



## Effect of pH on the Synthesis of Silica Sol-Gel Tetraethylorthosilicate-Trimethylchlorosilan (TEOS-TMCS)

Artha Monica Andini<sup>a</sup>, Choiril Azmiyawati<sup>a</sup>, Adi Darmawan<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science and Mathematics, Diponegoro University, Tembalang, Semarang, Indonesia

\* Corresponding author: [adidarmawan@live.undip.ac.id](mailto:adidarmawan@live.undip.ac.id)

<https://doi.org/10.14710/jksa.25.11.394-398>

### Article Info

#### Article history:

Received: 5<sup>th</sup> October 2022

Revised: 10<sup>th</sup> December 2022

Accepted: 20<sup>th</sup> December 2022

Online: 31<sup>st</sup> December 2022

#### Keywords:

Silica; TEOS; TMCS; pH variation

### Abstract

Sol-gel synthesis of silica employing the co-precursor trimethylchlorosilane (TMCS) and the precursor tetraethylorthosilicate (TEOS) was accomplished. The purpose of this investigation was to ascertain how pH affected the properties of synthetic silica. The synthesized hydrophobic silica was characterized using FTIR, TGA, and GSA to determine the effect of pH adjustment on the functional group characters, thermal properties, and pore morphology. The ratio between TEOS/TMCS was fixed at 75:25 and varied the pH (4, 6, 7, 8, and 10) and the calcination temperature (without calcination, 300°C and 500°C). FTIR analysis showed that the number of C-H and Si-OH groups in the xerogel decreased with increasing calcination temperature. Xerogel formed at pH 6 provides the highest thermal stability among other pHs. The results from the BET analysis revealed that changes in pH directly affect the physical characteristics of the surface, making the resulting gel network less rigid and more susceptible to shrinkage of pore volume and diameter in the atmosphere. Meanwhile, in an alkaline medium, continuous condensation will occur so that the pore diameter and volume decrease. The high pore diameter and volume imply that pH 7 is ideal for preparing xerogels.

### 1. Introduction

Nanomaterial technology has been widely used in various industries, such as health, construction, textiles, food, medicine, computers, and machinery [1]. One example of nanomaterials is nanoparticles which are currently the center of attention because they can be used to develop better industrial functions and products. The material that has been widely used to manufacture nanoparticles is silica. The structure of nanoparticles depends on the method and conditions of particle preparation. Various silica gels have been synthesized using the sol-gel method [2], reverse microemulsion, and flame synthesis. However, sol-gel is a promising method for synthesizing silica particles due to its ability to control particle size, size distribution, and surface morphology [3].

Silica can be used as a hydrophobic glass coating material, one of which is to produce a material that has a self-cleaning hydrophobic surface [4]. However, silica only synthesized from its alkoxysilane will have

hydrophilic properties. In the silica gel synthesis process, additional modifiers such as methyltriethoxysilane (MTES) and trimethylchlorosilane (TMCS) can change the material properties from hydrophilic to hydrophobic [5].

Hamidah *et al.* [6] conducted a study using water glass and TMCS as a modifying agent with a particular concentration and immersion time to form a hydrophobic film layer on glass. The determining factor for creating a hydrophobic film layer is the replacement of silanol groups on the glass surface with alkyl groups from TMCS. Silica made from 3.6% water glass and 1.5 M TMCS solution with a modification time of 9 to 13 hours tends to experience an increase in the contact angle where the 13-hour modification time produces a contact angle of 118°.

Research by Nizar [7] found that manufacturing TEOS-based silica aerogel and using a modifier in the form of TMCS affected the particle size of the resulting sample. SEM characterization shows that TMCS

immersion of 15 mL obtained an average diameter of 6.868432 nm–67.03631 nm, while for immersion of 25 mL, the size is 2.181567 nm–25.36593 nm.

In order to obtain materials with the desired properties, it is essential to control various hydrolysis and condensation process parameters, such as solvent, catalyst, pH, or temperature [8]. The structure of silica gel is highly dependent on the pH of the precursor sol, where pH controls the speed of the sol-gel reaction and affects the character of the resulting silica gel [9].

