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FABRICATION OF TERNARY SILICA-CALCIUM-MAGNESIUM AEROGELS: EFFECT OF FEEDING RATE AND MOLAR RATIO ON PROPERTIES

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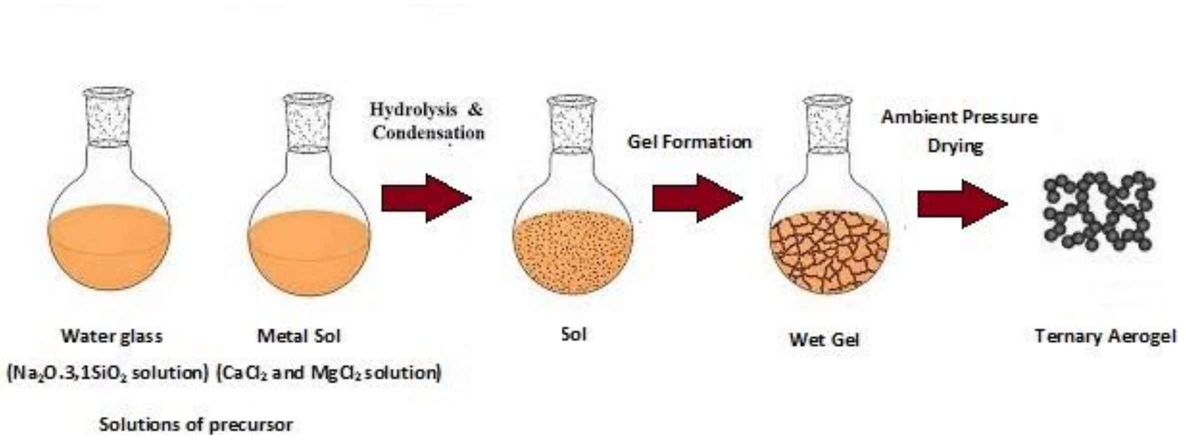
Highlights

- Si/(Ca:Mg) ternary aerogels were synthesized via the solvent exchange method
- The molar ratio of Si/(Ca:Mg) have remarkable effect on final properties
- Ambient-dried ternary aerogels with unique properties should be used in several applications

Graphical Abstract



Flowchart of the Silica-Calcium-Magnesium ternary aerogel production

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ABSTRACT: The silica-calcium-magnesium ternary aerogels were prepared by a solvent exchange method and a subsequent ambient pressure drying process. The effect of process parameters such as feeding rate (9-70 mL.min^{-1}) and molar ratio (Si/(Ca:Mg) = 1:1 - 3:1) on the material characteristics including density, elemental content, surface area, pore size, pore volume, and morphology of powders were investigated. Aerogels were characterized by Fourier transform infrared spectroscopy (FTIR), inductively coupled plasma optical emission spectroscopy (ICP-OES), scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET), Barrett–Joiner–Halenda (BJH) and tapping density analysis. It was found that the molar ratio of Si/(Ca:Mg) could remarkably affect the surface area and density of aerogels, while the feeding rate had slight effect. The resultant aerogels exhibited high specific surface areas. The results showed that the aerogel has a Si/(Ca:3Mg) molar composition obtained with 9 mL.min^{-1} had the highest surface area (524 m^2.g^{-1}). The increase of Ca to Mg molar ratio caused a decrease in the surface area and density of samples. The resultant aerogels are promising candidates as adsorbents to remove various contaminants.

Keywords: *Ambient pressure drying, Co-doped silica, Pore structure, Structural evolution, Ternary aerogel*

1. INTRODUCTION

Silica aerogels are three-dimensional porous nanostructures which have exceptional and unique features such as high porosity (80-99 %), high surface area (up to1200 m^2.g^{-1}), low density (down to 0.003 g.cm^{-3}) and low thermal conductivity (0.005-0.021 W (m·K)$^{-1}$) [1,2]. Accordingly, silica aerogels have attracted great attention in various applications ranging from thermal insulation to the aerospace sector during the past decades [3].

