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The Effect of Synthesis Parameters on Structure and Properties of Silica Xerogels

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Abstract

Introduction: Sol gel derived silica matrices have many promising features such as high homogeneity, product purity, chemical and physical stability and porosity. These porous materials with nanosized pores enable loading of numerous biologically active substances into matrices.

Objective: The aim of this study was to investigate the effect of synthesis parameters on structure of silica xerogels.

Methods: The effect of two different catalysts (NH_4OH and HCl), drying temperature and water content on properties of xerogels were studied. Chemical composition and structure of xerogels were analyzed by Fourier Transfer Infrared Radiation (FTIR) and Scanning Electron Microscopy (SEM), respectively. Specific surface area and pore size of xerogels were examined by BET.

Results: FTIR results confirmed the forming of Si-O-Si bonds which proved condensation of silanols. According to results, acid-base catalyst, lower temperature for drying and lower water content caused to form crack free xerogels. SEM results showed that acid-base catalyzed xerogels were more porous and pores of acid-base catalyzed xerogels were cylindrical while acid catalyzed xerogels had plate like pores. BET results represented that using higher drying temperature, higher water content and acid-base catalyst increased pore size of xerogel. Also BET results proved that these xerogels had nanosized pores(~4nm).

Conclusion: We conclude that different active substances can be entrapped in xerogels by changing synthesis parameters and achieving different pore sizes.

Keyword: Silica, Xerogel, Sol gel, Catalyst, Drying temperature

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1. Introduction

The sol gel method has been active area of research for the past last three decades and it is highly efficient due to the low temperature of the chemical process, product purity, high homogeneity, ability to insert numerous biologically active substances during preparation. In addition, one could release this molecules in a controlled manner through the network pores into surrounding liquid.[1-4] Silica xerogels obtained via this method are nontoxic and biocompatible in vivo and they cause no adverse tissue reactions and degrade in the body to silicic acid, $Si(OH)_4$, which would be eliminated through the kidneys. These material have a wide range of application fields such as catalysis, controlled drug release, implants, packaging and surgery tools [1, 5, 6].

Basically the sol gel process means the synthesis of an inorganic network by chemical reaction in solution at low temperature. It involves the production of a colloidal suspension which is called sol by mechanically mixing a liquid alkoxide precursor, such as tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS), water, a cosolvent and acid or base catalyst . After gelation a wet gel forms a globally connected solid matrix, which after drying forms the dry gel state, called xerogel [7, 8]. Different polymeric structures such as linear, entangled chains, cluster and colloidal particles can be achieved depending upon the water: alkoxide molar ratio (R), pH, temperature, catalyst and solvent [9]. In this article two different catalyst (HCl and NH_4OH), water content and drying temperature were used to prepare xerogels. Properties of these xerogels were analyzed by FTIR, SEM and BET.

2. Material and Methods

Tetraethylorthosilicate ($TEOS,Si(OC_2H_5)_4$) was purchased from sigma-Aldrich chemical company, Ammonia(NH_4OH), hydrochloric acid(HCl) and ethanol were purchased from Merck company.

five samples of Silica xerogels with different catalysts, water content and drying temprature were prepared by the sol gel method. For preparing xerogels, solution of TEOS and ethanol were mixed for 30 min then water, HCl (0.01M) as catalyst were added and stirred for 30 min to form homogenous sol. For producing acid catalyst xerogel, sol is covered with parafilm and left for gelation. For preparing acid-base catalyst xerogel, after 24 hours, NH_4OH (1M) was added to sol to form continuous gel. The sol composition and drying temperature are listed in table1.

Table 1: Composition of sols

sample	TEOS[ml]	Ethanol[ml]	H_2O[ml]	HCl 0.01M[ml]	Ammonia [ml]	Drying temprature [ºC]
1	11.4	23.4	4	0.1	0	27
2	11.4	23.4	6	0.1	0	27
3	11.4	23.4	4	0.1	2	27
4	11.4	23.4	6	0.1	2	27
5	11.4	23.4	6	0.1	2	80

Table 2: properties of silica xerigels

sample	Gelation time	Surface area[m^2/g]	Average pore diameter[nm]
1	31680	-	-
2	10080	-	-
3	5	689.6	3.953
4	1	734.6	4.489
5	1	560.2	3.576