This research will be carried out by synthesizing hydrophobic thin film silica with Tetraethoxysilane-Trimethylchlorosilane (TEOS-TMCS) precursors with a fixed TEOS-TMCS concentration ratio and varying the pH of the solution to obtain the optimal pH in the synthesis of hydrophobic thin film silica with Tetraethoxysilane-Trimethylchlorosilane (TEOS-TMCS) precursors. Furthermore, an analysis will be carried out using Fourier-transform infrared spectroscopy (FTIR), Thermogravimetric Analysis (TGA), and Gas Sorption Analysis (GSA) to determine the effect of variations in pH during the synthesis process on the characteristics of the resulting thin layer silica. This study aims to assess the influence of pH on the hydrophobicity of TEOS-TMCS silica xerogel silica.

## 2. Methods

### 2.1. Materials

The materials used were tetraethylorthosilicate (TEOS) (Merck), ethanol pro-analysis (Merck), ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) (Merck), trimethylchlorosilane (TMCS) (Sigma-Aldrich), acetic acid pro-analysis ( $\text{CH}_3\text{COOH}$ ) (Merck).

### 2.2. Synthesis of Silica Xerogel

The premix solution was prepared by mixing 1 M  $\text{NH}_4\text{OH}$  and ethanol with a molar ratio of 1:50, followed by magnetic stirring. A 50 mL premix solution and TEOS-TMCS (2.84 mL: 0.54 mL) were put into each of five Schott bottles, and  $\text{CH}_3\text{COOH}$  was added to adjust the solution to various pH variations (4, 6, 7, 8, and 10). The solution was then stirred for 2 hours at a low temperature. The aerogels formed were stored in a petri dish at room temperature until dry and then oven-dried at 60°C for 2 hours. After drying, the xerogel was crushed with a mortar. The calcination temperature was varied to 300°C and 500°C to determine the stability and changes in hydrophobicity of the resulting xerogel.

### 2.3. Characterization of Silica Xerogel

The formed xerogels were then characterized using GSA, TGA, and FTIR to determine the structural and morphological characters of the resulting xerogels. The silane groups and their group ratios were identified using FTIR. The background reduction and deconvolution of the peaks from the spectra were carried out using the fityk program. TGA was used to determine the thermal stability in maintaining its hydrophobicity. The surface area of the resulting xerogel was determined by the Brunner-Emmett-Teller (BET) method.

## 3. Results and Discussion

### 3.1. Analysis of TEOS-TMCS Functional Groups

Fourier Transform Infrared (FTIR) was used to analyze and identify functional groups and types of bonds found in TEOS-TMCS. The results of the FTIR spectra of the TEOS-TMCS are shown in Figure 1, which shows that pH and calcination temperature variations affect the position, shape, and intensity of the TEOS-TMCS absorption peaks.

