Journal of
NANOSTRUCTURES
JNS
NANOSTRUCTURES
JNS.kashanu.ac.ir

Synthesis and Characterization of Hydrophobic Silica Aerogel by Two Step(Acid-Base) Sol-Gel Process

Azadeh Tadjarodi[a]*, Marzieh Haghverdi[b], Vahid Mohammadi[b], Masoud Rajabi[c]
[a]Departments of Chemistry, Iran University of Science and Technology, Tehran, Iran
[b]Department of Chemistry, Faculty of Science, Imam Khomeini International University, Qazvin, Iran
[c]Department of Material Science, Faculty of Engineering, Imam Khomeini International University, Qazvin,Iran

Article history:
Received 3/6/2013
Accepted 15/8/2013

Keywords:
Silica aerogel
Sol-gel
Acid-base catalyst
Surface modification
Trimethylchlorosilane

**Corresponding author:*
E-mail address*:*
tajarodi@iust.ac.ir
Phone: +98 21 77240516
Fax: +98 21 77491204

Abstract

The silica aerogel was prepared by the acid–base sol–gel polymerization of tetraethylorthosilicate precursor followed by ambient pressure drying. The prepared silica aerogels were characterized by Fourier transform infrared (FT-IR), Thermo-gravimetric and differential thermal analysis (TG/DTA), X-ray diffractometer (XRD), Energy dispersive X-ray microanalysis (EDX), Brunauer–Emmitt–Teller (BET) and Scanning electron microscopy (SEM). The result silica aerogel is a light and crack-free solid with very low bulk density 0.027 g /cm^3, high specific surface area 655.58 m^2/ g and large pore volume 0.4831 cm^3/ g. The average size of particles was calculated using a Microstructure Measurement program and Minitab statistical software.

1. Introduction

In recent years, silica aerogels have attracted considerable research interest due to their applications as adsorbents, catalysts[1, 2] light weight thermal and acoustic insulating systems [3-6], waste management (gas absorption, radioactive waste confinement[2, 6-9] and host materials for drug delivery systems[10-12].Silica aerogels are the transparent nano-porous form of silica with high specific surface area, low density, high porosity, low thermal conductivity and low index of refraction [13-17]. At present, various methods were used to prepare silica aerogel such as vapor-phase reaction, sol gel, thermal decomposition and supercritical drying [18, 19]. The most common route to synthesize silica aerogels is sol-gel polymerization of silicon alkoxides such as tetra orthosilicate (TEOS), which leads to obtain a hydrophilic silica aerogel [2, 20-22]. The role of TEOS in preparation of silica aerogel is to strengthen the gel against crack formation. Hydrophilic silica aerogels are sensitive to moisture because of the presence of active OH end groups in the silica network. Therefore, it is necessary to modify the surface with organic groups (hydrophobic reagents). For this purpose, there are different surface modifying agents such as dimethyldichlorosilane (DMDCS), Hexamethyl-dislioxane (HMDSO), phenyltrimethoxysilane (PTMS), and hexamethyldisilazane (HMDZ) [2]. In the present work, hydrophobic aerogels were prepared using trimethylchlorosilane (TMCS). Also, in order to compare the physical and hydrophobic properties of the aerogels, the time interval was varied from 6 to 24 h before adding the basic catalyst. In this paper, the mentioned method for making silica gel involves hydrolysis and poly condensation process of tetraethoxysilane (TEOS) as shown by following reactions [23]:

$$Si(O{-}R)_4+4H_2O \longrightarrow Si(OH)_4+4R{-}OH \quad (1)$$

$$Si(OH)_4+Si(OH)_4 \rightarrow (OH)_3Si{-}O{-}Si(OH)_3+H_2O \quad (2)$$

2. Experimental procedure

2.1. Materials

The chemicals used for the preparation of silica gel, were tetraethoxysilane (TEOS), ethanol (EtOH), and oxalic acid ($C_2H_2O_4$), ammonium hydroxide (NH_4OH), hexane and trimethylchlorosilane (TMCS). All the chemical reagents were purchased from Merck Co. and used without further purification.

