



Processing of sol–gel silica using gamma radiation

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Abstract

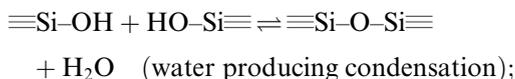
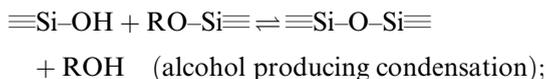
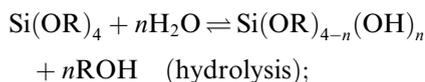
The affect of gamma radiation on the structure of silica gels obtained using tetramethoxysilane (TMOS) as chemical precursor and molar ratios TMOS:H₂O varying from 1:4 up to 1:32 was studied. The structure of the silica gels produced was determined by X-ray diffraction and nitrogen gas sorption. The samples were irradiated with ⁶⁰Co γ-rays to doses of 200 Gy. The xerogels obtained under gamma radiation had larger specific surface area and pore volumes than the gels obtained using a conventional sol–gel process. The observed variation in those quantities was 2–100 times larger. Gamma radiation promotes an overall stabilization of the polymerization process, resulting in more reproducible structures. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Sol–gel process have been studied and developed since the process is well suited for preparing materials and designing devices with specific properties [1–6]. The sol–gel preparation of materials starts from a solution containing mainly metal-organic compounds such as metal alkoxides [1,4,5]. The solution is changed to a sol, in which clusters of molecules or fine particles are dispersed in the liquid as a result of hydrolysis and polycondensation of the compounds [1,4,5]. In most cases, the sol is gelled by further reaction. Heating of the gelled mass to higher temperatures changes the gel to a glass, ceramic or composite [2].

In the silica-based sol–gel process, typically a silicon alkoxide, for example tetraethoxysilane (TEOS) or tetramethoxysiloxane (TMOS) and an amount of water are dissolved in a mutual solvent in the presence of a catalyst (acid or basic). Three bimolecular nucleophilic reactions are generally used to describe the process [1]:



where R is an alkyl group such as CH₃, C₂H₅, C₃H₇, or C₄H₉ and *n* varies from 1 to 4. The actual

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complexity of the process is not indicated by this simplified representation, though, because many different intermediates are formed during the reaction [7]. The macroscopic consequence of this complex sequence of reactions is the conversion of the initial liquid to a gel, which becomes a rigid solid after loss of solvent [8]. A variety of physical and chemical factors (e.g., temperature, pressure, pH, concentration of reagents and catalysts) affect the polymerization process and thus the properties of the final product [1–6].

Chemical changes in material irradiated with photons with energies greater than a few eV are the result of reactions between ions and excited molecules and, in many systems, of free radicals formed from them [9]. The effects of ionizing radiation on organic compounds, colloids and the radiation syntheses of inorganic chemicals and organometallic compounds are described by several authors [9,10]. Zhu et al. [11] explored the possibility of using γ -radiation of a colloidal solution combined with the sol–gel process to prepare glass–metal composites.

In our work we study the effect of γ -radiation on the structure of silica gels obtained from the sol–gel process.

2. Experimental

Silica gels were made from tetramethoxysilane ($\text{Si}(\text{OCH}_3)_4$, Aldrich Chemical; grade assay 98%, cat. no. 21,847-2, used without further purification) hydrolyzed with deionized water (electrical conductivity $\sim 0.05 \mu\text{S cm}^{-1}$ at 298 K). Neither acid nor basic catalyst nor a mutual solvent was used. Tetramethoxysilane solutions using molar ratios of TMOS to H_2O equal to 1:4; 1:8; 1:16 and 1:32 were prepared [12,13].

Two different experiments were prepared. In the first one, the reactions were carried out under ambient pressure and at room temperature (typically 23–27°C) with stirring to homogenize the solution for periods of time varying from 20 min for molar ratio equal to 1:32 up to 100 min for solution with molar ratio of 1:4. The homogenized solutions were poured into a flask (polystyrene or polymethyl methacrylate) which could be sealed.

The wet gels were aged at room temperature for about 4 weeks, then dried at room temperature for 2 weeks, followed by further heat treatment to 700°C in an oven.