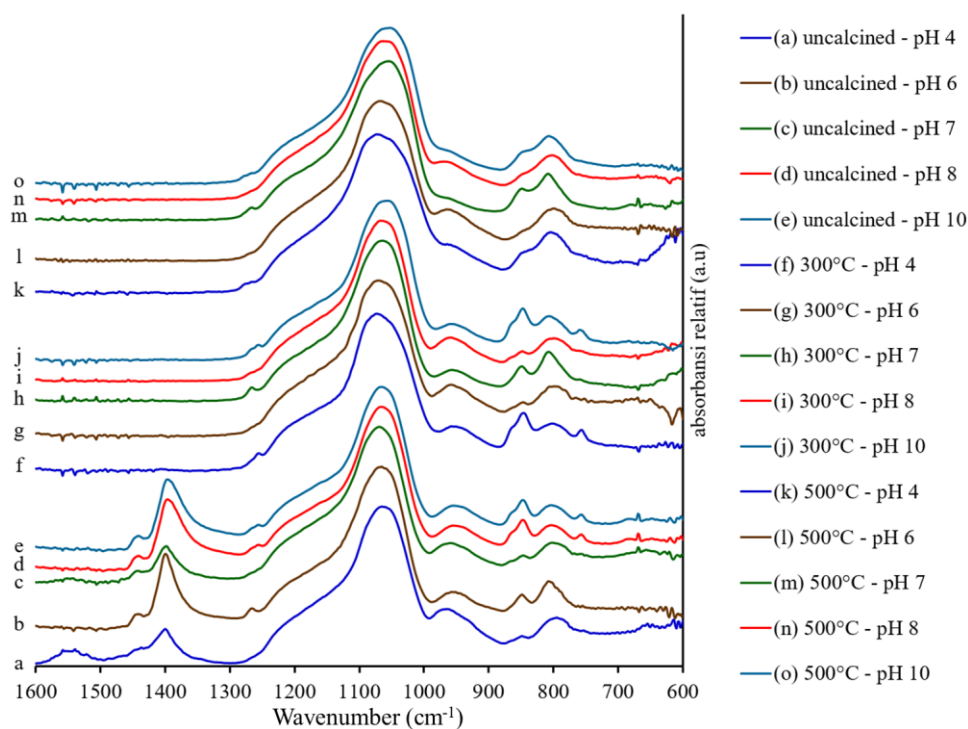


Figure 1. TEOS-TMCS sol-gel FTIR spectra

Figure 1 shows the role of the co-precursor and the effect of setting the calcination temperature from the peaks of the resulting absorption bands. According to Sulastri and Kristianingrum [10], the sol-gel process produces compounds containing siloxane groups (Si-O-Si), silanol (Si-OH), and modified silica groups, which are denoted -Si-OM. In research Li *et al.* [11], strong peaks were found at 1085  $\text{cm}^{-1}$  and 457  $\text{cm}^{-1}$ , indicating the presence of Si-O-Si group vibrations. The peak at 955  $\text{cm}^{-1}$  indicates a Si-OH stretching vibration [12]. As well as the peaks of the stretching and bending vibrations of the Si-CH<sub>3</sub> bands are at 2963  $\text{cm}^{-1}$ , 1257  $\text{cm}^{-1}$ , and 847  $\text{cm}^{-1}$ . In this study, the pH of the solution and calcination temperature were adjusted. And in the FTIR results of all samples, there were peaks in the range of 880–760  $\text{cm}^{-1}$  indicating stretching vibrations and bending of the Si-CH<sub>3</sub> bands, vibration peaks in the range 950–900  $\text{cm}^{-1}$  indicate the stretching vibration of Si-OH, and the vibration band in the range of 1100–1000  $\text{cm}^{-1}$  indicates vibration of the Si-O-Si group.

In Figure 1, the sol-gel without calcination has several different vibrational peaks compared to the calcined sol-gel, which appear at 1460–1360  $\text{cm}^{-1}$  indicating the stretching and bending bands of the C-H groups, while the peaks of these bands do not appear on the sol-gel with calcination treatment. Some differences in the peaks can be seen in the vibrational peaks in the range of 950–900  $\text{cm}^{-1}$ , which appear more sloping, indicating Si-OH stretching vibrations, as well as peaks in the range of 880–760  $\text{cm}^{-1}$ , which show stretching vibrations and bending of the Si-CH<sub>3</sub> bands. In conclusion, the higher the heating treatment on the sol-gel, the presence of C-H and Si-OH groups will also decrease.

### 3.2. Analysis of Thermal Stability and Decomposition of TEOS-TMCS Sol-Gel Decomposition

Characterizing decomposition and thermal stability of TEOS-TMCS sol-gel samples using a Thermogravimetric Analyzer (TGA) by examining the change in sample mass as a function of temperature in scanning mode or as a function of time in isothermal mode. The results of the TGA curve of the TEOS-TMCS sol-gel are shown in Figure 2. The variation in pH affects the shape of the TEOS-TMCS sol-gel curve.

