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RESEARCH PAPER

Cost-Effective Preparation of Silica Aerogel with Excellent Porosity through Efficient Gel-Drying in a Supercritical Medium

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ABSTRACT

In this study, a simple and novel supercritical dryer system was designed to drying of wet gel, aiming for the removal of the high energy-consumption equipment such as pump and strong compressor. The system is capable to provide the supercritical state in the fluid, only using the control of thermodynamic conditions. To ensure the proper efficiency of the developed dryer system, the silica aerogel was successfully derived from tetraethyl orthosilicate as starting material of silica. The amorphous phase of silica was identified by XRD analysis. The specific surface area and average pore size were measured at about 659 m^2/g and 22 nm, respectively, via the BET method. The N_2 adsorption-desorption isotherm curve shows the type IV isotherm, indicating the mesoporous structure with cylindrical and capillary pores. The bulk density and porosity were measured at about 0.11 g/cm^3 and 95%, respectively. The TEM and FESEM micrographs indicate porous and interconnected structures along with open mesopores in the range of 10-30 nm. These results confirm the proper efficiency and performance of the designed supercritical dryer system.

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INTRODUCTION

Over the last decade, aerogels are of particular importance owing to their exceptional properties such as high surface area, high porosity, ultra-low density, high thermal insulation value, ultra-low dielectric constant, low index of refraction and high optical transmission [1-3]. These excellent features make the porous materials suitable to use as a catalyst, heat insulation, adsorbent, sensor, and other industrial application [4-6]. Aerogel is a synthetic lightweight porous material with extremely low density derived from a gel [7]. Out of all aerogels, silica aerogel is considered an extremely important and applicable material and is used in various industrial and technological applications [8-10].

Silica aerogels can be easily prepared by the sol-gel method from Tetraethoxysilane (TEOS) as silicon sources [9]. At the first step of the synthesis, the reactive hydroxyl groups are produced by hydrolysis of the alkoxide group's molecules [11, 12]. Then, condensation reactions between hydroxyl groups result in the formation of a sol [13]. By giving aging time to wet gel, further condensation takes place which leads to the linking of particles to each other and the formation of a 3D network of porous gel [14]. The silica aerogels will be obtained by drying wet gel.

Drying of wet gel is conventionally performed by replacing the liquid phase of a wet gel with

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a gas in a supercritical dryer [15, 16]. These systems work above the supercritical pressure and temperature of the fluid that requires high energy, resulting in a costly process and limiting industrial-scale production. Considering the high energy consumption of the process, the design of this system with the approach of reducing energy consumption is of almost importance.

In this study, we design a novel supercritical dryer setup without using high energy-consuming equipment of the pump and a strong compressor, which can create a supercritical state with mild and controlled conditions. The performance of this designed system was evaluated by successfully drying a wet gel containing silica nanoparticles. This silica wet gel was conventionally prepared by the sol-gel method from TEOS as a silica precursor.

MATERIALS AND METHODS

Synthesis Procedure

The tetraethyl orthosilicate (TEOS, 99 %wt), ethanol (C_2H_5OH, 99.9 %v/v), ammonia (NH_3, 30 %wt), and hydrochloric acid (HCl, 37 %wt) were provided by Sigma-Aldrich Chemical Co.

to dry the alcogel under standard conditions, a supercritical drying system with low energy consumption was required. For this purpose, a supercritical drying setup was fabricated to convey the fluid to a supercritical state, according to Fig. 1. In the designed system, the adjustable high pressure (up to 150 bar) can be provided only by controlling the thermodynamic conditions (temperature and pressure) without the need for strong compressors. In this study, the CO_2 supercritical fluid was used to eliminate the liquid component of wet gel, whereas the designed supercritical dryer is also suitable for ethanol, methanol, and acetone fluids.

First, the conditions for condensation of carbon dioxide were provided by cooling the reactor. Afterward, a stream of liquid carbon dioxide from the CO_2 cylinder flowed into the reactor, at constant pressure. The liquid carbon dioxide was obtained by inserting a pipe near the bottom of the cylinder, which leads to the removal of the energy-consumption device of the pump.

