



Research Article / Araştırma Makalesi

EFFECT OF ACID TYPE AND GELATION pH ON THE STRUCTURAL PROPERTIES OF SILICA AEROGELS PREPARED BY USE OF RICE HULL BIOSILICA

Burcu KARAKUZU¹, Tülay Merve TEMEL¹, Sevil YÜCEL^{1*}, Pınar TERZİOĞLU², Yeliz ELALMIŞ¹

¹*Yıldız Technical University, Faculty of Chemical and Metallurgical Engineering, Department of Bioengineering, Esenler-İSTANBUL*

²*Muğla Sıtkı Koçman University, Faculty of Sciences, Department of Chemistry, MUĞLA*

Received/Geliş: 25.01.2016 Revised/Düzeltilme: 07.03.2016 Accepted/Kabul: 14.03.2016

ABSTRACT

In this study, the experimental results of the surface area, morphology, and density of silica aerogels obtained at different preparation conditions are reported. The aerogels have been produced by sol-gel process followed by ambient pressure drying. Rice hull ash silicate solution was used as an inexpensive precursor. The type of acids and gelation pH has strongly affected the structural properties of the final products. The silica aerogels have a well-developed nanoporous structure and a high specific surface area. The densities, pore sizes and specific surface areas of the silica aerogels were in the range of 0.273-0.849 g cm⁻³, 3.24-10.22 nm, and 238-726 m²g⁻¹, respectively.

Keywords: Ambient pressure drying, rice hull, silica aerogel.

PİRİNÇ KABUĞU BİYOSİLİKASI KULLANILARAK HAZIRLANAN SİLİKA AEROJELLERİN YAPISAL ÖZELLİKLERİNE ASİT TİPİ VE JELLEŞME pH'ININ ETKİSİ

ÖZ

Bu çalışmada, farklı hazırlama koşullarında elde edilen silika arojellerin yüzey alanı, morfoloji ve yoğunluğuna ait deneysel sonuçlar rapor edildi. Arojeller sol-jel yönteminin ardından ortam basıncında kurutma ile üretildi. Pirinç kabuğu külü silikat çözeltisi ucuz bir başlatıcı olarak kullanıldı. Asit çeşidi ve jelleşme pH'ı son ürünün yapısal özelliklerini son derece etkiledi. Silika arojeller iyi gelişmiş nano-gözenekli bir yapıya ve yüksek spesifik yüzey alanına sahiptir. Silika arojellerin yoğunlukları, gözenek çapları ve spesifik yüzey alanları sırasıyla 0.273-0.849 g cm⁻³, 3.24-10.22 nm ve 238-726 m²g⁻¹ aralığındadır.

Anahtar Sözcükler: Ortam basıncında kurutma, pirinç kabuğu, silika arojel.

* Corresponding Author/Sorumlu Yazar: e-mail/e-ileti: syucel@yildiz.edu.tr, tel: (212) 383 46 34

1. INTRODUCTION

In this new century, aerogels attract more attentions from both academic and industrial fields because of their excellent properties as high porosity (85–99.8 %), low density (as low as 0.003 g cm⁻³), low thermal conductivity (as low as 0.01 W/m K), and large specific surface area (up to 1200 m² g⁻¹). In general, aerogels classified into inorganic, organic, and composite aerogels. Silica aerogels are inorganic oxides that are the most extensively studied one [1]. Silica aerogels are highly porous and lightest materials that have various applications in aerospace, catalyst supports, drug delivery systems, insulation materials, paints and varnishes, optics, etc. [2].

Conventionally, silica aerogel production is employed by using expensive starting materials like silicon alkoxides followed by supercritical drying or freeze-drying method. However, traditional production hinders the large-scale production of silica aerogels because of being expensive, energy intensive and dangerous. Therefore, the reduction of costs and risks by using low-cost silica sources and ambient pressure drying method are the key points through the commercialization. An agricultural waste, rice hull ash, which is rich in amorphous silica, is an appropriate candidate for silica aerogel production.