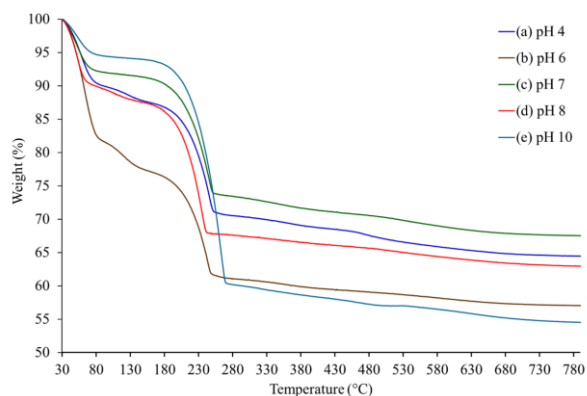


Figure 2. TGA curve of the TEOS-TMCS xerogel

From Figure 2, the role of TMCS as a co-precursor and the effect of pH on the shape of the resulting curve

can be seen. According to Pambudi and Zainuri [13], the TGA curve provides information about the weight loss of the sample against a given temperature change in the range of 0–1300°C. Ivanov *et al.* [14] found that the TEOS-TMCS aerogel curve did not show a reduction in mass at 0–140°C, which indicated that water or alcohol was not contained in the aerogel because it is hydrophobic. The drastic mass reduction of about 50% occurs due to chlorine (Cl) decomposition and the oxidation of the -CH<sub>3</sub> group attached to the main silica chain. Meanwhile, in the TEOS aerogel sample without a co-precursor, the TGA curve experienced a mass reduction of 10% and ended at 160°C, indicating that the solvent was adsorbed. A 5% reduction in mass from 250–800°C means a pyrolysis reaction of the organic compound residue. According to this study, mass decreased significantly in most curves between 31°C and 75°C.

This study showed a decreased mass that was not too significant at a temperature range of 31–75°C in most of the curves. Mass reductions of 9.4%, 7.6%, 9.9%, and 5.2% occurred at pH 4, 7, 8, and 10, respectively. Meanwhile, at pH 6, there was a significant mass decrease of 16.2%. This indicates that at pH 6 the adsorbed solvent decreased more than at other pHs and also experienced a slight decomposition of chlorine and oxidation of the -CH<sub>3</sub> group. The decrease in mass over this temperature range indicates the presence of adsorbed solvent contained in the xerogel. A significant decrease in mass occurred in the temperature range of 170–270°C at pH 4, 6, 7, 8, and 10, respectively, by 15.8%, 14.2%, 16.8%, 18.5%, and 33.2%. The decrease in mass over this temperature range indicates the decomposition of chlorine (Cl) and the oxidation of the -CH<sub>3</sub> group attached to the main silica chain.

The first derivative of the TGA curve is called derivative thermogravimetry (DTG). DTG solves the overlap reaction by changing the experimental conditions, which can change the relative speed of the overlapping reaction and produce a better resolution. In DTG, the change in mass with temperature ( $\text{dm}/\text{dT}$ ) is plotted against temperature or time. The results of the DTG curve from the TEOS-TMCS sol-gel are shown in Figure 3. The pH variation affects the shape of the TEOS-TMCS sol-gel curve.

