larger mesopores, which could be useful for some applications, and the higher silica concentration did not compromise the density significantly while potentially offering more mechanical strength.

Prior research by H. Izutsu et al. reported that when using TEOS as a precursor and tartaric acid as a gelation agent, the $-\text{COOH}$ group coordinated with the silica ion and formed a $\equiv\text{Si}-\text{O}-\text{OC}-$ structure. [30] A TGA analysis was conducted using AG-T-a as an example to determine whether this bond occurs when using sodium silicate as a raw material

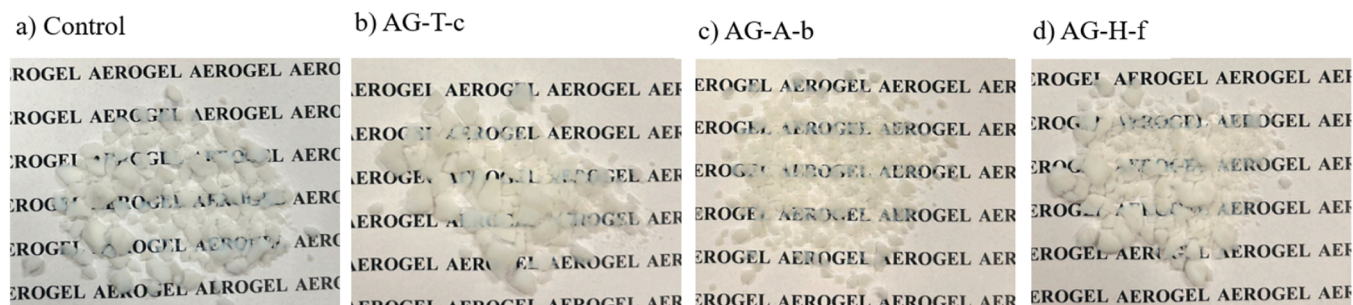


Fig. 2. Photos of selected silica aerogels produced with ion exchange resin (a), and each gelation agent b-c.

Table 2

Properties of silica aerogels produced without any sodium removal: thermal conductivity (λ), BET specific surface area (SSA_{BET}), average desorption pore width, bulk density (ρ_b), skeletal density (ρ_s), porosity, water contact angle (WCA), and wt% of soluble Na^+ present in the aerogels determined by IC.

Name	λ (mW/m•K)	SSA_{BET} (m ² /g)	Pore width (nm)	ρ_b (kg/m ³)	ρ_s (g/cm ³)	Porosity (%)	WCA	Na^+ (wt%)
AG-T-a	23.9 ± 0.1	828 ± 18	7.6 ± 0.7	125 ± 2	2.31	94.6 ± 0.9	146.2°±0.7	1.80
AG-T-b	30.3 ± 0.2	890 ± 20	7.9 ± 0.7	133 ± 1	2.63	94.9 ± 0.2	146.5°±0.4	1.94
AG-T-c	22.3 ± 0.1	966 ± 23	10.8 ± 0.9	83 ± 4	2.71	97.0 ± 1.4	151.1°±2.4	0.47
AG-T-d	22.2 ± 0.3	591 ± 11	16.6 ± 1.6	113 ± 8	1.72	95.0 ± 3.6	151.7°±1.1	1.15
AG-T-e	25.7 ± 0.4	555 ± 12	10.8 ± 1.0	99 ± 1	1.96	95.0 ± 0.4	151.8°±0.9	0.47
AG-T-g	26.1 ± 0.3	262 ± 4	18.0 ± 1.6	171 ± 8	1.88	90.9 ± 4.0	151.1°±0.1	4.36
AG-A-a	30.1 ± 0.3	181 ± 2	6.5 ± 0.1	188 ± 3	1.88	90.0 ± 1.7	150.3°±0.7	6.35
AG-A-b	18.9 ± 0.2	668 ± 13	11.0 ± 1.4	95 ± 9	2.08	95.4 ± 4.3	150.8°±0.8	0.73
AG-A-c	42.0 ± 0.6	139 ± 2	6.2 ± 0.3	230 ± 10	1.90	87.9 ± 5.2	151.8°±0.9	7.67
AG-A-d	19.0 ± 0.1	712 ± 15	13.8 ± 1.5	87 ± 3	1.72	94.9 ± 2.0	146.1°±1.1	0.70
AG-A-e	60.2 ± 0.4	226 ± 3	7.1 ± 0.78	250 ± 4	1.90	86.8 ± 2.3	147.1°±0.6	4.40
AG-H-a	56.8 ± 0.4	267 ± 4	10.3 ± 0.8	294 ± 6	1.92	84.7 ± 2.9	147.4°±0.2	5.63
AG-H-b	42.6 ± 0.3	264 ± 2	14.1 ± 0.8	270 ± 7	1.89	85.7 ± 3.5	150.1°±0.6	3.58
AG-H-d	23.0 ± 0.1	518 ± 8	17.8 ± 2.4	113 ± 7	1.84	93.9 ± 3.7	151.5°±0.3	0.19
AG-H-e	34.1 ± 0.2	237 ± 1	15.5 ± 0.4	207 ± 10	1.92	89.2 ± 5.4	149.4°±1.5	4.22
AG-H-f	22.1 ± 0.1	1006 ± 18	11.9 ± 1.7	53 ± 4	1.57	96.7 ± 2.6	150.9°±0.9	0.21
Control	26.7 ± 0.1	689 ± 15	8.6 ± 0.9	116 ± 10	2.19	94.7 ± 4.6	148.3°±0.8	0.02

