Highly porous silica networks derived from gelatin/siloxane hybrids prepared starting from sodium metasilicate

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Abstract

The formation of polymeric hybrid materials of siloxanes with gelatin (GE) starting from sodium metasilicate as the silica source, and their transformation into silica under different conditions have been studied. Gelatin/silicate hybrid nanocomposites were obtained by acid precipitation of mixed gelatin and sodium silicate solutions. Porous xerogels with large BET areas ($452\,m^2/g$) constituted by closed packed microspheres (1 μm diameter) containing residual gelatin in microporous domains were obtained after thorough extraction of gelatin with water from the nanocomposites. By calcination at 550 °C the residual gelatin occluded in the micropores was eliminated and a highly microporous silica (BET area $834\,m^2/g$) with microspherical morphology was produced. Blanks were prepared in order to establish the role of GE in the process. Silica samples obtained under the same conditions but without gelatin also have large BET areas but they are mesoporous (40–100 Å), presenting an irregular morphology on a micron scale. The morphological and textural differences between both silica types demonstrate the nanocomposite structure of the hybrids, making evident the templating role of gelatin in the formation of the silica network.

1. Introduction

The combination of organic polymers with siloxanes under mild chemical conditions has been used for the preparation of polymeric organo-inorganic hybrids in the form of films for membranes or coatings, or as precursors for the preparation of porous materials [1–7]. This has been done mainly by using the sol–gel process [8]. A controlled sequence of hydrolyses and condensations starting from an alkoxysilane like tetraethyl orthosilicate in alcohols and other polar solvents leads to a solution or colloidal suspension of siloxane polymers (sol) [9]. At this stage, or at the beginning of the

process, it is possible to incorporate a soluble organic polymer in the sol. Yet only recently has the study of the use of biopolymers to obtain hybrids started to be studied, mainly because these materials are related to biomimetic processes. The presence of functional groups such as amino, amide or carboxyl in some polymers can allow compatibilization of the polymeric phase dominions with inorganic matrices at a submicroscopic level through hydrogen bonding with Si—OH groups.

In previous work we have found that chitosan, a polysaccharide of natural origin that contains amino and amide functional groups in its structure, easily forms hybrids with precursors of silica or titania prepared by the sol–gel method. These hybrids have al-

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lowed the preparation of homogenous and flexible films [10,11] or their transformation into oxides with high surface area and porosity [12,13].

Moreover, it was found that under certain conditions chitosan can acts as a template for the morphology of the final oxide [12,13]. Assuming that other biopolymers could have a similar effect in the preparation of inorganic oxides, in this work we have undertaken a study of the formation of hybrids of siloxanes with gelatin (GE).

GE is a heterogeneous mixture of water-soluble proteins of a high molecular weight obtained from collagen and its water solution readily forms gels at temperatures under 30 °C. It would be expected that the amino acid residues contained in its protein structure could make possible an association with silanol groups through hydrogen bonds. This connectivity should allow good compatibility between both components leading to the formation of a hybrid composite. It should be mentioned that recently hybrid Gelatin/siloxane films have been prepared with potential application as a scaffold for bone tissue engineering by using the sol–gel method [14].

In this work we have prepared GE/siloxane hybrids starting from sodium metasilicate as the silica source, and we have studied the transformation of this product into silica under different conditions.

It is well known that most of the commercial silica gels are prepared starting from soluble glass, i.e. sodium metasilicate (Na_2SiO_3). Normally the synthesis is carried out by forming first a silicate hydrosol containing polysiloxane chains through acidification, followed by cross-condensation reactions between them leading to silica networks. The aim of this study was to make use of the expected tendency of this biopolymer for association with silicate hydrosols in order to modify the characteristics of the products. Then the preparation and characterization of blanks was carried out in order to establish a potential role of GE in the process. The effects of compositions and synthesis conditions on the morphology, BET area and porosity of the final products are described in detail.

2. Experimental

Commercial sodium metasilicate 50–52° Bé, $d = 1.526$ and commercial gelatin from porcine skin, Bloom 240, were used as received.

2.1. Preparation of GE/silica composites

Sodium metasilicate solution (8.2 ml) was added by dropping it on different amounts of 3% aqueous GE solutions, previously prepared at 45 °C with magnetic stirring for about 2 h, in order to get the desired SiO_2/

GE mass ratios. The resulting mixed solutions were either (a) gelatinized by cooling or (b) precipitated with hydrochloric acid.