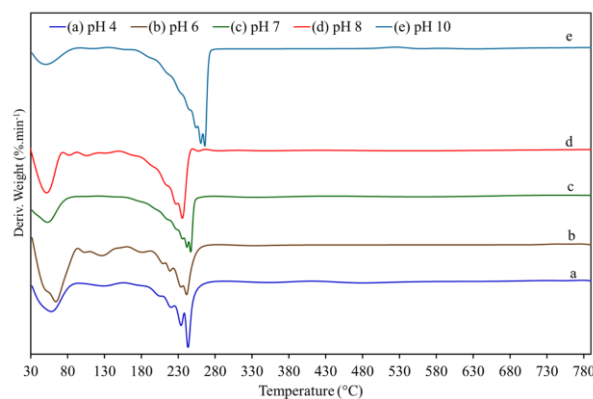
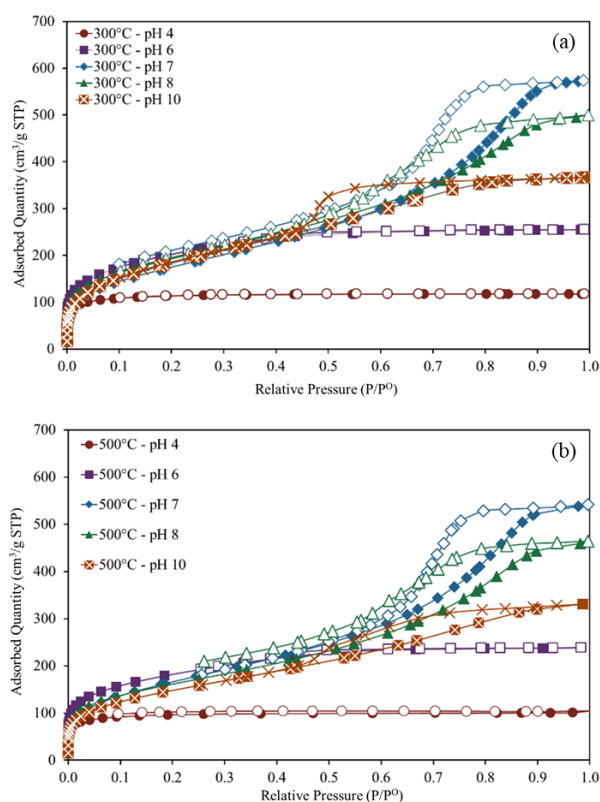


Figure 3. DTG curve of TEOS-TMCS xerogel

The DTG peak indicates the mass loss rate per unit of time and can be used to determine the maximum temperature of mass loss precisely when overlapping reactions occur. This study obtained initial peaks at pH 4, 6, 7, 8, and 10 at 58, 65, 52, 51, and 50°C, respectively. The initial peak indicates the start of thermal decomposition and solvent loss. Significant peaks of pH 4, 6, 7, 8, and 10 were at 243, 240, 247, 235, and 266°C, respectively. The significant peak indicates the decomposition of chlorine (Cl) and the oxidation of the  $-CH_3$  group attached to the main silica chain.

### 3.3. Identification of the Physical Properties of TEOS-TMCS Sol-gel Surfaces

A gas Sorption Analyzer (GSA) is used to identify the physical properties of a material, including surface area, pore volume, pore radius, pore distribution, and others.



**Figure 4.** (a) GSA curve of xerogel at 300°C calcination and (b) GSA curve of xerogel at 500°C calcination

Figure 4 shows the role of variations in the pH of the sol-gel solution on the shape of the resulting curve. The results of the isothermal adsorption/desorption analysis from Li *et al.* [11] found that the shape of the curve experienced a change in the area covered, which was more significant from sample 1:11 to sample 1:5. In contrast, the value of the TMCS ratio increased, it caused an increase in the ratio of larger mesopores and a decrease in the ratio of smaller mesopores.

In this study, it is shown that pH had a direct effect on the process of producing xerogel. It was proven on the calcination curve at 300°C the relative pressure during absorption isotherms experienced an increase in the area covered by the order from the smallest to the largest area of pH 4, 6, 10, 8, and 7. The sample curve calcined at

500°C relative pressure on isothermal absorption experienced an increase in the area covered by the order from the smallest area to the largest area, which is the same as the calcination at 300°C. The similarity of the 300°C calcination temperature results and 500°C shows that the xerogel’s calcination temperature does not significantly affect the physical properties of the resulting pores. However, the pH highly affects the physical properties of the pores, especially in acidic conditions, where the hydrolysis process is rapid and the gelation process is slow. In contrast, condensation is fast in alkaline conditions, hydrolysis is slow, and gelation is fast. A too-acidic pH also contains a lot of  $H^+$ , which can make the siloxy groups protonated and cannot produce a rigid gel [15]. Alkaline pH causes the condensation process to occur continuously. Then the optimal pH for synthesizing TEOS-TMCS xerogel was carried out at a solution pH of 7.