2.1. Gamma irradiation

In the second type of experiments, the TMOS solutions were irradiated with a ^{60}Co γ -ray source (Gammacell 220, Atomic Energy of Canada). The solution was poured into the cobalt-60 gamma cell 10 s after the addition of the reagents (TMOS + H_2O) into the reaction flask (perfluoroalkoxy resin – PFA), which was then sealed. The solutions were stirred to homogenize with a special device (patent pending). The irradiation conditions are summarized in Table 1.

The wet gels appeared homogeneous and translucent after irradiation. They were aged and heat treated as the gels obtained in the first part of the experiments.

2.2. Structural analysis

After the thermal treatment, X-ray diffractograms (XRD) of the xerogels obtained from the non-irradiated and irradiated solutions were obtained (Geigerflex, Rigaku) at a scanning rate of $0.13^\circ \text{ s}^{-1}$ in the 2θ range from 25° to 35° , using graphite-monochromated $\text{Cu-K}\alpha$ radiation [13]. The gas sorption, BET method, (Autosorb 1, Quantachrome) was measured. The specific (BET) surface area, total pore volume and mean pore radius of dry gels were determined by a standard nitrogen adsorption–desorption technique [14].

Table 1
Typical gamma irradiation conditions

| TMOS: H_2O molar ratio | Stirring time (min) | Irradiation time (min) | Gamma dose (Gy) |
|---|------------------------|---------------------------|--------------------|
| 1:4 | 120 | 320 | 190 |
| 1:8 | 100 | 330 | 200 |
| 1:16 | 100 | 310 | 180 |
| 1:32 | 50 | 310 | 180 |

3. Results

The gels appeared to be almost completely amorphous and no peaks attributable to crystalline materials were detected in the XRD. Fig. 1 gives the XRD pattern of typical gels: (a) obtained from a non-irradiated solution TMOS:H₂O molar ratio of 1:32 and (b) gel obtained from a γ -irradiated solution TMOS:H₂O molar ratio of 1:32.

The specific surface area, specific pore volume and average pore radii for all xerogel compositions are presented in Fig. 2.

The observed average pore radius varied approximately from 1.1 to 1.6 nm for irradiated samples. The largest pore radius correspond to gels made with 1:32 M TMOS:H₂O molar ratio. For gels made with 1:4 M molar ratio we observed (Fig. 2) a standard deviation of 1.2 nm. The specific pore volume and the specific surface area of all samples (irradiated and non-irradiated) increased as the molar ratio increased from 1:4 to 1:32 M.

Nitrogen adsorption–desorption isotherms for irradiated and non-irradiated samples are shown in Figs. 3 and 4.

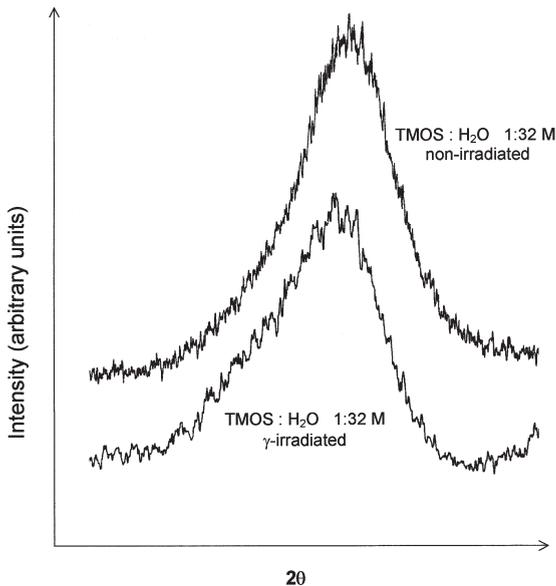


Fig. 1. Typical XRD patterns of irradiated and non-irradiated xerogels.