2.2. Synthesis of silica aerogels by a two steps acid–base catalyzed sol–gel process followed by ambient pressure drying

Silica alcosols were prepared in a 250 mL beaker in two steps as follows: in the first step, tetraethoxysilane (TEOS), ethanol (EtOH) and oxalic acid were mixed under constant stirring conditions for 15 min. In the subsequent step, the base catalyst (NH_4OH) was added drop by drop to the acid catalyzed sol while stirring at time intervals 6 and 24h. In order to compare the physical and hydrophobic properties of the aerogels, the time interval was varied from 6 to 24 h before adding the basic catalyst. The molar ratio of TEOS: EtOH: H_2O (acidic): H_2O (basic): was kept constant at 1:6.9:3.5:2.2, respectively, along with the oxalic acid (0.01M) and NH_4OH(0.5M). Gelation and aging of alcosols last for 12 hours. After the sols were set, a small quantity of ethanol was added over the gels in order to prevent the evaporation of pore solvent, the shrinkage and cracking of the gel. The alcogels were aged for 6 h in ethanol at room temperature. Before the surface modification of the gel was carried out, the present ethanol in the alcogels was exchanged with a nonpolar solvent such as hexane in order to avoid the reverse reaction of surface modification, which generally occurs in polar solvents. For this purpose, the alcogels were kept in hexane solvent (50 mL) for 12 h. Then, the surface modification was carried out by immersing the alcogels in a hexane bath containing trimethylchlorosilane (TMCS). The molar ratio of TEOS/TMCS was kept constant at 2. Silica aerogels were obtained by the atmospheric drying of the gels in an oven at 65 °C for 4 h, 80 °C for 2 h and 120 °C for 2 h[24]. In order to obtain fixed weight of silica aerogel, the sample pieces were heated in an oven at 120°C for an hour and then desiccated.

2.3. Characterization

The surface modification was confirmed using fourier transform infrared (FT-IR) spectroscopy (Shimadzu-8400S) in the range of 400-4000 cm^{-1} using KBr pellets. Thermal stability of the hydrophobic silica aerogels in terms of retention of hydrophobicity was observed using thermo-gravimetric and differential thermal analysis

(TG/DTA Perkin Elmer). X-ray diffractometer (XRD:Philips, model: X'Pert MPD) was used to determine the phases of nanosilica. Quantitative chemical analyses of modified silica were accomplished by Energy dispersive x-ray microanalysis (EDX, Model Philips XL-30).The specific surface area and pore size distribution of aerogels were determined by Brunauer–Emmitt–Teller (BET) method (BET, Model Belsorp-mini). The microstructure (morphology) of nano-porous silica aerogel was observed using scanning electron microscopy (SEM) analyzer (Model Philips XL-30). The packing bed density of the aerogel sample was obtained by filling them in a cylindrical column of known volume and the density was calculated from its mass to volume ratio [25]. Two different densities are used to characterize silica aerogels: bulk density and skeletal density. Bulk density (ρ_b) is defined as the ratio of the aerogel's mass to its volume. The skeletal density of these particles is supposed to be very close to that of the bulk solid. These values were obtained by using helium picnometry. The percent of volume shrinkage and porosity of the aerogels have been determined as follows :

$$\%\text{volume shrinkage} = \left(1 \quad \frac{Va}{Vg}\right) * 100$$

$$\%\text{Porosity} = \left(1 - \frac{\rho_b}{\rho_s}\right) * 100$$

Where, V_a and V_g are the volume of aerogel and alcogel, respectively, ρ_s is the skeletal and, ρ_b is the bulk density of the silica aerogel [26].

3. Results and discussion

3.1. Surface modification and hydrophobic properties of the TEOS-based aerogels

Figs. 1 (a) and (b) show the FT-IR spectra of TMCS modified TEOS- based silica aerogel. The absorption peaks at 3432 cm^{-1}, are related to the hydroxyl groups. The absorption peaks at 2965(CH_3 stretching) and 852 (Si-CH_3 bending) cm^{-1} are attributed to surface modification of hydrogels by TMCS[27-29]. The observed strong peaks at 458, 1055, 1385 and 1642 cm^{-1} are related to the bending of the O–Si–O and Si–O–Si vibrations, Si–O–Si and Si-H_2O vibrations, respectively [30]. The intensity of absorption peaks of O–H at 3432 and 1642 cm^{-1} decreased for 24h of aging period due to replacement of hydroxyl with tri-methyl groups [30, 31].

