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Preparation of SiO_2 Aerogel from Rice Husk Ash

CUI Sheng[a, b], YU Shu-wen[a], LIN Ben-lan[a], SHEN Xiao-dong[a, b], GU Danming[a]

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/MaterialsA

Silica was leached from rice husk ash as sodium silicate by NaOH treatment. Using water glass as silica sources, SiO_2 aerogel was prepared via sol-gel process and ethanol supercritical drying. Based on gelation time and porous characteristics of SiO_2 aerogel, the optimum gel preparation technology was determined, such as silica concentration 6.0wt.%, gelation at pH value 5.0 and aging in H_2O/EtOH. By the way, the density was as low as 0.0713g/cm^3, specific surface area 729.82m^2/g, the hole size 3.39cm^3/g, the average pore size 16.32nm, and the size distribution uniform.

Silica aerogel is a structure controllable light nanoporous solid material, which is composed of colloidal particles gathering each other. Silica aerogel have numerous excellent properties because of its unique structure with nanoporous network, high specific surface area[1], super low density[2], high porosity, low thermal conductivity[3], low dielectric constant[4], catalysis and sorption properties[5], et al. The outstanding properties of silica aerogel make it have broad application prospects in catalysis sorption, optics, low-temperature physics, laser experiments, space investigations, microelectronics, electrical engineering, and acoustics as highly efficient heat insulators and trapping media for the analysis or purification of gas.[6] At present, SiO_2 aerogel were prepared by a sol-gel process using kinds of precursors, for example, tetraethyl orthosilicate (TEOS),[7] tetramethyl orthosilicate (TMOS)[8] and other organic silicon compounds, forming a continuous network structure of SiO_2 aerogel in solution, and removing the solvent in gel pores based on supercritical drying, thereby obtaining a lightweight porous SiO_2 aerogel. Sarawade[9] and He[10] et al synthesized silica aerogel using TEOS by sol-gel process and ambient pressure drying route. Rassy[11] et al prepared silica aerogels by the sol-gel process and dried by the CO_2 supercritical method, in which the SiO_2 produced from tetramethoxysilane (TMOS) and methyltrimethoxysilane (MTMS) in different proportions. However, the raw materials of organic silicon compounds are expensive and have a potential toxicity and other issues, which limit the mass production and commercial applications of SiO_2 aerogel in terms of both cost and safety. Therefore, the use of cheap and abundant waste resources, such as high silicon content of rice husk in recent years, is attached more and more importance to prepare SiO_2 aerogel.

In the preparation process of SiO_2 aerogel, the gel parameters, such as pH value[12] and silica content[13], which have a significant effect on density, specific surface area, bore diameter, pore volume and even the final properties of the synthesized aerogel, determine the physical properties of the gel,. Therefore, it is significantly important for obtaining SiO_2 aerogel with good performance to control gel parameters. The preparation of SiO_2 gel can be divided into one-step and two-step process[14-15]. For the one-step, the catalyst was directly added into solution to form SiO_2 aerogel, in this way, the backbone structure of which has such characteristic, namely SiO_2 particles larger and specific surface area smaller; For the two-step, first forming the silicic acid under acidic condition, and then adjusting the pH value to prepare SiO_2 gel by alkaline catalyst, the network skeleton of which through two-step process have owned smaller particles and larger specific surface area, which is more suitable in modification and graft of aerogel.

Many works in relation to using rice husk have been done for the preparation of SiO_2 aerogel. Rajanna[16] et al described an improved process for preparation of silica aerogel microparticles (SAMs) for drug delivery from rice husk ash (RHA), an inexpensive source rich in biocompatible silica. Tadjarodi[17] et al prepared SiO_2 aerogel from rice husk ash by sol–gel method and dried under atmospheric pressure. In this paper, making homemade rice husk ash as raw material, generating sodium silicate solution by treatment and investigating the impact of the species of alkali and the concentration and reaction time of alkali to the water glass quality in extraction process, then combined with the two-step sol-gel method and ethanol supercritical drying[15,18-20] to prepare SiO_2 aerogel. By comparing the effects of different parameters and aging gel liquid to gel process and the properties, the gel preparation process and parameters of SiO_2 aerogel were determined by RHA.

In this study, the water glass and the silica aerogel were prepared as follows. For the water glass, we performed the water glass, a

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[a] *College of Material Science and Engineering, Nanjing Tech University, Nanjing 210009, China. E-mail: scui@njtech.edu.cn; Tel: +8613813960913*
[b] *Nanjing Tech University Suqian Advanced Materials Institute, Suqian 223800, China. E-mail: xdshen@njtech.edu.cn*

† Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x

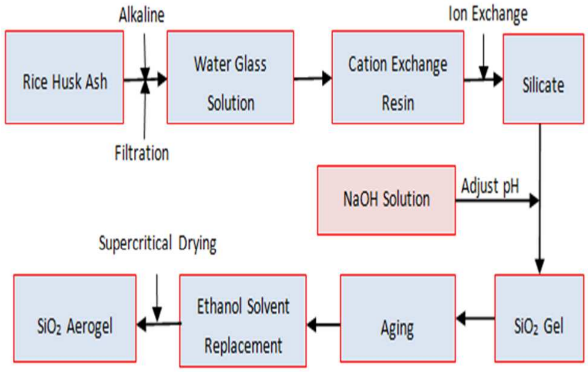


Fig.1 Overall flowchart for preparing SiO_2 aerogel from rice husk ash via supercritical drying

certain amount of rice husk ash with 1mol/L NaOH solution by mixing in three-necked flask was heated and stirred until the reaction solution began to boil, and recorded the initial response time. During the reaction, the water evaporated quickly, and the condenser was required to reflux. After a period of time, close the heating unit, cool the solution at room temperature, and then subject to suction filtration to remove the unreacted residue, which was dried and weighed to calculate the dissolution rate of SiO_2, the collected filtrate namely was the sodium silicate, and saved in the brown bottle for the detection and follow-up experiments. For the silica aerogel, based on ion exchange resin pre-treatment method[21] the Na-type 732 cation exchange resin was done for pre-processing and transformation. First, the resin was repeatedly washed, soaked with deionized water, so that it was thoroughly swollen, removing mechanical impurities in it. Then the solvend in resin was removed by 1mol/L hydrochloric acid solution and sodium hydroxide solution respectively soaking for 12h. Finally, they were washed with deionized water until the pH value was about 7, namely which could be used. Then the water glass solution with a certain SiO_2 content at 10mL/min speed was taken to prepared the silicic acid with the pH value of 2.1 ~ 2.3 via the exchange column of the cation exchange resin with pretreatment. Then the NaOH solution with 1mol/L was used as a catalyst, and adjusted the pH to a certain value, continued stirring for 5 min, poured into moulds and then got SiO_2 gel. After aging, substitute with ethanol solvent, and finally dry by ethanol supercritical, during which controlled the drying pressure 10 MPa and the drying temperature 270℃, the gel could be obtained SiO_2 aerogel. Specific process was shown as figure 1.

In order to be better for the material characterization, the modulus of sodium silicate[22], which was the ratio of the number of moles of SiO_2 and Na_2O in sodium silicate solution, was determined. we measured the content of SiO_2 and Na_2O and then calculated the modulus of sodium silicate in sodium silicate solution by acid-base titration[23]. First, weighing 15g NaF was added to the beaker containing 250 mL of water with the temperature of 60 ℃ ~ 90 ℃ and kept the supersaturated solution at room temperature . Then taking the water glass solution 10mL was placed in the flask with 250mL for sample preparation during NaF solution heated. On the same time, the NaF supersaturated solution was added into the conical flask with 50 ml, dropping 10 drops of methyl red indicator till the solution turned yellow, and using HCl standard solution with 0.5mol/L was titrated to the red and hardly changed, then continued to add 2mL ~ 5mL; Second, using NaOH standard solution of 0.5 mol/L was titrated till yellow appeared, using pH test paper determined the end point of titration, measuring the volume V_4 of HCl standard solution that NaF alkaline solution consumed.

After the above, there would be a titration test. The water glass solution for 5 ml was taken into the conical flask, in which was dropped 10 drops of methyl red indicator, and the 0.5 mol/L HCl standard solution was titrated into the solution from yellow to reddish to end, writing down the standard volume V_1 of the consumption, i.e., the concentration of Na_2O was determined. Second, 50 mL NaF supersaturated solution was added, shaking the solution colour to the yellow, and dropping 0.5 mol/L HCl standard solution until the solution from yellow to red, and then continued dropping 2 mL ~ 5 mL, writing down the volume V_2 of consumed HCl standard solution for the second time. Finally, using the 0.5 mol/L NaOH standard solution dropped back, measuring the pH value with pH paper while the solution was dripped, until the pH value of the solution was the same as blank test, recording the volume V_3 of consumed NaOH standard solution. The reaction equations were as followed,

$$Na_2O{\bullet}mSiO_2 + 2HCl + (m-1)H_2O = 2NaCl + mH_2SiO_3 \tag{1}$$

$$H_2SiO_3 + 6NaF + H_2O = Na_2SiF_6 + 4NaOH \tag{2}$$

$$NaOH + HCl = NaCl + H_2O \tag{3}$$

According to the reaction happened in the titration process, it could be calculated for the content of SiO_2 and Na_2O in water glass,

$$n(SiO_2) = (V_2 - V_3 - V_4) / 8 \tag{4}$$

$$n(Na_2O) = V_1 / 4 \tag{5}$$

The water glass module *m* could be represented as:

$$m = n(SiO_2) / n(Na_2O) = (V_2 - V_3 - V_4) / 2V_1 \tag{6}$$

In addition, the SiO_2 dissolution rate[24] was used to represent the conversion rate of the reaction of the rice husk ash and the alkali. The SiO_2 content of the rice husk ash was high in experiment, more than 99%[25], so the SiO_2 dissolution rate could be represented the following formula,

$$SiO_2 \text{ dissolution rate} = (W_0 - W_1) / W_1 \times 100\% \tag{7}$$

and the time, when the sol was poured into a mould, was set as the starting time, and the mould was inclined 45°, when the liquid didn't flow clearly within the mould, the gel has been occurred, this time was recorded as the gel time. Besides, the line shrinkage rate of SiO_2 aerogels prepared in the experiment were cylindrical block material, so the diameter of which could be calculated the line shrinkage rate of aerogel through measured directly,

$$\Delta d = (d_1 - d_2) / d_1 \times 100\% \tag{8}$$

Formula: d_1 was the diameter of the SiO_2 wet gel, d_2 was the diameter of SiO_2 aerogel, the diameter was measured by vernier caliper, the precision of which was 0.02 mm.