The structure of aerogels may be changed due to the sol-gel process parameters. In the present study, enterprises have been carried out to investigate the influence of two different acid (nitric and citric acid) and gelation pH (4-9) on the structural properties of silica aerogels by ambient pressure drying method. In this method, solvent exchange was carried out using ethanol and a small quantity of TEOS in ethanol was used to alter the surface of silica wet gel. Finally, n-heptane was used to remove TEOS/ethanol. The properties of aerogels were investigated by using BET, SEM, and FT-IR technique.

2. EXPERIMENTAL SECTION

2.1. Materials

The local rice hull ash sample was obtained from the Yetiş Food Factory (Turkey). Citric acid (C₆H₈O₇), ethanol, nitric acid (HNO₃), tetraethoxysilane (TEOS), and n-heptane were purchased from Merck (Darmstadt, Germany).

2.2. Sodium Silicate Preparation from Rice Hull Ash

The sodium silicate solution was prepared according to the method of Yücel et.al. [3]. Primarily rice hull ash was burned at 600°C for 5 hours. Acid leaching was carried out by treating rice hull ash (40 grams) with HCl solution (6M) and then heated up to its boiling point for two hours under reflux. The rice hull ash and acid mixture was filtered. The acid leached rice hull ash was dried at 80°C for 20 minutes. The dried ash was boiled in 1M NaOH solution (240 mL) in a covered flask for an hour. The mixture was filtered and the undissolved residues were washed with distilled water (400 mL). The obtained sodium silicate solution was cooled down to room temperature in polypropylene bottles.

2.3. Silica Aerogel Preparation

The procedure for preparation of silica aerogel is demonstrated in Figure 1. The silica hydrogel was prepared by neutralizing the sodium silicate solution with nitric acid (or citric acid) (1 M) to pH 4. The obtained gel was aged for 18 h at room temperature. After aging the gel was washed three times with distilled water to remove excess sodium salts resulted from the neutralization. Subsequently, the water in the gel was replaced by a solution of 20 vol% H₂O/ethanol by aging for 24 h at room temperature. After that, the pretreated gel was aged in 70

vol% TEOS/ethanol solution for 18 h at room temperature. Then, it was aged again for 4 h at 70°C. The TEOS/ethanol solution in the gel was replaced by washing three times with n-heptane. The gel was aged for 24 h at room temperature with two times replacement of fresh n-heptane. The mixture was centrifuged. Finally, it was dried in 6 h intervals at 50°C, 60°C and 70°C to obtain the silica aerogel.

The experiments were conducted at pH 4, 7 and 9.

2.4. Characterization

Nitrogen adsorption measurements were carried out at 77 K with an Automatic Surface Area and Pore Size Distribution Analyzer (Micromeritics, TriStar II 3020) to determine the pore size, pore volume and specific surface area of the aerogel samples. Specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. Single point total pore volume was estimated from the adsorbed N₂ volume at 0.95 relative pressure (P/P₀) values. Barrett-Joiner-Halenda (BJH) method was used to estimate pore size and pore volume by using desorption branch of the isotherm. In this study it is accepted that micropore width is less than 2 nm, mesopore width is between 2-50 nm, and macropore width is larger than 50 nm [4].

The chemical structure of aerogel samples was confirmed by using FT-IR spectrometry (Thermo Scientific Nicolet iS10, USA) in the wave number range of 700 to 4000 cm⁻¹.

The apparent density of silica aerogels was calculated from the measured weight and the volume. The porosity of aerogels was estimated according to the true density of silica (2.19 g cm⁻³) and the apparent density of silica aerogel [5].

