Modelling and optimisation of sodium silicate based silica aerogel synthesis using response surface methodology

Seyed Saeed Mirzaee[1], *Esmaeil Salahi*[1] ✉, *Ali Khanlarkhani*[2]

[1]*Ceramics Department, Materials and Energy Research Center, Karaj, P.O. Box 31787-316, Iran*
[2]*Nano-Technology and Advanced Materials Department, Materials and Energy Research Center, Karaj, P.O. Box 31787-316, Iran*
✉ *E-mail: e-salahi@merc.ac.ir*

Published in Micro & Nano Letters; Received on 10th February 2018; Accepted on 2nd March 2018

The purpose of this work was to model and optimise the preparation of silica aerogel using low-cost material and modified sol–gel process. A central composite design was employed to optimise the synthesis factors. Among all factors discussed in literatures, silica concentration, gelation time and hydrophobic agent amount were the most efficacious ones. All experiments were performed at the same conditions, but the elected factors were varied in five levels. The response (density of silica aerogel) was fitted by quadratic regression model to find the optimal condition. Computation results showed that the minimum density of silica aerogel was achieved at silica concentration of 4.12 g/l, acid amount of 14.46 ml and trimethylchlorosilane (TMCS) consumption of 10.39 ml. The best density of silica aerogel was 0.078915 g/cm^3 and the specific surface area determined by Brunauer–Emmett–Teller (BET) analysis was 780 m^2/g.

1. Introduction: Silica aerogel is a promising material in modern technologies and has received great attention due to its inimitable characteristics. Some of these unique physical properties such as low density, high porosity and high specific surface area are just some of its unique physical properties. Despite its superior properties, manufacturing cost of silica aerogel restricted its application. There are two main challenges to scale up the production of aerogels: (i) the use of expensive and hazardous silica sources such as silicon alkoxides, and (ii) the cost of drying process applied to prevent structure collapse [1, 2].

Currently, a lot of researches have been concentrated to overcome these problems to lower the cost and time of aerogel production [3, 4]. Sodium silicate is the cheapest source of silica that is easily dissolved in water and does not pose any risk of flammability. However, before initiating the gelation, sodium ions must be replaced with proton to form a silicic acid [5, 6]. Recently, the ambient pressure drying (APD) method has attracted much attention due to its potential to reduce the cost of aerogel synthesis. APD is a set of operations including solvent exchange following by surface modification to minimise forces exerted onto the gels during drying [7, 8]. APD is perhaps the cheapest method compared to the other drying processes, but the consumption of the silylating agent must be considered because it is the costly part of APD. Therefore, it seems necessary to evaluate the synthesis parameters.

There are many factors in sol–gel process that affect the final properties of silica aerogel. Duraes *et al.* [9] studied the effect of drying condition on the microstructure of silica aerogel. Bangi *et al.* [10] surveyed H_2O/Na_2SiO_3 molar ratio on density and thermal conductivity of silica aerogel in both acidic and basic pH. Rao *et al.* [11] focused on the different protic solvent and demonstrated that the isopropanol and methanol resulted in lower density. Sarawade *et al.* [12] reported the effect of washing pH and ageing time on physical and textural properties of modified and unmodified silica aerogel. Rao *et al.* [13, 14] investigated the physical and hydrophobic properties of the silica aerogels with various and mixed silylating agents. In another work, Gurav *et al.* [15] investigated on the ratio of H_2O/Na_2SiO_3 and acid/Na_2SiO_3 and their results showed that the graph of the density versus both ratios have the stationary points revealing the best proportion.

As briefly described above, many researchers focused on factors affecting silica aerogel synthesis. In some cases, the results are incompatible. This may be due to 'one factor at a time' approach that ignores the interactions between factors. Considering that the study of the interactions between factors requires a large number of experiments, the empirical method seems almost impossible. Design of experiments (DOE) is an applicable tool to reduce the number of experiments by involving statistical analysis. Response surface methodology (RSM) is designed by Wilson and Box for optimisation in chemical industry. Among all RSM techniques, central composite design (CCD) is a popular one. The CCD method is widely used in optimisation of chemical reactions. There are three design points in CCD: (i) factorial points (2^k), (ii) star points or axial points ($2k$) and central points (n). So, the number of experiments will be $N=2^k+2k+n$, where k is the number of factors to be evaluated [16]. It is obvious that the experiments in CCD are much lower than other empirical methods.