Through the comparison, there was large distinguish between Mineral SiO_2 and the SiO_2 of rice husk ash in property. The former existed in the form of the crystal, stabilizing; the other presented in the form of the hydrate amorphous, high activity, which was more likely to react with alkali. Therefore, the SiO_2 of rice husk ash was extracted by alkali in experiment, generating a certain modulus of water glass solution. In the process of alkali extraction, the SiO_2 dissolution rate of rice husk ash and the modulus of water glass were considered mainly. The dissolution rate of SiO_2 reflected the utilization ratio of raw material, and the modulus showed the

Tab.1 Effect of NaOH amount on the extraction rate of SiO_2 and water glass modulus

$n(SiO_2) : n(NaOH)$	Extraction rate of SiO_2 (%)	Measured modulus	Theoretical modulus
5 : 3	81.21	3.08	3.33
3 : 2	89.58	2.73	3.00
5 : 4	93.47	2.36	2.50
1 : 1	93.83	1.84	2.00
3 : 4	94.12	1.31	1.50

composition of water glass, affecting the physical and chemical properties of water glass, which was the important indicator. In experiment, the influence for the types and dosage of alkali and reaction time on the dissolution rate of the SiO_2 and the modulus of water glass were studied.

In the experiment, the SiO_2 of rice husk ash was extracted by NaOH and Na_2CO_3 respectively, and the reaction equation was,

$$2NaOH + mSiO_2 = Na_2O \bullet mSiO_2 + H_2O \quad (9)$$

$$Na_2CO_3 + mSiO_2 = Na_2O \bullet mSiO_2 + CO_2 \quad (10)$$

Found in study, it was not satisfactory for the reaction result of Na_2CO_3 solution and rice husk ash, according to the stoichiometric ratio of the ingredients of the reaction equation (10), the dissolution rate was not high, only when the amount of Na_2CO_3 was doubled, the rate of dissolution would improve. Therefore, it could be considered for the reaction of Na_2CO_3 solution and the rice husk ash as the following formula,

$$2Na_2CO_3+mSiO_2+(1+x)H_2O = Na_2O \bullet mSiO_2 +2NaHCO_3 + xH_2O \quad (11)$$

Known from the formula, the amount of Na_2CO_3 doubled, because $NaHCO_3$ solution didn't decompose when heated, resulting in the cost of Na_2CO_3 increasing, while the alkaline of NaOH was strong, which was easier to react with rice husk ash. So it was decided to use NaOH to extract SiO_2 of rice husk ash.

The amount of alkali had some effect on the reaction, the chemical reaction between NaOH and rice husk ash proceeded by equation (9), in which m was theoretical modulus of generating water glass. The molar amount of NaOH was determined by m value of the equation in experiment, followed by adding different amounts of NaOH solution reacting with the rice hull ash for 4 h, obtaining a different amount of corresponding to alkali the extraction rate of SiO_2 and the modulus of water glass, as shown the table 1. It could be found from table 1, the dissolution rate of SiO_2 increased with the increase of NaOH content, which reached 90 % above when the molar ratio of SiO_2 and NaOH was 5: 4, and when the NaOH content continued increasing, the dissolution rate of SiO_2 added indistinctively. Then the modulus of water glass reduced with the amount of NaOH increased, and the high modulus of sodium silicate solution could be obtained when the amount of alkali was little. Because the rice husk ash contained a small amount of impurity and the result of SiO_2 didn't completely react, the measured modulus of water glass was lower than theoretical. The relative content of rice husk ash was bigger in the system and the material mixed unevenly when the dosage of NaOH was less, leading the lye couldn't fully react with SiO_2 of rice husk ash, so the dissolution rate of SiO_2 was low, while the modulus of water glass was not low because of the actual content of the alkali solution small; Afterwards, the rice husk ash mixed with alkali solution more fully, with the increase of dosage of NaOH, the amount of sodium silicate that generated in the reaction of NaOH and SiO_2, and the dissolution rate of SiO_2 increased, but due to the large amount of NaOH solution, leading to the modulus of sodium silicate small eventually; With the further increase for the amount of NaOH, the dissolution rate of SiO_2 increased little, however, the modulus of sodium silicate had greatly reduced. Therefore, the dosage of alkali should be chosen with the dissolution rate of SiO_2 high and the modulus of sodium silicate moderate, namely, $n(SiO_2):n(NaOH)=5:4$.