Since silica aerogels are potential candidates for a wide variety of applications, scientists are actively studying on the production of aerogels with suitable properties to be used in different branches of industry. The range of aerogels can be efficiently increased by incorporating a minor component to the silica aerogel [4]. Many researchers have focused on the preparation of different types of silica aerogels such as silica [5], alumina-silica [6, 7,8], copper-silica [4], titania-silica [9,10], zirconia-silica [11,12], vanadium-silica [13], calcium-silica [14], and alumina-silica-titania [15, 16] aerogels. The charming point of multi-component aerogel production is the possibility of processing their structural, textural, and catalytic properties according to specific requirements [16]. However, the production of multi-component aerogels is generally complicated and expensive depending on the different hydrolysis rates of the starting sols and supercritical drying method. The surface areas of multi-component aerogels are generally low compared to the traditional silica aerogels. The commercialization of hybrid aerogels can be enhanced via the optimization of process parameters and also by employing simple ambient pressure

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drying processes instead of supercritical drying [17, 18].

The present study aimed to synthesize silica-calcium-magnesium ternary aerogels using water glass as silica precursor via ambient pressure drying method. To the best of our knowledge, this is the first study investigating the effect of different synthesis parameters such as feeding rate (9-70 mL.min^{-1}) and Si/(Ca:Mg) molar ratio on the structure and properties of silica-calcium-magnesium ternary aerogels. The properties of the aerogels were carried out using FT-IR, ICP-OES, SEM, and N_2 adsorption-desorption techniques to describe their structural evolution.

2. MATERIAL AND METHODS

2.1. Materials

Calcium chloride dihydrate ($CaCl_2.2H_2O$), Magnesium chloride hexahydrate ($MgCl_2.6H_2O$), n-Heptane (for analysis) and Ethanol (absolute, ≥99.0%) purchased from Merck KGaA (Darmstadt, Germany). Sodium Silicate ($Na_2O.3,1SiO_2$, Module-2 - Bome 36-50) Chem Pure purchased from Ege Kimya (Istanbul,Türkiye).

2.2. Preparation of silica-calcium-magnesium ternary aerogels

The silica sol was prepared by diluting water glass ($Na_2O.3,1SiO_2$) with distilled water (1:4 v/v). The metal sol was prepared by dissolving the appropriate amount of $CaCl_2.2H_2O$ and $MgCl_2.6H_2O$ in distilled water (150 mL). Then the metal sol was fed into the silica sol via a peristaltic pump (Heidolph Pumpdrive 5201, Germany) at a feeding rate of 9, 35 or 70 mL/min while the silica sol was constantly stirred. The precipitate was further vigorously stirred for 15 minutes. The reaction flask was capped with a watch glass and then the precipitate was aged for 24 hours at 50 °C in an oven dryer (Elektro-mag, Turkey). After the aging step, the gel was washed with distilled water (300 mL) to remove the excessive sodium salts. Subsequently, the gel was soaked in ethanol (150 mL) and stirred vigorously using a mechanic stirrer (Heidolph RZR 1, Germany) for 1 minute to remove water from the pores. The mixture was filtered and the same solvent exchange step was repeated for a second time. However in the second cycle instead of filtering the ethanol, the gel was aged in ethanol for 24 hours at 50 °C. Then ethanol was replaced with n-heptane using the same procedure. The surface modification of gels was achieved by aging in n-heptane for 24 hours at 50 °C. Finally, the mixture was filtered and the gels were dried in gradually at 70 °C for 20 hours, 90 °C for 2 hours and 110°C for 2 hours in an air dryer.

Table 1. The molar composition of produced silica-calcium-magnesium aerogels

Composition	Si/(Ca:Mg) ratio
Si/(Ca:3Mg)	1/1
Si/(Ca:Mg)	1/1
Si/(3Ca:Mg)	1/1
2Si/(Ca:3Mg)	2/1
2Si/(Ca:Mg)	2/1
2Si/(3Ca:Mg)	2/1
3Si/(Ca:3Mg)	3/1
3Si/(Ca:Mg)	3/1
3Si/(3Ca:Mg)	3/1

After the determination of a suitable feeding rate, the aerogels were produced with different molar ratios of Si/(Ca:Mg) (shown in Table 1). The molar ratio of silica to total of calcium and magnesium was taken as 1:1, 2:1 and 3:1 and also, the ratio of calcium and magnesium between each other was selected as 1:1, 1:3, and 3:1.

2.3. Characterization of silica-calcium-magnesium ternary aerogels

Surface area, pore size and pore volume of aerogels were determined using a Micromeritics TriStar II 3020 surface area and pore distribution analyzer at 77 K. The BET method was used to estimate the specific surface area of aerogels (SBET), while the BJH method was used for pore size and pore volume calculation. The SEM was conducted using a modal of ZEISS EVO® LS 10. FTIR spectra were recorded with a Shimadzu IR Prestige 21 spectrometer. The ICP-OES were performed by Shimadzu ICPE-9000 to determine the elemental composition of aerogels. The tapping density was evaluated as described by Temel et al. [3].