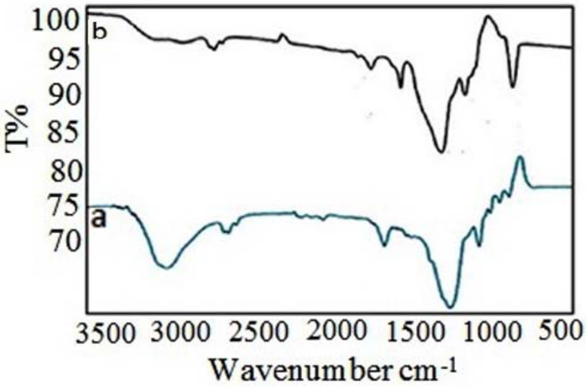


Fig. 1. FT-IR spectra of the prepared modified silica aerogels: (a) T = 6h, (b) T = 24h.

Figs. 2 (a) and (b) illustrate TG and DTA curves of the prepared aerogels in the temperature range of 25–700 °C, in nitrogen at a heating rate 20 °C /min. From the start of the experiment until the temperature of around 100 °C, the recorded amount of weight loss due to loss of water present in the sample and the external water molecules bound by surface tension. The second weight loss step at 370 °C is related to hydrophobicity of silica aerogels. At higher than this temperature, the oxidation of the methyl groups, responsible for the hydrophobicity of aerogels, will be occurred. Also an observed exothermic peak for both samples in DTA curve at this temperature indicates that hydrophobicity of silica aerogels can be maintained up to about 370°C.

The surface modification of the aerogels by non-polar groups is an indispensable step before the ambient pressure drying. Because it prohibits the formation of new siloxane bonds between the adjacent silica clusters and thereby the irreversible shrinkage of the gel. In the present studies, the surface of the alcogels was organically modified by tri-methyl groups present in the trimethylchlorosilane according to the following chemical reaction:

$$\mathrm{Si\text{-}OH+(CH_3)_3Si\text{-}Cl} \longrightarrow \mathrm{Si\text{-}O\text{-}Si\text{-}(CH_3)_3+HCl} \qquad (3)$$

The surface modification of the gels according to the reaction (3) was confirmed by means of FT-IR spectroscopy. The presence of Si–CH_3 peaks at FT-IR spectrum confirms the surface modification of the aerogels and the attachment of –Si–CH_3 groups from the TMCS to the silica aerogel surface. Thermogravimetric (TG) analysis of the TMCS modified aerogels was performed to confirm the oxidation temperature for the –CH_3 groups [23].

3.2. Physical properties of the TEOS-based aerogels

Herein, silica aerogel was prepared by a two steps acid–base catalyzed sol–gel process followed by ambient pressure drying. The present solvent in the alcogel was replaced by a non-polar solvent such as hexane prior to the surface modification step. It was found that ethanol and hexane play an important role in obtaining monolithic and uniform silica aerogels.

It has been observed that the bulk density of the aerogels decreased from 0.039 to 0.027 g cm^{-3} with the increasing of time from 6 to 24 h(Table 1).

With the increasing of time, the hydrolysis of TEOS precursor approaches completeness and leads to the formation of the silica network. For lower T values, the result gel network is relatively weaker because of the incomplete hydrolysis of the TEOS.