The figure 2 showed the effect of reaction time on the extraction

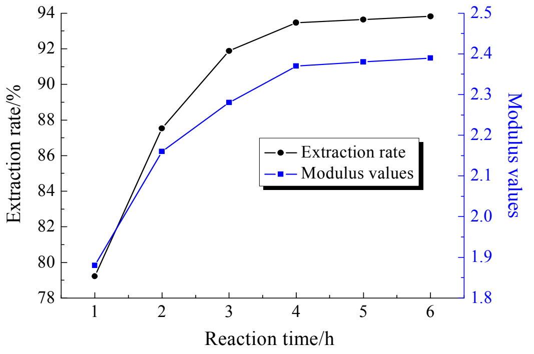


Fig.2 Effect of reaction time on the extraction rate of SiO_2 and water glass modulus ($n(SiO_2)$: $n(NaOH)$=5:4 and the NaOH concentration of 1 mol/L)

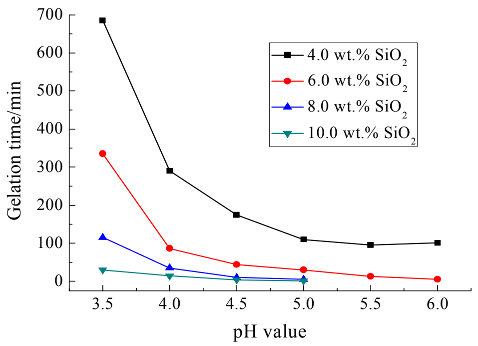


Fig.3 Change in gelation time with the variation of pH value and SiO_2 concentration

rate of SiO_2 and water glass modulus under the condition that the molar ratio of NaOH and SiO_2 was 5:4 and the concentration of lye was 1 mol/L. Seen from figure 2, when the dosage of alkali was determined, the extraction rate of SiO_2 and water glass modulus increased with reaction time increasing. However, the extraction rate of SiO_2 and water glass modulus no longer changed when the reaction to reach a certain time. Because the higher the concentration of NaOH, the faster the reaction rate, and the extraction rate of SiO_2 and water glass modulus increased obviously in the early stage of the reaction; When the reaction arrived the later, the concentration decreased, and the water glass increased that generated in solution at the same time, causing the reaction rate reduced, the extraction rate of SiO_2 and water glass modulus gradually stabilized. The reaction time using alkali extraction was determined for 4 h according to the extraction rate of SiO_2 and water glass modulus.

In the process of preparation of aerogels, it was vital for the gelation process of SiO_2 aerogel, which determined the structure and properties of SiO_2 aerogel. The silicate, using water glass extracted in experiment, was obtained by cation exchange resin and ion exchange, then realize the gelation with NaOH solution by adjusting pH value. Gelation time was important index in the process of gel formation, the preparation process of gel would be more if gel time cost too long, or the gel would be out of control due to if gelation time too short. In practice, therefore, the reasonable gelation time was neither long nor short. In order to accurately control gel process, first, the pH value of gel and the content of SiO_2 in sodium silicate for gel time should be studied, the experiment result is shown in figure 3. The gel time got short while the pH value of gel increased in the different content of SiO_2 gel. When the pH was 3.5 ~ 5.0, the pH value increased, the gel time shortened sharply; When the pH was 5.0 ~ 6.0, the gel time changed less obviously. It was that the isoelectric point [26] of SiO_2 sol was between 1 and 3 of pH value, the polycondensation of silicon hydroxyl was nucleophilic substitution process, the reaction rate of which was proportional to the concentration of OH^- [27]. So the concentration of OH^- increased gradually and the rate of polycondensation reaction with the increase of pH value, leading to the gel time reduced. Besides, when the pH value was certain, the content of SiO_2 in sodium silicate increased, the gel time got short. When the content of SiO_2 was less than 4.0 wt. %, no matter how many catalysts joined, the gel couldn't form; and when the content of SiO_2 was greater than 10.0 wt. %, the gel could form immediately with the catalyst added just, but there were a lot of bubbles, uneven and broken easily through this way. For this phenomenon, the concentration was low with the content of SiO_2 less, and particle collisions had a small chance, leading to the rate of polycondensation reaction decreased and the gel time increased, even the gel could not form finally; The concentration of the particles increased with the content of SiO_2 increased, and the polycondensation reaction greatly accelerated, forming a three-dimensional network structure of SiO_2 gel.

In addition, found in the process of adding alkaline catalyst, there was a little ivory phenomenon with NaOH solution quickly joined one-time in gel, which was equably transparent when NaOH solution slowly added (about 5 drops per minute). When the alkaline catalyst joined fast, the SiO_2 particles grew rapidly because of the concentration of NaOH high locally, resulting in a loss of liquidity of the sol in a short time and forming the gel, and some of SiO_2 particles produced ivory phenomenon because of precipitate formed. On the other hand, when the alkaline catalyst added slowly, the smaller SiO_2 particles generated in system first, and the positively charged layer surface formed quickly and dispersed stably in solution. Then the positively charged layer surface was destroyed when the alkaline catalyst continued to be added, prompting SiO_2 particles grew older and crosslinking, eventually, forming a uniform structure of SiO_2 gel. Therefore, in the next experiment, the gel could be formed by adjusting pH with alkaline catalysts added at 5 drops/min.