To ensure the performance of the designed setup, the silica aerogel was conventionally synthesized by applying this system for the drying step as follows: 1 ml TEOS was mixed with 9 ml ethanol as solvent. To hydrolysis of ethyl groups in TEOS and formation of silanol groups (Si-OH), 1 ml deionized water was poured into the solution at room temperature. 1 drop of HCl as a catalyst of the hydrolysis stage was injected into the reaction medium. The solution was mixed under mechanical stirring for 30 min, obtaining a “sol” organic phase containing silicic acid with a pH value of about 3. Afterward, ammonia as a catalyst of the sol condensation stage was dropwise added into the prepared sol to increase the pH of the reaction mixture up to 8. Then, the solution was poured into the mold and the gelation of the sol was observed after approximately 30 min. The obtained gel was immersed in ethanol overnight at room temperature for an aging time. Finally, the silica aerogel was derived via drying of the obtained wet gel by using a supercritical fluid of

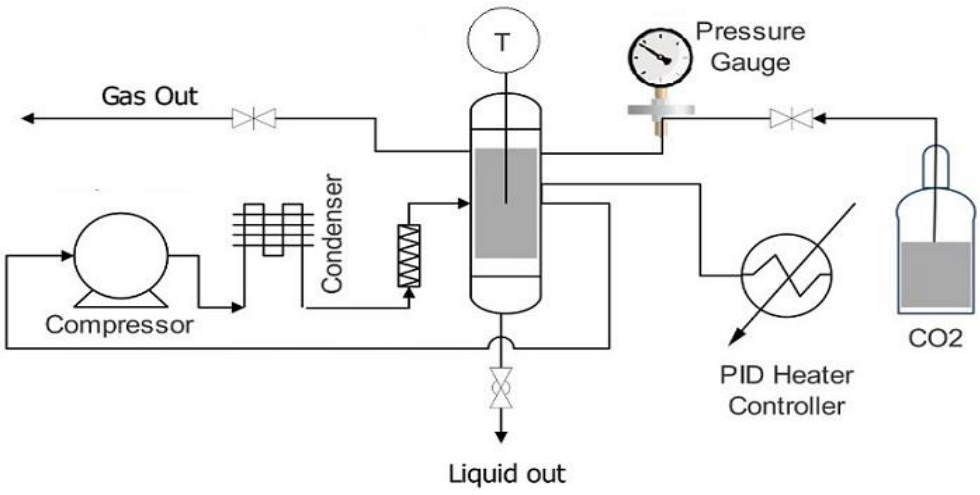

Fig. 1. Schematic of designed supercritical dryer system

carbon dioxide at 100 bar and 40 °C for 4 h.

Characterization

X-ray diffraction pattern (XRD, PANalytical X'Pert-Pro, Netherland) in the range of 10° to 80° was used to specify the structure and relative configuration of obtained silica aerogel. The chemical properties of silica aerogel were investigated by using the Fourier transform infrared spectroscopy (FT-IR, Magna-IR 550 spectrometer, Nicolet Co.) in the range from 400 to 4,000 cm^{-1}. Brunauer–Emmet–teller analysis (BET, Belsorp 28 system, Japan) was applied to measure the specific surface area of silica aerogel, and nitrogen adsorption-desorption isotherm at 77 K was obtained by an automatic system. Before analysis, the sample was degassed for 5 h under vacuum at 300 °C. The microstructure observation was carried out by field emission scanning electron microscopy (FESEM, MIRA3 TESCAN, USA) and transmission electron microscopy (TEM, CM120 Philips, Netherland) micrographs. The apparent density was defined by measuring the weight of a given volume. The bulk density (ρ_b) was determined by the mass of the given volume, and then porosity was calculated through $(1-\rho_b/\rho_s)\times100$, which skeleton density is 2.2 g/cm^3 [17].

