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3-*n*-propyl-1-azonia-4-azabicyclo[2.2.2]octanechloride/silica hybrid polymer. A morphologic study in relation to the organic content

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Abstract

The 3-*n*-propyl-1-azonia-4-azabicyclo[2.2.2]octanechloride/silica hybrid polymer was synthesized, using the sol–gel method, by varying the organic content. The samples were characterized using infrared spectroscopy (FTIR), scanning electron microscopy (SEM), N_2 adsorption–desorption isotherms and thermogravimetric analysis. The polymer morphology could be controlled by the choice and amount of the organic precursor added. The dispersion of the organic/inorganic phases was shown to be in molecular or nanometric level. The organic content elevation produced a decrease in the surface area and pore volume due to the organic pore blocking effect.

Keywords: Sol–gel; Xerogels; Dabco

1. Introduction

The sol–gel method for preparing hybrid silica based polymers has gained scientific importance in the last decade, due to its extensive possible applications [1–6]. This method, based on the hydrolysis and polycondensation reactions of silicon alkoxides with organosilanes, is an advantageous process if compared with other covalent-bonding methods for obtaining hybrid systems, because the resulting xerogels can be synthesized at room temperature with homogeneity and purity. Additionally, by using the sol–gel process it is possible to obtain materials with different forms, such powders, membranes, monoliths, films, etc. However, the molecular structure and microstructure of these hybrid polymers, prepared with multi-component systems, are not completely understood [7]. Little changes in the synthesis conditions, like the solvent, the precursor used, the gelation temperature, etc. produce drastic changes in the physicochemical properties of the resulting materials [8–11]. These differences are related to the thermodynamic and kinetics of reactions that take place in the sol–gel process.

Recently we have obtained a new charged hybrid xerogel the 3-*n*-propyl-1-azonia-4-azabicyclo[2.2.2]octanechloride silsesquioxane polymer (dabco/silica silsesquioxane) with a high organic loading [12]. This material presented very interesting properties such high water solubility and capacity for forming a stable thin film on surfaces containing aluminum oxide. The presence of dabco group bonded in these surfaces allowed its use as metal sorbent. It was also observed that the solubility of this polymer is decreased with decreasing organic content. This fact could bring about the interest in study the preparation of a new sequence of insoluble charged dabco/silica hybrid polymers with potential application as a metal sorbent, mainly due to its unusual ability to form stable complexes with a ligand/metal 1:1 stoichiometry [13]. Additionally, priory paper using silica-gel grafted with dabco groups showed selectivity to perchlorate ion making possible to develop a new potentiometric sensor for this ion [14].

Thus, in this work, the preparation of dabco/silica xerogel polymer in an insoluble form was studied. Five samples were synthesized, varying the organic loading in the synthesis from 2 to 40%, in order to understand the influence of the organic content on the morphology of this

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system. The samples were characterized by using infrared spectroscopy, elemental CHN analysis, thermogravimetric analysis, N_2 adsorption–desorption isotherms and scanning electron microscopy (SEM).

2. Experimental

2.1. Synthesis of 3-n-propyl-1-azonia-4-azabicyclo[2.2.2]octanechloride xerogel polymer (dabco/silica)

The 1,4-diazabicyclo[2.2.2]octane (DABCO) (20 mmol) (Acros), previously sublimed, were dissolved in 40 ml of an ethanol/acetone (Merck) solution (1:1), and 20 mmol of 3-chloropropyltrimethoxysilane (CPTMS) (Acros) were added. This mixture became upon reflux conditions, in argon atmosphere and stirring, at near 90 °C for 48 h. The product of reaction, 3-*n*-propyltrimethoxysilane-1-azonia-4-azabicyclo[2.2.2]octanechloride (DABCOSIL) was used as organic precursor in the sol–gel synthesis. In the previous DABCOSIL solution it was added, under stirring, ethyl alcohol (10 ml), twice distilled water, maintaining the water/TEOS molar ratio 4/1, HF (0.1 ml) and tetraethylorthosilicate (TEOS) (Acros). The resulting pH was between 3 and 4 for all samples. The DABCOSIL molar percentile, in relation to TEOS, was 2, 5, 10, 25 and 40%. The mixture was stored for 15 days, just covered without sealing. The gel was then washed with acetone and dried at 90 °C for 1.5 h and the resulting dabco/silica xerogel polymers were assigned as X2, X5, X10, X25 and X40, respectively.