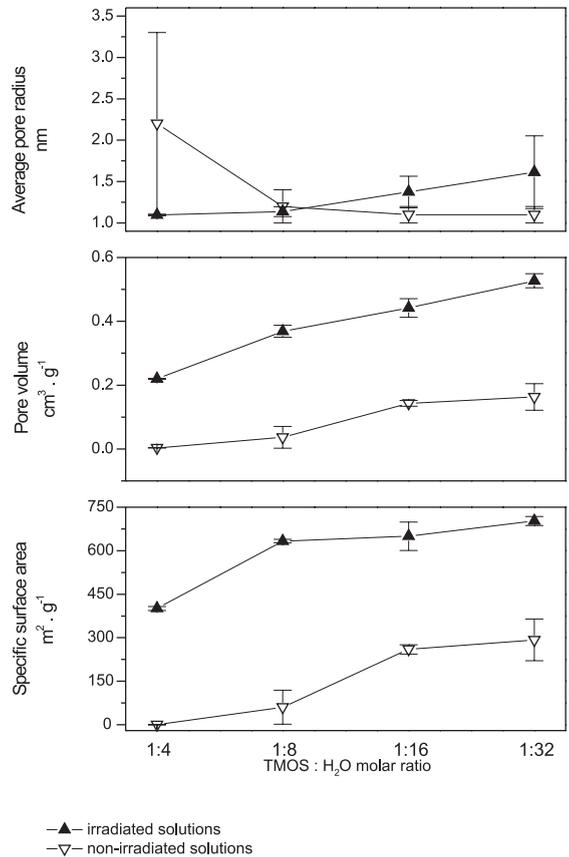


Fig. 2. Specific surface area, specific pore volume and average pore radii for irradiated and non-irradiated xerogels. Lines are drawn as guides for the eye.

4. Discussion

The specific surface areas increased with increasing water content as does the pore volume (Fig. 2). This trend, reported previously [15], was attributed to an increase in the hydrolysis rate as water concentration increases. The increased hydrolysis rate increased the condensation rate and, hence, cross-linking of the polymeric chains. This cross-linking process causes the development of a particulate microstructure, which is not as dense as silica gels with less cross-linking [16].

The observed (see Fig. 2) effects of γ -radiation on the silica gel structures were increases of specific surface area and specific pore volume for all TMOS:H₂O molar ratios. We observed a larger

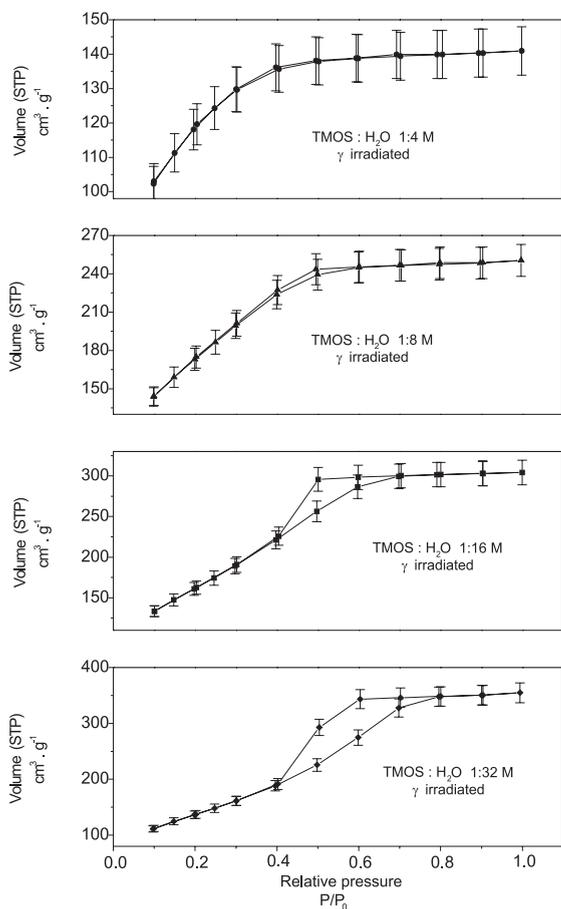


Fig. 3. Nitrogen adsorption–desorption isotherms for γ -irradiated xerogels. Lines are drawn as guides for the eye.

change in average pore radius for the non-irradiated 1:4 M ratio sample and for larger water contents the observed average pore radii were larger for γ -irradiated gels. The γ -radiation apparently caused formation of greater amount of structural voids in the silica gel network. An effect of γ -radiation is that the structure of the irradiated gel is more homogeneous and more reproducible.