(Fig. 4). The overall weight loss was ~12 wt%, with no DTG peaks below 350 °C. A broad peak in the 350 °C – 500 °C range was assigned to the loss of CH_3 groups from the TMCS surface modification. [31] Suggesting that no detectable tartaric acid remained in the gel or bonded to the silica network, as H. Izutsu reported a sharp DTG peak in the 250 °C – 350 °C range assigned to the decomposition of the tartaric acid. The AG-T-a sample exhibited a similar TGA curve to the control sample, with a slight shift in the CH_3 peak that can be attributed to the variations in the network structure, such as specific surface area (Table 2). A study by U. Bangi et al. investigating the addition of tartaric acid to a sodium silicate solution did not report the coordination of the acid to the silica network, which is in line with the presented findings. [5]

3.1.2. Acetic acid

Acetic acid-catalyzed aerogels followed a similar trend to tartaric acid ones. AG-A-b and -d showed the highest performance across all samples, with thermal conductivity as low as 18.9 mW/m•K, which is slightly lower than that of a commercial sample (19.0 mW/m•K). Similar to AG-T-c, the pH of gelation was 5.0–6.5, while the other AG-A samples gelled at a higher pH. The silica-to-acid ratio for AG-A-b and -d was 1.5, which also correlates with AG-T-c (Si:acid = 3), as acetic acid is monoprotic and has one bonding site for a sodium ion. AG-A samples with a Si:acid of 3 (a, c) performed poorly and resembled xerogels due to high shrinkage after drying. Hence, lower Si:acid ratios are required when using acetic acid as a gelation agent to achieve a sol with a pH closer to the neutral range and facilitate sodium removal and hydrolysis of silica species. Notably, prior research also reported a high-quality aerogel synthesized at pH~6 using acetic acid, with no sodium removal techniques. [9]

Silica concentration in the sol also had an effect on aerogel properties, although not as significant as the silica-to-acid ratio. Under acidic conditions, a lower Si wt% of 3 (AG-A-b) resulted in a higher hydrophobicity (150.8°) than a Si wt% of 4.5 (AG-A-d), which had a water contact angle of 146.1°. This is likely due to a lower density alcogel network allowing easier access to TMCS than a higher density one. At the same time, AG-A-b had a lower average pore width and higher bulk density, potentially indicating a higher degree of shrinkage during drying due to its weaker silica network. Overall, these two samples are of comparable properties, with AG-A-b having the benefit of utilizing fewer raw materials.

3.1.3. Hydrochloric acid

Hydrochloric acid (AG-H) was tested to investigate how acid strength affects gelation. Due to its high dissociation constant, HCl reacted rapidly with sodium silicate, and a gel formed once the pH dropped

below 10, at which the solubility of silica species is extremely low. This, combined with high NaCl concentrations, likely led to poor connectivity of the silica network. Unlike other samples, this gel was more opaque and crumbled easily, likely due to the presence of salt (NaCl) as well as a weaker silica network. The resulting aerogel had a white color and was in powder form. As gelation occurred at pH~10, its mechanism differs from that of the other samples produced. Under basic conditions, particle growth occurs via Ostwald ripening, although the presence of salt (NaCl) promotes aggregation and decreases the gelation time by reducing the repulsive interactions between sol particles. [16] Additionally, ions with high electronegativity were found to have a stronger effect on particle growth, which may contribute to the difference in gelation times between organic acids (OH^-) and inorganic ones (Cl^-). [32]

First, two samples were gelled at pH 10 (AG-H-a, -b) with varying Si wt% and Si:acid ratios (Table 1). Sample AG-H-b with lower values for those parameters performed slightly better than AG-H-a (Table 2), similarly to the acetic and tartaric acid-catalyzed samples. A lower silica-to-acid ratio was attempted for AG-H-c, but gelation did not occur, potentially due to low Si wt%. Following parameter optimization, gelation occurred at pH 5, 7, and 9 for samples H-d, H-f, and H-e, respectively. Here, the variation in Si-to-acid ratio had an effect on the resulting properties, with lower ratios of 1.7 (H-d) and 1.8 (H-f) yielding aerogels with respective thermal conductivities of 23.0 and 22.1 mW/m•K. Similarly, AG-H-e with a ratio of 2.4 performed better than AG-H-a and -b gelled at pH 10 with respective Si:acid ratios of 4.3 and 3.2. The drawback of HCl as a catalyst lies in the difficulty of controlling gelation conditions. It was observed that when the sol pH is below ~10, gelation occurs almost simultaneously, limiting the achievable parameter variations.

The first stage of this work did not include any intentional removal of sodium to observe its effects on the aerogels and the efficiency of the APD solvent exchange process in removing it. The three acids used in this study as gelation catalysts yielded varying results and required different parameters. Aerogel properties depended on synthesis conditions, including the pH of the sol, the Si wt% in the gel, and the silica-to-acid molar ratio. However, another factor that affects the properties of aerogel is the presence of impurities.

3.1.4. Sodium removal during solvent exchange

To quantify the soluble sodium that remained in the aerogels post-drying, they were washed with water, and an IC analysis was done on the liquid (Table 2, Table 1S). The first question was to identify the factors contributing to variations in Na wt%. Aerogels prepared from sols with higher Si wt% contained more sodium after the drying stage,

which was expected as such sols would also have more sodium to begin with. Additionally, a lower-density silica network has higher permeability, which can promote salt formation and its removal during the solvent exchange steps. [5] The time of gelation does not seem to correlate with the Na wt% in aerogels, meaning that the polymerization rate does not affect the formation or removal of salt (Table 1). Notably, there were some outliers, indicating that the synthesis parameters also have an effect on sodium removal. Using tartaric acid as a gelation agent appears to significantly reduce residual sodium in aerogels, likely because it provides two binding sites rather than one for acetic and hydrochloric acids. As discussed earlier, lower silica-to-acid ratios resulted in less Na⁺ detected in aerogels. Hydrochloric acid was less efficient at Na⁺ removal, and acetic acid-catalyzed aerogels were varied in their Na⁺ content, showcasing the significant effect of the silica-to-acid ratio on the Na⁺ removal efficiency. These variations can also be caused in part by slight differences in the solubility of the respective sodium salts in ethanol. Disodium tartrate is classified as insoluble in ethanol by Commission Regulation (EU), NaCl is slightly soluble in ethanol (0.065 g/100 g ethanol at 25°C) [33], and sodium acetate is slightly soluble in ethanol (~2 g/100 g ethanol at RT) [34]. Hence, the efficiency of sodium removal depends on the stability and solubility of these salts in solvents used for solvent exchange.

