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Study of the effect of DCCA and hydrofluoric acid contents on metric and topological parameters of silica membranes

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In this work we studied the effects of drying control chemical additive (DCCA's), for instance formamide, N,N-dimethylformamide and propylene carbonate as well as the effect of hydrofluoric acid on structural parameters related to the evaluation of pore connectivity and permeability of sol-gel membranes. In order to study the effect of drying additives, we used a molar ratio additive/alkoxide of 1/1. We used several molar ratios HF/alkoxide to allow an evaluation of the effect of hydrofluoric acid on the textural properties and permeability of the samples. The influence of those parameters on pores interconnectivity and permeability was studied using a combination of geometric modeling and experimental evaluation of the volume fraction of pores (V_v), the surface area density (S_v), the average pore size and bulk density. Using different DCCA's and different concentrations of hydrofluoric acid we obtained membranes with different textural properties and permeability. The elevated interconnectivity of these membranes suggests the feasibility of their utilization in separation and impregnation processes.

1. Introduction

The structure of ceramic membranes can be modified by changing their pore geometry and the chemical properties of the pore-solids interfaces [1]. In both situations the interaction among the fluid present inside the pores with the solid walls affect the gas and solution separation and transport properties [1].

The amorphous structures obtained via sol-gel processing determine pore structure. Control of this structure is necessary for applications such as membranes and porous matrices [2]. The possibility of designing the geometry of the pore network is certainly an advantage of sol-gel materials.

In porous amorphous solids, such as silica gels, the main metric properties used for geometric description are the volume fraction of pores (V_v) and the surface area density (S_v). An important topological property is the connectivity of pore density (G_v) [3, 4].

The connectivity of an isolated volume can be defined as the number of independent closed curves which can be drawn inside the volume and which can not be continuously deformed one to another and can not shrink to form a point without leaving the volume [4]. A fundamental topological theorem states that the connectivity of a surface or a closed feature is equal to its genus (G). The genus can be associated with the largest number of cuts, which can be made on the surface of a body without creating a new part [5].

Using geometric models it is possible to evaluate the topological parameters from experimental measurements of V_v and S_v. In this work a cylindrical model developed by Vasconcelos [3, 4] is used. This work is an extension of previous ones [3, 4, 6] and its goal is the evaluation of the effect of some DCCA's and hydrofluoric acid on the structural parameters of silica gels and their affect on the connectivity and permeability.

1.1. Modeling the pore structure

To use the cylindrical model [3, 4, 6], we assumed that the entire volume and all the surface area are associated with the branches (B) of the structure. The nodes (N) represent the points in which the branches meet one another and they have no volume or surface area [3, 4, 6].

The expression for evaluating genus density is

$$G_v = B_v - N_v + P_v, \quad (1)$$

where N_v is the number density of nodes and P_v is the number density of separated parts or isolated pores.

B_v can be written as [3, 4, 6]

$$B_v = \frac{S_v^3}{(16\pi V_v(1 - V_v))}. \quad (2)$$

In order to solve Equation 1 and to obtain parameters B_v, N_v, G_v and P_v, it is assumed that the initial coordination number of pores (number of branches connected to a single node), NC, is equal to 4. The Equation 1 can be used for the conditions in which the coordination number varies from NC = 4 to NC = 2. During this stage N_v is constant and given by [3, 4, 6]

$$N_\mathrm{v} = \frac{B_\mathrm{v}^0}{2} \tag{3}$$

where B_v^o is the number density of branches for the initial conditions of the sample (as dried silica gel).

When NC varies from 4 to 2 the relative value of P_v is represented as being constant at one, what means that the pore structure is completely interconnected [4].

1.2. Evaluation of permeability

The permeability is a parameter frequently used to describe a property of a porous material [6]. In spite of that, the expressions commonly used to evaluate the permeability of materials use only the metric parameters volume fraction of pores (V_v) and the average pore radius (r_P) [7].

The coefficient of permeability (k_P) is commonly used to represent the intrinsic component of permeability. A general representation of k_P is the following [2, 9]:

$$k_\mathrm{P} = \frac{V_\mathrm{v} r_\mathrm{P}^2}{c} \tag{4}$$

where c is a constant associated with the tortuosity of the pore network (with a value of 8 for cylindrical pores).