RESULTS AND DISCUSSIONS

X-ray diffraction analysis was applied to study the formation and phase identification of synthesized silica aerogel, and the result was demonstrated in Fig. 2. The major broad diffraction peak at around $2\theta = 22.8°$ is attributed to the amorphous phase of silica based on JCPDS PDF data (29-0085) [2]. Also, no sharp peak appeared in the diffractogram, confirming the formation of the amorphous phase of silica aerogels [18] .

FT-IR spectrum of prepared silica aerogel was presented in Fig. 3. The broadband appeared around 3430 cm^{-1} demonstrating the O–H stretching vibrations due to the existence of hydrogen-bonded among silanol groups [19]. The observed band around 1630 cm^{-1} is related to deformation vibrations of physically absorbed water [20]. The absorbs around 466 cm^{-1} and 799 cm^{-1} corresponded to symmetric stretching vibrations and bending mode of Si—O covalent bonds in the structure of silica. On the other side, the weak band at 965 cm^{-1} is indicated by the in-plane stretching vibrations of silicon–oxygen bonds [20]. Furthermore, the existence of Si–O–Si covalent bonds and the formation of silica network structure were confirmed by observation of intense bands around 1091 cm^{-1}, which are due to the transversal and longitudinal optical modes of asymmetric stretching vibrations of the Si–O–Si, respectively [4]. These identified bonds have been proven to the successful formation of silica networks.

N_2 adsorption-desorption isotherm was performed to investigate the pore shape of