Samples AG-A-a and AG-A-b had the same Si wt% of 3 but Si:acid ratios of 3.0 and 1.5, respectively, and Na⁺ wt% of 6.35 and 0.73, respectively (Table 2). This trend is also present for the AG-A-c and AG-A-d, as well as for the HCl-catalyzed samples. While the absolute amount of sodium present originally was the same, adding different molar amounts of acid appeared to have an effect on the quantity of salt in the aerogel post-drying. A potential explanation could be that more acid added initially leads to the precipitation of a sodium salt, which can be removed during the solvent exchange as it has low solubility in ethanol. Sodium ions alone reside within the silica network, making them less accessible and harder to remove during solvent exchange due to the electrostatic interactions with the Si-OH groups on the network surface. [12,32]

Prior research showed similar trends for sodium removal in H₂SO₄-catalyzed gels. There, ethanol (a low-polarity solvent) was added to the sol prior to gelation in order to decrease the solubility of Na⁺ and SO₄²⁻ ions, leading to their precipitation and removal by filtration. This resulted in a significant decrease in sodium ion content in the sols compared with both the ion-exchange method and the raw sodium silicate sol. However, the microstructure analysis showed that ethanol addition to the sol results in poor homogeneity and clustering. [12]

However, the correlation between amounts of acid added and Na⁺ content in AG-A and AG-H gels was not observed for tartaric acid-catalyzed samples. While they contained less Na⁺ compared to acetic and HCl-catalyzed gels, some variations were present. Two pairs of aerogels with the same Si wt% and varying Si:acid ratios (AG-T-a and -d; -c and -e) showed a negative correlation for the first pair and almost no difference for the second. Potentially, since tartaric acid is diprotic, all AG-T samples had low enough Si:acid ratios, allowing for sufficient hydrolysis and sodium removal during the gelation step. This shows that excessive acid not only results in a low pH, which is not ideal for silica network formation, but also has adverse effects on sodium removal efficiency.

Apart from the synthesis parameters, the variations in aerogel properties and sodium removal efficiency in samples catalyzed by different acids can be attributed to a combination of factors such as the ionic strength of the pore solution and its effect on electrostatic repulsion between silica particles and subsequent rate of condensation; the solubility and stability of sodium salts in the solvent; and the potential interactions of organic ions (acetate and tartrate) with the silanol groups or hydrogen bonding that may affect the microstructure of the resulting aerogels.

The relationship between Na⁺ wt% in aerogels and their thermal conductivity and bulk density was investigated. A correlation is

observed: lower Na⁺ content is associated with reduced density and thermal conductivity, consistent with previous research. [21] Interestingly, the data are split into two clusters, where at Na⁺ < 2 wt% (7 data points), the aerogel properties are less scattered. But at Na⁺ > 3.5 wt% (8 data points), the variation among samples is spread around a larger range (Table 2). Additionally, no samples had 2.0 – 3.5 Na⁺ wt% regardless of the initial amount of sodium in the sol. This suggests that, in the first case, the gelation agents were effective at removing sodium at the sol-gel stage, which is attributed to an optimized silica-to-acid ratio, as discussed earlier. In the second case, the Na⁺ remained in the network either due to higher density for hydrogels with more solid contents (Si wt%) or due to an insufficient amount of acid added, which had a negative effect on initial network formation, leading to decreased efficiency of sodium removal during the solvent exchange steps. Hence, the cluster of samples with lower quality and higher Na⁺ wt% can be explained by overall suboptimal sol conditions or by insufficient removal of sodium by the gelation agent.

Therefore, it can be concluded that when enough acid is present in the sol-gel stage of the synthesis (Si:acid of ~1.5 for monoprotic acids, and ~3 for diprotic acids), the salt precipitated from its interaction with the sodium ions makes it easier to remove in the solvent exchange series, even when no intentional sodium removal steps are performed.

3.1.5. Scalability and sustainability

The findings show that the conditions of the sol-gel stage have an effect not only on the properties of silica aerogel but also on the efficiency of sodium removal from the silica network. Hence, it was determined that samples AG-T-c, -A-b, and -H-f yield the highest-quality material with low density and thermal conductivity, minimal sodium content, and high specific surface area. The methodology is consistent across all three samples and can be considered cost-effective, as it uses sodium silicate as the raw material, avoids the need for ion-exchange resin, and employs ambient-pressure drying. Additionally, all samples contain the lowest amount of silica at only 3 wt%, but due to their low bulk density, they produce the same volume of material as samples with higher Si wt%.