2. Experimental procedure

Sol-gel silica membranes were prepared by acid catalysis of tetraethyl ortosilicate (TEOS, Aldrich Corp.) and deionized water. Nitric acid (pH = 1.5) was used as catalysts. To evaluate the influence of HF in the structural parameters and permeability of silica gel membranes, we used various HF/TEOS molar ratios: 0, 0.015, 0.030, 0.060 and 0.12. In order to study the influence of some DCCA's (formamide, N,N-dimethylformamide and propylene carbonate), we use a DCCA/TEOS molar ratio of 1/1. The sols were cast into cylindrical containers and the gelation occurred at room temperature. The aging of the gels was carried out at 80°C. The specimens were dried at 110°C for 48 h.

After drying the samples were analyzed by BET method, using an automatic gas sorption machine (Autosorb 1, Quantachrome) for volume and surface area. The average pore radius was estimated from $r_\mathrm{p} = 2V_\mathrm{p}/S_\mathrm{p}$. Bulk density was determined by mercury picnometry. The bulk density measurements were repeated six times for each sample.

3. Results and discussion

Table I shows the data obtained for specific surface area of pores (S_p), specific volume of pores (V_p), average pore radius (r_p) and bulk density (ρ_v) for silica gel membranes obtained with HF as a polymerization agent and with different DCCA's. Fig. 1 shows the isotherms for the different membranes. The membranes exhibit isotherms of type IV, according to the BDDT classification originally proposed by Brunaer and coworkers, which is characteristic of a mesoporous (2–50 nm pore diameter) material [2]. The isotherms exhibit a broad loop with the desorption branch being steeper than the adsorption branch. This type of hysteresis loop is classified as type H2, which is characteristic of the so-called ink-bottle pores that have pore cavities larger in diameter than the openings (throats) leading into them [2, 10]. The membranes obtained with DCCA's exhibit different textural properties. Samples obtained with propylene carbonate and samples obtained without additive exhibit a finer pore structure, with a higher surface area and a smaller pore size. Samples obtained with formamide and N,N-dimethylformamide have larger bulk density.

Applying the cylindrical model (Equation 2) and Equation 1 to the pore structure of the silica-gel membranes, we obtained the topological data shown in Table II. The connectivity density of pores (G_v), varied

TABLE I Structural parameters of membranes catalyzed with HF and prepared with different DCCA's

Sample	S_p (m^2/g)	V_p (cm^3/g)	r_p (nm)	ρ_v(cm^3/g)
HF	360 ± 29	1.21 ± 0.09	6.8 ± 0.3	0.65 ± 0.03
HFF	279 ± 22	0.84 ± 0.07	15 ± 0.8	0.77 ± 0.04
HFD	300 ± 24	0.82 ± 0.07	11 ± 0.6	0.80 ± 0.05
HFPC	656 ± 52	1.17 ± 0.09	3.4 ± 0.2	0.69 ± 0.04

HF—no DCCA; HFF—formamide; HDF—N,N-dimethylformamide; HFPC—propylene carbonate.

TABLE II Geometric parameters and permeability of membranes catalyzed with HF and prepared with different DCCA's

Sample	V_v	$S_\mathrm{v} \times 10^{-6}$ (cm^{-1})	$G_\mathrm{v} \times 10^{-19}$ (cm^{-3})	$k_\mathrm{p} \times 10^{19}$ (m^2)
HF	0.73 ± 0.05	8.0 ± 0.64	5 ± 2	4.1 ± 0.7
HFF	0.65 ± 0.05	6.1 ± 0.48	2.0 ± 0.8	183 ± 35
HFD	0.64 ± 0.05	6.6 ± 0.53	2.5 ± 0.9	97 ± 19
HFPC	0.72 ± 0.06	14 ± 1.1	14.8 ± 0.6	10 ± 2

HF—no DCCA; HFF—formamide; HDF—N,N-dimethylformamide; HFPC—propylene carbonate.