3. RESULTS AND DISCUSSION

3.1. Effect of the feeding rate on the properties of silica-calcium-magnesium ternary aerogels

Feeding rate may have an important role in the textural properties and morphology of materials [19]. The variation of surface area, pore size, pore volume and density of aerogels due to the feeding rate of the sol was demonstrated in Table 2. It is obvious from the results that the surface area of aerogels increased slightly with the decreased feeding rate. The maximum BET-specific surface area (469 $m^2 g^{-1}$) occurred in the aerogel with 9 $mL.min^{-1}$ feeding rate. Increasing the feeding rate from 9 to 70 $mL.min^{-1}$, led to the decrease of surface area to 433 $m^2.g^{-1}$ and also the pore size. The aerogels had mesopore sizes ranging from 3.15-4.44 nm which shows that the particles were small [3]. Additionally, the mesopore volumes of aerogels were in the range of 0.26 to 0.37 $cm^3.g^{-1}$. When the tapping density of aerogels was investigated, the aerogel obtained with 9 $mL.min^{-1}$ feeding rate tendered the lowest density value (0.287 $g.cm^{-3}$). Keeping these in view, further experiments were conducted using 9 $mL.min^{-1}$ feeding rate.

Table 2. Effect of the feeding rate on the textural properties and density of silica-calcium-magnesium ternary aerogels

Feeding rate ($mL.min^{-1}$)	SBET ($m^2.g^{-1}$)	BJH Pore size* (nm)	Pore volume ($cm^3.g^{-1}$)	Density ($g.cm^{-3}$)
9	469	4.44	0.37	0.287
35	468	3.25	0.27	0.487
70	433	3.15	0.26	0.393

* The pore size values were obtained from the desorption part of the N2 adsorption-desorption isotherm

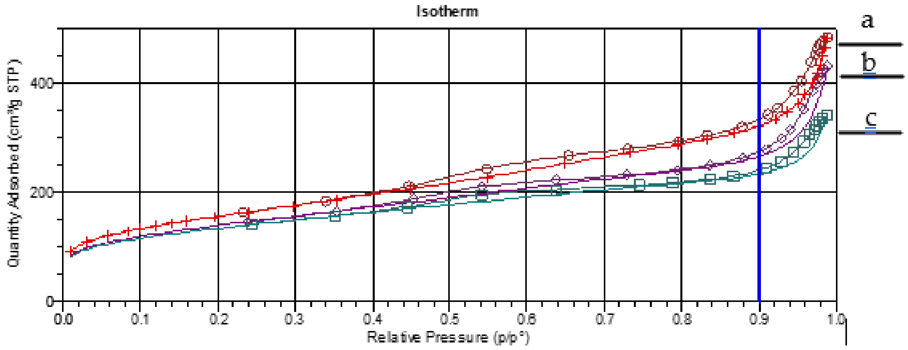

Figure 1. N_2 adsorption/desorption isotherms of the aerogels prepared with a) 9 b) 35 c) 70 $mL.min^{-1}$ feeding rate

Figure 1 shows the N_2 adsorption-desorption isotherms of silica-calcium-magnesium ternary aerogels. A type IV isotherm with a combination of H1-type hysteresis loops was encountered for the aerogels. These indicate the presence of interconnected mesopores with cylindrical geometries and open at both ends. It is clear from the N_2 sorption isotherms that the volume adsorbed increases slowly at low relative pressure. This result can be attributed to the fact that the samples contain little amount of micropores [15].

Table 3. Effect of the feeding rate on the elemental content of silica-calcium-magnesium ternary aerogels

Feeding rate (mL.min^{-1})	Elemental content (%)			
	Si	Ca	Mg	Na
9	94.08	1.37	4.19	0.36
35	88.65	2.14	9.21	<0.123
70	93.68	1.89	4.43	<0.123

The effect of the feeding rate on the elemental content of silica-calcium-magnesium ternary aerogels is given in Table 3. The feeding rate of metal sol slightly effected the elemental content of ternary aerogels. It was determined that the incorporation of Ca and Mg was higher when the feeding rate was 35 mL.min^{-1}. The incorporation trend was similar for 9 mL.min^{-1} and 70 mL.min^{-1} feeding rates.