The results of the previous studies show that among all the factors, concentration of silica, gelation time and amount of hydrophobic agent, are the most efficacious parameters on the final density of silica aerogel. The purpose of this Letter is to estimate the simultaneous effect of these parameters on the response of bulk density and to determine the optimal values for the production of silica aerogel. Therefore, The RSM was utilised using three variables, 'silica concentration', 'acid addition' (which directly affects the gelation time) and 'TMCS consumption' on the final density of silica aerogel. The magnitude of these parameters was selected based on pervious works [6, 10, 15].

2. Materials: Sodium silicate solution (Merck, 1.05621, SiO_2/Na_2O: ~3) was diluted with deionised water to make 150 ml sol containing 3–5 g/l silica (pH ~12.3). The sol becomes to gel by adding 2 M nitric acid (HNO_3, Merck, 1.00456). The silica sol just before the gelation had a pH ranging 10–10.5. To strengthen the gel structure, it was remained in deionised water for 12 h. Na^+ ion removal was performed by washing the wet gel several times with distilled water. Then, solvent exchange was carried out in two steps. At first, capillary water was replaced with methanol (CH_3OH, Merck, 106009) as intermediary solvent. To ensure complete replacement of water, this step repeated twice in 24 h. The second step is the exchange of pore liquid (in this case methanol) with a liquid which has lower surface tension [in this case hexane ($CH_3(CH_2)_4CH_3$, Merck, 104368)] in

12 h. Surface modification was performed by introducing trichloromethylsilane ($ClSi(CH_3)_3$, Merck, 102333) to the wet gel at 45°C in 12 h. Then the surface modified gel was dried under ambient pressure at 45°C for 5 h and ultimately dried at 80°C for 5 h to get hydrophobic silica aerogel.

3. Design of experiment: A circumscribed central composite design was employed for the designed experiment of this research. Effects of three factors, namely 'silica concentration', 'acid addition' and 'TMCS consumption' on response of aerogel density were evaluated. There were five levels for each factor as shown in Table 1. The design had a total of 17 runs including 8 factorial points, 6 axial points and 3 replicates at the centre points. The complete quadratic model for three-factor CCD is described in the following equation:

$$Y = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k} b_{ii} x_i^2 + \sum_{i=1 j=i+1}^{k} b_{ij} x_i x_j + \varepsilon \qquad (1)$$

Table 1 Factors and levels in the CCD

Factor	Level				
	$-\alpha$	−1	0	+1	$+\alpha$
x_1 (g/l) (silica concentration)	3.1591	3.5	4	4.5	4.8409
x_2 (ml) (acid addition)	13.6591	14	14.5	15	15.3409
x_3 (ml) (TMCS consumption)	9.6591	10	10.5	11	11.3409

where Y is the response; b_0, b_i, b_{ii} and b_{ij} are model constant, the linear coefficients, the quadratic coefficients and the interaction coefficients, respectively; x_i and x_j are independent variables.

4. Results and discussion: In accordance with CCD procedure, 17 experiments including 8 factorial, 6 axial and 3 centre points were performed to evaluate the effect of three factors and their interactions on density of silica aerogel. Experimental and predicted values of density are illustrated in Table 2. Based on experimental results, the following coded second-order polynomial equation (2), which is provided by Design Expert software (version 7.0.0, Stat-Ease, Inc. USA), was appropriately fitted on the empirical data

(see (2))

The sign and the absolute amount of each coefficient indicate the positive/negative effect of the variable on the response [17]. So, the uncoded equation (2) is as below:

(see (3))

The purpose of this model was to describe the interaction of factors affecting the response at the investigated range. The results of analysis of variance (ANOVA) test are presented in Table 3. The significance of each model terms could be determined by prob>F <0.05 while values >0.1 indicate the model terms are not significant. Among all model terms in this case A, C, AB, AC, A^2, B^2 and C^2 are significant, B is not significant and BC is insignificant. The model F-value of 684.10 implies the model is significant.