In procedure (a) the solution was kept at 4 °C during 3–4 h and the resulting gel was dried for 24 h at 70 °C, then washed with distilled water, and finally calcined at 550 °C for 2 h. In procedure (b) the solution was precipitated in ca. 60 ml of 1 N HCl, reaching a final pH of 1.2–1.3. In this method the reaction mixture was decanted overnight and then filtered. The precipitate was dried, washed or extracted with distilled water at different stages during the synthesis as explained bellow, and finally calcined.

2.2. Washing and extraction procedures

Samples prepared by method (b) were washed thoroughly with distilled water after filtration, after drying or after calcination. Different results were obtained in each case (see Table 2). However, samples with higher BET areas were obtained when the dry products were extracted with water in a Soxhlet apparatus during 24 h prior to calcination.

2.3. Thermal treatment

The xerogels were dried at 70 °C for 20 h and finally calcined in air in a programmed temperature Nabertherm S27 furnace at 550 °C for 2 h, or at the temperature and time predetermined for a specific experiment, with a temperature gradient of 10 °C/min.

2.4. Characterization

Specific surface area, pore size and pore size distribution of the samples were determined with a Micromeritics ASAP 2010 apparatus at −196 °C using nitrogen as the adsorption gas. Morphologies were examined on micrographs obtained by Scanning Electron Microscopy (SEM) (Siemens Autoscan). FTIR spectra (Bruker Vector 22) were taken to verify the absence of residual organic compounds. Simultaneous (DTA/TGA) thermal analyses were carried out in the range of 20–800 °C in a Netzsch STA 409C instrument under air and at the rate of 10 °C/min. Sodium analysis was done by Inductively Coupled Plasma–Atomic Emission Spectroscopy (ICP-AES) with a Perkin Elmer P-400 Sequential instrument.

2.5. Silica blanks

Blanks were prepared from sodium metasilicate under similar conditions as the hybrid xerogels but without GE (samples B1 and B2, Table 2) in order to study the templating role of gelatin in the synthesis. In this case, no precipitation of the silicate solutions in diluted HCl

was seen. After removal of solvent in a rotary evaporator, the resulting gels were dried, washed and calcined in a similar way as the mixed GE/siloxane products.

3. Results

3.1. BET areas and pore characteristics

The BET areas of silica samples obtained from gels prepared by gelatinization (method (a)) of mixed GE/siloxane solutions with different GE:SiO$_2$ weight ratios are shown in Table 1. The dried gels were washed with distilled water before or after calcination. Only marginal

differences were detected, and only the results of samples washed before the calcination step are shown in this Table. In all cases the resulting BET areas were small and thereafter no further work was done using this method. Table 2 shows the BET area and pore characteristics of silica samples prepared starting from xerogels obtained by acid precipitation of mixed GE/siloxane solutions (method (b)). This Table also shows the data obtained for two blanks prepared in a similar way, but without GE. The preparation and characterization of the blanks (samples B$_1$ and B$_2$) was done in order to study the templating role of gelatin in the synthesis by modeling not only the pore structure but also the morphology of the particles of the final silica. In Table 2, samples M$_{11}$ and M$_{12}$ are not properly silica, but porous hybrid xerogels.

Fig. 1(a) presents the nitrogen sorption isotherms showing pore size distribution for sample M$_{10}$, which corresponds to a silica with a large BET area obtained after calcination of a water-extracted GE/siloxane xerogel sample. On the other hand, the corresponding textural characteristics of a blank sample (B$_2$) are presented in Fig. 1(b). This sample was milled after the drying procedure at 70 °C and thoroughly washed prior to calcination.

Table 1
Silica samples obtained by gelatinization of mixed GE/siloxane solutions at 5 °C

Sample	BET surface (m^2/g)	GE/SiO$_2$ (w/w)	Observations
M$_1$	4.1	1:2	Washed before calcination
M$_2$	6.7	1:5	Washed before calcination
M$_3$	3.0	1:1	Washed before calcination
M$_4$	4.1	2:1	Washed before calcination

Table 2
Silica samples obtained by precipitation of mixed GE/siloxane solutions in 1 N HCl

Sample	BET area (m^2/g)	Gelatin/SiO$_2$ ratio (w/w)	Pore vol.% (cm^3/g)	Pore ϕ (Å)[a]	Micropore area (m^2/g)	Observations
B$_1$	723	Blank	0.67	37	0	Washed after calcination
B$_2$	494	Blank	0.95	96	0	Washed after drying
M$_5$	146	1:3	—	—	—	Washed after calcination
M$_6$	237	1:10	—	—	—	Washed after calcination
M$_7$	487	1:5	0.23	<20	212	Washed after drying 70 °C
M$_8$	552	1:5	0.27	<20	381	Washed after drying 200 °C
M$_9$	587	1:5	0.28	<20	387	Washed after calcination
M$_{10}$	834	1:5	0.42	<20	278	Extracted after drying 70 °C
M$_{11}$	452	1:5	0.53	43	0	Id. M$_{10}$ without calcination
M$_{12}$	394	1:5	0.36	32	0	Id. M$_{11}$ after drying 200 °C/4 h