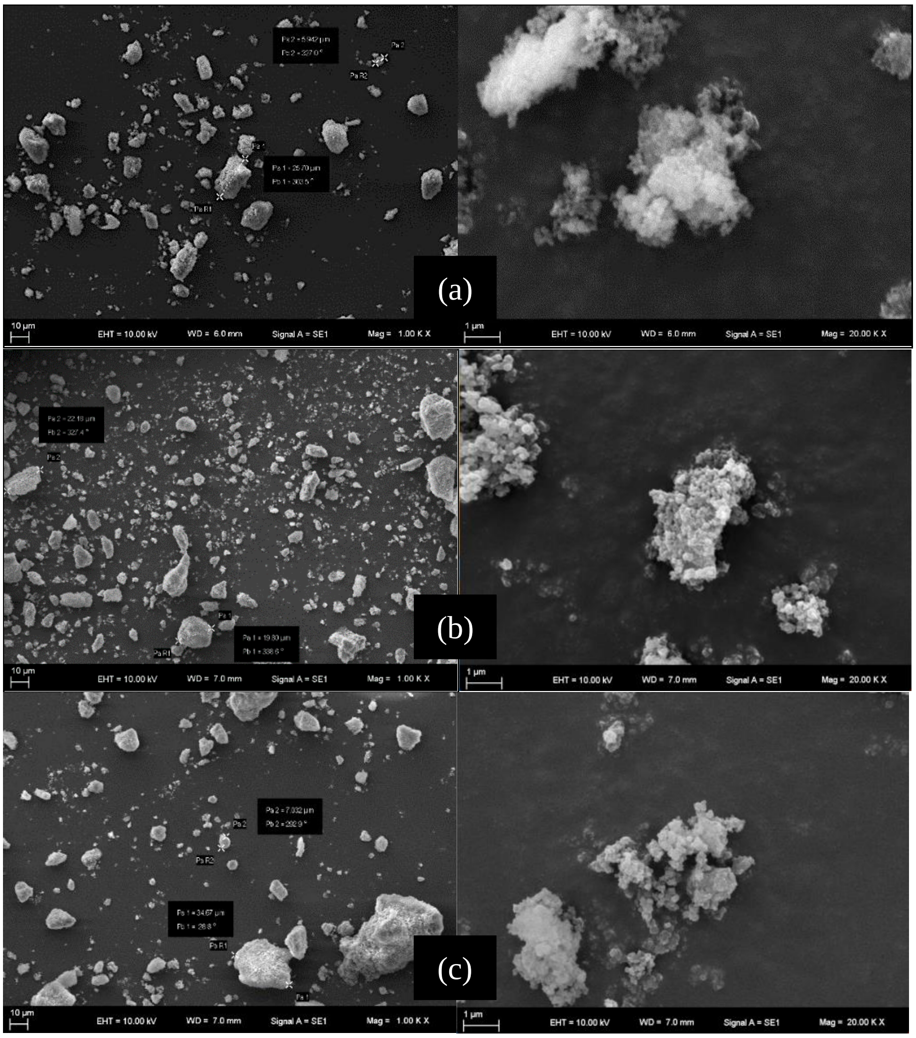

Figure 2. SEM micrographs of aerogels prepared with a) 9 mL.min^{-1}, b)35 mL.min^{-1}, c)70 mL.min^{-1} feeding rate

Figure 2 displays SEM micrographs of the ternary aerogels prepared with different feeding rates. The micrographs reveal that the aerogel prepared with 35 and 70 mL.min^{-1} feeding rate was made of small agglomerates of spherical particles. Interestingly, the aerogel prepared with 9 mL.min^{-1} are observed to be composed of cloud-like nanoclusters. This further verifies the previous N_2 adsorption/desorption results.

3.2. Effect of the molar ratio on the properties of silica-calcium-magnesium ternary aerogels

Initial sol parameters including the precursors for the silica and other components, the molar composition of precursors, water content, and catalyst considerably affects the pore characteristics and other properties (e.g. morphology, transparency etc.) of the final aerogels [20]. The effect of the molar ratio on surface area, pore size, pore volume and density of aerogels is given in Table 4. It was clear that the variation in molar ratio had a considerable effect on the textural properties of aerogels. All the ternary aerogels exhibited high surface area except 3Si/(3Ca:Mg) aerogel (161 $m^2.g^{-1}$), small pore volume (≤ 0.37 $cm^3.g^{-1}$), and small pore size (≤5.46 nm). The increase of Si to (Ca:Mg) molar ratio led to a decrease in surface area while the increase in density. When the Si to (Ca:Mg) molar ratio increased from 1 to 3 the surface area of aerogel decreased from 524 to 393 $m^2\,g^{-1}$. The surface area and density of samples decreased with the increase of Ca to Mg molar ratio in the ternary system whereas, a reverse trend was found for the pore sizes. Conversely, the surface area and density of aerogels increased with the increment of the Mg to Ca molar ratio. When all these results are evaluated together it could be seen that the Si/(Ca:3Mg) sample had the highest surface area (524 $m^2.g^{-1}$).