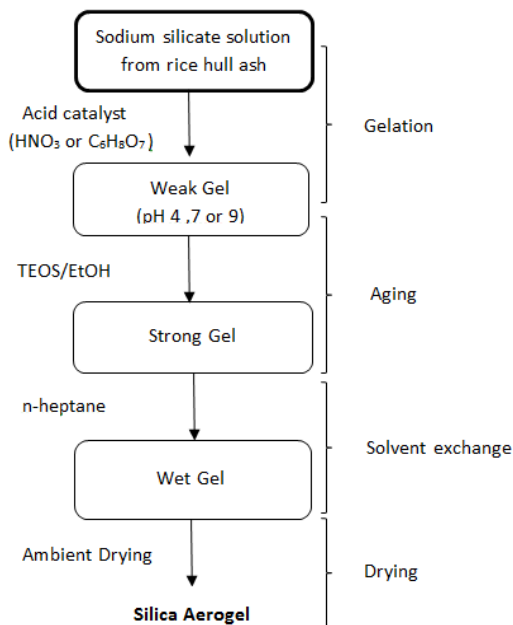


Figure 1. The flowchart of silica aerogel preparation

3. RESULTS AND DISCUSSION

Although aging time, aging temperature, precursor, solvent, and trimethyl silylating agent types are fundamental aerogel process parameters affecting the properties of final product, acid

type and gelation pH are also among the key variables. The type of acid and the pH of medium directly affects hydrolysis and condensation reaction rates and thus the mechanism of reaction.

3.1. FT-IR Studies

Figure 2 shows the FT-IR spectrums of silica aerogels. The peaks at around 3400 cm^{-1} and 1640 cm^{-1} are assigned to $-\text{OH}$ groups. The spectrum exhibits the asymmetric and symmetric bending of the $\text{Si}-\text{O}-\text{Si}$ bonds at around 1050 cm^{-1} and 792 cm^{-1} , respectively [6].

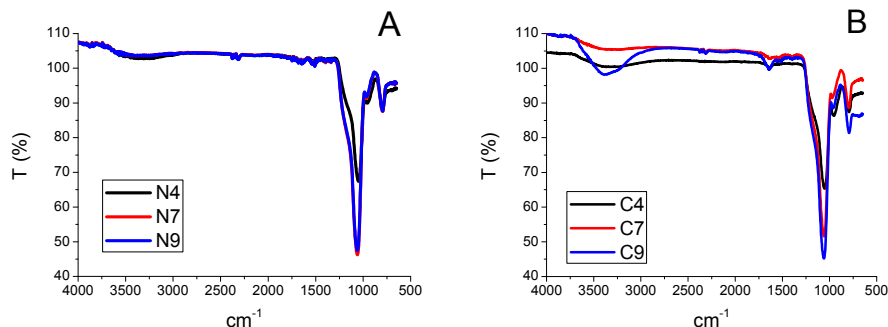


Figure 2. FT-IR spectrum of silica aerogels obtained at different gelation pH with A) nitric acid and B) citric acid

3.2. Nitrogen Adsorption

Table 1 shows the average pore size, single point total pore volume, mesopore volume, and specific surface area of the aerogels prepared at various pH values with different acids. The specific surface area of aerogels varies within a wide range depending on the acid type and gelation pH. It seems that at the same gelation pH, the surface area was higher for the silica aerogels prepared in the presence of citric acid and lower for those prepared in the presence of nitric acid. The BET surface area of silica aerogels was in the range of $238\text{--}726\text{ m}^2\text{ g}^{-1}$. As can be seen from Table 1, BET surface area decreases with the increase of gelation pH for both citric and nitric acid gelled aerogel samples. Maximum specific surface area ($726\text{ m}^2\text{ g}^{-1}$) was obtained with citric acid at gelation pH 4. Pore size and mesopore volume is also affected by the gelation pH and maximum values were obtained at aerogel samples gelled at pH 7 for both citric and nitric acid. According to the results present in Table 1, mesopore fraction of citric acid gelled aerogels is higher than nitric acid gelled aerogels.