Table 2 DOEs by CCD for density of silica aerogel

Run	Silica concentration, g/l	Acid addition, ml	TMCS consumption, ml	Density, g/cm^3	
				Observed	Predicted
1	3.50	14.00	11.00	0.126816	0.126771
2	4.00	14.50	9.66	0.088012	0.088906
3	3.50	15.00	11.00	0.138587	0.137643
4	4.50	14.00	11.00	0.100775	0.099598
5	4.50	14.00	10.00	0.110599	0.110231
6	4.00	14.50	10.50	0.080000	0.079884
7	4.50	15.00	11.00	0.092767	0.091861
8	4.00	15.34	10.50	0.086830	0.088364
9	4.84	14.50	10.50	0.130460	0.132124
10	4.50	15.00	10.00	0.104006	0.102494
11	4.00	14.50	11.34	0.095201	0.096336
12	3.16	14.50	10.50	0.167795	0.168160
13	4.00	13.66	10.50	0.085233	0.085728
14	4.00	14.50	10.50	0.079500	0.079884
15	3.50	15.00	10.00	0.118556	0.118175
16	3.50	14.00	10.00	0.107709	0.107303
17	4.00	14.50	10.50	0.080500	0.079884

$$\begin{aligned} \text{Density} = {} & 0.080 - 0.011 \times A + 7.836 \times 10^{-4} \times B + 2.209 \times 10^{-3} \times C \\ & - 4.652 \times 10^{-3} \times A \times B - 7.525 \times 10^{-3} \times A \times C + 0.025 \times A^2 \\ & + 2.532 \times 10^{-3} \times B^2 + 4.503 \times 10^{-3} \times C^2 \end{aligned} \qquad (2)$$

$$\begin{aligned} \text{Density} = {} & 3.45826 - 0.23401 \times \text{Silica} - 0.21774 \times HNO_3 - 0.25345 \times \text{TMCS} \\ & - 0.01861 \times \text{silica} \times HNO_3 - 0.030301 \times \text{Silica} \times \text{TMCS} \\ & + 0.09936 \times \text{Silica}^2 + 0.010129 HNO_3^2 + 0.018013 \times \text{TMCS}^2 \end{aligned} \qquad (3)$$

doi: 10.1049/mnl.2018.0093

Table 3 ANOVA test for CCD in the case of silica aerogel density

Source	Sum of squares	df	Mean square	*F*-value	*p*-value Prob>*F*
model	9.549×10^{-003}	8	1.194×10^{-003}	684.10	<0.0001
A-silica	1.567×10^{-003}	1	1.567×10^{-003}	898.34	<0.0001
B-HNO_3	8.386×10^{-006}	1	8.386×10^{-006}	4.81	0.0597
C-TMCS	6.663×10^{-005}	1	6.663×10^{-005}	38.18	0.0003
AB	1.732×10^{-004}	1	1.732×10^{-004}	99.24	<0.0001
AC	4.530×10^{-004}	1	4.530×10^{-004}	259.64	<0.0001
A^2	6.956×10^{-003}	1	6.956×10^{-003}	3986.56	<0.0001
B^2	7.229×10^{-005}	1	7.229×10^{-005}	41.43	0.0002
C^2	2.286×10^{-004}	1	2.286×10^{-004}	131.02	<0.0001
residual	1.396×10^{-005}	8	1.745×10^{-006}	—	—
lack of fit	1.346×10^{-005}	6	2.243×10^{-006}	8.97	0.1037
pure error	5.000×10^{-007}	2	2.500×10^{-007}	—	—
Cor total	9.563×10^{-003}	16	—	—	—

There is only a 0.01% chance that, this large 'model *F*-value' could occur due to noise. The 'lack of fit *F*-value' of 8.97 implies the lack of fit is not significant relative to pure error. The 'predicted *R*-squared' of 0.9918 is in reasonable agreement with the 'adjust *R*-squared' of 0.9971 and the signal-to-noise ratio of 91.847 indicates that this model can be used to navigate the design space.