During the silica-calcium-magnesium ternary aerogel preparation process, various bonds (e.g. Si-O-Si, Si-OH) were produced by hydrolysis reaction. Hereby, bonds interconnect to form a three-dimensional network structure [21]. Therefore, the variation of textural properties could be attributed to the different hydrolysis and condensation reaction rates of the chemicals (e.g. the cation exchange reaction of CaO with SiO- groups to form $Ca(OSi-)_2$ and the (Mg, Ca) O replaced with the Na_2O in the N_2OnSiO_2) [22]. We propose that too much Ca might diminish the cross-linking degree of the bonds which results in the deterioration of the pore structure of aerogel. In this situation, compact particles form and thus a reduction in the specific surface area occurs due to the lack of nitrogen access into some of the pores. However, the incorporation of magnesium led to the occurrence of porous agglomerates in the network accordingly raises the surface area.

The pore volume of ternary aerogels ranged from 0.23 to 0.37 $cm^3.g^{-1}$. In general, the porosity of aerogels was related not only to the pore size but also to the number of pores [23]. In this study, the porosity of the aerogels depends substantially on the pore size. This indicates that probably the number of pores was almost equal for all the samples and their sizes primarily effect the pore volume.

Table 4. Effect of the molar ratio on the textural properties and density of silica-calcium-magnesium ternary aerogels

Molar Composition of Aerogels	**S_{BET} ($m^2.g^{-1}$)**	**BJH Pore size (nm)**	**Pore volume ($cm^3.g^{-1}$)**	**Density ($g.cm^{-3}$)**
Si/(Ca:3Mg)	524	4.37	0.33	0.366
Si/(Ca:Mg)	469	4.44	0.37	0.287
Si/(3Ca:Mg)	420	4.93	0.37	0.266
2Si/(Ca:3Mg)	514	3.22	0.29	0.473
2Si/(Ca:Mg)	434	3.50	0.29	0.385
2Si/(3Ca:Mg)	242	5.16	0.30	0.245
3Si/(Ca:3Mg)	393	3.21	0.23	0.569
3Si/(Ca:Mg)	301	4.20	0.29	0.397
3Si/(3Ca:Mg)	161	5.46	0.28	0.313

The reported textural properties of binary and ternary silica aerogels are summarized in Table 5. The surface area of different aerogels varied from 158 $m^2.g^{-1}$ to 524 $m^2.g^{-1}$. Thus, the surface area as well as pore size and pore volume of aerogels can differ by many factors including molar composition and process parameters.

Table 5. Comprasion of textural properties of silica-calcium-magnesium ternary aerogels with hybrid aerogels

Aerogel Type	S_{BET} ($m^2.g^{-1}$)	Pore size (nm)	Pore volume ($cm^3.g^{-1}$)	Reference
Alumina/Silica	231	31.7	1.86	[24]
Ceria/Silica	404	-	-	[25]
Iron/Silica	158	-	0.27	[26]
Zirconia/Silica	395	10.9	1.09	[11]
Alumina/Titania/Silica	235	22.6	1.29	[15]
Calcium/ Silica	198	4.37	0.203	[14]
Calcium/Magnesium/Silica	524	4.37	0.33	In this study

The variation of molar ratio had no effect on the type of N_2 adsorption–desorption isotherms (not given). The type isotherms of the aerogel were determined to be of type IV which is characteristic of mesoporous materials [27].

The SEM micrographs of aerogels prepared with various Si-, Ca- and Mg molar ratios are given in Fig 3-5. As can be seen from SEM images, aerogels are composed of small particles and pores. The diameters of the particles were in the range 2-80 µm. Aerogels consisted of irregular agglomerates that were formed by spherical nanoparticles. Agglomerates had a grape-like appearance. We supposed that the grape-like structure was made up of spherical particles and also a porous spongy structure was formed spontaneously. The samples with higher Mg molar ratio had bigger agglomerates compared with the samples with higher Ca molar ratio (Fig.4 a-c). This verifies that the particle growth of the aerogels was limited by the incorporation of calcium.