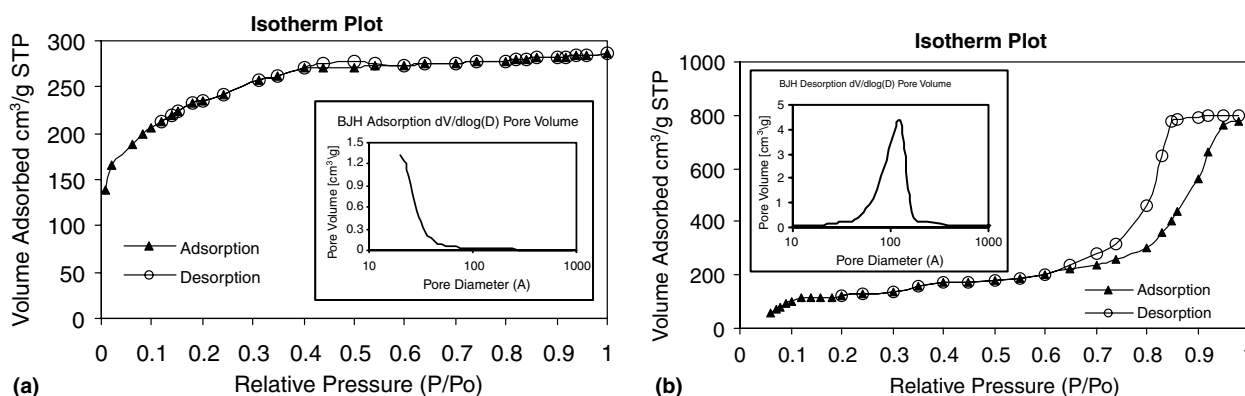[a] Maximum observed in the pore size distribution curves.

Fig. 1. Nitrogen sorption isotherms showing the pore size distribution of silica samples: (a) prepared by calcination of gelatin/silica xerogels previously extracted with water (sample M$_{10}$) and (b) blank prepared from a xerogel washed after the drying at 70 °C (sample B$_2$).
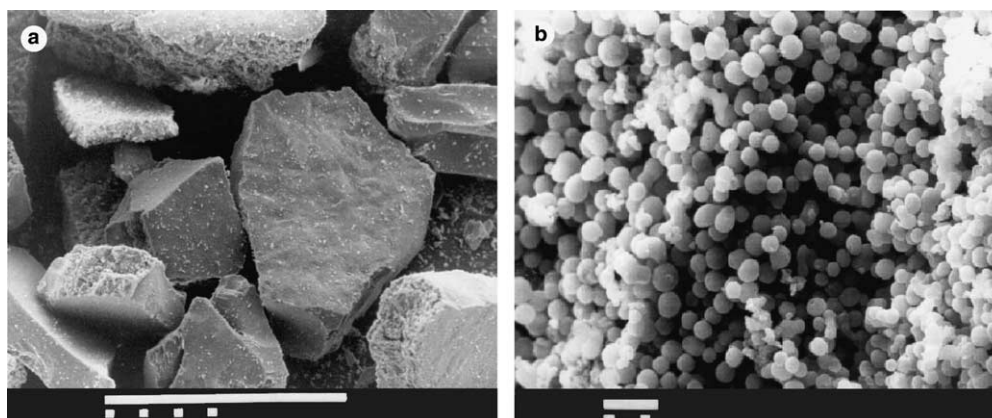
Fig. 2. SEM micrographs of (a) dried silica/gelatin xerogel after extraction with water, and (b) the same sample, at greater magnification, showing the microspherical morphology of the particles. The bar size corresponds to 1000 μm in Fig. 2(a) and 10 μm in Fig. 2(b).
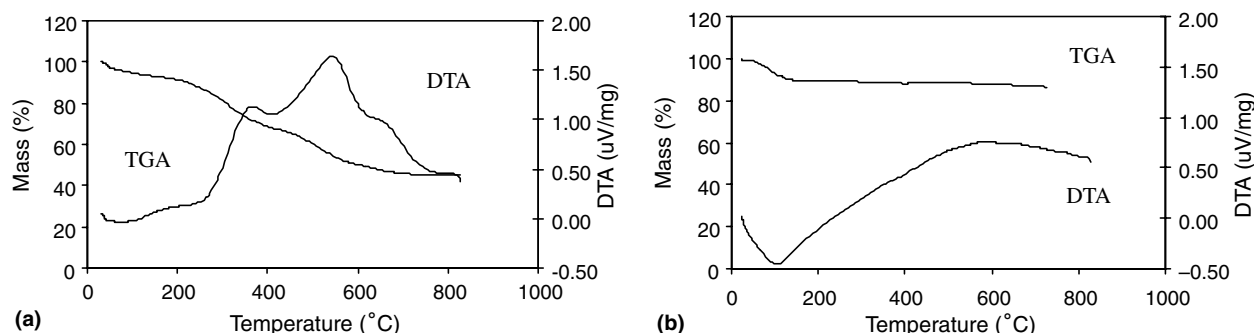