However, it is crucial to consider the scalability and sustainability of the protocol in order to address the industrial relevance of this process. The first point of difference is the gelation time, which is relevant for large-scale production. This makes AG-H-f (<1 min) more time-efficient than AG-A-b (30 min) and AG-T-c (90 min). The silica-to-acid ratio also varies, and diprotic tartaric acid allows for the highest ratio of 3, decreasing raw material requirements. Monoprotic species require a lower ratio of 1.5–1.8. Secondly, the costs and environmental impact of gelation agents should be considered. The carbon footprint per kg of tartaric, acetic, and hydrochloric acids produced is 4.60, 1.69, and 0.616 kg CO₂ eq, respectively. [35–37] With the correction for different silica-to-acid molar ratios needed, hydrochloric acid is 5.4 times lower in kg CO₂ eq than acetic acid and 18.1 times lower in kg CO₂ eq than tartaric acid. Prior research also reported the high environmental impact of tartaric acid when compared with both organic and inorganic acids. [38,39]

Another aspect relevant to the production of aerogels is the cost, which varies significantly among the gelation agents. Based on current market prices, hydrochloric acid is approximately 5 times cheaper than acetic acid and 50 times cheaper than tartaric acid, after accounting for the different molar amounts of acid required in each case. Therefore, while tartaric acid as a catalyst was more resilient to parameter changes than the other two acids, it is economically and environmentally unfavorable.

3.2. Sodium removal techniques

3.2.1. Sodium removal by washing aerogel

The presence of sodium has been shown to adversely affect the properties of silica aerogel. [21] Since Na⁺ was detected in all aerogel

samples, the quality of these samples is expected to improve upon separation from the salt. The first method of intentional sodium removal (1) included washing aerogels in water post-drying, with AG-T-c, AG-A-b, and AG-H-b selected for this study (Fig. 1). This section discusses the efficiency of washing as a Na^+ removal method, as well as the effect of water on the aerogel properties.

A thermogravimetric analysis was conducted on selected aerogels before and after washing to investigate their thermal stability and to confirm the removal of salt by this method (Fig. 3 a, b). The first notable difference is the overall weight loss among samples. AG-T-a shows behavior similar to the control sample, while AG-A-e and AG-H-a exhibit additional peaks and a higher overall weight loss at lower temperatures. This could be attributed to varying contents of Na^+ among these aerogels (1.80, 4.40, and 5.63 wt%, respectively). Some water evaporation of ~ 4.4 wt% was observed at around $40 - 100^\circ\text{C}$ for AG-A-e and AG-H-a, likely due to the hygroscopic nature of NaCl. Then, a mass loss of around 5 wt% observed for all aerogels in the region of $350^\circ\text{C} - 450^\circ\text{C}$ is attributed to the evaporation of organic CH_3 groups added during surface modification for hydrophobicity. [31] Peaks at $800^\circ\text{C} - 900^\circ\text{C}$ seen for A-e and H-a with respective losses of 6.8 wt% and 13.5 wt% are potentially caused by the decomposition of NaCl, which was reported to occur at 820°C . [40] After the washing, aerogels were analyzed again (Fig. 3 c, d). Samples AG-A-e1 and AG-H-a1 still experienced ~ 5 wt% water loss at $40 - 110^\circ\text{C}$, which could be water trapped in the pores of aerogels. Due to the lower surface area of these aerogels compared with AG-T-a1, this water may be harder to access. However, the sharp DTG peaks observed for AG-A-e and AG-H-a in the $800 - 900^\circ\text{C}$ range are not present in the washed samples. Therefore, this suggests that the washing step successfully dissolved the majority of NaCl present.

Next, the properties of washed aerogels were evaluated and compared with the original samples (Table 3). An interesting trend was

observed with the BET data, as most samples showed a decrease in specific surface area, with a simultaneous increase in the average desorption pore widths (Figure S4). The pore size distributions appeared to be narrower post-washing, with lower micropore counts (Fig. 4). Prior research by Chal et al. reported similar results when subjecting aerogels to very humid (90% RH) environments. [41] They were linked with potential hydrolysis of the Si-O-Si bonds, bonds between silica and a hydrophobic group, or present Si-OH groups resulting from incomplete hydrophobization. In the case of Si-O-Si bond hydrolysis, the gel would undergo increased recondensation during drying, leading to partial structural collapse and a reduction in specific surface area. Current findings propose that similar microstructural effects occur for hydrophobic silica aerogels when exposed to water directly for a short amount of time (1 h). At the same time, B. Chal et al. reported an increase in hydrophilicity of aerogels exposed to humidity, while this study observed the opposite effect. However, it can also be linked to the dissolution of NaCl, having a bigger impact on hydrophobicity than the effects of water on the silica network. The water contact angle generally increased for the aerogels that contained higher amounts of salt pre-washing (e.g., AG-T-a, AG-A-e, AG-H-a). Similarly, the samples with higher Na^+ wt% experienced either a decrease or a slight increase in bulk density, while samples with lower Na^+ contents mostly had an increase in bulk density.

The morphology of selected samples was analyzed with SEM (Fig. 5). While no notable differences were observed before and after washing in AG-T-c and AG-A-b, AG-H-b, they appear to be less dense post-washing, with larger particle clusters. Prior research reported that hydrogel washing yields aerogels with larger macropores, which stems from Na^+ hindering the condensation reaction during gelation, thereby reducing the homogeneity of the silica network. [12]