**Table 1.** Effect of pH and calcination temperature on surface physical properties

pH	BET surface area (m <sup>2</sup> /g)		Pore volume (cm <sup>3</sup> /g)		Pore diameter (4V/A by BET) (nm)	
	300°C	500°C	300°C	500°C	300°C	500°C
4	368.11	313.7	0.182	0.162	2.028	2.117
6	690.99	624.34	0.394	0.368	2.243	2.32
7	615.58	585.32	0.887	0.833	5.52	5.436
8	673.07	562.34	0.774	0.711	4.462	4.924
10	645.23	517.17	0.567	0.512	3.349	3.818

The BET surface area, pore volume, and pore diameter results of the calcination xerogel samples at 300 and 500°C did not show significant differences (Table 1). However, the pH value of the xerogel setting greatly affects the BET surface area, pore volume, and pore diameter results. The smallest yield was found on the BET surface area at pH 4, while the best results were obtained at pH 6. These results could be caused by pH 4 having a high concentration of  $H^+$ , which can protonate siloxy groups but cannot generate a rigid gel, causing volume shrinking when the gel is heated to produce xerogel [15]. Optimal results at pH 6 are probably caused by the hydrolysis and condensation processes that both take place optimally, which can make the resulting surface area optimal.

The volume and pore diameter increased with the order of the samples at pH 4, 6, 10, 8, and 7. A solution in acidic conditions caused the volume and pore diameter of the sample to be small because the hydrolysis rate was fast, and the  $=Si-O-Si=$  formation reaction was running slowly, preventing the formation of a rigid gel network [16]. The network will shrink the volume and pore diameter as the calcination temperature increases. Shrinkage in volume and pore diameter also occurs when the solution is in very alkaline conditions because the condensation process will continue so that it will form agglomerates [17]. In conclusion, the best pore volume and diameter can be obtained by synthesizing the TEOS-TMCS sol-gel at pH 7.

#### 4. Conclusion

Silica xerogel was successfully synthesized via the sol-gel method using TEOS as a precursor and TMCS as a co-precursor by varying the pH (4, 6, 7, 8, and 10) and calcination temperature (300 and 500°C). The characterization results showed that pH 6 provides the best thermal stability because it undergoes chlorine decomposition and oxidation of the  $-CH_3$  group. The results of the analysis of the BET method, the condition of the solution at pH 7 is the optimal condition for producing samples with large pore diameters and volumes.