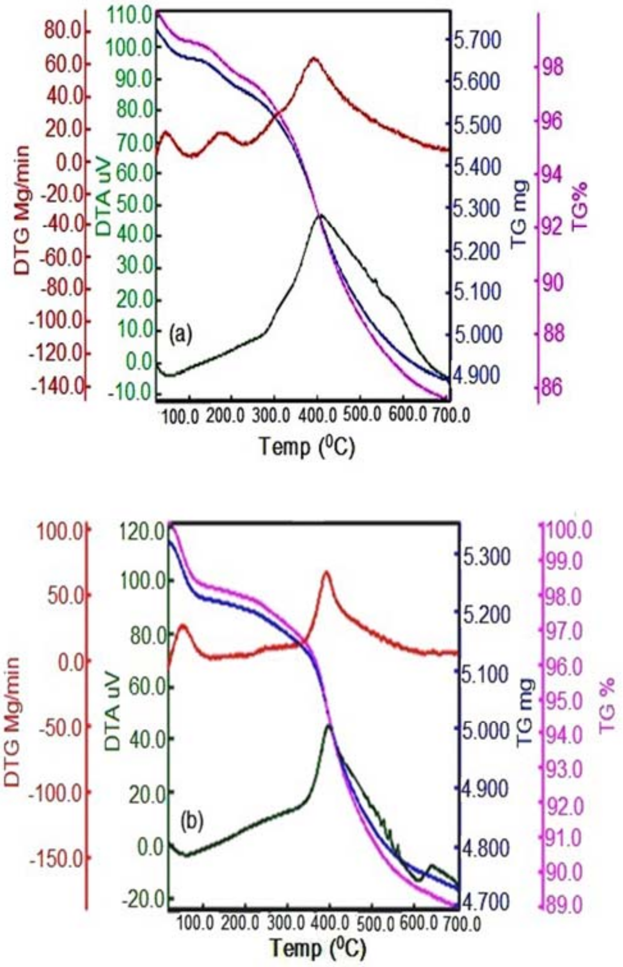


Fig. 2. TGA curves of the prepared modified silica aerogels: (a) T = 6h, (b) T = 24h.

Figs. 3 (a) and (b) illustrate X-ray diffraction patterns of TMCS modified TEOS-based silica aerogel at 6 and 24h times. There is a broad peak between 20 and 30^{o} (2θ) in both graphs. These patterns are characteristic of amorphous SiO_2 [32].

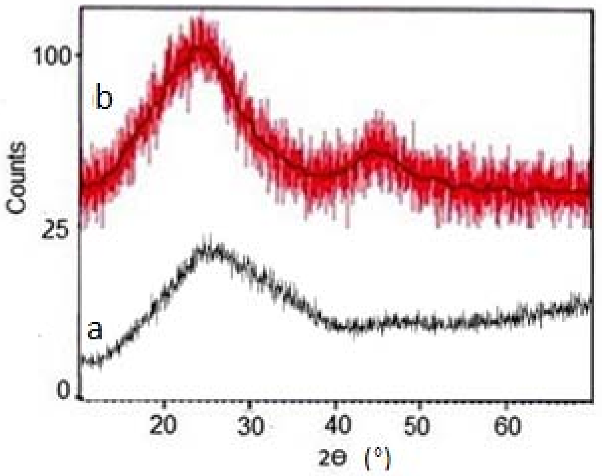


Fig. 3. XRD patterns of TMCS modified silica aerogel: (a) T = 6h, (b) T = 24h.

3.3. Textural properties of the TEOS-based aerogels

In the synthesis of silica aerogel by a two steps acid–base catalyzed sol–gel process, the effect of the basic catalyst (NH_4OH) at different time intervals on the physical and textural properties of the resulting aerogels has been investigated. It has been observed that the surface area of the aerogels enhanced from 618.81 to 655.58 m^2 g^{-1} with the increasing time from 6 to 24 h. This is because of the efficient surface modification of the gels by the tri-methyl groups before the ambient pressure drying. The enhancement in the surface area with an increase in the T value can be attributed to the fact that the gels with higher T values shrink less than those obtained for the lower T values. With the increasing time, condensation reaction is longer because the sols including high silica lead to form a dense silica network with relatively smaller pores. Also cumulative pore volume and average pore diameter are decreased and surface area is increased. But for lower T values, sols having less silica content, upon gelation, lead to the development of a gel network in which the silica chains are quite separated from each other and form bigger pores. Surface area is decreased and cumulative pore volume and average pore diameter are increased. Specific surface area, pore volume and average pore diameter of the aerogel have been given in Table 2. The obtained nitrogen adsorption– desorption isotherms at 77 K are depicted in Figs. 4(a) and (b).

It presents the amount of the gas adsorbed at equilibrium as a function of the partial pressure (p/p_o). The nitrogen physisorption isotherms obtained for all samples exhibited Type IV hysteresis loops, which are generally observed in mesoporous materials [33].The desorption cycles of the isotherms showed hysteresis loops in all of the aerogels, which were attributed to capillary condensation occurring in the mesopores.