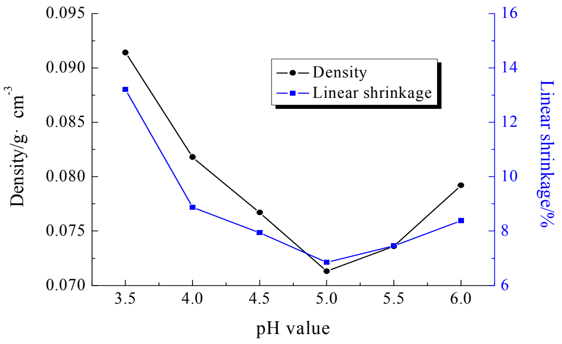
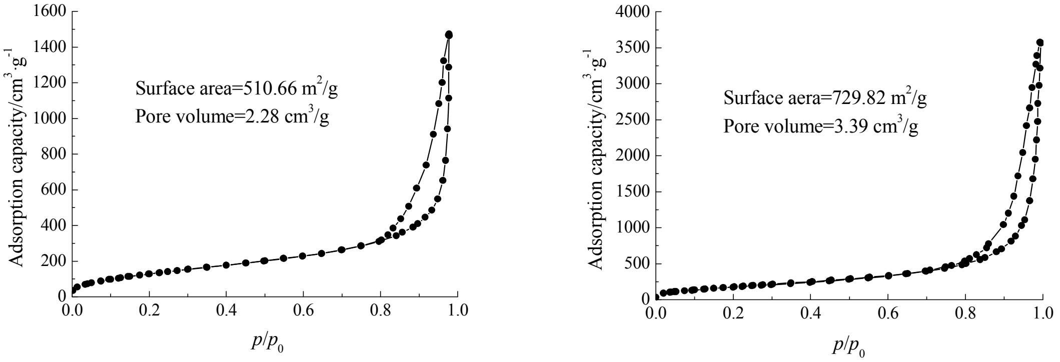


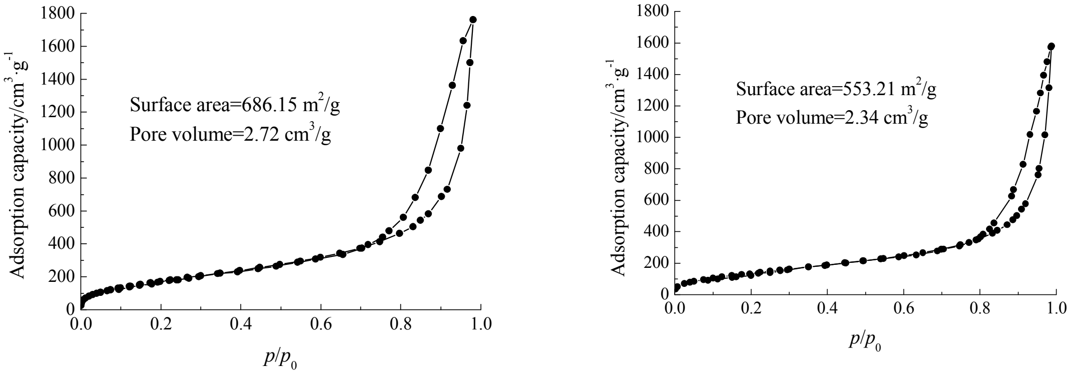
Fig.4 Change in density and linear shrinkage of aerogel with the variation of pH value (the SiO_2 content of water glass was 6.0wt. %)

The relationship between the density and the linear shrinkage rate of SiO_2 aerogel with the variation of pH value was shown in figure 4, and the content of SiO_2 aerogel was 6.0 wt. % in water glass. As seen from the picture, the change in the density and line shrinkage rate of SiO_2 aerogel with the variation of pH value were basically identical. When the pH value of gel was the range of 3.0 ~ 5.0, the density of aerogel and linear shrinkage decreased with pH value increased, and reached minimum when the pH value was 5.0, respectively, 0.0713 g/cm^3 and 6.85%. However, the density and linear shrinkage of aerogel started to rise as pH value increased further, and the density rose to 0.0713g/cm^3 and the linear shrinkage increased to 8.34%.

In order to further research the effect rule of pH value on the structure and properties of SiO_2 aerogel, the aerogel samples was tested by BET in different pH values, and obtained N_2 adsorption-desorption isotherms as shown in figure 5. The adsorption-desorption isotherms of SiO_2 aerogels obtained at different pH values all were type IV, which presented adsorption hystersis loop of adsorption curve and stripping curve without coincidence, and the adsorption hysteresis loop type belong to the H1, proving all SiO_2 aerogel were mesoporous materials at both ends of the cylindrical hole structure. Among them, when the gel pH = 5.0, the specific surface area and pore volume of the aerogel was the largest, respectively, 729.82 m^2/g and 3.39 cm^3/g; when the pH increased or decreased, specific surface area and pore volume of the aerogel also reduced, which was consistent with the change of density of aerogel at different pH value.