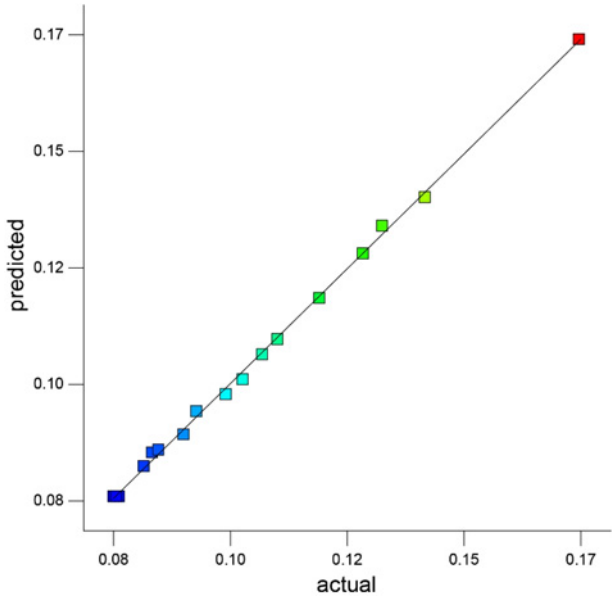

Fig. 1 *Normal probability plot of predicted and actual value for silica aerogel density*

The normal probability plot, which is used to identify substantive departures from normality, is depicted in Fig. 1. As it can be seen, the data are close to straight line which means that the data are approximately normally distributed. This behaviour is another reason to prove the suitability of the proposed model [18].

The response surface and contour diagram for the density of silica aerogel as a function of silica concentration and acid addition at different TMCS consumption are presented in Fig. 2. It is observable that the silica content has greater effect on the density than the acid addition. The density of aerogel decreases with initially increase in silica concentration reaching a minimum state, but further increase leads to increase in density at constant amount of acid [19]. As it can be seen, this minimum state shifts to the higher silica content and the density of aerogel enhances with increasing in TMCS consumption. It is necessary to change the pH of the solution to form interconnected silica network. Due to the basic nature of sodium silicate, acid addition is required. As we know, the network forms in moderate pH [20]. So, the amount of acid should modify at different silica concentration. This is the reason for the movement of the minimum points.

The effect of silica concentration and TMCS consumption on the density of silica aerogel at the different amount of acid is illustrated in Fig. 3. It seems that these graphs follow the same trend as above-mentioned figure. This is due to the interactive and concurrent effects of investigated parameters. TMCS is needed as surface modifying agent in the air pressure drying method. The low amounts of TMCS make the surface hydroxyl groups remaining unmodified, resulting in shrinkage and increased density, on the

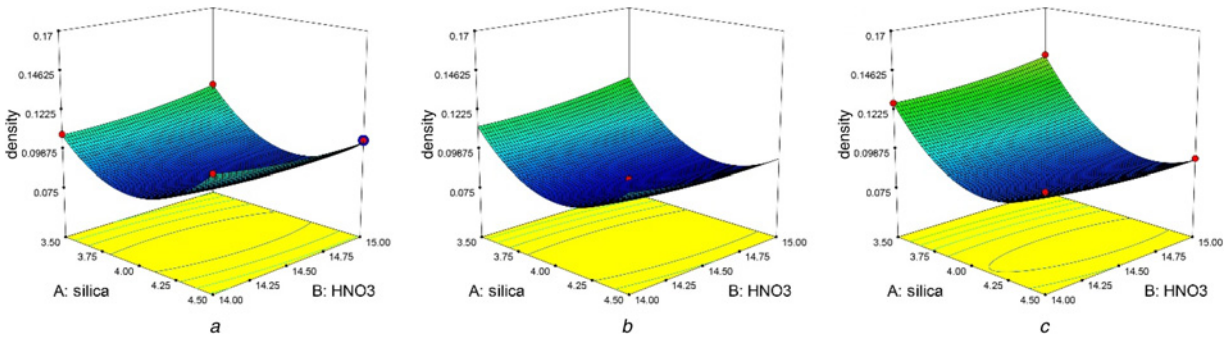

Fig. 2 *Effect of silica concentration and acid addition on the density of silica aerogel at*
a 10 ml TMCS consumption
b 10.5 ml TMCS consumption
c 11 ml TMCS consumption