2.2. Elemental analysis

The organic content of the xerogel polymers was analyzed using a CHN Perkin Elmer M CHNS/O Analyzer, model 2400, in triplicate, after heating the samples at 100 °C, under vacuum for 1 h.

2.3. Infrared analysis

Self-supporting disks of the xerogel polymers, with an area of 5 cm^2, weighing ca. 100 mg were prepared. The disks were heated for 1 h at 150 °C, under vacuum (10^{-2} Torr). The IR cell used in this work present two sections, an oven that consists of an electrical filament on the external wall of the cell and another section with two KBr windows for submitting the sample to the infrared beam, using a mobile support. The two sections are pressed together using a viton o-ring. The sample can be heated under vacuum and then moved to the infrared beam. Thus the sample is not exposed to the external environment [15]. The equipment used was a Shimadzu FTIR, model 8300. The spectra were obtained with a resolution of 4 cm^{-1}, with 100 scans.

2.4. Thermal analysis

The dabco/silica xerogel polymers were submitted to thermal gravimetric analysis (TGA), using nitrogen atmosphere. The equipment used was a Perkin Elmer TGS 2 thermogravimetric analyzer. The samples were heated from room temperature to 800 °C at a rate of 10 °C min^{-1}.

2.5. Scanning electron microscopy

The dabco/silica xerogel polymers were analyzed with a Jeol model JSM 5800 scanning electron microscope, with 20 kV and 60,000 times of magnification. The primary aggregated particle size and its standard deviation were determined by using the Quantikov software [16].

2.6. N_2 adsorption–desorption isotherms

The nitrogen adsorption–desorption isotherms of polymers, degassed at 150 °C, were determined at the liquid nitrogen boiling point in a homemade volumetric apparatus, with a vacuum line system employing a turbo molecular Edward vacuum pump. The pressure measurements are made using capillary Hg barometer and an active Pirani gauge. The specific surface areas of hybrid materials were determined from the BET (Brunauer, Emmett and Teller) multipoint method [17] and the pore size distribution was obtained using BJH (Barret, Joyner, and Halenda) method [18].

3. Results and discussion

The dabco/silica xerogel synthesis was performed in two steps. Firstly the 3-*n*-propyltrimethoxysilane-1-azonia-4-azabicyclo[2.2.2]octanechloride (DABCOSIL) was obtained from the reaction of DABCO with CPTMS, as

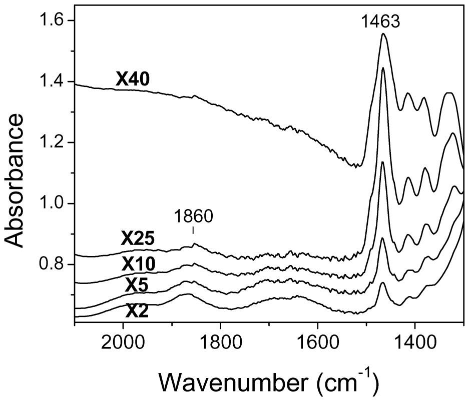
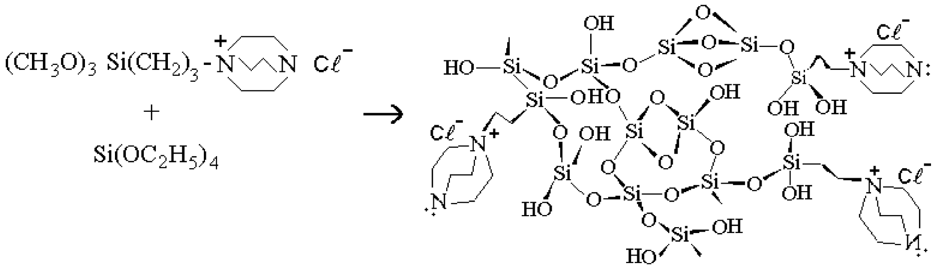


Fig. 1. Infrared absorbance spectra of the dabco/silica xerogel polymers with different organic content, obtained at room temperature after heating to 150 °C, in vacuum.

described by Eq. (1):

$$N(C_2H_4)_3N + Cl(CH_2)_3Si(OCH_3)_3 \rightarrow N(C_2H_4)_3N^+ \times (CH_2)_3Si(OCH_3)_3Cl^- \quad (1)$$

Afterwards, the DABCOSIL was used as organic precursor in sol–gel process. The DABCOSIL was added to a TEOS solution and the gelation occurred as described by Eq. (2).