Table 1. Characterization of the modified silica aerogels by drying at atmospheric pressure

Sample	%Volume shrinkage	% Moisture	Density (g/cm^3)	%Porosity
Addition of NH_4OH after 6 hours	97.84	3.74	0.039	98.18
Addition of NH_4OH after 24 hours	97.23	4.27	0.027	98.77

Table 2. Results of BET for the modified silica aerogels

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore size (nm)
Addition of NH_4OH after 6 hours	618.81	0.4848	3.1339
Addition of NH_4OH after 24 hours	655.58	0.4831	2.9475

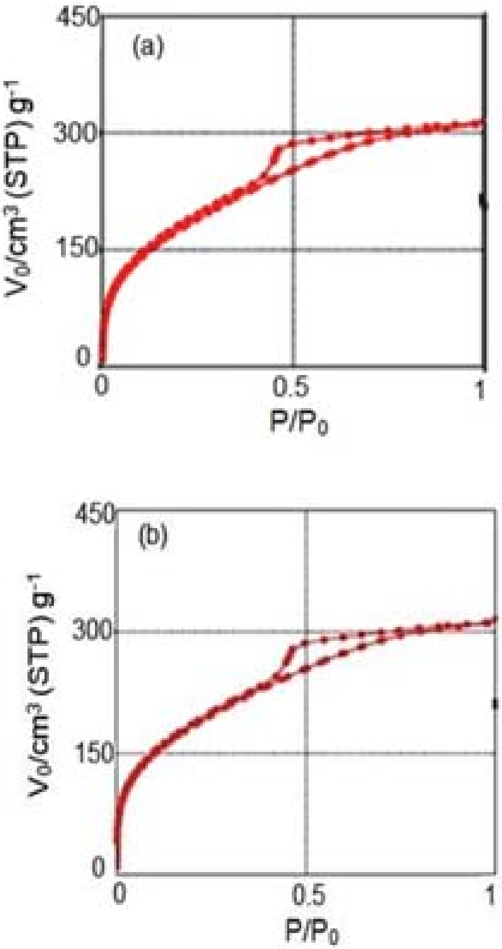


Fig. 4. N_2 adsorption/desorption isotherms of the prepared modified silica aerogels: (a) T = 6h, (b) T = 24h.

Figs. 5(a) and (b) illustrate pore size distribution (PSD) profiles of the TEOS-based aerogels synthesized at the ambient pressure. A significant change has been observed in the PSD profiles of the result aerogels at various T values. The peak pore diameter shifted to higher value as the time increased from 6 to 24 h.

Figs. 6a and 6b show the SEM images of the prepared silica aerogels in EtOH/TMCS/Hexane solution for modification of the wet gels for T = 6h and 24h, respectively. The SEM images of the prepared silica aerogels have porous network structure. There are white parts in the surface of the aerogel and the black parts, which are bulges and pores, respectively. The size of particles is below 100 nm, and the particle distribution of aerogels is uniform for using EtOH/TMCS as the modification solution. The EDX analysis confirms that the obtained aerogels at both times only contain Si and no impurity exists (Fig. 7).

The average size of the nanoparticles was determined using the Microstructure Measurement program and Minitab statistical software, in which the average size of the particles found, is 34.75 nm (T = 6h) and 38.8 nm (T = 24h).