Fig. 3. TGA and DTA thermograms carried out under air for (a) a dried GE/siloxane xerogel and (b) a similar sample after extraction with water.

3.2. Morphological characterization

SEM showed that the morphology of the dried GE/siloxane xerogels and that of the final silica samples obtained after calcination were similar. Fig. 2(a) shows micrographs of pieces of dried xerogel samples after extraction. At greater magnification, Fig. 2(b) shows that the pieces are conformed by a close packing of microspheres about 1 μm in diameter, with a low degree of dispersion. Such morphology is not present in blank samples at a similar scale of magnification.

3.3. Thermal analysis

For easy comparison, Fig. 3 shows, at the same scale, the thermograms corresponding to simultaneous DTA/TGA thermal analyses performed on similar xerogel samples dried at 70°C/24 h, where one of them (Fig. 3(a)) was calcined and then washed to eliminate residual NaCl (Table 2, sample M_7) and the other (Fig. 3(b)) was extracted with water during 24 h in a Soxhlet apparatus in order to remove gelatin and NaCl (Table 2, sample M_{10}).

4. Discussion

4.1. Textural properties

In Table 1 it is seen that silica samples obtained by gelling of the solutions (method (a)) have a very low BET area, suggesting that in the gel formed by cooling the gelatin is not intimately associated with the silica network. In this case the siloxane solution is probably retained as the liquid phase inside the network of the gel formed by the biopolymer. That is, the gel-former is GE and not the siloxane component.

On the other hand, when mixed solutions are precipitated in hydrochloric acid, the calcined samples correspond to microporous silica with a large surface area (Table 2), suggesting an intimate association, probably at the molecular level, between both phases. In this case the precipitate formed corresponds to a siloxane-based xerogel in which GE macromolecules remain occluded in the inorganic network as explained below. During further calcination, GE is eliminated leaving a microporous silica sample. In a series of preliminary experiments (samples M_5, M_6, M_9) it was found that the higher BET areas were obtained starting from mixed solutions with a w/w GE/SiO$_2$ ratio of 1:5. Moreover,

the samples with higher BET areas were obtained by GE extraction instead of GE elimination by calcination (Table 2, sample M_{10}).

As seen in Fig. 1(a), the nitrogen sorption isotherms of sample M_{10} are typical of microporous materials, with the maximum located in the pore size range of <20 Å, the mean pore diameter being 26.6 Å (by desorption). However, the pristine extracted but non-calcined sample (M_{11}) shows a lower BET area and the absence of microporosity. However, clearly the micropores are blocked. This indicates either that water could not remove GE occluded in micropores or that there was water remaining inside the micropores. This latter assumption was discarded because after further drying for 4h at 200 °C the BET area and porosity remained practically unchanged (sample M_{12}). This sample is mesoporous, with a maximum located at 34 Å without microporosity (Table 2). Only after the calcination process does a considerable micropore area appear ($278 m^2/g$), but maintaining the mesoporous and external area of the original sample. This result suggests that the microporosity is originated by GE macromolecules encapsulated in the siloxane network. Absorptions due to GE in sample M_{11} are not visible in FTIR spectrum probably due to insufficient sensibility. The DTA/TGA and DSC/TGA results discussed below confirm this assumption.

4.2. Morphological considerations

SEM micrographs of silica samples prepared from xerogels obtained by precipitation in hydrochloric acid show monolithic pieces (Fig. 2(a)) constituted by close packing of regular sized microspheres (1 μm) (Fig. 2(b)). Considering the above results, these microspheres are probably microporous. It should be mentioned that separately neither the gelatin nor the silicate solutions form precipitates by treating them similarly with acid. This suggests that the precipitation of the combined GE/silicate solutions could be due to the association of both components to form hybrid molecular species in the solution. On the other hand, when the pure silicate solutions are mixed in a similar way with hydrochloric acid and then evaporated, the resulting solid after washing and calcination produces a mesoporous silica with irregular morphology. These products can be considered as blanks to establish the role of GE in samples prepared in a similar way, but starting from mixed GE/siloxane solutions (Table 1).