(2)

It was observed by CHN elemental analysis (Table 1) that the final organic content is related to the DABCOSIL precursor quantity added and this trend was also verified by infrared spectroscopy and thermogravimetric analysis. A linear relation between the organics added in the synthesis and the final organic content present in the resulting solid was not observed. Effects as solvent dilution caused by low organic concentration in the synthesis or organic saturation in very high organic concentration were already observed and can explain variations in this linearity [19]. The infrared spectra are shown in Fig. 1. The band intensity of CH_2 bending modes (δHCH) of DABCO and propyl groups that appears at 1463 cm^{-1} increases from X2 to X40 sample, in agreement with the CHN results (Table 1). The inorganic phase can be identified by the typical silica overtone band at ca. 1860 cm^{-1}, due to structural modes of Si–O–Si framework. This band is most poorly defined on samples that present higher organic content, indicating that the silica inorganic framework is fractionated with the organics. Therefore, we can consider that the organic–inorganic phase dispersion should occur at the molecular or nanometric level [20,21].

The curves obtained from thermogravimetric analysis are shown in Fig. 2. The organic content increases from X2 to X40 sample, and the organic phase is thermally very stable at least up to 300 °C, for all samples. This high thermal stability was interpreted taking into account the covalent bonded organic–inorganic interface.

Table 1 also presents some morphological data of the dabco/silica xerogel polymers obtained from the N_2 adsoption–desorption isotherms. The increase in the organic content produces a decrease in the surface area as well as in the pore volume. These results indicate that the surface organic coverage of the pores results in a partial reduction of the pore free volume [22].

The N_2 adsorption–desorption isotherm curves are shown in Fig. 3. The curves of the samples X40 and X25, which have a higher organic content, are not well defined. These samples have lower porosity (Table 1). However, the isotherms obtained for the samples X10, X5 and X2, are typical type IV, characteristic of mesopore materials [23]. The desorption curves show a hysteresis at high relative pressure. This behavior is observed when the equilibrium pressure of condensation differs from the equilibrium pressure of evaporation, thus the amount of desorbed nitrogen is lower than that adsorbed, in a same P/P_0 region. Hysteresis behavior is very common in hybrid sol–gel systems [11,24], and it indicates the occurrence of a small capillary condensation due to the organics present, the disordered micropores structure, the presence of bottle shape pores and N_2 network-percolation effects [25–27].

The pore size distribution curves are shown in Fig. 4. It was possible to observe that the samples X40 and X25 have no mesoporous structure while the X10 and X5 samples show an appreciable amount of mesopores with a diameter of about 8 nm. These larger pores are also present in the lowest organic concentrated sample (X2) but now there is another predominant mesopore size region with maximun diameter of 6 nm that was not present in the other samples. Therefore, the pores with lower diameter, present in the X2

Table 1
CHN elemental analysis and morphological data

Sample	Precursor added DABCOSIL molar percentile (%)	Elemental analysis[a] (mmol g^{-1})	BET surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})
X2	2	0.39	306	0.56
X5	5	0.44	139	0.32
X10	10	0.97	119	0.29
X25	25	1.87	39	0.049
X40	40	2.31	34	0.044

[a] Millimoles of organic groups per gram of polymer.