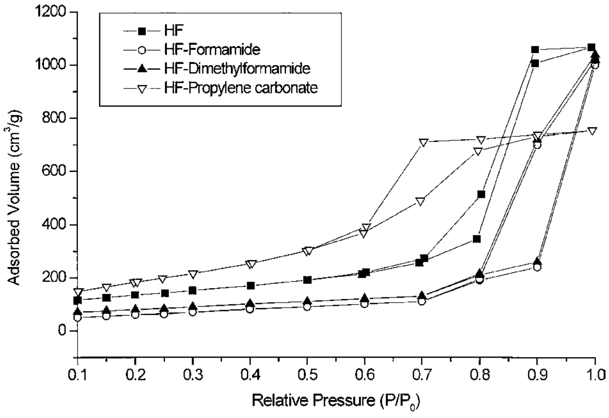

Figure 1 Isotherm for silica gel membranes obtained with HF as a polymerization agent and with different DCCA's. (Should appear in item 3_Results and Discussion, after the first paragraph)

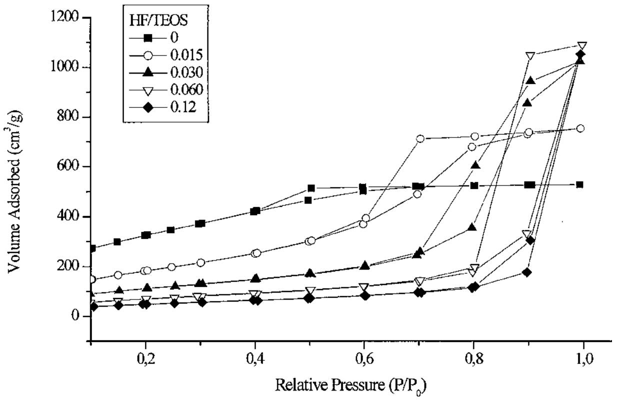

Figure 2 Isotherm for membrane obtained with propylene carbonate and nitric acid as the catalyst (HF\TEOS = 0) and for membranes obtained with different concentrations of HF. (Should appear in item 3_Results and Discussion, after the 4° paragraph)

TABLE III Structural parameters of membranes catalyzed by HNO_3 at pH 1.5 and by mixtures of HNO_3 and HF at different concentrations, prepared with propylene carbonate as DCCA

HF:TEOS molar ratio	S_p (m^2/g)	V_p (cm^3/g)	r_p (nm)	ρ_v (cm^3/g)
0	1167 ± 93	0.82 ± 0.04	1.4 ± 0.07	1.3 ± 0.14
0.015	656 ± 52	1.17 ± 0.09	3.4 ± 0.2	0.69 ± 0.04
0.030	392 ± 31	1.59 ± 0.08	7.8 ± 0.4	0.38 ± 0.02
0.060	246 ± 20	1.69 ± 0.08	13.1 ± 0.7	0.44 ± 0.02
0.120	170 ± 14	1.63 ± 0.08	18.4 ± 0.9	0.36 ± 0.09

TABLE IV Geometric parameters of membranes catalyzed by HNO_3 at pH 1.5 and by mixtures of HNO_3 and HF at different concentrations, prepared with propylene carbonate as DCCA

HF:TEOS molar ratio	V_v	$S_v \times 10^{-6}$ (cm^{-1})	$G_v \times 10^{-19}$ (cm^{-3})
0	0.64 ± 0.03	26 ± 2.0	73 ± 2.5
0.015	0.72 ± 0.06	14 ± 1.1	14.8 ± 0.6
0.030	0.78 ± 0.04	8.62 ± 0.68	3.7 ± 0.13
0.060	0.79 ± 0.04	5.41 ± 0.44	0.94 ± 0.03
0.120	0.78 ± 0.04	3.74 ± 0.31	0.31 ± 0.05

from 2.0×10^{19} cm^{-3} for membranes obtained with formamide and 3.0×10^{20} cm^{-3} for the membrane obtained with propylene carbonate. The membrane obtained with formamide as DCCA has the highest permeability (k_P).

It has been shown in a previous work [11] that these DCCA's affect the early stages of the sol-gel process. Silica gels obtained with amide additives present a more cross-linked network and consequently a coarser pore texture. The mesoporous membrane obtained without drying chemical additive exhibit a low monolithicity, ca. 50%, while the monolithicity of the membranes obtained with DCCA is higher than 90%. Mesoporous membranes obtained with propylene carbonate present the highest monolithicity (100%) when heat-treated up to 600°C at a heating rate of 1°C/min.

