

Influence of Processing Variables on the Pore Structure of Silica Gels Obtained with Tetraethylorthosilicate

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In this work it was evaluated the influence of the type and concentration of the acid catalyst and the gelation temperature on the structure of pores of silica gels obtained with TEOS. The values of the major structural parameters related to the pores such as volume fraction of pore (Vv), surface area per unit volume (Sv), the average pore size (r_p) and the connectivity of pores (Gv), obtained in this work showed the possibility of tailoring the pore structure of silica gels by changing the processing variables. For the HF catalyzed gels the values of average pore radius varied from 6.8 nm to 21.6 nm, and the gelation time varied from 2 min to 140 min. For the gels obtained in this work the activation energy for gelation (E) was found to be 11.8 kcal/mole.

Keywords: silica, sol-gel, nanostructure

1. Introduction

A new generation of ceramic materials of high structural and unique properties has been emerged with the sol-gel processing, due to the possibility of manipulation and control of the nanostructure, which occurs from the first stages of the gel formation¹⁻³.

Porous membranes have been used in separation processes of mixtures, solutions and suspensions involving species of different sizes and chemical nature. These applications require the use of porous materials with specific structural characteristics⁴.

The sol-gel processing is considered to be the most practical one for ceramic membrane synthesis, specially due to the possibility of designing the geometry of the pore network and the feasibility of obtaining narrow pore size distributions. Thus, acting in the processing conditions, one can change the pore structure and adapt the permeability of the silica monoliths to the different separation process desired^{4,5}.

In this work it is carried out an analysis of the porous structure of silica gels obtained via hydrolysis of tetraethylorthosilicate (TEOS). It was evaluated the influence of the acid catalyst and the gelation temperature on the structural parameters of the silica gels.

2. Experimental

Sol-gel silica was prepared by acid catalysis of tetraethylorthosilicate (TEOS, Aldrich Corp.) and deionized

water, with ethanol (Merck Corp.) used as solvent. As catalyst, nitric acid (HNO₃, Merck Corp.), hydrofluoric acid (HF, Merck Corp.) and hydrochloric acid (HCl, Merck Corp.) were used. The molar ratio H₂O/TEOS was 16 and molar ratio ethanol/TEOS was 6.

The sols were cast into cylindrical containers. The gelation of the sols obtained via HCl, HNO₃ and various concentrations of HF occurred at room temperature. In order to study the influence of the gelation temperature in the structural parameters of the silica gel, the gelation was also carried out at different temperatures, for gels catalyzed with a mixture of HNO₃ (pH = 1.5) and HF (0.03 M). In this set of experiments, the gelation temperatures used were 27 °C, 40 °C, 50 °C e 60 °C.

The aging of the gels was carried out at 60 °C during 48 h. The drying was made at 80 °C during 48 h. After drying the samples were analyzed using an automatic gas sorption machine (Autosorb 1, Quantachrome Corp.) for specific volume, specific surface area and average pore size. Bulk density was evaluated by mercury pycnometry.

The gelation time (t_{gel}) was arbitrarily taken as the time at which the viscosity of solution increased suddenly. The viscosity measurements were performed in a viscosimeter with agitation velocity and temperature control (η Realogic).

The monolithicity was evaluated using the ratio between the weight of the largest entire part of the gel and the total weight of the gel after drying.

3. Results

3.1. Influence of the type and concentration of the catalyst

The values of pH, gelation time (t_{gel}) (at room temperature), specific surface area (S_p), specific pore volume (V_p) and average pore radius (r_p) for the silica gels obtained via acid catalysis of TEOS using HNO_3 , HCl and HF , with an acid/TEOS molar ratio (M) of 0.1, are listed in Table 1. Table 2 presents the data obtained for t_{gel} , S_p , V_p and r_p for gels fabricated with TEOS and catalyzed with HNO_3 (pH = 1.5) and HF (with concentrations of 0.02; 0.03; 0.04; 0.06; 0.08 and 0.12 M). The variation of t_{gel} and r_p with HF concentration are shown in Fig. 1 and Fig. 2, respectively. Table 3 presents the data on volume fraction of pores (V_v), solid-pore surface area per unit volume (S_v), genus (G_v) and permeability (K_p) for the silica gels.