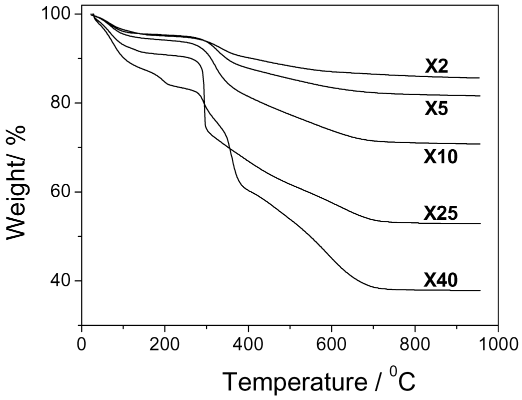


Fig. 2. Thermogravimetric curves of dabco/silica xerogel polymers with different organic content.

sample, disappear with increasing organic content. This result suggests that the organic pendant groups cover the pore surface with a consequent pore-blocking effect, as already observed for similar hybrid polymers [22,28]. However, in contrast to the cited papers the pore-blocking effect seems to occur in the pores with smaller size, in the present work

The SEM images are shown in Fig. 5. The organic content influences the xerogel polymer microstructure. In the X2 image it is possible to observe that the sample consists of large particles (ca. 800 nm) with a primary particled structure. The average diameter of these primary particles, calculated by using the Quantikov software [16], was 82 nm, with a standard deviation of 15 nm. For the X40 sample, the primary particles are not seen. The X40 sample consists of large compacted particles. These difference in the microstructure can explain the low surface areas and pore volumes of the samples with higher organic content (Table 1).

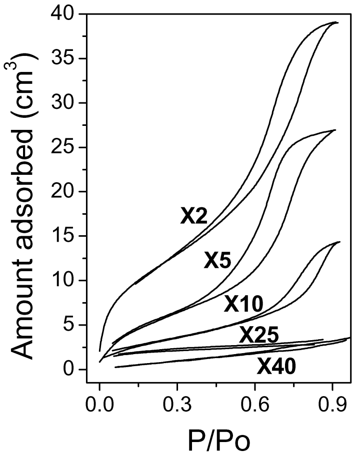


Fig. 3. N_2 adsorption–desorption isotherms for dabco/silica xerogel polymers with different organic content previously degassed at 150 °C for 2 h.

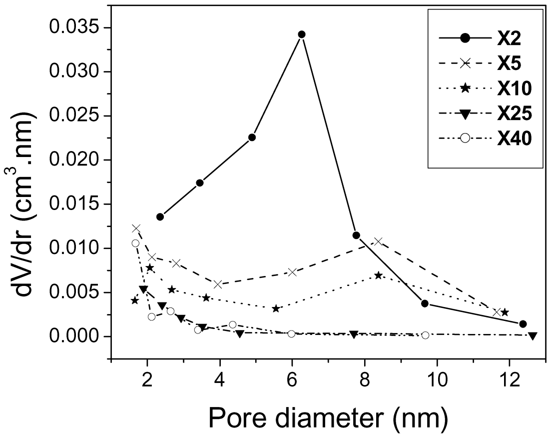


Fig. 4. Pore size distribution of dabco/silica xerogel polymers with different organic content, obtained by using BJH method.

4. Conclusions

The synthesis of a sequence of insoluble and thermally stable 3-*n*-propyl-1-azonia-4-azabicyclo[2.2.2]octanechloride/silica hybrid xerogel polymers with organic content varying from 0.39 to 2.31 mmol g^{-1} was performed. The dispersion of the organic/inorganic phases was shown to be at the molecular or nanometric level, resulting in an homogeneous fractional silica network. The morphology of the polymers was drastically influenced by the organic

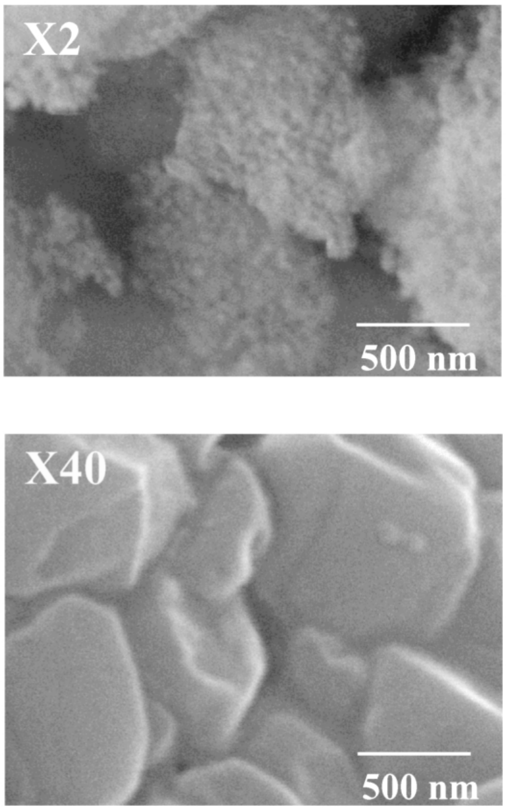


Fig. 5. SEM images of dabco/silica xerogel polymers. The magnification was 60,000 ×.