Overall, the results showed that washing aerogels with water, even

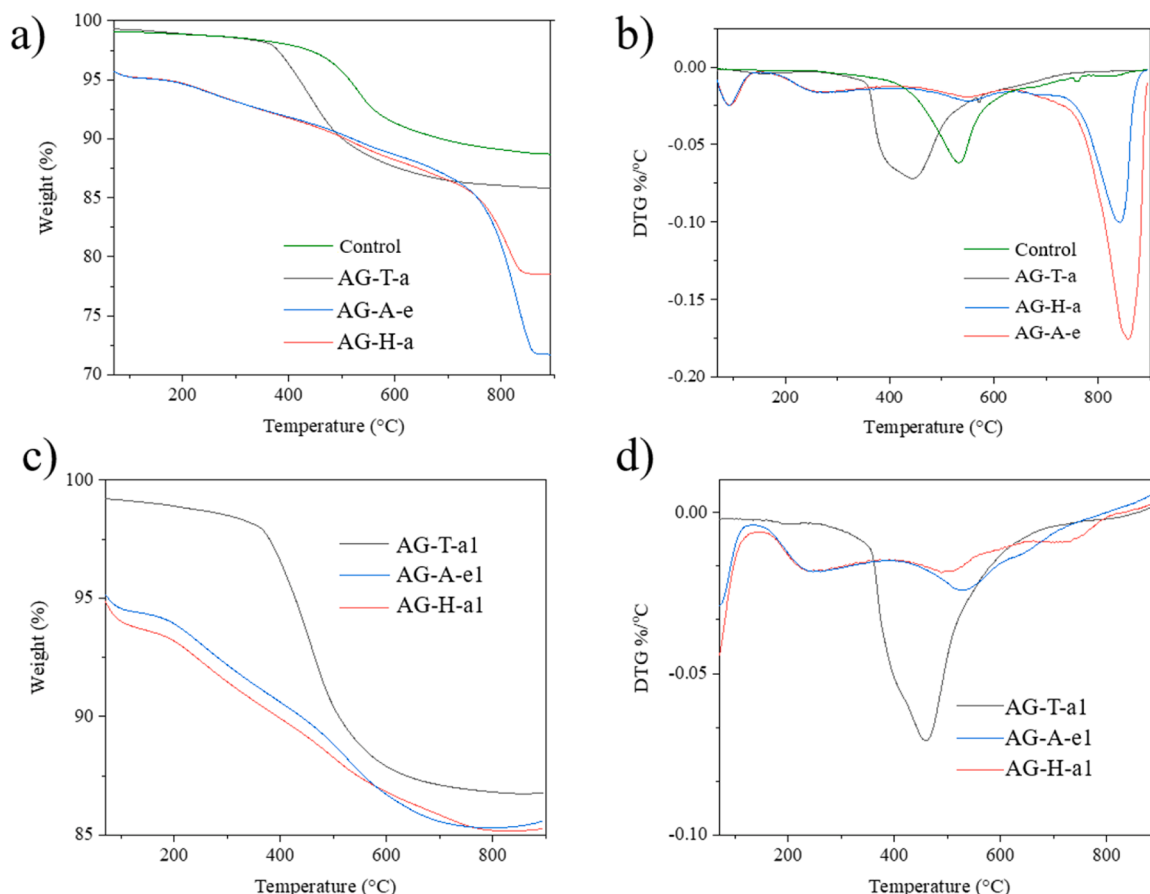


Fig. 3. Thermogravimetric analysis (TGA) of a) aerogel samples, c) washed aerogel samples; DTG curve of b) aerogel samples, d) washed aerogel samples.

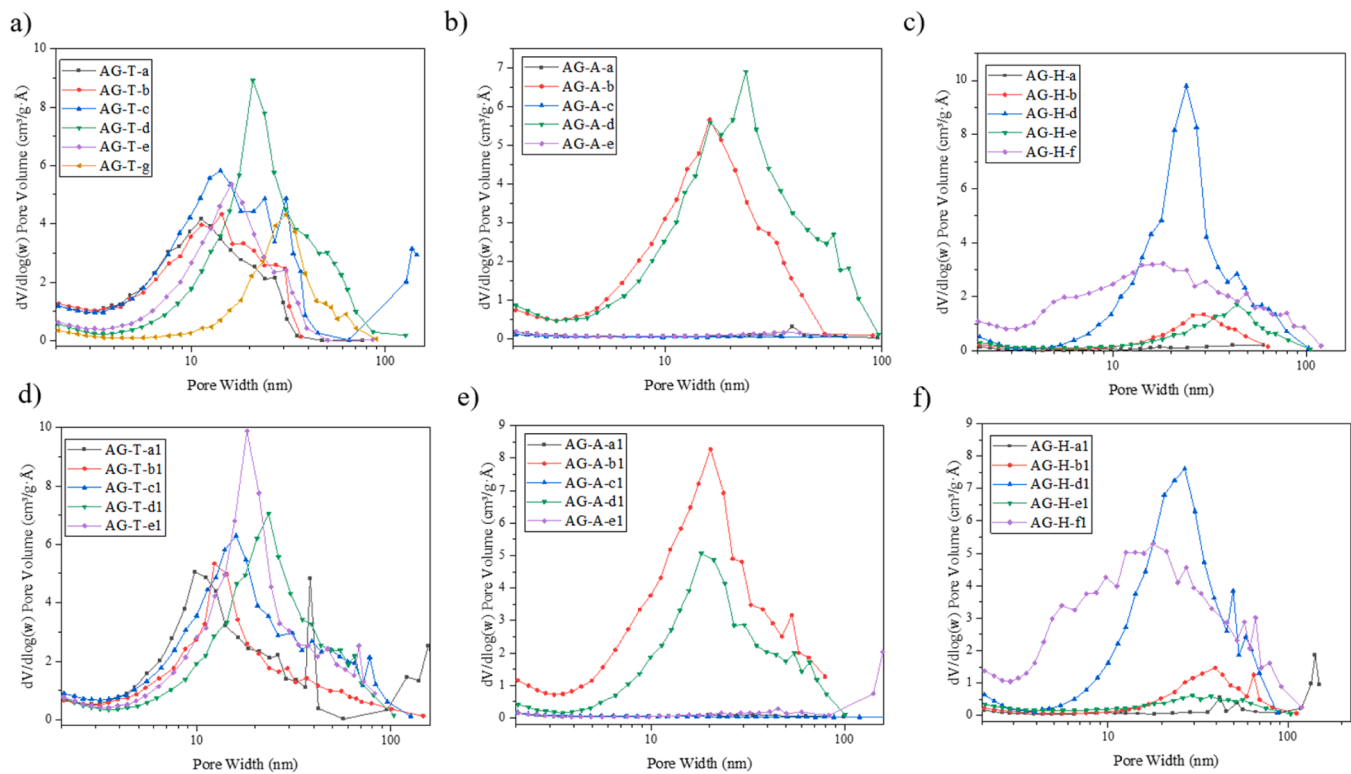


Fig. 4. Pore size distributions of silica aerogels before a)-c) and after d)-f) washing calculated with the BJH theory.