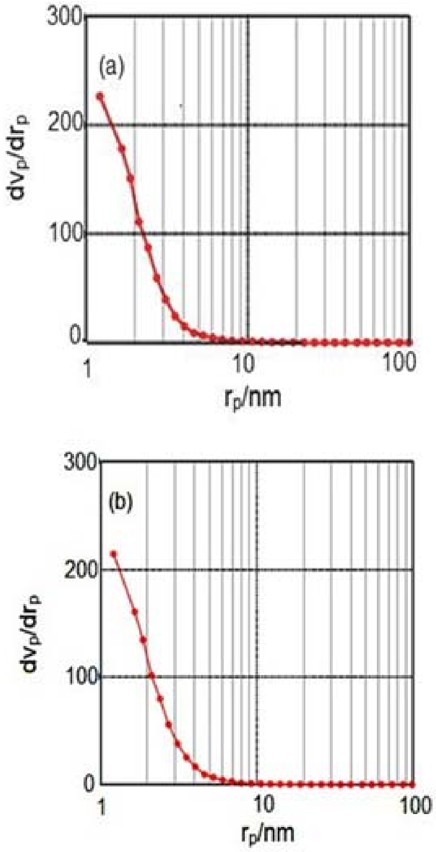


Fig. 5. Differential pore size distributions of the prepared modified silica aerogels: (a) T = 6h, (b) T = 24h.

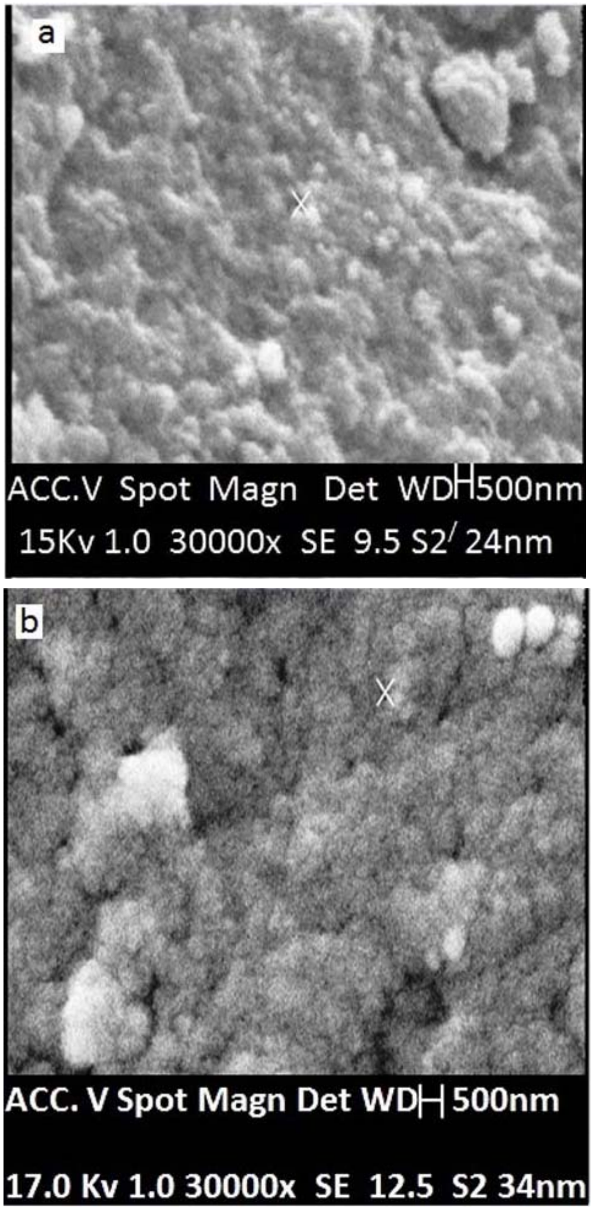
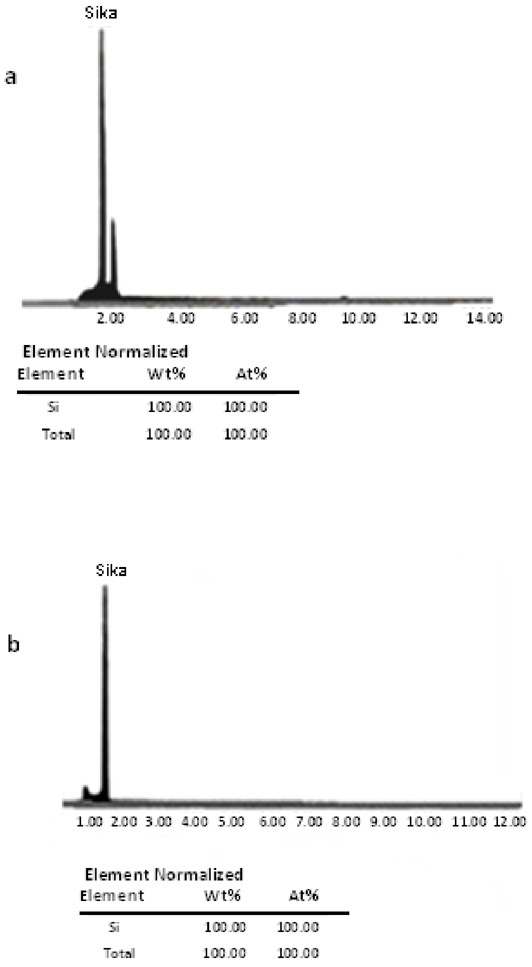