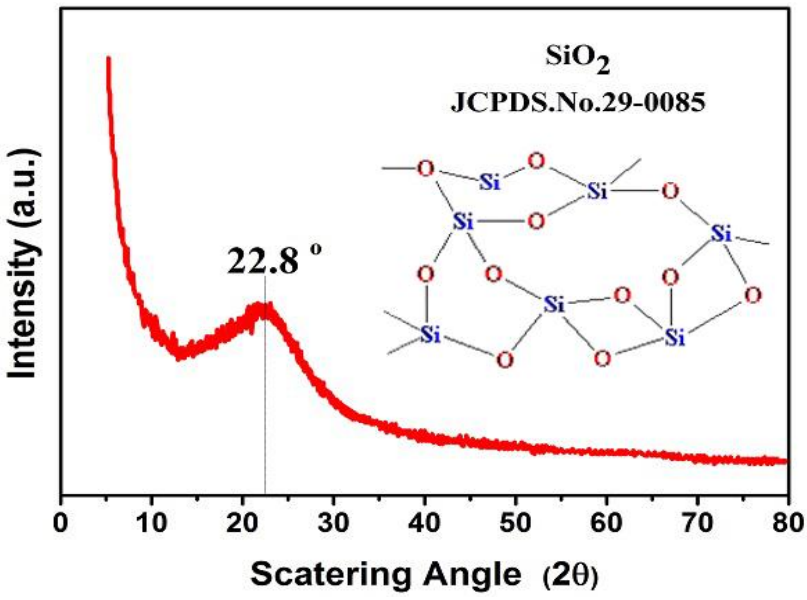

Fig. 2. The XRD profile of obtained silica aerogel

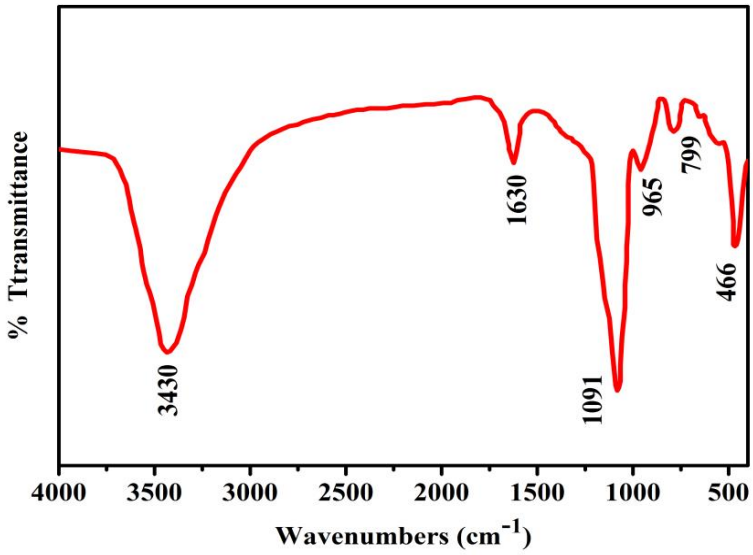

Fig. 3. The FT-IR analysis of obtained silica aerogel

SiO_2 aerogel. The obtained isotherm in Fig. 4. a shows a rapid increase at high relative pressure and a hysteresis loop, which refers to the type-IV isotherm, indicating the mesoporous structure of silica aerogel [4]. The appeared hysteresis loop reveals the existence of mesopores in the form of cylindrical and capillary pores in the 3-dimension structure of silica aerogel [21]. The maximum amount of the adsorbed nitrogen gas at a relative pressure of 0.99 is about 2380 cm^3/g. Also, the pore size distribution in Fig. 4. inset displays a nonuniform distribution of micro-mesopore in the range of 1.1-40 nm.

In addition, the physical properties of synthesized silica aerogel were listed in Table 1. As is clear, the surface area measured by Brunauer–Emmet–Teller (BET) analysis was obtained 659 m^2/g for prepared silica aerogel, which indicates a high

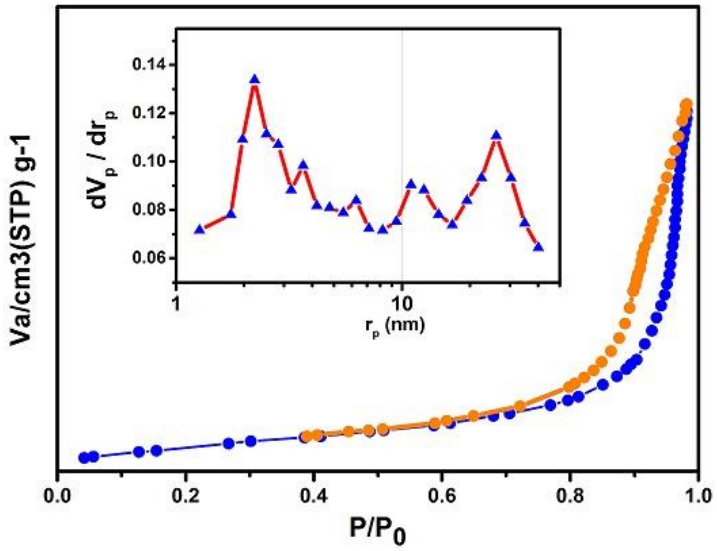

Fig. 4. N_2 adsorption-desorption isotherms of SiO_2 aerogel, and the pore size distributions (inset)

Table 1. Physical properties of synthesized silica aerogel

Specific surface area (m^2/g)	Average pore size (nm)	Total Pore volume (cm^3/g)	Density (g/cm^3)	Porosity (%)
659.74	22.29	3.67	0.11	0.95