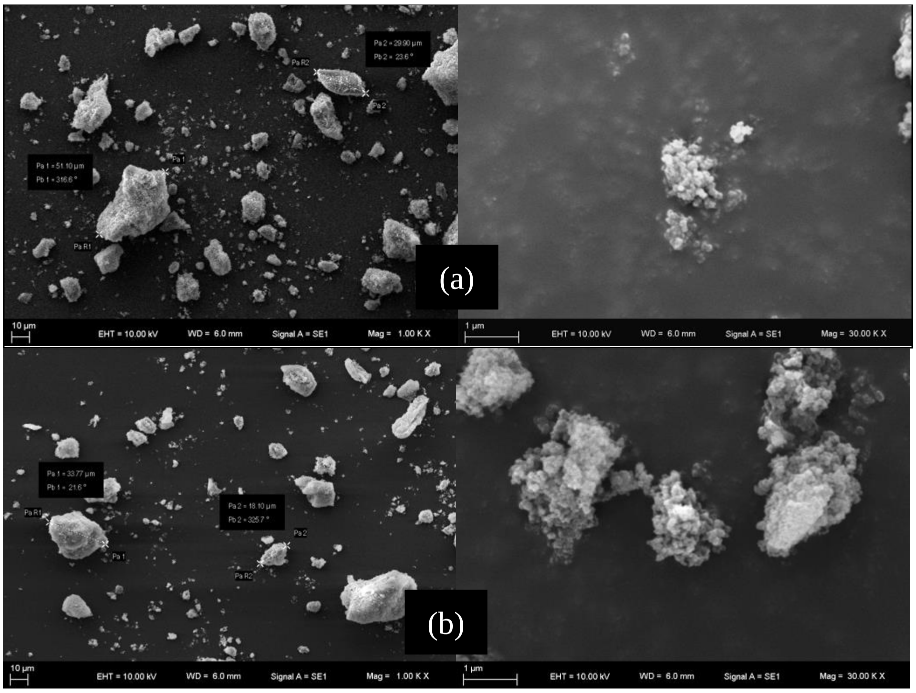

Figure 3. SEM micrographs of aerogels with (a) Si/(Ca:3Mg), (b)Si/(3Ca:Mg) molar composition