content, higher organic content produced a decrease in the surface area and pore volume as well as in the physical appearance of the samples, as observed by SEM. These facts show that it is possible to prepare hybrid xerogel polymers with desired characteristics.

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References

[1] Shea KJ, Loy DA. Chem Mater 2001;13:3306–19.
[2] Hsiue G-H, Lee R-H, Jeng R-J. Polymer 1999;40:6417–28.
[3] Lu Z, Lindner E, Mayer HÁ. Chem Rev 2002;102:3543–78.
[4] Lev O, Wu Z, Bharathi S, Glezer V, Modestov A, Gun J, Rabinovich L, Sampath S. Chem Mater 1997;9:2354–75.
[5] Levy D, Esquivias L. Adv Mater 1995;7:120–9.
[6] Schmidt H, Jonschker G, Goedicke S, Mennig M. J Sol–Gel Sci Technol 2000;19:39–51.
[7] Pavan FA, Gushikem Y, Moro CC, Costa TMH, Benvenutti EV. Colloid Polym Sci 2003;281:173–7.
[8] Kim K-M, Adachi K, Chujo Y. Polymer 2002;43:1171–5.
[9] Boury B, Corriu RJP. Adv Mater 2000;12:989–92.
[10] Pavan FA, Gobbi SA, Moro CC, Costa TMH, Benvenutti EV. J Porous Mater 2002;9:307–11.
[11] Burleigh MC, Markowitz MA, Spector MS, Gaber BP. J Phys Chem B 2001;105:9935–42.
[12] Arenas LT, Langaro A, Gushikem Y, Moro CC, Benvenutti EV, Costa TMH. J Sol–Gel Sci Technol 2003;28:51–6.
[13] Moreira WC, Gushikem Y, Nascimento OR. J Colloid Interface Sci 1992;150:115–20.
[14] Fernandes JR, Kubota LT, Gushikem Y, Neto GO. Anal Lett 1993;26: 2555–63.
[15] Foschiera JL, Pizzolato TM, Benvenutti EV. J Braz Chem Soc 2001; 12:159–64.
[16] Pinto LCM. PhD Thesis, Universidade de São Paulo, IPEN; 1996.
[17] Brunauer S, Emmett PH, Teller E. J Am Chem Soc 1938;60:309–19.
[18] Barret EP, Joyner LG, Halenda PP. J Am Chem Soc 1951;73:373–80.
[19] Pavan FA, Franken L, Moreira CA, Costa TMH, Benvenutti EV, Gushikem Y. J Colloid Interface Sci 2001;241:413–6.
[20] Schubert U, Hüsing N, Lorenz A. Chem Mater 1995;7:2010–27.
[21] Habsuda J, Simon GP, Cheng YB, Hewitt DG, Diggins DR, Toh H, Cser F. Polymer 2002;43:4627–38.
[22] Pavan FA, de Magalhães WF, de Luca MA, Moro CC, Costa TMH, Benvenutti EV. J Non-Cryst Solids 2002;311:54–60.
[23] Brunauer S, Deming LS, Deming WS, Teller E. J Am Chem Soc 1940; 62:1723–46.
[24] Lim MH, Stein A. Chem Mater 1999;11:3285–95.
[25] Brinker J, Scherer GW. J Non-Cryst Solids 1985;70:301–22.
[26] Gregg SJ, Sing KSW. Adsorption, surface area and porosity. London: Academic Press; 1982. pp. 111.
[27] Sing KSW. Adv Colloid Interface Sci 1998;76:3–11.
[28] Boury B, Corriu RJP, Strat VL. Chem Mater 1999;11:2796–803.