Fig. 6. SEM images of the prepared modified silica aerogels: (a) T = 6h, (b) T = 24h.

Rao *et al*. obtained the best quality silica aerogel in terms of low density, high percentage of porosity and high hydrophobicity with the molar ratio of TEOS: EtOH: acidic H_2O : basic H_2O : OXA: NH_4OH : HMDZ at 1 : 8 : 3.75 : 2.25 : 6.23×10^{-5} : 4×10^{-2} : 0.36, respectively, by ambient pressure dried method. Silica aerogels produced with low density (0.092 g/cm^3), high percentage of porosity (96.15%)[21]. Also, it has been reported the preparation of silica aerogels with the different mono, di and tri alkyl or aryl silylating agents such as MTMS, MTES, VTMS, PTMS, PTES, DMDMS, TMMS, TMCS, BTSA, HMDZ. Silica aerogels obtained with low density (0.105 g/cm^3), high percentage of porosity (94.61%) by using the tri alkyl silylating agents [22]. In this work, we studied the physical and hydrophobic properties of the aerogels and the time interval from 6 to 24 h before adding the basic catalyst. The surface area of the obtained aerogels increased from 618.81 to 655.58 m^2 g^{-1}, the bulk density of the aerogels decreased from 0.039 to



Element Normalized

Element	Wt%	At%
Si	100.00	100.00
Total	100.00	100.00

Element Normalized

Element	Wt%	At%
Si	100.00	100.00
Total	100.00	100.00

Fig. 7. EDX analysis of the prepared modified silica aerogels: (a) T = 6h, (b) T = 24h.

0.027 g/cm^3 and high percentage of porosity increased from 98.18 to 98.77. Also, in order to minimize the drying shrinkage, the surface of the gels was modified by using trimethylchlorosilane before drying at ambient pressure. With comparison this research and similar works [21,22], we found that with the increasing of time from 6 to 24 h before adding the basic catalyst and by using surface modifying agent (TMCS), silica aerogels obtained with low density, high percentage of porosity and high surface area.

4. Conclusions

In summary, nano-porous silica aerogel was synthesized by a two steps acid-base catalyzed sol-gel process followed by ambient pressure drying. The surface area of the obtained aerogels increased from 618.81 to 655.58 m^2 g^{-1} and the bulk density of the aerogels decreased from 0.039 to 0.027 g/cm^3 cm^{-3} with an increase in the T value from 6 to 24 h, respectively. In order to minimize the drying shrinkage, the surface of the gels was modified by using trimethylchlorosilane (TMCS) before the ambient pressure drying and avoids the condensation reactions between the silica clusters. In order to get the aerogels with the suitable physical and hydrophobic properties, the time interval was varied from 6 to 24 h before adding the basic catalyst.

Acknowledgment

The authors are grateful to Imam Khomeini International University and Department of Chemistry, Iran University of Science and Technology for the financial support and using from laboratory equipments for this work.

References

[1] S. Maury, P. Buisson, A. C. Pierre, J. Mo.Catal. B: Enzymatic 269 (2002)19-20.

[2] P. R. Aravind, P. Shajesh, G. D. Soraru,K.. G. K. Warrier, J. Sol-Gel Sci. Technol. 54 (2010) 105-117.

[3] M. Schmidt, F. Schwertfeger, J. Non-Cryst. Solids. 225 (1998) 364-368.

[4] V. Gibiat, O. Lefeuvre, T. Woignier, J. Pelous, J. Phalippou, J. Non-Cryst.Solids. 186 (1995) 244-255.