3.2. Influence of the gelation temperature

The values of the processing variables and the physical properties of the silica gels obtained with the various gelation temperatures are shown in Table 4. Fig. 3 shows the relation between gelation time and gelation temperature obtained in this work.

4. Discussion

Commonly, t_{gel} can be decreased by processing parameters that increase the condensation rate^{5,7}. For silica gels, gelation is typically faster in the presence of a base or HF than when using other acids, as indicated in Table 1. The

pore structure of the gels obtained in different conditions is quite different. The specific surface area of the gels varied from 727 m^2/g (HNO_3) to 98 m^2/g (HF). The specific volume of pores changed from 0.42 cm^3/g (HNO_3) to

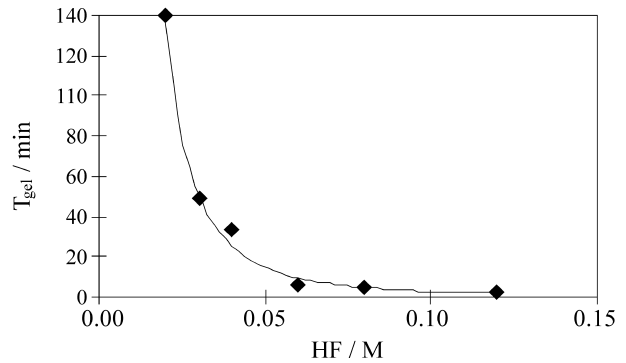


Figure 1. Gelation time as a function of HF concentration.

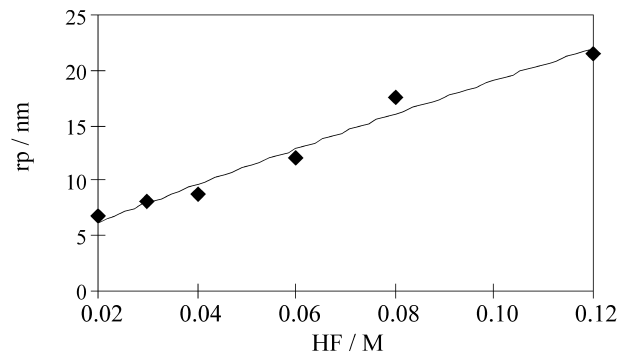


Figure 2. Average pore radius as a function of HF concentration.

Table 1. Values of gelation time (t_{gel}), specific surface area (S_p), specific pore volume (V_p) and average pore radius (r_p) for the silica gels obtained through acid catalysis of TEOS using HCl , HNO_3 and HF .

Acid acid/TEOS = 0.1	pH	t_{gel} (min)	S_p (m^2/g)	V_p (cm^3/g)	r_p (nm)
HNO_3	0.5	2880 ± 60	727 ± 22	0.42 ± 0.02	1.2 ± 0.1
HCl	0.8	660 ± 10	532 ± 16	0.85 ± 0.04	3.2 ± 0.1
HF	1.5	9.0 ± 0.1	98 ± 3	1.56 ± 0.08	31.6 ± 1.3

Table 2. Values of gelation time (t_{gel}), specific surface area (S_p), specific pore volume (V_p), average pore radius (r_p) and bulk density (ρ_v) of silica gels catalyzed by mixtures of HNO_3 and HF at different concentrations.