Table 3

Properties of washed aerogels with a calculated difference in property from the unwashed aerogels.

Name	SSA _{BET} (m ² /g)	Pore width (nm)	ρ_b (kg/m ³)	WCA
AG-T-a	678 ± 15	10.1 ± 1.8	117 ± 12	147.5°
a1	(−18%)	(+32%)	(−7%)	(+0.9%)
AG-T-b	631 ± 11	12.0 ± 1.4	146 ± 8	149.7°
b1	(−29%)	(+51%)	(+10%)	(+2.2%)
AG-T-c1	780 ± 17	11.8 ± 1.8	103 ± 8	152.5°
	(−19%)	(+10%)	(+25%)	(−0.2%)
AG-T-d	623 ± 12	14.9 ± 1.5	105 ± 4	151.7° (0%)
d1	(+5%)	(−10%)	(−7%)	
AG-T-e	689 ± 14	13.5 ± 2.2	118 ± 5	151.5°
e1	(+24%)	(+19%)	(+19%)	(−0.2%)
AG-T-g1	329 ± 4	21.3 ± 1.9	179 ± 9	151.1° (0%)
	(+25%)	(+18%)	(+5%)	
AG-A-a1	179 ± 3	7.4 ± 0.6	142 ± 2	151.9°
a1	(−1%)	(+14%)	(−25%)	(+1.0%)
AG-A-b1	979 ± 17	12.3 ± 1.9	97 ± 4 (+2%)	152.2°
b1	(+47%)	(+12%)		(+0.9%)
AG-A-c1	177 ± 3	5.55 ± 0.1	208 ± 1	151.2°
c1	(+28%)	(−10%)	(−9%)	(−0.4%)
AG-A-d1	458 ± 8	15.3 ± 1.7	85 ± 4 (−2%)	150.3°(+2.9%)
d1	(−36%)	(+11%)		
AG-A-e1	220 ± 4	15.3 ± 2.2	251 ± 11	150.0°
e1	(−3%)	(+115%)	(0%)	(+2.0%)
AG-H-a1	203 ± 3	13.5 ± 1.4	256 ± 14	150.2°
a1	(−24%)	(+31%)	(−13%)	(+1.9%)
AG-H-b1	254 ± 2	17.0 ± 0.4	256 ± 2	151.4°
b1	(−4%)	(+20%)	(−5%)	(+0.9%)
AG-H-d1	570 ± 9	17.2 ± 2.1	118 ± 9	151.0°
d1	(+10%)	(−3%)	(+5%)	(−0.3%)
AG-H-e1	230 ± 1	9.9 ± 0.4	198 ± 4	151.5°
e1	(−3%)	(−36%)	(−5%)	(+1.4%)
AG-H-f1	1180 ± 19	10.3 ± 1.1	55 ± 1 (+5%)	150.1°
f1	(+17%)	(−14%)		(−0.5%)
Control	917 ± 22	11.6 ± 1.6	112 ± 6	149.7°
	(+33%)	(+36%)	(−4%)	(+0.9%)

for a short period, affects their properties and, in some cases, negatively, such as an increase in bulk density or a decrease in specific surface area. At the same time, it is successful in removing sodium salt that remains in the gels (Figure S2, Figure S3). These findings can be used as a way to tune the properties of aerogels, for example, in cases where slightly larger pore sizes are required. However, as a method of sodium removal, this approach varied depending on the sample, making it less reliable than other methods.

3.2.2. Sodium removal by hydrogel washing

Removing sodium by washing the hydrogels in water has been reported in several studies and shown to be effective. [5,12,42] Aerogels from each acid catalyst were synthesized and washed with water after the aging step (AG-T-c2, AG-A-b2, AG-H-b2). Samples T-c and A-b were chosen due to their high insulation properties, and sample H-b due to its high wt% of sodium. The aim is to see how the washing of hydrogels affects the properties of the final material compared to no intentional sodium removal sample (0) and post-drying washing (1) (Fig. 1). As discussed earlier, washing aerogels in the post-drying step (1) affected their properties due to potential hydrolysis; it is possible that a similar process would happen with this approach as well. The experimental work was conducted to determine whether the properties of these samples are better without or with washings, and, if so, at which stage. It is hypothesized that washing the sample with high Na contents would be more beneficial than washing the gels with low Na wt%.

The results showed that this method is effective at removing sodium ions, with a decrease in Na⁺ wt% of 23%, 81%, and 31% for AG-T-c2, AG-A-b2, and AG-H-b2, respectively, when compared with unwashed aerogels (Table 4). By analyzing the liquid phase from the washing, it was determined that this method removed 46.9, 42.9, and 54.8 Na⁺ wt% for each hydrogel, respectively. However, for T-c2 and A-b2, the quality decreased, with a 20% and 33% increase in bulk density, among other properties. While prior research showed that water washings, when done over 24 h, result in lower-density aerogels (~ 6% decrease), this is not the case for the first two samples analyzed. [5] One potential reason

