



Relationship analysis of processing parameters with micro and macro structure of silica aerogel dried at ambient pressure



Zahra Talebi Mazraeh-shahi ^a, Ahmad Mousavi Shoushtari ^{a,*}, Majid Abdouss ^b, Ahmad Reza Bahramian ^c

^a Department of Textile Engineering, Amirkabir University of Technology, Hafez Ave, Tehran, Iran

^b Department of Chemistry, Amirkabir University of Technology, Hafez Ave, Tehran, Iran

^c Polymer Engineering Department, Faculty of Chemical Engineering, Tarbiat Modares University, Tehran, Iran

ARTICLE INFO

Article history:

Received 24 January 2013

Received in revised form 23 April 2013

Available online 12 June 2013

Keywords:

Silica aerogel;
Ambient pressure drying;
Surface modification;
Reaction parameters;
Micro structure

ABSTRACT

In the present study, tetraethoxysilane (TEOS) aerogel was produced by a two-step catalytic process at ambient pressure drying under different synthesis conditions. The relationship of the key processing parameters such as EtOH/TEOS, H₂O/EtOH molar ratios and synthesis temperature with micro and macro structures of the synthesized aerogel has been analyzed. The effectiveness degree of each key processing parameter in the microstructure and then the effects of microstructure changes on the morphology and physical properties including the density and porosity were also evaluated.

The results apparently showed that the processing temperature presented the highest effectiveness on the pore structure, porosity and density of the synthesized aerogels. Synthesizing at the temperature of 30 °C gave rise to a dense structure with very small pore size (3 nm) and porosity of 59% which exhibited a type-I adsorption–desorption isotherm. Other processing parameters affected the micro and macro structure but their effects were less significant compared to the temperature effect.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Silica aerogels are known as unique porous materials containing more than 90% air and less than 10% solid silica in the form of a highly cross-linked network structure [1]. These materials have large specific surface area, low density high porosity, very low thermal conductivity and low index of refraction [1–3]. Due to their outstanding properties, in recent years silica aerogels have been used in several advanced applications such as catalysts, thermal insulators, acoustic impedance and drug delivery systems [4–8].

They are usually synthesized by traditional sol–gel chemistry followed by a supercritical drying technique to avoid destruction of the porous structure due to the effect of capillary stress [9,10]. The sol–gel synthesis involves acid or base catalyzed hydrolysis and condensation of silicon alkoxides [11].

However, supercritical drying is an expensive and very risky technique due to high cost of production and the requirement for the autoclave at high pressures and temperatures in the presence of organic solvents. These limitations have hindered the commercial development of aerogel production through this technique [2,10]. Therefore in recent years, developed drying techniques have been presented. One of these new drying techniques is a rapid supercritical extraction method (RSCE) in which a hydraulic hot press is used [12–15]. Also, silica aerogels can be produced by an atmospheric pressure drying method

in which the network strengthening and surface modification occur prior to the drying. According to this method at the surface modification stage, the hydrophobic groups are formed on the silica surface avoiding condensation reactions to occur during the drying stage [2,10].

TEOS based silica aerogel having the ethanol byproduct of the polycondensation of Si(OC₂H₅)₄ is less hazardous compared to Tetramethoxysilane (TMOS) based silica aerogel due to higher toxicity of the methanol byproduct of the polycondensation of Si(OCH₃)₄ [16].

In the case of TEOS silica aerogel preparation, various procedures have been presented by different investigators. Table 1 shows their procedures and the main properties of the obtained products.

The effect of various precursors on the physical properties of silica aerogels reported in the literature has shown that the PEDS and TMOS aerogel present narrow and uniform pores with very small SiO₂ particles while TEOS aerogel demonstrated the lowest surface area and non-uniform pores with larger SiO₂ particles of the network [17]. The surface chemical modification with considerable changes in the physical properties of TEOS silica aerogel using different co-precursors has also been reported in which co-precursors with smaller size and fewer number of alkyl groups in combination with ethoxy groups gave rise to the hydrophobic aerogels with the higher optical transmission [18].

The sol–gel parameters demonstrate a strong effect on the texture and properties of silica aerogel. Synthesized aerogels using the TEOS precursor in the presence of oxalic acid catalyst have been reported in the literature. Rao et al. investigated the preparation conditions effect

* Corresponding author. Tel.: +98 21 64542638; fax: +98 21 66400245.
E-mail address: amousavi@aut.ac.ir (A.M. Shoushtari).

Table 1
Preparation conditions and physical properties of TEOS silica aerogel.

Precursor	TEOS	TEOS/PTES	TEOS/DMCS	TEOS/ETES	TEOS	TEOS
Molar ratio of precursor:EtOH:H ₂ O	1:5:7	1:5:7	1:5:7	1:5:7	1:3:4	1:3.9:3.5
Catalyst	Citric acid	Oxalic acid	Oxalic acid	Oxalic acid	HCl/HF	HCl
Drying method	SCD ^a	SCD	SCD	SCD	SCD	APD ^b
Gelation time	2.2 days	10.5 days	3 days	14 days	–	1.5 h
Porosity (%)	87.89	87.26	90.92	88.32	–	80
Bulk density (kg/cm ³)	230	247.1	190.6	245.2	–	430
Surface area (m ² /g)	800	–	–	–	863	987
References	[17]	[18]	[18]	[18]	[19]	[2]

^a Supercritical drying.