(a) pH=3.0 (b) pH=5.0



(c) pH=5.5 (d) pH=6.0

Fig.5 N_2 adsorption-desorption isotherms of SiO_2 aerogels obtained at different pH values

The figure 6 was the pore size distribution of SiO_2 aerogels obtained at different pH values. When the pH value was 3.0, the average pore size of aerogel was 9.84 nm, and the distribution was wide in the scope of 5 nm ~ 25 nm; When the pH value was 5.0, the average pore size of aerogel was 16.32 nm, the range of which narrow, mainly focused in 10 nm ~ 20 nm; When the pH value increased to 5.5 and 6.0, the average pore size of aerogels were 20.46 nm and 24.73 nm respectively, which was the range between 10 nm and 40 nm. It could be found by comparing different distribution of pore size of aerogel, when the pH value was 5.0, the aperture size distribution of SiO_2 was relatively uniform and centralized, illustrating the porous network structure of aerogel was uniform, too, so the density was relatively small, while the pH value were 3.0, 5.5 and 6. 0, the gel had different aperture size distribution, hence the density of aerogel was bigger. For one possible reason, the hydrolysis rate of silica was inconsistent with polycondensation rate in the process of sol-gel [28-29]. The hydrolysis reaction rate of silicic acid was much greater than the polycondensation when the gel pH value was lesser, and there were large amounts of silicate monomers in system, which was conducive to nuclear reaction, thus forming more nuclear, but the size was smaller, and resulting low crosslinking and loose structure of the polymer gel. Therefore, the phenomenon of local reunion was more serious and gel contraction was bigger, leading to the aerogel density bigger, specific surface area and pore volume smaller, pore size distributed. The polycondensation reaction rate of silicate accelerated with the increase of gel pH value, when pH = 5.0, the hydrolysis rate and condensation rate corresponded, i.e. the polycondensation reaction would happen immediately followed hydrolysis of silicate, and therefore the concentration of monomer was relatively low in system, contributing to the growth and crosslinking of nuclear, and becoming perfect structure and high intensity of micelle gel. So the contraction of gel would reduce in the process of solvent replacement and drying of solvent, and the density of aerogel was small, specific surface area and pore volume

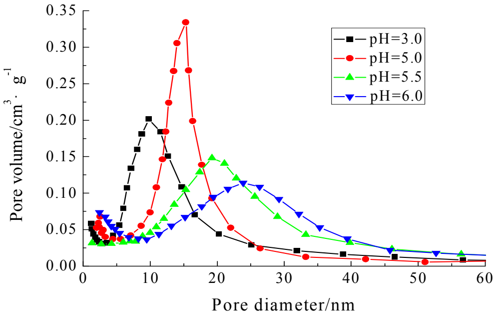


Fig.6 Pore size distribution of SiO_2 aerogels obtained at different pH values

Tab.2 Effect of SiO_2 concentration on the properties of aerogel

SiO_2 concentration (wt.%)	Line shrinkage (%)	Density (g/cm^3)	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
4.0	13.76	0.0565	553.27	1.96	10.45
6.0	6.85	0.0713	729.82	3.39	16.32
8.0	5.23	0.0876	714.36	3.43	16.74
10.0	1.47	0.124	642.59	2.38	12.21

large, pore size distribution more homogeneous. However, the polycondensation reaction would be very fast if the pH value was very high, resulting in the SiO_2 particles large, increasing the brittleness of gel, making the density of aerogel increased, specific surface area and pore volume decreased, aperture large and the distribution range very wide.

As a result, when pH = 5.0, the density of SiO_2 aerogel was the least and specific surface area the largest, the pore size distribution was uniform and the microstructure fine. So the pH = 5.0 was the best as the preparation of SiO_2 aerogel.

The content of SiO_2 had a great influence on the structure and properties of aerogels, too. Known from the table 2, when the pH value was 5.0, the density of aerogel increased and the line shrinkage decreased with the increase of SiO_2 concentration. This was because of the crosslinking degree of gel low and the gel strength weak when the SiO_2 concentration was small, so the gel was very difficult to maintain the integrity of porous structure and it had big line shrinkage, leading to the density of aerogel low. On the contrary, the gel strength was improved and the line shrinkage rate of aerogel reduced with the increase of SiO_2 concentration. When the SiO_2 concentration increased to 10.0 wt. %, the gel had a dense network structure and the intensity was high, making the aerogel line shrinkage rate was only 1.47%, but at the same time, the solid content of SiO_2 aerogel was also high per unit volume, so the density of aerogel was higher, reaching 0.124 g/m^3.