[5] J. Chwastowski, J. Figiel, A. Kotarba, K. Olkiewicz, L. Suszycki, J Nucl. Instrum. Methods Phys. Res. A. 504 (2003) 222-227.

[6] T. Woignier T, J. Reynes, J. Phalippou, J. L. Dussossoy, N. N. Jacquet- Francillon, J. Non-Cryst. Solids. 225 (1998) 353-357.

[7] T. Woignier, J. Reynes, J. Phalippou, J. L. Dussossoy, J. Sol-Gel Sci. Technol. 19 (2000) 833-837.

[8] J. Reynes, T. Woignier, J. Phalippou, J. Non-Cryst. Solids. 285 (2001) 323-327.

[9] T. Woignier, J. Primera, M. Lamy, C. Fehr, E. Anglaret, R. Sempere, J. Phalippou, J. Non-Cryst. Solids. 350 (2004) 299-307.

[10] C.E. Carraher, J. Polymer News. 30 (2005) 386-388.

[11] J. M.Schultz, K.I. Jensen, F. H. Kristiansen, J. Solar Energy Mat. Solar Cells. 89 (2005) 275-285.

[12] E. K. Chul, S.Y. Jong, J. H. Hae, J. Sol-Gel Sci. Technol. 49 (2009) 47-52.

[13] L.W. Hrubish, J. Chem. Ind. 17 (1990) 824-827.

[14] J. Fricke, J. Aerogels, Springer verlag, Berlin, 1986.

[15] R. J. Ayen, P. A. Iacabula, J. Rev. Chem. Eng. 5 (1988) 157-198.

[16] M. Schneider, A. Baiker, J. Catal. Rev. Sci. Eng. 37(1995) 515-556.

[17] A. P. Rao, A. V. Rao, K. H. Bangi, J. Sol-Gel Sci. Technol. 47 (2008) 85-94.

[18] H. Tamon, T. Kitamura, M. Okazaki, J. Colliod Interf. Sci. 19 (1998) 353-359.

[19] A. O. Rami, E. R.Houssam, J. App. Surf.Sci. 257 (2010) 276-281.

[20] P. Rao, A. V.Rao, J. Sol-Gel Sci. Technol. 36 (2005) 285-292.

[21] P. Rao, G. M. Pajonk, A.V. Rao, J. Mater. Sci. 40 (2005) 3481-3489.

[22] A. P. Rao, A.V. Rao, G. M. Pajonk, J. Appl. Surf. Sci. 253 (2007) 6032-6040.

[23] A. Hilonga, K. J. Kil, P.B. Sarawade, K. H. Taik, J. Alloys Compd. 487 (2009) 744-750.

[24] P.B. Sarawade, K. J. Kil, K. H. Kun, K. H. Teak, J. Appl. Surf. Sci. 254 (2007) 574-579.

[25] P.M. Shewale, A. V. Rao, A. P. Rao, J. Appl. Surf. Sci. 254 (2008) 6902-6907.

[26] L. Jyoti, A. Gurav, A.V. Rao, D. Y.Nadargi, P. Hyung-Ho, J. Mater. Sci. 45 (2010) 503-510.

[27] V.M. Gun’ko, M.S. Vedamuthu, G.L. Henderson, J.P. Blitz, J. Colloid Interface Sci. 228 (2000) 157-170.

[28] N. Hering, K. Schriber, R. Riedel, O. Lichtenberger, J.Woltersodorf, J. Appl.Organo-metallic Chem. 15 (2001) 879-886.

[29] P.M. Shewale, A. V. Rao, A. P. Rao,S. D. Bhagat, J. Sol-Gel Sci. Technol. 49 (2009) 285-292.

[30] L. Jiu Wang, S. Yu Zhao, M. Yang, J. Mat. Chem. Phy. 113 (2009) 485-490.

[31] D. Y. Nadargi, S. S.Latthe, A. V. Rao,J. Sol-Gel Sci. Technol. 49(2009)53-59.

[32] N. Thuadaij, A. Nuntiya, J. Sci. 35 (2008) 206-211.

[33] S.D. Bhagat, Y. H. Kim, M. J. Moon, Y. S. Ahh, J. G. Yeo, J. Solid State Sci. 9 (2007) 628-635.