^b Ambient pressure drying.

on the physical and hydrophobic properties of ambient pressure dried silica aerogels that were produced by TEOS and hexamethyldisilazane (HMDZ) as a silylating agent at 200 °C in the presence of oxalic acid. They were obliged to apply very long durations for solvent exchange, surface modification and drying steps in the synthesis process [20]. However in the presented work, we managed to reduce the time of steps mentioned above using HCl as a catalyst and TMCS as a silylating agent (Fig. 1).

On the other hand, a few results on two-step HCl–NH₄OH catalyzed aerogels in particular ambient pressure dried silica aerogels have been reported [21–23].

By varying the sol-parameters, microstructure (pore size, particle size and pore size distribution) and physical properties of the aerogels may be alerted which have been reported by some researchers [1,2,20]. However, few works have been carried out on the relationship between the key processing parameters with microstructure, morphology and physical properties of ambient pressure dried silica aerogels. Also the effectiveness degree of each key processing parameter in the micro and macro structure has not been studied.

The aim of this work is to find out the relationships of the key processing parameters such as EtOH/TEOS, H₂O/EtOH and TEOS:HCl:NH₄OH molar ratios, and synthesis temperature with micro and macro structures of the two-step HCl–NH₄OH catalyzed aerogels produced at ambient pressure using the TEOS precursor. The effectiveness degree of each key processing parameter in the microstructure, morphology and physical properties of the resultant aerogels is also evaluated.

2. Experimental

2.1. Materials

Tetraethoxysilane (TEOS) and Trimethylchlorosilane (TMCS) were purchased from Merck Co. The solvents used in the production of aerogels including ethanol and n-hexane were supplied from Scharlau Co.

2.2. Aerogel sample preparation

Two-step aerogels were prepared from TEOS, H₂O, EtOH, HCl and NH₄OH at different molar ratios (Table 2) according to the flowchart shown in Fig. 1. In the first step, TEOS was hydrolyzed by mixing with H₂O (molar ratio of TEOS/H₂O = 1:1), EtOH and HCl for 1.5 h at 60 °C. The pH = 3 was adjusted for all samples except A8 which was set at pH = 2 in this step. The second step (gelation) consisted of mixing the remaining water and NH₄OH after cooling the sol to room temperature. The sol was kept at 50 °C (except A9) for gelation. The pH = 8 was adjusted for all samples in this step. After gelation, the samples were aged in ethanol 2 times within 24 h. Further, the samples were washed in n-hexane 2 times within 24 h. Then the surface modification was carried out by 5% TMCS in the solvent of n-hexane for 12 h at 45 °C (except the A9 sample). Finally the samples were washed with n-hexane two times within 24 h. The ambient

pressure drying was performed in 12 h at room temperature and then 24 h at 50 °C.

2.3. Characterization of aerogel samples

The microstructure and morphology of silica aerogels were observed using field emission scanning electron microscopy (FE-SEM, Hitachi S4160, Japan) with magnification of 100,000. Nitrogen adsorption

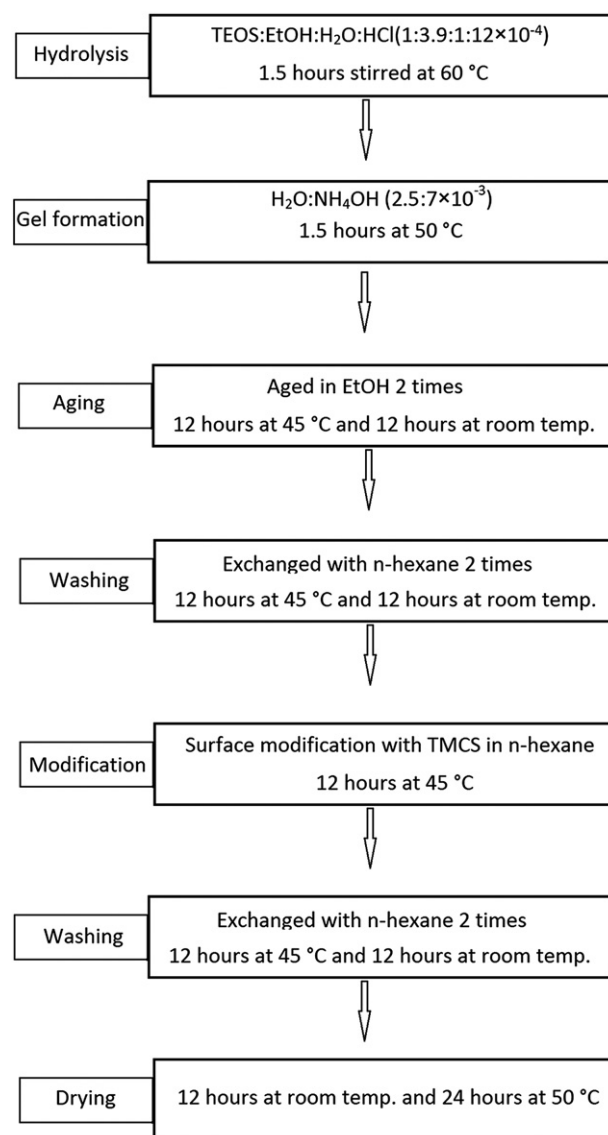


Fig. 1. General scheme for the preparation of silica aerogel samples by the ambient pressure dried method.

Download English Version:

<https://daneshyari.com/en/article/7903565>

Download Persian Version:

<https://daneshyari.com/article/7903565>

[Daneshyari.com](https://daneshyari.com)