Table 1. Specific surface area (S_{BET}), pore size, mesopore volume (V_{meso}) and single point total pore volume (V_{T}) of silica aerogels

Acid type	Gelation pH	S_{BET} ($\text{m}^2\text{ g}^{-1}$)	Pore size (nm)	V_{meso} ($\text{cm}^3\text{ g}^{-1}$)	V_{T} ($\text{cm}^3\text{ g}^{-1}$)	$V_{\text{meso}}/V_{\text{T}}$ (%)
Nitric acid	4	673	3.24	0.313	0.449	69.7
	7	296	10.22	0.756	1.174	64.4
	9	238	9.08	0.437	0.919	47.6
Citric acid	4	726	3.37	0.397	0.523	75.9
	7	341	9.43	1.051	1.062	99.0
	9	261	8.45	0.485	0.900	53.9

The N₂ adsorption–desorption isotherms are given in Fig. 3. Adsorption-desorption isotherms of aerogel samples produced are Type IV, which is the characteristic of mesoporous materials [7, 8]. Isotherms of aerogel samples prepared with nitric and citric acid exhibited hysteresis loop, which is owing to the capillary condensation in the mesopores. Hysteresis loops of the samples gelled at pH 7 and 9 are H2 type, whereas aerogel samples gelled at pH 4 are H1 according to the IUPAC classifications. H2 type hysteresis loops represent pores with non-uniform size or shape, such as ink-bottle shape [9] and H1 type hysteresis loops represents cylindrical pores [10].

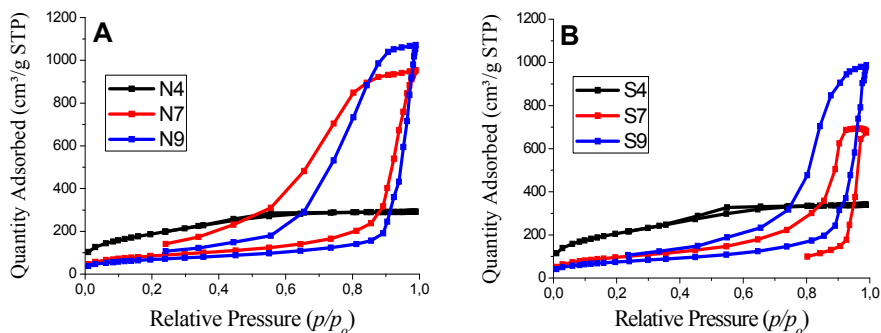


Figure 3. Nitrogen adsorption–desorption isotherms of aerogel samples prepared with nitric acid (A) and citric acid (B)

Pore size distribution profiles of prepared aerogel powders are given in Fig. 4. Aerogel samples gelled at pH 4 with both nitric and citric acid show narrow pore size distribution compared with pore size distribution profiles of aerogel samples gelled at pH 7 and 9. Furthermore, aerogel samples gelled at pH 4 exhibited small pore size and high specific surface area (Table 1) compared with aerogel powders prepared at pH 7 and 9, which have wider pores.

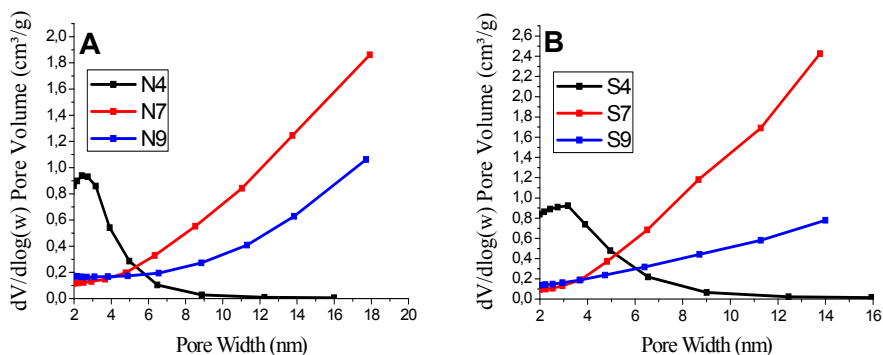


Figure 4. Pore size distribution profiles of the aerogel samples prepared with nitric acid (A) and citric acid (B)