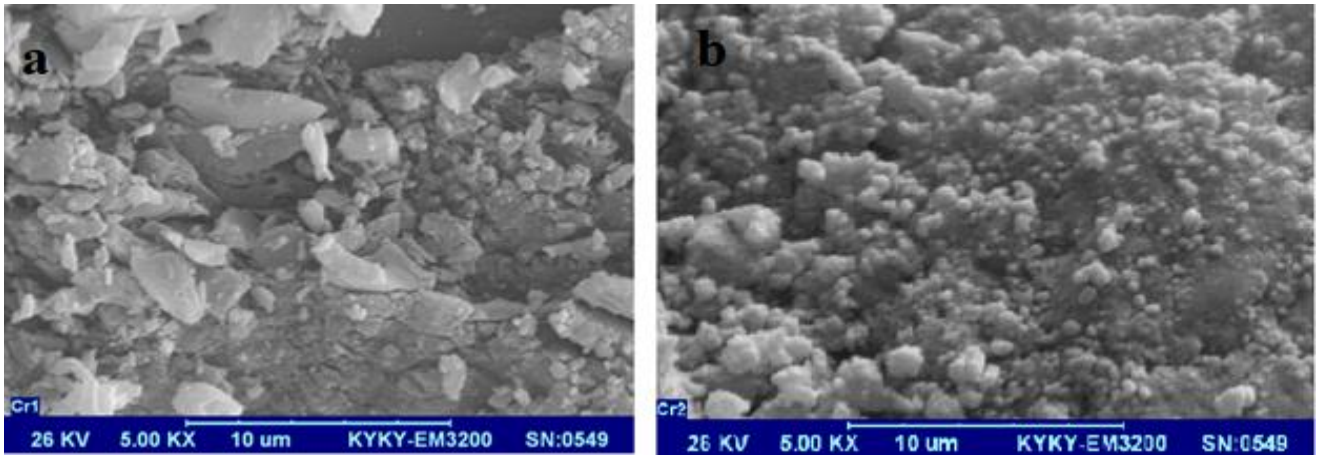

Figure 1: (a) acid catalyzed xerogel, b) acid-base catalyzed xerogel

A FTIR spectrometer (EQUINOX55- BRUKER) was used for analysis of chemical composition. The spectra were measured over rang of 400-4000 cm^{-1}. BET technique (micromeritics-Gimini237-america) based on nitrogen gas adsorption was used for measurement of specific surface area and pore size of xerogels. Scanning Electron Microscopy (SEM, VEGAM0- TESCAN Germany) was used to study microstructure of xerogels.

3. Results

The Effect of type of the catalyst and drying temperature on the gelation time, surface area and pore size of the matrices are listed in table 2. Clearly, there are significant differences in properties of xerogels. For acid-catalyzed samples, surface area and pore size were too small to be measured with BET technique. It is obvious that, xerogels with highest water content have highest surface area and pore size because by evaporating the water more porous xerogels are achieved. Increasing the drying temperature decreases the surface area and pore size of matrices because wet silica network surrounds the pores that are filled with ethanol and water. When the gel is dried in higher tempratures, ethanol and water quickly evaporate and the gel ages by additional cross linking of unreached –OH and –OR groups. This will

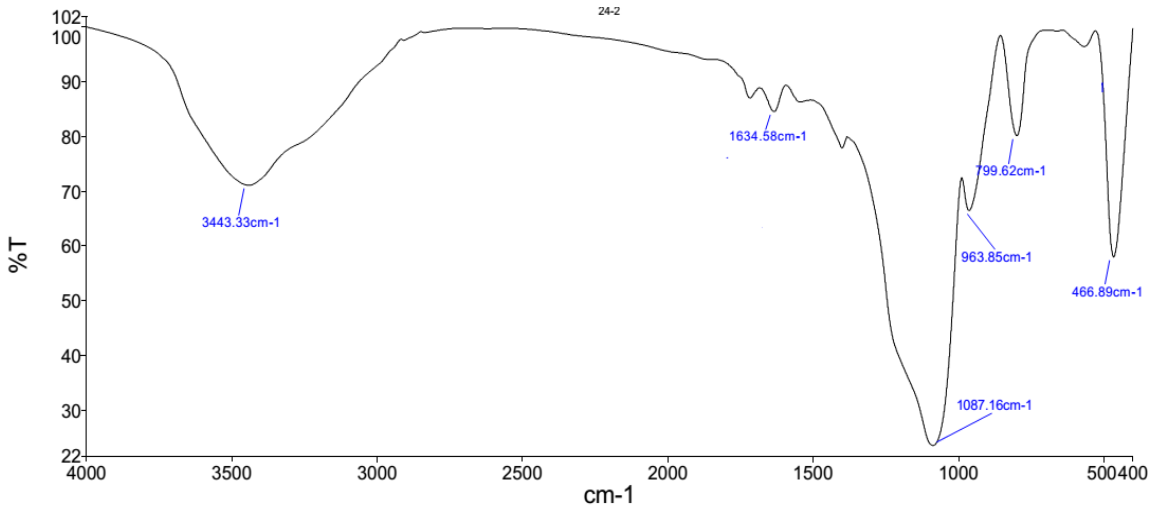

Figure 2: FTIR spectra of silica xerogel

cause the network collapse, which results in less pore size and surface area.

The SEM images of acid catalyzed and acid-base catalyzed xerogels are shown in figure1. The acid-base catalyzed xerogels are more particulated. The fast polymerization of hydrolyzed silanols in the presence of base catalyst, favors formation of seprated clusters, as it was excpected. Acid-base catalyzed xerogels were more porous. Pores of acid-base catalyzed xerogels were cylindrical, while acid catalyzed xerogels had plate like pores.

FTIR spectra of all samples of silica xerogels are similar. Figure 2 present FTIR spectra of one of the silica xerogels. Peaks at 466 cm^{-1}, 799 cm^{-1} and 963 cm^{-1} are, respectively, assigined to Si-O-Si asymmetric bending, symmetric stretching viberation of Si-O-Si bonds of ring structures and C-H rocking in CH_3 in TEOS. Peaks at 1087 cm^{-1} and 1634 cm^{-1} are, respectively, related to Si-O-Si symmetric stretching in cyclic structures and viberation of water molecules. The spectral range of 2750-3750 cm^{-1} in all samples is associated to H-bonded SiOH stretching vibration and H-bonded water.[1, 4, 7, 10]

4. Conclusion

Properties of the sol gel method made it powerful approach for loading numerous biological substances in matrices and use them as drug carriers. Different morphology and physical properties can be achieved by altering synthesis parameters like water content, type of catalyst and drying temperature. Silica xerogels with highest water content exhibited the highest surface area and pore size. Increasing drying temperature decreases surface area and pore size of xerogels. Acid catalyzed xerogels are more porous and have higher surface area and larger pore size (4.4 nm). We conclude that different active substances can be entrapped in xerogels by changing synthesis parameters and achieving different pore sizes.

Conflict of Interests

The authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest, or non-financial interest in the subject matter or materials discussed in this manuscript.

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No Applicable.

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