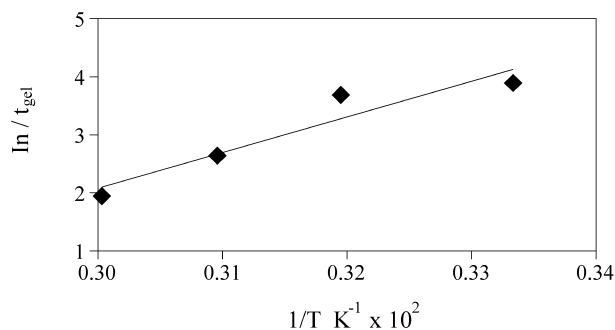
HF (mol/L)	t_{gel} (min)	S_p (m^2/g)	V_p (cm^3/g)	r_p (nm)	ρ_v (g/cm^3)
0.02	140 ± 7	360 ± 10	1.21 ± 0.05	6.8 ± 0.3	0.65 ± 0.01
0.03	49 ± 3	305 ± 9	1.23 ± 0.06	8.1 ± 0.3	0.54 ± 0.01
0.04	33 ± 2	344 ± 10	1.49 ± 0.07	8.7 ± 0.3	0.54 ± 0.03
0.06	6.0 ± 0.3	268 ± 8	1.61 ± 0.08	12.0 ± 0.5	0.55 ± 0.01
0.08	5.0 ± 0.1	168 ± 5	1.50 ± 0.07	17.5 ± 0.7	0.53 ± 0.01
0.12	2.0 ± 0.1	148 ± 4	1.60 ± 0.08	21.6 ± 0.9	0.51 ± 0.01

Table 3. Values of volume fraction of pores (V_v), solid-pore surface area per unit volume (S_v), genus (G_v) and permeability (K_p) for the silica gels catalyzed with HNO_3 and HF.

HF (mol/L)	V_v	S_v (10^6 cm^{-1})	G_v (10^{16} cm^{-3})	K_p (10^{-14} cm^2)
0.02	0.79 ± 0.04	2.34 ± 0.10	75.9 ± 18.4	4.6 ± 0.7
0.03	0.66 ± 0.04	1.67 ± 0.08	20.7 ± 5.8	5.5 ± 0.8
0.04	0.80 ± 0.08	1.86 ± 0.16	40.6 ± 18.6	7.6 ± 1.3
0.06	0.89 ± 0.06	1.47 ± 0.07	31.4 ± 8.8	15.9 ± 2.4
0.08	0.80 ± 0.05	0.89 ± 0.04	4.3 ± 1.2	30.4 ± 4.4
0.12	0.82 ± 0.06	0.75 ± 0.06	2.8 ± 0.8	47.6 ± 7.3

Table 4. Values of gelation time (t_{gel}), monolithicity, specific surface area (S_p), specific pore volume (V_p), average pore radius (r_p) and bulk density (ρ_v) of silica gels obtained with the various gelation temperatures.

Gelation temperature ($^{\circ}\text{C}$)	t_{gel} (min)	Monolithicity (%)	S_p (m^2/g)	V_p (cm^3/g)	r_p (nm)	ρ_v (g/cm^3)
27 ± 1	49 ± 2	94 ± 3	305 ± 9	1.23 ± 0.06	8.1 ± 0.3	0.54 ± 0.01
40 ± 1	40 ± 2	100 ± 1	461 ± 14	1.65 ± 0.08	7.2 ± 0.3	0.65 ± 0.01
50 ± 1	14.1 ± 0.2	100 ± 1	382 ± 11	1.34 ± 0.07	7.0 ± 0.3	0.64 ± 0.01
60 ± 1	7.1 ± 0.1	94 ± 3	314 ± 9	1.13 ± 0.06	7.2 ± 0.3	0.64 ± 0.01

**Figure 3.** Gelation time as a function of gelation temperature.

1.56 cm^3/g (HF) and the pore radii changed from 1.2 nm (HNO_3) to 31.6 nm (HF).