Structure and properties of aerogels are greatly influenced by gelation pH. Because condensation reactions are favored and hydrolysis reactions are restricted under alkali conditions,

formed particles are fewer in number but larger and denser than particles formed under acidic conditions. Thus, aerogel samples obtained under alkali condition have larger pores and smaller surface area than aerogel samples obtained under acidic conditions [11]. Lee et. al. [12] investigated the effect of pH (3.0-5.0) on the properties of silica aerogel that was prepared from water glass precursor in the presence of a base catalyst (ammonia) followed by ambient pressure drying and found similar results. Average pore diameter and BET surface area of prepared silica aerogels was about 20 nm, and about 700-750 m²g⁻¹, respectively. Kim et al.[13] reported that silica aerogels synthesized from sodium silicate solution using base catalyst with and without glycerol (gelated at pH 4) and aged in TEOS/ethanol solutions (TEOS percentage between 30-70%) were mesoporous, and had pore diameter and BET surface area between 14.1-18.5 nm and 347-634 m²g⁻¹, respectively. Results obtained in this study, especially specific BET surface area results are in agreement with the studies mentioned above.

3.3. Density and Porosity (%)

Table 2 shows the properties of aerogels synthesized by using nitric acid or citric acid. From the table, it was observed that higher gelation pH yields lower density silica aerogels. This can be explained by the coalescing of primary particles (dimers and oligomers) to form large clusters involving very large pores under alkali conditions [14]. In this study, the silica aerogel with the lowest density (0.273 g cm⁻³) was obtained by using nitric acid at pH 9. Also, citric acid gave a similar density as 0.277 g cm⁻³ at the same gelation pH. The porosity of silica aerogels was varied from 61.23 to 87.53 %. Nanoporous silica aerogels have a high porosity ranging from 75 to 99% [15]. Therefore, pH 7 and pH 9 are suitable to reach high porosity levels under these experimental conditions.

Table 2. Density of silica aerogels obtained at various gelation pH

Acid Type	Gelation pH	Density ^a (g cm ⁻³)	Porosity (%)
Nitric Acid	4	0.849	61.23
	7	0.294	86.58
	9	0.273	87.53
Citric Acid	4	0.751	65.71
	7	0.432	80.27
	9	0.277	87.35

^aAverage of three measurement

In accordance with the previous publications, the specific surface area and pore volume of silica aerogels decrease with the decreasing density [14, 16].

4. CONCLUSION

The major findings of the present work are as follows:

- (i) The properties of final product depend on the acid type and gelation pH.
- (ii) The silica aerogels produced using citric acid (gelation pH 4) have been found to have the highest surface area as 726 m² g⁻¹, while, silica aerogels produced using nitric acid (gelation pH 9) have been found to have the lowest surface area as 238 m² g⁻¹. As the acidity of the reaction mixture increased, the surface area and density of silica aerogels increased, too.
- (iii) The smallest pore size was obtained at pH 4 for both nitric and citric acid gelled aerogels (3.24 nm and 3.37 nm, respectively), while, the biggest pore size was obtained at pH 7 for both of the acids (10.22 nm and 9.43 nm, respectively).
- (iv) Silica aerogel powders obtained at pH 4 exhibited H1 type hysteresis loop, while, aerogel

samples obtained at pH 7 and 9 exhibited H2 type hysteresis loop. Thus, aerogel samples produced at pH 4 contain cylindrical pores, while samples produced at pH 7 and 9 contain ink-bottle shape pores.

(v) Aerogel samples obtained with citric acid have higher mesopore fraction than aerogel samples obtained with nitric acid.

(vi) The synthesized silica aerogel showed properties of 0.273–0.849 g cm⁻³ density and 61.23–87.53 % porosity.