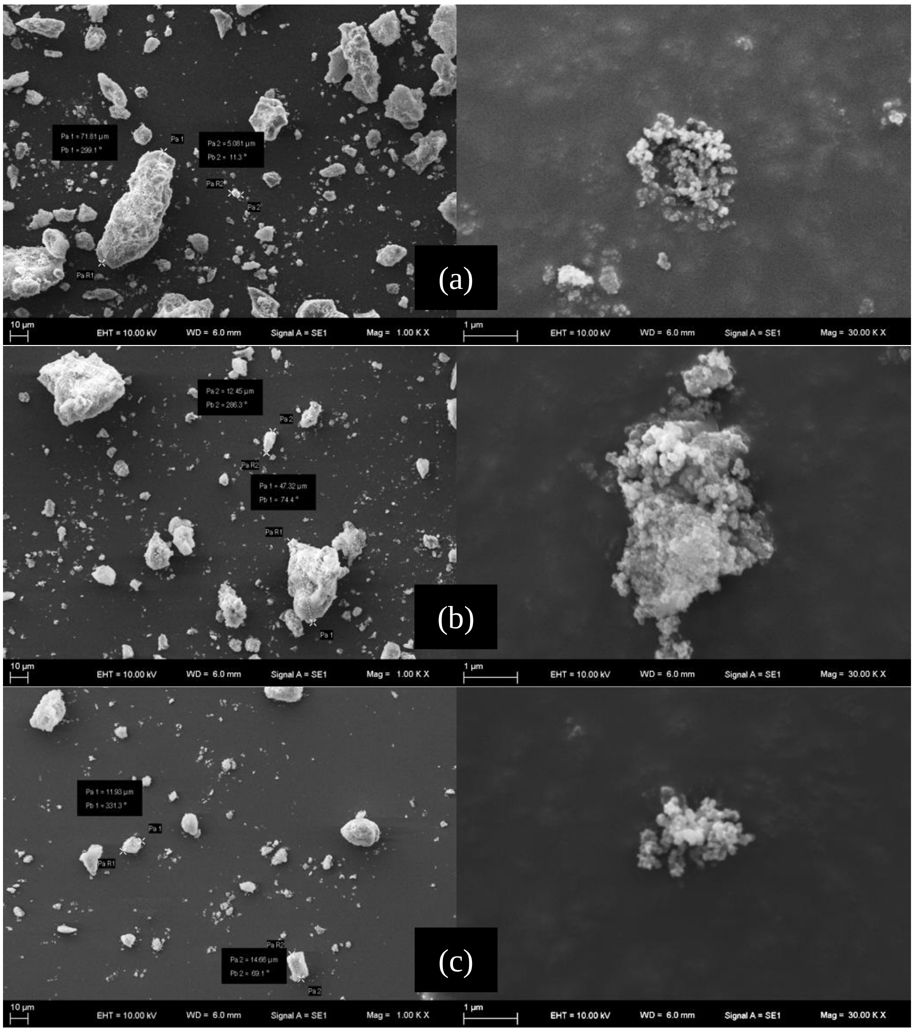

Figure 4. SEM micrographs of aerogels with (a)2Si/(Ca:3Mg), (b)2Si/(Ca:Mg), (c)2Si/(3Ca:Mg) molar composition

Figure 6 presents the FTIR analysis of the silica-calcium-magnesium ternary aerogels. Pure silica aerogel is known to exhibit the asymmetric and symmetric vibration of the three-dimensional Si–O–Si work at nearly 1062 and 794 cm^{-1}, respectively as previously reported by Temel et. al. [3]. For the ternary aerogels, FT-IR showed that the 1062 cm^{-1} band shifted towards a lower wave number (1010 cm^{-1}). The shift confirms the incorporation of Ca and Mg to the network. Similar result was reported by Wu [27] for metal incorporated silica aerogels. The other main difference was the formation of a peak at about 1450 cm^{-1} with the increased Ca amount (Fig. 6 c). This behavior may result from the formation of calcium carbonate due to the reaction of surface adsorbed carbon dioxide with calcium [15]. In addition, the board band between 3750 and 3200 cm^{-1} and centered at about 1630 cm^{-1} ascribed to the surface adsorbed OH groups (water).