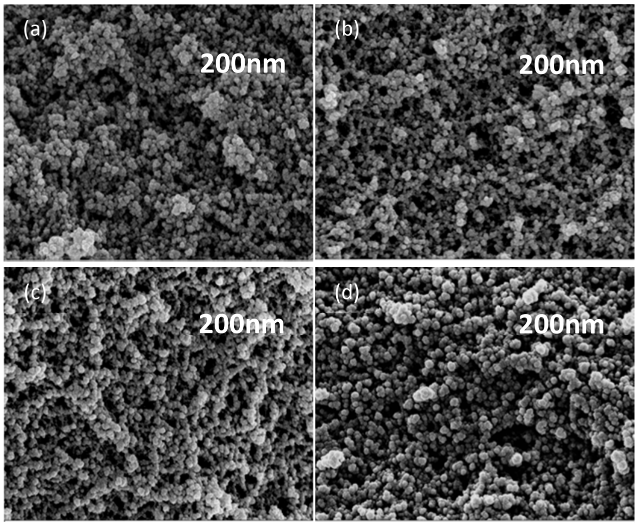


Fig.7 FE-SEM images of aerogels obtained with different SiO_2 concentrations

(a) 4.0 wt% SiO_2; (b) 6.0 wt% SiO_2; (c) 8.0 wt% SiO_2; (d)10.0 wt% SiO_2

Found from table 2 yet, the SiO_2 concentration had great influence on the pore structure of the aerogel. The aerogel shrunk significantly because of the gel strength weak when the SiO_2 concentration was 4.0 wt. %, causing pore volume and pore diameter of aerogels very little, and specific surface area reduced. When the SiO_2 content was 10.0 wt. %, large amount of SiO_2 particles quickly formed a dense gel structure in solution, leading to smaller aperture of aerogel, and pore volume and specific surface area also reduced accordingly. Therefore, SiO_2 content, too high or too low, was not conducive to form porous aerogel network structure, which had a high specific surface area, high pore volume and uniform pore size distribution. The nature of the aerogel was the best when SiO_2 concentration was 6.0 wt. % and 8.0 wt. % as shown in table 2, pore volume were 3.39cm^3/g and 3.43 cm^3/g, average pore diameter were 16.32nm and 16.74nm. Moreover, specific surface area very high, reaching 729.82m^2/g and 714.36 m^2/g, the relevant properties is already very close to SiO_2 aerogel materials by TEOS as the raw material prepared. However, when the gel pH value was 5.0 and SiO_2 concentration was 8.0 wt. %, the gel time is shorter, only 5 min, against the experimental operation; and gel time increased to 30 min when SiO_2 content was 6.0 wt. %, so it was more appropriate to prepare SiO_2 aerogel when the SiO_2 concentration was 6.0 wt. % in water glass solution.

Figure 7 was the FE-SEM images of aerogels obtained with different SiO_2 concentrations. Known from the picture, when the SiO_2 concentration was 4.0 wt. %, the aerogel particles were small, which had a clear phenomenon of reunion, and pore size distribution was uneven, pore formed between the particles was small, and the pore between aggregate was larger, it was caused because of the SiO_2 concentration low and gel strength poor, leading to uneven contraction. When the SiO_2 concentration is 10.0 wt. %, the aerogel particles of the composition was larger with structure more loose and porosity larger. When the SiO_2 concentration was 6.0 wt. % and 8.0 wt. %, the aerogel presented a nano porous continuous network structure, constituting a network frame of SiO_2 particles with sleekness and good uniformity. The analysis result of FE-SEM images was in line with the rule followed the change of SiO_2 concentrations in properties.

Finally, the effect of aging liquid on aerogel was analysed in the experiment. Aging[30] is one of the indispensable phases during the preparation of SiO_2 aerogel. The aerogel would produce a large shrinkage, if aging was not treated properly, the aerogel would appear the phenomenon such as pore size distribution uneven, cracking and even broken; And after aging treated, the strength of gel network frame improved and the flexibility of the skeleton

Tab.3 Effect of aging solution on the properties of SiO_2 aerogel

Aging Liquid	Line Shrinkage (%)	Density (g/cm^3)	Specific Surface Area (m^2/g)	Pore Volume (cm^3/g)	Average Pore Diameter (nm)
H_2O/EtOH	6.85	0.0713	729.82	3.39	16.32
TEOS/EtOH	3.78	0.0684	761.56	2.92	13.89

increased, besides, the contraction of aerogel significantly decreased, so SiO_2 aerogel owned the property of high quality by this way. The gel was treated by H_2O/ EtOH and TEOS/ EtOH with 30% concentration apart, comparing the influence of two different aging liquid on the nature of SiO_2 aerogel.

Gel enhancement mechanism was different in different aging solution. When the gel aged in H_2O/EtOH solution, smaller particles dissolved and deposited in the larger particles due to the different solubility among different radius of curvature of surface, or to say, SiO_2 particles dissolved from the surface and precipitated on the contact between particle neck of the negative curvature radius, making the gel network structure uniform, crosslinking degree increased and gel strength improved. When aged in TEOS/EtOH solution, the TEOS in solution would enter into the holes of the gel and react with the hydroxyl groups on network skeleton by silica keys (Si-O-Si) connected on the gel skeleton, supporting gel network structure, and resisting better shrinkage and cracking in the process of drying.

The infrared spectra of SiO_2 aerogel aging in two different aging liquid was shown from figure 8. There were obvious characteristic absorption peaks[28] of the network skeleton in SiO_2 aerogel at the wave number of 1089cm^{-1}, 799 cm^{-1} and 463 cm^{-1}, among them, the characteristic absorption peaks of SiO_2 aerogel aging by TEOS/EtOH was stronger than that by H_2O/EtOH, proving the number of silicon-oxygen bond (Si-O-Si) in aerogel increased when TEOS was connected to the network frame after TEOS/EtOH aging. The aerogel by TEOS/EtOH aging appeared a $-CH_3$ absorption peak at 2982cm^{-1} and $-CH_2$ absorption peak at 2935cm^{-1} and 1390 cm^{-1}, these were all connected with $-OC_2H_5$ in TEOS, at the same time, the absorption peak intensity of silicon hydroxyl (Si-OH) at 962cm^{-1} and aerogel physical adsorption abated, showing further that the TEOS had been connected to the network of SiO_2 aerogel skeleton.