For the γ -irradiated xerogels (Fig. 3), the isotherm for the 1:4 M sample is type I [14], indicating a microporous material, though there is evidence of vestiges of a hysteresis loop, characteristic of capillary filling of mesopores [14]. As the water content increased (up to a molar ratio of 1:32) the volume of gas absorbed increases (Figs. 3

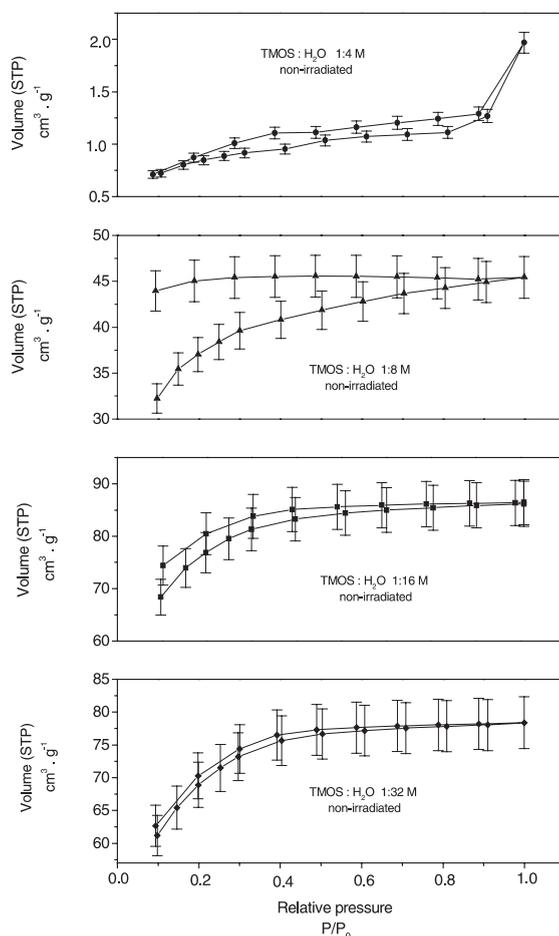


Fig. 4. Nitrogen adsorption–desorption isotherms for non-irradiated xerogels. Lines are drawn as guides for the eye.

and 4), while the isotherms become progressively more like those of type IV [14]. Based on the shapes of the isotherms of the irradiated samples, we suggest a more irregular nitrogen adsorption–desorption process. Again, an effect of γ -radiation is to reduce the irregularity.

5. Conclusion

Silica xerogels gelled while being exposed to gamma radiation had larger specific surface area and specific pore volumes than gels obtained using a conventional sol–gel process.

Gamma radiation promotes an overall stabilization of the polymerization process, resulting in more reproducible structures.

References

- [1] J.F. Brinker, G.W. Scherer, *Sol–Gel Science the Physics and Chemistry of Sol–gel Processing*, Academic Press, New York, 1990.
- [2] S. Sakka, T. Yoko, *Ceram. Int.* 17 (1991) 217.
- [3] R.J.P. Corriu, D. Leclercq, *Angew. Chem. Int. Ed. Engl.* 35 (13/14) (1996) 1420.
- [4] L.L. Hench, J.K. West, *Chem. Rev.* 90 (1) (1990) 33.
- [5] L.L. Hench, W.L. Vasconcelos, *Ann. Rev. Mater. Sci.* 20 (1990) 269.
- [6] D.L. Meixner, P.N. Dyer, *J. Sol–Gel Sci. Technol.* 14 (1999) 223.
- [7] J. Sanchez, A. McCormick, *J. Phys. Chem.* 96 (1992) 8973.
- [8] M.A. Cowen, S.L. Gilbert, M. Gonsalves, A.R. Hillman, S. Bruckenstein, *J. Chem. Soc., Faraday Trans.* 92 (6) (1996) 1079.
- [9] R.J. Woods, A.K. Pikaev, *Applied Radiation Chemistry: Radiation Processing*, Wiley, New York, 1994.
- [10] M. Hässinky (Ed.), *Actions chimiques et biologiques des radiations*, vols. 1–15, Masson, Paris, 1955–1971.
- [11] Y. Zhu, Y. Qian, M. Zhang, Z. Chen, G. Zhou, *J. Mater. Chem.* 4 (10) (1994) 1619.
- [12] W.L. Vasconcelos, PhD thesis, University of Florida, Gainesville, 1989.
- [13] A.M.M. Santos, DSc thesis, Universidade Federal de Minas Gerais, Belo Horizonte, 1998, in Portuguese.
- [14] S. Lowell, J.S. Shields, *Powder Surface Area and Porosity*, 3rd Ed., Chapman and Hall, London, 1991.
- [15] C.J. Brinker, K.D. Keefer, D.W. Shaefer, R.A. Assink, B.D. Kay, C.S. Ashley, *J. Non-Cryst. Solids* 63 (1984) 45.
- [16] M.D. Curran, D.D. Pooré, A.E. Stiegman, *Chem. Mater.* 10 (1998) 3156.