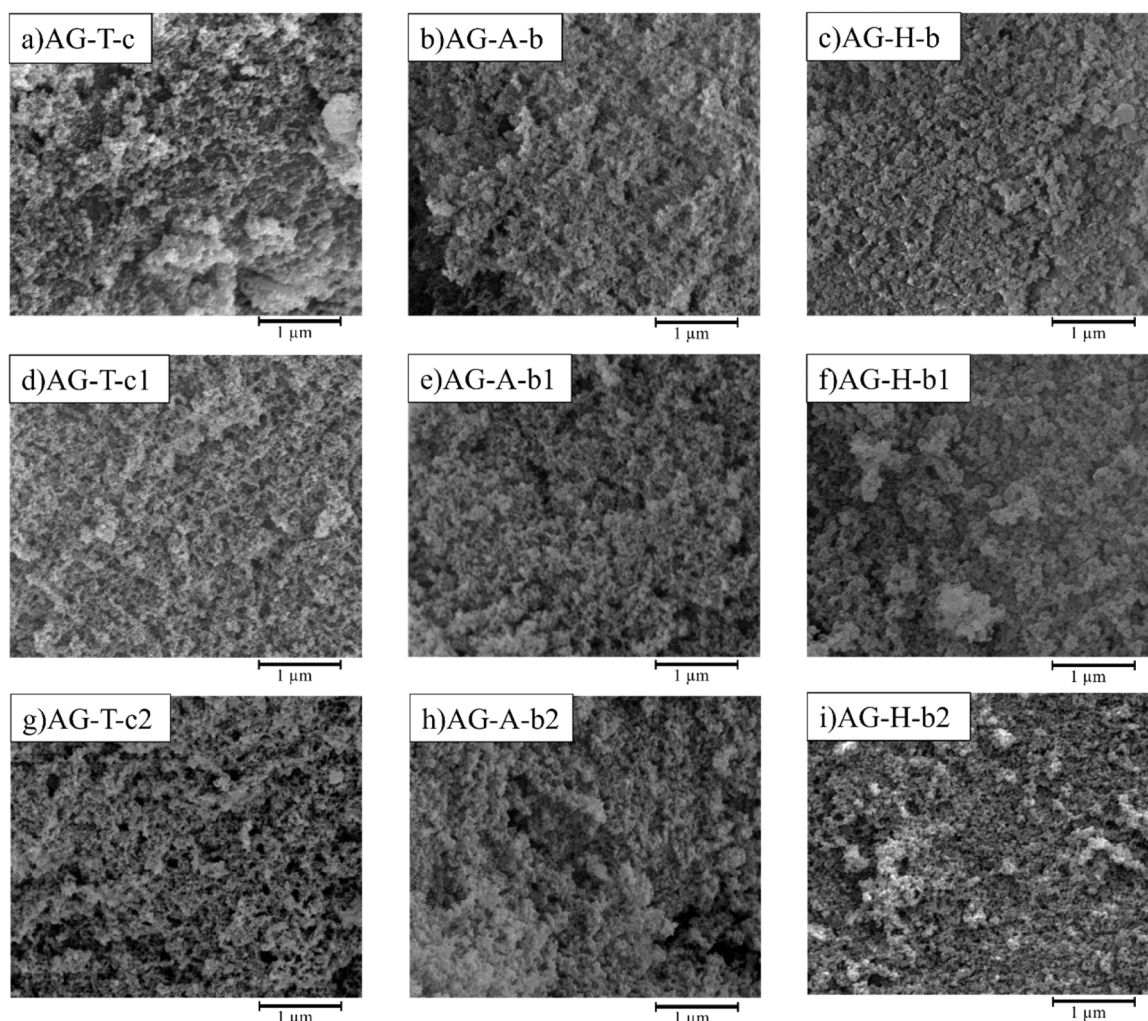


Fig. 5. SEM images of aerogels prepared without any sodium removal (a-c), aerogels washed after drying (d-f), and aerogels washed after gelation (g-i).

Table 4

Properties of silica aerogels washed after the gelation step, following the sodium removal method (2). Values in brackets represent the % of the change in properties compared to aerogels produced without any sodium removal.

Name	λ (mW/m $\cdot$ K)	SSA_{BET} (m ^{2} /g)	Pore width (nm)	ρ_b (kg/m ^{3})	ρ_s (g/cm ^{3})	Porosity (%)	WCA	Na $^+$ (wt%)
AG-T-c2	22.3 $\pm$ 0.04 (0%)	754 $\pm$ 19 (-22%)	11.7 $\pm$ 1.7 (+9%)	99 $\pm$ 2 (+20%)	1.60	93.8 $\pm$ 1.3 (-3%)	150.5° (-1.5%)	0.36 (-23%)
AG-A-b2	26.3 $\pm$ 0.3 (+39%)	512 $\pm$ 11 (-23%)	14.1 $\pm$ 2.2 (+29%)	126 $\pm$ 5 (+33%)	1.73	92.7 $\pm$ 2.7 (-3%)	152.3° (+1%)	0.14 (-81%)
AG-H-b2	32.3 $\pm$ 0.1 (-24%)	198 $\pm$ 1 (-25%)	10.3 $\pm$ 0.4 (-27%)	225 $\pm$ 10 (-17%)	1.78	87.4 $\pm$ 5.4 (+1%)	151.7° (+1%)	2.46 (-31%)

could be that, in current research, washing was done in a shaker, which could have led to damage to the silica network. Similar to method (1), the BET surface area decreased, and the average pore width increased, which could indicate hydrolysis of the silica network. Sample AG-H-b2 actually experienced an improvement in quality, with a 24% decrease in thermal conductivity and a 10% decrease in bulk density. In the SEM image, it appears less dense, with a more uniform network and smaller particle size. Additionally, its properties are better than those of AG-H-b1, which underwent the washing step post-drying (Table 3).