Therefore, it can be concluded that rice hull ash is an economically practical silica source for aerogel production. The aerogel production can be carried out as a commercial process using rice hull ash by ambient drying method.

Acknowledgments / Teşekkür

The authors are grateful to the Yıldız Technical University Projects Office for the financial support through an extensive research project (Project No: 2015-07-04-KAP-05).

REFERENCES / KAYNAKLAR

- [1] Wang J., Zhou Q., Song D., et al., “Chitosan–silica composite aerogels: preparation, characterization and Congo red adsorption”, *J Sol-Gel Sci Technol*, 76,501–509, 2015.
- [2] Pierre A.C., Pajonk G.M. “Chemistry of aerogels and their applications”. *Chem Rev.*, 102, 11, 4243–4265, 2002.
- [3] Yücel S., Terzioğlu P., Aydın-Sinirlioğlu Z., et al., “Synthesis, Characterization, *In Vitro* Degradability and Bioactivity of Strontium Substituted Rice Hull Ash Silica Based Melt Derived 45S5 Bioactive Glass”, *Journal of Engineering and Natural Sciences*, Sigma 33, 23-32, 2015.
- [4] Tzong-Horng L., Chun-Chen Y., “Synthesis and surface characteristics of nanosilica produced from alkali-extracted rice husk ash”, *Mater. Sci. Eng., B*, 176, 521–529, 2011.
- [5] Shi F., Wang L., Liu J., “Synthesis and characterization of silica aerogels by a novel fast ambient pressure drying process”, *Mater Lett*, 60, 29–30, 3718–3722, 2006.
- [6] Shewale P. M., Rao A. V., Rao A. P., “Effect of different trimethyl silylating agents on the hydrophobic and physical properties of silica aerogels”, *App Surface Sci*, 254, 6902–6907, 2008.
- [7] Tadjarodi A., Haghverdi M., Mohammadi V., “Preparation and characterization of nanoporous silica aerogel from rice husk ash by drying at atmospheric pressure”, *Mater. Res. Bull.*, 47, 2584–2589, 2012.
- [8] Leofanti G., Padovan M., Tozzola G., et al., “Surface area and pore texture of catalysts”, *Catal. Today*, 41, 207–219, 1998.
- [9] Bhagat S.D., Kim Y.H., Moon M.J., et al., “A cost-effective and fast synthesis of nanoporous SiO₂ aerogel powders using water-glass via ambient pressure drying route”, *Solid State Sci.*, 9, 628–635, 2007.
- [10] Yan X. X., Deng H. X., Huang X. H., et al., “Mesoporous bioactive glasses. I. Synthesis and structural characterization”, *J. Non-Cryst. Solids*, 351, 40, 3209-3217, 2005.
- [11] Sinkó K., “Influence of Chemical Conditions on the Nanoporous Structure of Silicate Aerogels”, *Materials*, 3, 704-740, 2010.
- [12] Lee S., Cha Y. C., Hwang H. J., et al., “The effect of pH on the physicochemical properties of silica aerogels prepared by an ambient pressure drying method”, *Mater Lett*, 61, 3130–3133, 2007.
- [13] Kim C. E., Yoon J. S., Hwang H. J., “Synthesis of nanoporous silica aerogel by ambient pressure drying” *J Sol-Gel Sci Technol*, 49,47–52,2009.

- [14] Kocon L., Despetis F., Phalippou J., “Ultralow density silica aerogels by alcohol supercritical drying”, *J Non-Cryst Solids*, 225, 1998, 96–100.
- [15] Zhang H., Hong C., Qiao Y., “Synthesis, Structural and Thermal Properties of Nanoporous SiO₂-based Aerogels, *Advances in Nanocomposites - Synthesis, Characterization and Industrial Applications*”, ISBN: 978-953-307-165-7, InTech, 2011.
- [16] Chao X., Jun S., Bin Z., “Ultralow density silica aerogels prepared with PEDS”, *J Non-Cryst Solids* 355 (2009) 492–495.