The presence of HF has a strong influence on gelation time. Iler⁷ proposes that the polymerization process involves, temporarily, the expansion of coordination number of silicon from 4 to 5 or 6, and the effectiveness in the polymerization process of the fluorine anion is due to its smaller ionic radius compared to that of the hydroxyl group. According to the Iler theory, the polymerization reaction is catalyzed by hydroxyl groups at pH's greater than 2, while for smaller pH, the polymerization rates are proportional to the H^+ and F^- ionic concentrations. It can be seen from Table 2 that as the concentration of HF changes from 0.02 M up to 0.12 M the values of r_p , S_p , and V_p vary significantly. That means that the presence of HF introduces a different structural arrangement of the pore structure, probably, due to the

action of fluoride ions. It can be seen through Fig. 1, that the gelation time was found to vary between 2 min to 140 min. The average pore size increased for higher HF concentration, ranging from 6.8 nm to 21.6 nm, as can be seen through Fig. 2.

It can be noted by Table 3 that the pore connectivity or genus (G_v) is quite high. The values of G_v were obtained by using a geometric model proposed by Vasconcelos⁶. In that model, the expression used to evaluate the genus is obtained through correlating of the metric properties S_v and V_v , as follows⁶:

$$G_v = \frac{S_v^3}{32 \pi V_v (1 - V_v)} + 1 \quad (\text{A})$$

The coefficient of permeability (K_p) is commonly used to represent the intrinsic component of permeability. The representation of K_p using in this work is the following⁸:

$$K_p = \frac{V_v r_p^2}{16 c} \quad (\text{B})$$

where c is a constant (with a value of 8 for cylindrical pores).

As shown in Table 3, G_v decreases as the HF concentration increases, on the contrary of the permeability, which increases for higher HF concentrations. This result can be related to the fact that G_v is very high for all samples, which allows for the stronger effect of the larger values of r_p and

V_V associated to the samples with larger concentration in HF.

Since the hydrolysis and condensation reactions are thermally activated, as the temperature increases the gelation time decreases⁵, as can be seen by Fig. 3. The temperature dependence of gelation can be represented by an Arrhenius equation:

$$\ln(t_{gel}) = A + \frac{E}{RT} \quad (C)$$

where A is a constant, R is the ideal gas content, and T is temperature. The “activation energy”, E, for silica gels is found to be ~10-20 kcal/mole, depending on the catalyst and alkoxy group^{5,7}. For the gels obtained in this work, E is found to be 11.8 kcal/mole.

The high values of monolithicity obtained for different gelation temperatures denote that the higher gelation temperatures used in this work seems not to be inducing gradients of temperature in the polymeric solutions, which could lead to a decrease in the mechanical strength of the gels.

The values of V_p varied from 1.23 cm³/g for the temperature of 27 °C to 1.13 cm³/g for the temperature of 60 °C, presenting a maximum of 1.65 cm³/g for the gelation temperature of 40 °C. It can be seen by Table 4, a similar behavior of the specific surface area, which presents a maximum value of 461 m²/g for the gelation temperature of 40 °C. In spite of the significant influence of the gelation temperature in the gelation time, it was not verified any special tendency in the values of structural parameters of the silica gel with the variation of the temperature, for the samples used in this work.

5. Conclusions

The gelation time was changed from 2 min. to 140 min. by varying the HF concentration. For the HF catalyzed gels the values of average pore radius varied from 6.8 nm to 21.6

nm. For the gels catalyzed with HNO₃ and HCl, the gelation time obtained was higher and the pore structure was finer than for the HF catalyzed gels.

The values of G_v for HF catalyzed gel denote the high interconnectivity of the pore structure. The large values of K_p suggest the feasibility of using these gels as separation membranes.

The gelation temperature influences significantly the gelation kinetics. For the gels obtained in this work, the activation energy for gelation (E) is found to be 11.8 kcal/mole.

The results obtained in this work denote the possibility of tailoring the pore structure of the silica gels by changing some process variables, which is necessary for making separation membranes and catalysis support.

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