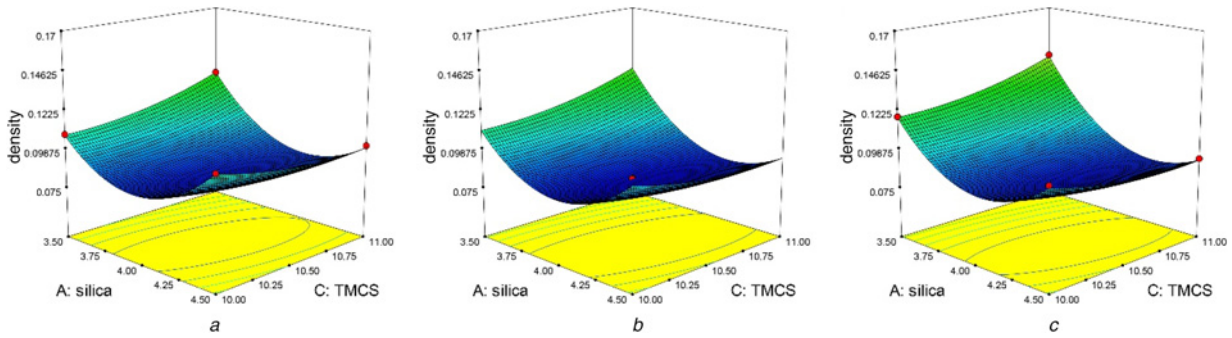

Fig. 3 *Effect of silica concentration and TMCS consumption on the density of silica aerogel at*
a 14 ml acid amount
b 14.5 ml acid amount
c 15 ml acid amount

other hand, excessive amounts of TMCS cause its accumulation in the surface and thereupon the density increases [21].

5. Optimisation of silica aerogel density: Numerical optimisation method was employed to determine the lowest response. The result of numerical calculation predicted that the lowest density in the range of the experiment was 0.078915 g/cm^3 for silica concentration of 4.12 g/l, acid addition of 14.46 ml and TMCS consumption of 10.39 ml. In order to reduce the cost of silica aerogel, TMCS consumption was set at minimum and other ranges were remained unchanged. The best outcome response was 0.0820507 g/cm^3 for silica concentration of 4.03 g/l, acid addition of 14.45 ml and TMCS consumption 10.00 ml. These results were checked empirically as a complementary test. The experimental values for these conditions were 0.0792 and 0.0819 g/cm^3, respectively, which showed a good agreement between experimental and predicted values indicating competency of the proposed model.

6. Conclusion: The processes of silica aerogel synthesis using sodium silicate solution as silica source were successfully modelled by employing the CCD method. The best conditions for density were achieved at silica concentration of 4.12 g/l, acid addition of 14.46 ml and TMCS consumption of 10.39 ml. Under this condition, the density of silica aerogel was 0.078915 g/cm^3. Therefore, it is demonstrated that low-density silica aerogels can be produced using low-cost sodium silicate and simple methods.

7 References

[1] Cheng X., Li C., Shi X., *ET AL.*: 'Rapid synthesis of ambient pressure dried monolithic silica aerogels using water as the only solvent', *Mater. Lett.*, 2017, **204**, pp. 157–160

[2] Pan Y., He S., Cheng X., *ET AL.*: 'A fast synthesis of silica aerogel powders-based on water glass via ambient drying', *J. Sol-Gel Sci. Technol.*, 2017, **82**, pp. 594–601

[3] Wang J., Zhang Y., Wei Y., *ET AL.*: 'Fast and one-pot synthesis of silica aerogels via a quasi-solvent-exchange-free ambient pressure drying process', *Microporous Mesoporous Mater.*, 2015, **218**, pp. 192–198

[4] Sink K.: 'Synthesis of aluminosilicate monolithic system by a novel fast ambient drying process', *Ceram. Int.*, 2016, **42**, pp. 5100–5106

[5] He S., Huang D., Bi H., *ET AL.*: 'Synthesis and characterization of silica aerogels dried under ambient pressure bed on water glass', *J. Non-Cryst. Solids*, 2015, **410**, pp. 58–64