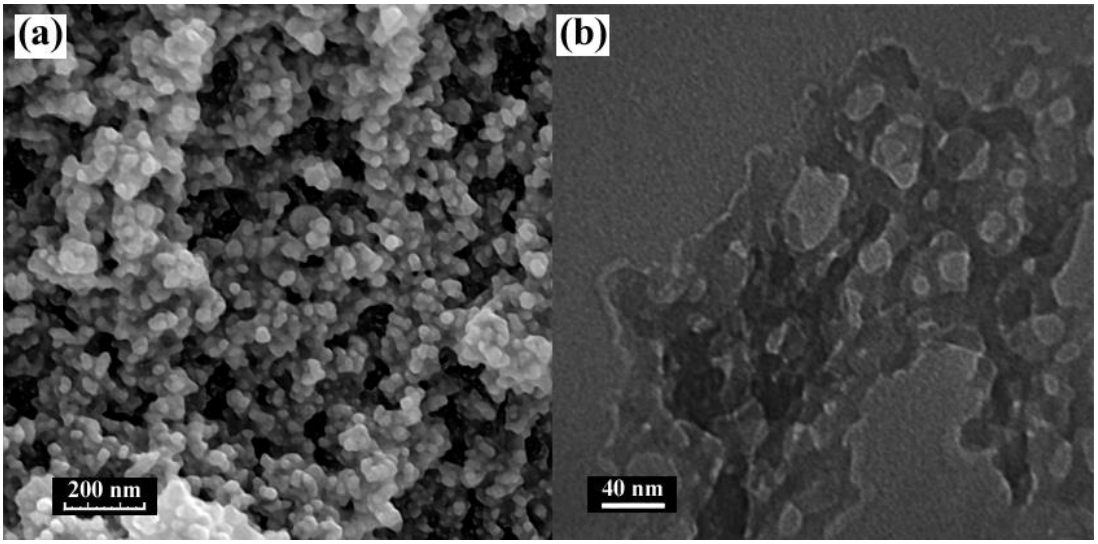

Fig. 5. SEM (a), and TEM (b) micrographs of obtained silica aerogel

surface area and is in line with the results of some previous studies [22-25]. Also, the average pore size and pore volume were determined at about 22 nm and 3.67 cm^3/g based on Barrett-Joyner-Halenda (BJH) methods. The bulk density and porosity of silica aerogel were calculated at about 0.11 g/cm^3 and 95 %, respectively. Anderson et al. [22] fabricated several hydrophobic silica aerogel by applying a rapid supercritical extraction system, and reportes the surface area between 550 to 770 m_2/g, and porosity about 96%. Gyori et al. [23] also used a static supercritical fluid extraction system for drying wet gels of silica. They report the surface area of these samples at about 497-874 m^2/g, and mesopore volume about 79-89% . These results demonstrated that the designed supercritical dryer system was successfully utilized to drying of silica aerogel with an acceptable efficiency compared to the conventional supercritical dryer.

TEM micrograph of prepared silica aerogel in Fig. 5. exhibited the three-dimensional network and interconnecting structure. The pore size distribution of porous silica aerogel was estimated to be in the range of 10-30 nm and the average size was approximately about 20 nm, confirming the presence of mesopores in the aerogel structure. The SEM micrograph in Fig. 5. b also demonstrated an interconnecting network and open mesopores along with a slight amount of aggregation [16]. The observed porous structure with a high number of open mesopores, as is clear in the TEM and SEM image, demonstrated the high porosity of synthesized silica and classified this material as an aerogel [2].

This observation in morphology and size distribution of mesopores indicated the appropriate process of drying and confirmed the proper performance of the designed supercritical dryer setup. On the other hand, in the supercritical drying method, due to the flow of fluid into the pores, a large number of open pores are created in the structure. Hence, the existence of open pores also confirms the good efficiency of the designed setup [16].

CONCLUSION

Aerogels as an applicable porous material, are obtained by drying a wet gel. The drying process

as a key step is conventionally performed via a supercritical dryer which is associated with high energy consumption, leading to an increase in the cost of aerogel production. Therefore, a supercritical dryer system was designed without the need for a pump and a strong compressor to reduce the energy consumption and cost of the process. The creation and control of supercritical states were conducted only by using thermodynamic conditions. To evaluate the proper performance and efficiency of the proposed supercritical dryer system, the silica aerogel was successfully synthesized by using the designed supercritical dryer. The sol-gel route was applied to the synthesis of silica aerogel from TEOS. The obtained high specific surface area, low density, and high porosity revealed the proper drying performance of the made setup. Also, a three-dimensional porous structure along with a large number of open pores confirms the suitable performance and acceptable efficiency of the designed dryer system.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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