The considerable difference in morphology and porosity between the silica prepared from the siloxane/gelatin mixed solution and the blanks prepared without gelatin can be attributed to the presence of this biopolymer. Probably gelatin acts as a template for the inorganic phase, generating hybrid xerogels constituted by microspherical particles, precursors of the final porous spheri-

cal silica particles with large surface area. By considering the protein structure of GE, it can be expected that an association of the amino acid residues with silanol groups through hydrogen bonds take place, allowing a good compatibility between both components, and leading to the formation of the hybrid composite. Experiments carried out by precipitating the mixed solution at pH > 1.4 resulted in final silicas with low BET area. Probably the association between GE and the silanol groups of the siloxane precursors requires a highly positively charged structure of the protein macromolecules of GE.

4.3. Thermal analysis

In the DTA curve of Fig. 3(a) it can be seen that the hybrid xerogel sample without gelatin extraction shows very strong exotherms at 365 and 543 °C, corresponding to the combustion of the organic phase. As expected, the weight decrease (TGA curve) of the sample after 150 °C, when all free or adsorbed water was already lost, is very important. This reaches about 45%, corresponding mainly to the eliminated organic phase and, to a much lower extent, to constituent water, i.e. water resulting from condensation between silanol groups.

This means that the hybrid xerogel contains about 40% GE. On the other hand, in the DTA curve of the precursor xerogel of sample M_{11} (Fig. 3(b)), after thorough extraction with water, no exothermic peaks assignable to organic combustion are visible. In this case the weight loss after 150 °C is very small (Fig. 3(b)). In order to discard the presence of water occluded in the exhaustively dried sample M_{12}, a simultaneous DSC/TGA analysis (not shown) was carried out due to its considerably higher sensibility. DSC showed the combustion peak of residual GE at 360 °C with a 3% weight loss, and a very low peak at 590 °C with a weight loss of 0.5%. Considering that the total BET area of this sample (M_{10}) corresponds roughly to the sum of the measured area of sample M_{11} ($452 m^2/g$) before calcination and the micropore area generated after the calcination process ($278 m^2/g$), it can be concluded that the microporosity observed after calcination is originated by the elimination of GE macromolecules forming microdomains in the silica matrix. Thereafter, dry xerogel samples before calcination (M_{11} and M_{12}) can be considered as porous, high surface area hybrid materials. The porosity of these materials could be due to interparticle aggregation processes similar to those of silica precursors without GE (samples B_1 and B_2). In all cases the liquid phase remaining after hybrid precipitation, treated as the blank samples, lead to porous silica with characteristics similar to those of B_2.

The high BET area of M_{11} indicates that a very stable structure of the silica network was already formed after drying the xerogel. At this stage a mesoporous silica matrix is present which turns into a microporous, higher BET area network through the calcination process.

Experiments with longer heating (6h at 550 °C) led to some reduction of the micropore area (205 m^2/g), but after further heating for 20h at 550 °C this area remained practically constant (203 m^2/g).

It should be mentioned that ICP analysis of final silica sample M_5 showed a considerable lower Na content (<0.005%) compared with samples washed after drying at 70 °C (M_7 = 0.01% Na), or washed after the calcination process (M_9 = 0.35% Na), where salt could be occluded in closed domains of the silica net.

5. Conclusions

The association of siloxane sols obtained from sodium metasilicate with the protein macromolecules of gelatin showed that gelatin/silicate hybrid nanocomposites can be obtained by acid precipitation of mixed gelatin and sodium silicate solutions. After thorough extraction of the gelatin, porous xerogels containing residual gelatin in microporous domains were obtained. Gelling of these solutions formed no similar hybrids. Porous silica samples obtained by calcination of hybrid xerogels are predominantly microporous (pore diameter <20 Å) with large BET areas (350–830 m^2/g) which depend on the preparation conditions. Silica samples obtained under the same conditions but without gelatin also have large BET areas, but they are mesoporous ($\approx$40–100 Å) showing an irregular morphology on a micron scale, in contrast with silica particles obtained from hybrid xerogels which have uniform spherical morphologies ($\approx$1 μm). These microspheres are microporous, showing, as discussed, the nanocomposite structure of the precursor hybrids and making evident the templating role of gelatin in the formation of the silica network.

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