Fig. 2 shows the isotherm for the membrane obtained with propylene carbonate and nitric acid as the catalyst and the isotherm for the membrane obtained with different concentrations of HF. According to the original BDDT classification [2], the isotherms obtained for the membrane without HF, is type I, being characteristic of a microporous solid (pore radii ≤ 1.0 nm). A high volume is adsorbed at the lowest relative pressure, which indicates a large volume of very small pores. The virtual lack of hysteresis in the desorption branch is generally interpreted to mean that the pores are smooth and cylindrical [2, 10]. The isotherms for the other membranes are type IV, with ink-bottle pores. Compared to the isotherm of the membrane without HF, less gas is adsorbed at low reltive pressures and a sudden increase in adsorption occurs at high pressure, indicating that mostly mesopores are present [2].

Structural parameters of the silica-gel membranes obtained with propylene carbonate as a drying additive and different concentrations of hydrofluoric acid are shown in Table III. From the results one can note that as the HF/TEOS molar ratio increases the surface area of the samples decreases, while the pore volume and the pore radii increase. The bulk density varied from 1.3 g/cm^3 for membrane without HF to 0.36 g/cm^3 for membrane with HF/TEOS molar ratio of 0.12. The pore volume varied from 0.82 cm^3/g for membrane without HF to 1.69 g/cm^3 for membrane with HF/TEOS molar ratio of 0.06. The presence of hydrofluoric acid leads to modifications in the structural arrangement of the pores structure for the membranes obtained with propylene carbonate. The average pore size increases for higher concentrations of HF, ranging from 1.4 to 18.4 nm. This information can be used to prepare a membrane with a tailored surface areas of pores. The same can be stated about volumes and sizes of pores, which is necessary for making engineered nanostructure for porous gels and membranes.

Table IV presents the results on volume fraction (V_v), surface area density (S_v) and genus density (G_v) for different membranes. The membranes obtained with HF exhibit volume fraction of pores in the range of 0.72–0.79. The membrane obtained without HF present V_v of 0.64. The interconnectivity of the membranes varied from 73×10^{19} cm^{-3} for membrane without HF to 3.1×10^{18} cm^{-3} for membrane with a HF/TEOS molar ratio of 0.12.

Since the interconnectivity of the porous network is an important parameter to determine the permeability of porous membrane, it is reasonable to introduce the genus in the expression to evaluate the coefficient of permeability of membranes. Vasconcelos [6] proposed an expression for a permeability geometric factor, P_g, which is obtained by introducing G_v directly into Equation 4:

$$P_g = \frac{D^2 V_v G_v}{4c} \qquad (5)$$

Table V shows the results of applying Equations 4 and 5 to the metric properties of silica gel membranes obtained with different concentrations of HF. The permeability of the membranes increased with the increasing in the concentration of hydrofluoric acid, as a consequence of the increasing in the pore size. The permeability geometric factor varied from 1.0×10^{-8}

TABLE V Permeability and permeability geometric factor (P_g) of membranes catalyzed by HNO_3 at pH 1.5 and by mixtures of HNO_3 and HF at different concentrations, prepared with propylene carbonate as DCCA

HF:TEOS molar ratio	$k_p \times 10^{19}$ (m^2)	$P_g \times 10^8$ (m^{-1})
0	1.6 ± 0.2	1.2 ± 0.56
0.015	10 ± 2	1.5 ± 0.91
0.030	59 ± 9	2.2 ± 0.11
0.060	169 ± 26	1.6 ± 0.79
0.120	331 ± 49	1.0 ± 0.50

m^{-1} for the membrane obtained with HF/TEOS molar ratio of 0.12 to 2.2×10^{-8} m^{-1} for membrane with HF/TEOS molar ratio of 0.030. These results show that while permeability (k_p) varies over 200 times among the samples, the permeability geometric factor (P_g) indicates only a twofold variation.

4. Conclusions

The sol-gel method allows the preparation of membranes with tailored pore structure. By using different DCCA's and hydrofluoric acid we obtained mesoporous membranes with different structural properties. The use of different concentrations of hydrofluoric acid and propylene carbonate leads to membranes with different structural properties. Membrane obtained without HF is microporous and exhibit large surface area and small pore size. Membranes obtained with HF are mesoporous and have large pore volumes and pore sizes. The connectivity of the membranes was found to be in the order of magnitude of 10^{20} cm^{-3}, which is extremely high and allows for the metric parameters to play important roles determining permeability.

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