#### References

- [1] A. K. M. Ayatullah Hosne Asif, Md. Zayedul Hasan, Application of nanotechnology in modern textiles: A review, *International Journal of Current Engineering and Technology*, 8, 2, (2018), 227-231 <https://doi.org/10.14741/ijcet/v.8.2.5>
- [2] Adi Darmawan, Riza Eka Saputra, Yayuk Astuti, Structural, thermal and surface properties of sticky hydrophobic silica films: Effect of hydrophilic and hydrophobic precursor compositions, *Chemical Physics Letters*, 761, (2020), 138076 <https://doi.org/10.1016/j.cplett.2020.138076>
- [3] Ismail Ab. Rahman, Vejayakumaran Padavettan, Synthesis of Silica Nanoparticles by Sol-Gel: Size-Dependent Properties, Surface Modification, and Applications in Silica-Polymer Nanocomposites—A Review, *Journal of Nanomaterials*, 2012, (2012), 132424 <https://doi.org/10.1155/2012/132424>
- [4] Vinayak V. Ganbavle, Uzma K. H. Bangi, Sanjay S. Latthe, Satish A. Mahadik, A. Venkateswara Rao, Self-cleaning silica coatings on glass by single step sol-gel route, *Surface and Coatings Technology*, 205, 23, (2011), 5338-5344 <https://doi.org/10.1016/j.surfcoat.2011.05.055>
- [5] Poonam M. Shewale, A. Venkateswara Rao, A. Parvathy Rao, Effect of different trimethyl silylating agents on the hydrophobic and physical properties of silica aerogels, *Applied Surface Science*, 254, 21, (2008), 6902-6907 <https://doi.org/10.1016/j.apsusc.2008.04.109>
- [6] Nur Hamidah, F. R. Meta, H. Setyawan, S. Affandi, Pelapisan hidrofobik pada kaca melalui metode sol-gel dengan prekursor waterglass, *Jurnal Teknik POMITS*, 1, 1, (2012), 1-4
- [7] Ahmad Nizar, Sintesis Dan Karakterisasi Silika Aerogel Berbasis Teos (Tetraethylorthosilicate) Menggunakan Metode Sol-Gel, *Inovasi Fisika Indonesia*, 5, 1, (2016), 7-10
- [8] Ahmed A. Issa, Adriaan S. Luyt, Kinetics of Alkoxysilanes and Organoalkoxysilanes Polymerization: A Review, *Polymers*, 11, 3, (2019), 537 <https://doi.org/10.3390/polym11030537>
- [9] Maryanne M. Collinson, Sol-Gel Strategies for the Preparation of Selective Materials for Chemical Analysis, *Critical Reviews in Analytical Chemistry*, 29, 4, (1999), 289-311 <https://doi.org/10.1080/10408349891199310>
- [10] Siti Sulastri, Susila Kristianingrum, Berbagai macam senyawa silika: Sintesis, karakterisasi dan pemanfaatan, *Prosiding Seminar Nasional Penelitian, Pendidikan dan Penerapan MIPA*, 2010
- [11] Ming Li, Hongyi Jiang, Dong Xu, Ou Hai, Wei Zheng, Low density and hydrophobic silica aerogels dried under ambient pressure using a new co-precursor method, *Journal of Non-Crystalline Solids*, 452, (2016), 187-193 <https://doi.org/10.1016/j.jnoncrysol.2016.09.001>
- [12] Julia C. Steinbach, Markus Schneider, Otto Hauler, Günter Lorenz, Karsten Rebner, Andreas Kandelbauer, A Process Analytical Concept for In-Line FTIR Monitoring of Polysiloxane Formation, *Polymers*, 12, 11, (2020), 2473 <https://doi.org/10.3390/polym12112473>
- [13] Dwi Ratna Setya Pambudi, Mochamad Zainuri, Pengaruh Waktu Tahan Proses Kalsinasi Prekursor Silika sebagai Material Pelapis Hidrofobik, *Jurnal Sains dan Seni ITS*, 5, 2, (2016), B80-B83
- [14] P. Ivanov, Y. Hristov, B. I. Bogdanov, P. Pashev, Synthesis of silica aerogel by surface modification, *Nauch. Trudy Rusensk. Univer*, 53, 10.1, (2014), 71-73
- [15] Thierry Woignier, Jean Phalippou, Florence Despetis, Sylvie Calas-Etienne, Aerogel processing, in: *Handbook of Sol-Gel Science and Technology*, Springer, Cham, 2018, [https://dx.doi.org/10.1007/978-3-319-32101-1\\_27](https://dx.doi.org/10.1007/978-3-319-32101-1_27)
- [16] Thongthai Witoon, Metta Chareonpanich, Effect of pore size and surface chemistry of porous silica on CO<sub>2</sub> adsorption, *Songklanakarinn Journal of Science & Technology*, 34, 4, (2012),
- [17] Huan Zhou, Jihong Sun, Bo Ren, Feng Wang, Xia Wu, Shiyang Bai, Effects of alkaline media on the controlled large mesopore size distribution of bimodal porous silicas via sol-gel methods, *Powder Technology*, 259, (2014), 46-51 <https://doi.org/10.1016/j.powtec.2014.03.060>