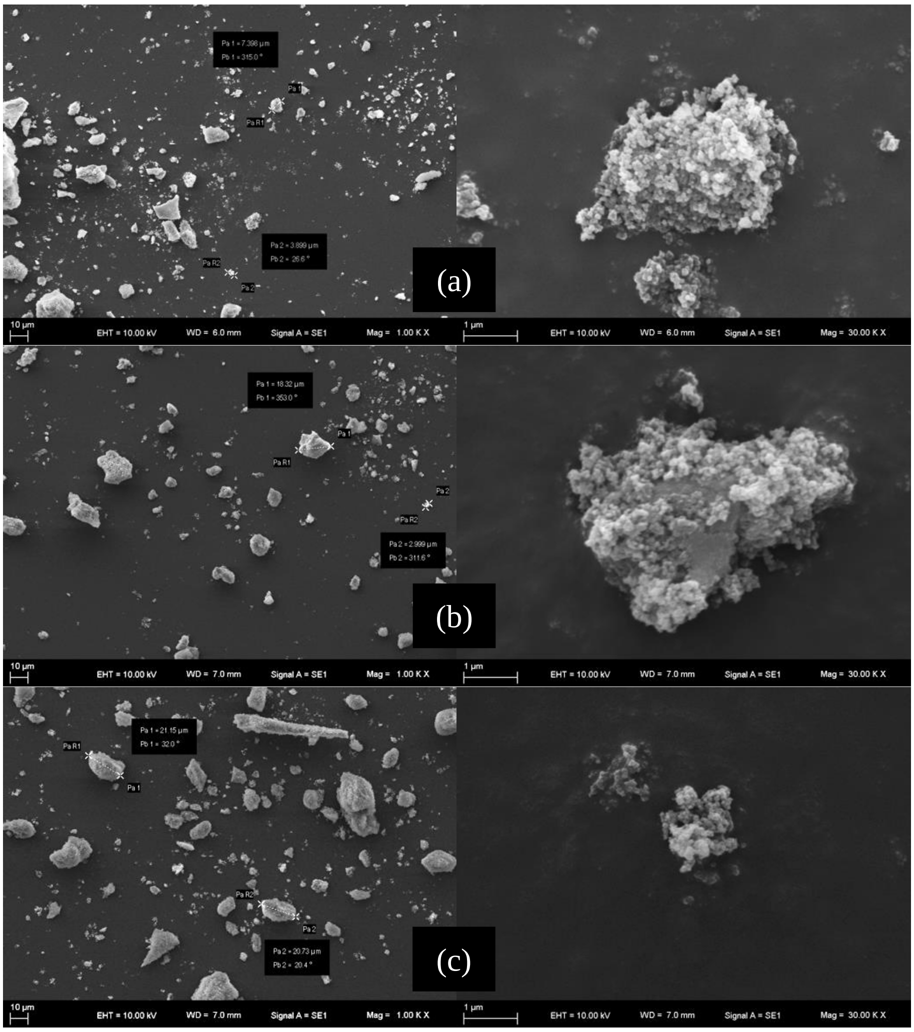

Figure 5. SEM micrographs of aerogels with (a)3Si/(Ca:3Mg), (b)3Si/(Ca:Mg), (c)3Si/(3Ca:Mg) molar composition

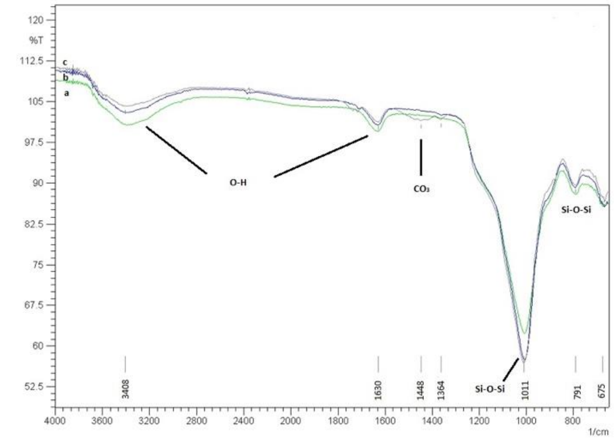

Figure 6. FT-IR spectra of silica-calcium-magnesium ternary aerogels with a)Si/(Ca:3Mg), b)Si/(Ca:Mg) c) Si/(3Ca:Mg) molar composition

Table 6. Effect of the molar ratio on the elemental content of silica-calcium-magnesium ternary aerogels

Sample	**Elemental content (%)**			
	Si	**Ca**	**Mg**	**Na**
Si/(Ca:3Mg)	94.06	0.75	4.73	0.46
Si/(Ca:Mg)	94.08	1.37	4.19	0.36
Si/(3Ca:Mg)	91.20	2.87	5.69	0.24
2Si/(Ca:3Mg)	90.50	0.89	8.25	0.36
2Si/(Ca:Mg)	92.11	2.67	4.60	0.62
2Si/(3Ca:Mg)	91.29	5.47	2.72	0.52
3Si/(Ca:3Mg)	90.51	1.96	6.33	1.20
3Si/(Ca:Mg)	89.88	4.45	4.81	0.87
3Si/(3Ca:Mg)	88.39	7.90	2.88	0.83

The effect of the molar ratio on the elemental content of silica-calcium-magnesium ternary aerogels is presented in Table 6. The results showed that there was small amount of sodium salts in the aerogel structure. The total incorporation of Ca and Mg increased with the increased silica content as expected.

4. CONCLUSIONS

It is important to control the process parameters during the aerogel production. A series of mesoporous silica-calcium-magnesium ternary aerogels with various feeding rates and Si/(Ca:Mg) molar ratio were prepared by a solvent exchange method followed by an ambient pressure drying method. The aerogel prepared with 9 mL.min^{-1} feeding rate exhibited a higher surface area (469 m^{2}·g^{-1}) than the samples prepared with higher feeding rates. All the aerogels were mesoporous confirmed with a type IV N_2 sorption isotherm. The surface area and density of aerogels were greatly affected by the Si/(Ca:Mg) molar ratio. The surface area and density of produced aerogels varied from 161 m^{2}.g^{-1} to 524 m^{2}.g^{-}1 and 0.245 g.cm^{-3} to 0.569 g.cm^{-3}, respectively. The surface area and density of aerogels increased with increasing Mg/Ca molar ratio from 1 to 3. The results showed that aerogels having different properties could be obtained by varying the process parameters.

Declaration of Ethical Standards

The authors declare that the study complies with all applicable laws and regulations and meets ethical standards.

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.

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Data Avaibility

Data will be made available on request.

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