While all aerogels had a small increase in hydrophobicity of 1–3%, the samples containing < 1 wt% Na $^+$ performed better without any sodium removal techniques (AG-T-c, AG-A-b). Aerogel AG-H-b containing 3.58 wt% Na $^+$ benefited from the washing, although its properties are still worse than those of other AG-H samples (e.g., H-d and H-

f). This suggests that the synthesis protocol and sol-gel conditions have a larger effect on aerogel properties than additional sodium removal processes. Upon optimizing the methodology, the sodium content can be minimized to yield a high-quality silica aerogel without the need for washings or ion-exchange resin.

In the context of silica aerogel synthesis, this study evaluates several synthesis parameters within a single framework, enabling direct comparison of their effects on aerogel properties and sodium removal efficiency. Prior research reported difficulties in achieving controlled gelation and a homogeneous silica network when employing strong inorganic acids as gelation catalysts. [12,43] The present findings demonstrate that diprotic organic acids facilitate uniform gelation while simultaneously removing sodium ions. This novel approach resulted in better performance than the control sample prepared via the traditional

ion-exchange resin. Moreover, the need for additional Na^+ removal steps is eliminated in the proposed protocol, which was found to negatively affect the aerogel quality by current findings, aligning with literature. [41] However, while tartaric acid exhibited the highest sodium removal efficiency, its higher cost and lower sustainability compared to mineral acids may limit its applicability, explaining the continued reliance on inorganic acids in environmentally focused studies. [44] By optimizing the sol-gel process for acetic and hydrochloric acids, this work shows that performance similar to tartaric acid-catalyzed gels can be achieved without additional purification steps. Overall, this research clarifies the role of sodium in silica aerogel production, and outlines synthesis pathways that minimize processing requirements while enhancing the properties of the material.

4. Conclusions

This study investigated parameter optimization for acid-catalyzed silica aerogel synthesis by comparing different gelation agents and sodium removal methods. The aim was to combine the methodology reported in prior research with novel approaches to identify the key factors that influence the properties of the resulting silica aerogel.

- (1) Tartaric acid as a catalyst yielded the most homogeneous aerogels with slight variation in their properties and residual sodium contents. This was linked to its high Na^+ removal efficiency at the sol-gel stage due to its diprotic nature. It was also found that the pH of the sol had a higher impact on the aerogel performance than other parameters, with samples gelled in a slightly acidic range yielding the best results.
- (2) Acetic and hydrochloric acids exhibited more variation in properties and sodium amounts with changes in synthesis parameters, emphasizing the importance of lower silica-to-acid ratios (1.5–2.0) for monoprotic catalysts. Using HCl, a strong inorganic acid, proved more challenging due to the difficulty of controlling the gelation conditions, specifically at sol pH below 10. HCl induces an alternative gelation pathway that differs from that of organic acids, which resulted in generally lower performance of the aerogels.
- (3) Relying on the solvent exchange process to remove residual sodium was possible under certain conditions. Those include using a low Si wt% for the sol, which minimized the amount of sodium in the early stage and increased gel permeability due to lower density, and catalyzing gelation with tartaric acid or acetic/hydrochloric acids at a low silica-to-acid ratio (1.5–2.0). Under these conditions, the Na^+ content in aerogels was recorded at 0.19 – 1.94 wt%, while samples that were made otherwise contained 3.58 – 7.67 Na^+ wt%.
- (4) Washing the aerogels with water in a shaker for 1 h resulted in a reduction of sodium but also a change in their properties. While the aerogels were hydrophobic, immersion in water led to an increase in density and a decrease in specific surface area for many samples, likely caused by the pore structure rearrangement and the dissolution of sodium salts. At the same time, it resulted in a notable increase in average pore widths due to hydrolysis and hydrophobicity due to sodium salt removal for most samples. However, adapting the parameters to remove sodium during solvent exchange rather than post-drying yielded the highest quality aerogels overall.
- (5) Washing the hydrogels with water post-aging step was also successful in removing the sodium with a 23–81% decrease compared to the original samples. However, similarly to aerogel washing, the properties worsened with an increase in density and a decrease in porosity for samples with low sodium contents post-drying. For the aerogel with high Na^+ wt%, adding a hydrogel washing step was beneficial overall and led to better properties when compared with the same sample washed post-drying. This

method is, therefore, applicable for samples that are not sufficiently purified during the solvent exchange steps, but is redundant for aerogels that are.

In conclusion, this research proposed several novel aerogel synthesis protocols using three acids as gelation agents and relying on the solvent exchange sequence to remove the residual sodium instead of implementing additional steps for its removal. The resulting aerogels have low thermal conductivity (18.9 – 22.3 mW/m•K), low bulk density (52.5 – 95.2 kg/m³), and high specific surface areas (712.2 – 1006.2 m²/g), while containing 0.21 – 0.70 Na^+ wt%.

CRediT authorship contribution statement

Schollbach Katrin: Writing – review & editing, Supervision. **H.J.H. Brouwers:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition. **Gauvin Florent:** Writing – review & editing, Supervision. **Borzova Marina:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Funding declaration

This research is funded by Project BRIMM (Bright Renovatie Isolatie voor woningschil door (Advanced) Materialen en Methodes) under Missiegedreven Onderzoek, Ontwikkeling en Innovatie (MOOI), grant number MOOI32007.

Supporting Information

Additional information on excess tartaric acid addition (Figure S1). Detailed SEM EDX analysis of selected samples before and after washing (Figures S2 and S3). BET adsorption-desorption curves for all samples (Figure S4). Detailed IC data used to quantify sodium and chlorine contents in washed samples (Table S1).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors acknowledge Barbara Zhilinskaya for her excellent contribution to the experimental work presented in this paper. Furthermore, the authors want to acknowledge Beatrice Cerrai for assistance with SEM measurements.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mtcomm.2026.115944.

Data availability

Data will be made available on request.

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