[6] Shewale P.M., Rao A.V., Gurav J.L., *ET AL.*: 'Synthesis and characterization of low density and hydrophobic silica aerogels dried at ambient pressure using sodium silicate precursor', *J. Porous Mater.*, 2009, **16**, pp. 101–108

[7] Lee J.S., Hong S.K., Hur N.J., *ET AL.*: 'Fabrication of spherical silica aerogel/magnetite nanocomposite particles', *Mater. Lett.*, 2013, **112**, pp. 153–157

[8] Bangi U.K.H., Park C.S., Baek S., *ET AL.*: 'Improvement in optical and physical properties of TEOS based aerogels using acetonitrile via ambient pressure drying', *Ceram. Int.*, 2012, **38**, pp. 6883–6888

[9] Duraes L., Ochoa M., Rocha N., *ET AL.*: 'Effect of the drying conditions on the microstructure of silica based xerogels and aerogels', *J. Nanosci. Nanotechnol.*, 2012, **12**, pp. 6828–6834

[10] Bangi U.K.H., Jung I.K., Park C.S., *ET AL.*: 'Optically transparent silica aerogels based on sodium silicate by a two-step sol-gel process and ambient pressure drying', *Solid State Sci.*, 2013, **18**, pp. 50–57

[11] Rao A.P., Rao A.V., Gurav J.L.: 'Effect of protic solvents on the physical properties of the ambient pressure dried hydrophobic silica aerogels using sodium silicate precursor', *J. Porous Mater.*, 2008, **15**, pp. 507–512

[12] Sarawade P.B., Kim J.K., Hilonga A., *ET AL.*: 'Synthesis of hydrophilic and hydrophobic xerogels with superior properties using sodium silicate', *Microporous Mesoporous Mater.*, 2011, **139**, pp. 138–147

[13] Rao A.P., Rao A.V., Pajonk G.M.: 'Hydrophobic and physical properties of the ambient pressure dried silica aerogels with sodium silicate precursor using various surface modification agents', *Appl. Surf. Sci.*, 2007, **253**, pp. 6032–6040

[14] Rao A.P., Rao A.V.: 'Improvement in optical transmission of the ambient pressure dried hydrophobic nanostructured silica aerogels with mixed silylating agents', *J. Non-Cryst. Solids*, 2009, **355**, pp. 2260–2271

[15] Gurav J.L., Rao A.V., Rao A.P., *ET AL.*: 'Physical properties of sodium silicate based silica aerogels prepared by single step sol–gel process dried at ambient pressure', *J. Alloys Compd.*, 2009, **476**, pp. 397–402

[16] Montgomery D.: 'Design and analysis of experiments' (John Wiley & Sons, New York, NY, USA, 2001)

[17] Savic I.M., Savic I.M., Stojiljkovic S.T., *ET AL.*: 'Modeling and optimization of energy-efficient procedures for removing lead(II) and zinc(II) ions from aqueous solutions using the central composite design', *Energy*, 2014, **77**, pp. 66–72

[18] Lee K.M., Abd Hamid S.B.: 'Simple response surface methodology: investigation on advance photocatalytic oxidation of 4-chlorophenoxyacetic acid using UV-active ZnO photocatalyst', *Materials*, 2015, **8**, pp. 339–354

[19] Shi H.X., Cui J.T., Shen H.M., *ET AL.*: 'Preparation of silica aerogel and its adsorption performance to organic molecule', *Adv. Mater. Sci. Eng.*, 2014, **2014**, Article ID 850420, doi: 10.1155/2014/850420

[20] Rao A.P., Rao A.V., Bangi U.K.H.: 'Low thermalconductive, transparent and hydrophobic ambient pressure dried silica aerogels with various preparation conditions using sodium silicate solutions', *J. Sol-Gel Sci. Technol.*, 2008, **47**, pp. 85–94

[21] Rao A.P., Pajonk G.M., Rao A.V.: 'Effect of preparation conditions on the physical and hydrophobic properties of two step processed ambient pressure dried silica aerogels', *J. Mater. Sci.*, 2005, **40**, pp. 3481–3489

doi: 10.1049/mnl.2018.0093