In table 3, the properties of SiO_2 aerogel were compared via two different aging liquid prepared. Could be seen from the table, the linear shrinkage rate and density of SiO_2 aerogel by TEOS/EtOH aging were smaller than H_2O/EtOH, because the TEOS could be connected to the network frame by silicon-oxygen bond (Si-O-Si) in the TEOS/EtOH aging, which was better for the improved effect on gel strength than in the H_2O/EtOH, leading to the line shrinkage rate smaller. Although the introduction of TEOS would increase SiO_2 content of aerogel quickly, for which the influence on shrinkage rate was more significant, making the final density of SiO_2 aerogel small. Besides, as a result of TEOS grafted on SiO_2 aerogel skeleton network, the roughness of aerogel skeleton particles increased, which was equal to make the surface area of the aerogel largen, but also caused that the pores of the aerogel was occupied by TEOS, resulting in pore volume and average pore diameter of aerogel smaller.

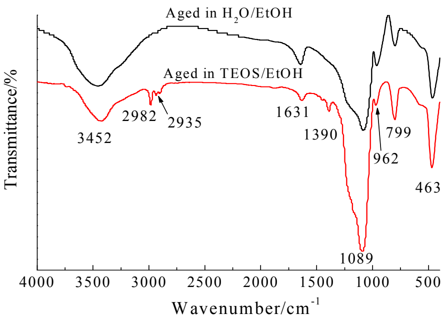


Fig.8 Pore size distribution of SiO_2 aerogels obtained at different pH values

To sum up, in TEOS/EtOH solution ageing, some situations of SiO_2 aerogel had been improved, such as shrinkage rate, density and specific surface area, but the effect was not obvious, on the contrary, pore volume and pore diameter of aerogel reduced. Besides, after TEOS aging, the number of the hydroxyl groups dropped largely on the surface of the gel, which was against to the next step of hydrophobic modification and amino modified of aerogel. In addition, the TEOS was expensive as raw materials, and had certain harm to human body, so H_2O/EtOH solution was decided to treat for aging based on the principle of low cost.

Conclusions

The silica was leached from rice husk ash as the silicon source, using alkali extraction reaction, sodium silicate solution was generated, and then the silicate was obtained by cation exchange resin and the gel formed through adjusting pH value by NaOH solution, finally, the light porous SiO_2 aerogel was successfully achieved by means of ethanol supercritical fluid drying. The main conclusions are as follows.

(1) It was better for NaOH than Na_2CO_3 in the SiO_2 extraction of rice husk ash. When the reaction time was more than 4 h, or the mole ratio of SiO_2 and NaOH less than 5:4, the dissolution rate of SiO_2 increased unobvious. Therefore, as the ideal condition, the concentration of NaOH solution 1 mol/L, n(SiO_2):n(NaOH)=5:4 and the reaction time 4 h, thus, the resulting modulus of sodium silicate solution was 2.36 and the dissolution rate of SiO_2 was 93.47%.

(2) When pH=5, the density of aerogel was minimum, specific surface area and pore volume the largest, and the specific surface area and pore volume of the aerogel reduced whether gel pH value increased or decreased. When the SiO_2 concentration is 6.0 wt. % and 8.0 wt. %, the specific surface area and pore volume of SiO_2 aerogel reached the maximum

value. And, the effect aging in TEOS/EtOH solution was less obvious than in H_2O/EtOH solution.

(3) Considering various factors, the SiO_2 concentration ultimately was determined to 6.0 wt.% in sodium silicate and got gel when pH = 5.0, after aged by H_2O/EtOH solutions, the SiO_2 aerogel could be obtained. Through the process, the obtained SiO_2 aerogel owned spongiform nano porous network structure, the density was as low as 0.0713g/cm^3, specific surface area 729.82m^2/g, the hole size 3.39cm^3/g, the average pore size 16.32nm, and the size distribution uniform, besides, the properties were similar to that of SiO_2 aerogel prepared from tetraethoxysilane (TEOS).

Acknowledgements

This work was financially supported by the NSAF (10976013), the Key Program of Natural Science Fund of Jiangsu Province (BK2010082), the Industry Program of Science and Technology Support Project of Jiangsu Province (BE2014128), the clinical medical special Program of Science and Technology Project of Jiangsu Province (BL2014074), Program for Changjiang Scholars and Innovative Research Team in University (No.IRT1146), Jiangsu Collaborative Innovation Center for Advanced Inorganic Function Composites and the Priority Academic Program Development of Jiangsu Higher Education Institutions. Any opinions, findings, and conclusions or recommendations expressed in this paper are those of the authors and do not necessarily reflect the views of these programs.

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