Porous silica derived from chitosan-containing hybrid composites

J. Retuert, R. Quijada, and V. Arias
Departamento de Quimica e Ingenieria Quimica, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile and Centro para la Investigación Interdisciplinaria Avanzada en Ciencia de los Materiales (CIMAT), Av. Beaucheff 850, Casilla 2777, Santiago, Chile

M. Yazdani-Pedram
Departamento de Quimica Orgánica y Físico Quimica, Facultad de Ciencias Químicas y Farmacéuticas, Olivos 1007, Casillo 233, Santiago, Chile and Centro para la Investigación Interdisciplinaria Avanzada en Ciencia de los Materiales (CIMAT), Av. Beaucheff 850, Casilla 2777, Santiago, Chile

In this paper, we report the preparation by the sol-gel technique of organic–inorganic hybrid composites containing the biopolymer chitosan incorporated in a siloxane-based inorganic network. The hybrid xerogels were transformed into porous silica particles by elimination of the organic phase. Surface characteristics of the silica samples can be easily tailored. In this way Brunauer–Emmett–Teller areas, pore volume, and pore diameter of the prepared silica can be predetermined within a wide range. Morphology of the particles at longer length scales can be designed to obtain either irregularly shaped particles with layered morphology or spherical particles. The results are explained on the basis of the cationic polyelectrolytic properties of chitosan, which allows easy association with siloxane oligomers, the precursors of silica in forming hybrid nanocomposites.

I. INTRODUCTION

Polymer hybrids are composites of organic polymers with inorganic components blended at the level of molecular dispersions and can be prepared in solution through sol-gel processing. Silica-based hybrids are the most widely studied materials in which the inorganic matrix is formed by the sol-gel reaction. A controlled sequence of hydrolyses and condensations starting from an alkoxysilane-like tetraethyl orthosilicate (TEOS) in alcohols and other polar solvents leads to a solution or colloidal suspension of siloxane polymers (sol). At this stage, or at the beginning of the process, it is possible to incorporate a soluble organic polymer in the sol. The basic reactions are

$$-\mathrm{Si}-\mathrm{OEt} + \mathrm{H_2O} \xrightarrow[-\mathrm{EtOH}]{} -\mathrm{Si}-\mathrm{OH}\ \text{(Hydrolysis)}$$

$$-\mathrm{Si}-\mathrm{OH} + \mathrm{EtO}-\mathrm{Si}- \xrightarrow[-\mathrm{EtOH}]{} -\mathrm{Si}-\mathrm{O}-\mathrm{Si}-\ \text{(Condensation)}$$

Further cross-condensations between siloxane polymers in the sol lead to the formation of a gel precursor of the silica matrix. In hybrid syntheses, organic polymer is present in the sol and can be dispersed homogeneously in the silica gel. Condensation between silanol groups consolidates the silica network largely during further thermal treatment of the gel.

$$-\mathrm{Si}-\mathrm{OH} + \mathrm{HO}-\mathrm{Si} \xrightarrow[-\mathrm{H_2O}]{} -\mathrm{Si}-\mathrm{O}-\mathrm{Si}-$$

Organic–inorganic polymer hybrids are attractive materials for optical devices, separation methods, sensors, structural materials, catalysts, and catalyst supports.[1,2] Porosity is a key property of materials, in particular those used for the preparation of catalysts, supports, and absorbents, where high surface area and control of pore size are important goals. Great advances have been made in the modeling of model porous structures with a high degree of order by using surfactants or amphiphilic block copolymers.[3,4] Moreover, the use of molds in combination with sol-gel has been applied to build oxidic suprastructures with predesigned architecture.[5] An alternative method for preparing porous silica with high surface area is based on the elimination of the organic component of hybrid polymer composites prepared by the sol-gel method.[6-11] Normally, preparation of polymer hybrids has been achieved by hydrolysis–condensation of tetraalkoxysilane in the presence of the appropriate organic polymer. Kure *et al.* found that molecular weight, functional groups, and the content of organic polymer segments in the hybrid stage have little influence on pore size.[8] However, Tomalia was able to control the pore size of porous silica by using the so-called "starburst" dendrimer as an organic polymer segment.[9] Recently, silicas with high surface areas could be obtained starting from siloxane-based hybrids containing poly(tetramethylene oxide) as the organic counterpart.[11] Furthermore, a dual pore structure was found in microporous silica prepared by pyrolysis of methacryloxypropyl groups in a hybrid precursor.[12] Variations of this method, consisting of the generation of porosity in hybrid xerogels by solvent extraction[13] or chemical elimination of the organic phase have also been reported.[14] Most of the papers on synthesis and transformation of polymer hybrids into porous oxides deal with synthetic polymers. However, the use of natural polymers for this work, despite their inherent complexity, can be interesting because of their renewable nature and their relation with biomimetic processes.

This work reports the preparation of hybrid composites containing the biopolymer chitosan incorporated into the inorganic network prepared by the sol-gel technique, and its transformation into porous silica by eliminating the organic phase. The use of chitosan for preparing hybrid materials is currently being examined in our laboratories.[15–18] Chitosan, poly-β-(1-4)-2-amino-2-deoxy-D-glucose, is the partially deacetylated product obtained by alkali treatment of chitin, an abundant biopolymer in the shells of crustaceans, and is a cationic polyelectrolyte due to amino-functionalities. This biopolymer readily associates with siloxane oligomers, precursors of silica via sol-gel, to form nanocomposites.

Because of the remarkable effect of reaction parameters on product characteristics, the preparation of silica/chitosan composites under a variety of experimental conditions has been investigated to study their effects on surface area and pore structure of the products. In particular, we have studied the formation of composites by using siloxane sols produced with both acidic and basic catalysts.

II. EXPERIMENTAL

A. Materials

Chitosan (CHI; Aldrich high molecular weight) (Aldrich, Milwaukee, WI) was used as the polymeric component. Molecular weight ($Mw = 1.2 \times 10^6$) was determined in CH_3COOH 0.1 M/NaCl 0.2 M as described previously.[19] The degree of deacetylation was 80.5% by ^1H- nuclear magnetic resonance spectroscopy.[20] TEOS (Aldrich), the precursor for the preparation of siloxane soluciones, was used as received.

A solution of TEOS in ethanol was hydrolyzed with aqueous HCl in ethanol to have a $TEOS:H_2O:HCl:EtOH = 1:1:0.01:10$ molar composition. This solution was kept at 50 °C in an open container for 3–4 days. The final volume was about half the initial. Distilled ethanol (azeotrope) was used, because it was noted that absolute ethanol removes added water, inhibiting the hydrolysis of TEOS. Eventually, more ethanol was added during the process to maintain the liquid level. Under these conditions, low-branched polysiloxanes should be produced. A similar procedure, but with ammonia as a basic catalyst, was used in some preparations.

B. Product synthesis

A 1% solution of CHI in dilute formic acid (5%) was prepared and filtered through a coarse sintered glass filter to remove microgels. The hybrids were prepared by mixing the freshly prepared solutions of CHI and siloxane sols. Relative amounts of each solution were predetermined from the CHI/SiO_2 ratio desired in the composite. The SiO_2:CHI molar ratio of the samples was calculated from the molecular weight of the monomeric unit of CHI (160.1). The solution was stirred for 1 h and then aged for 14 h. Xerogels were obtained from this solution either by removing the solvent in a rotavapor (method 1) or by precipitation in 0.5 N ammonia followed by separation of the resulting solid by filtration or centrifugation (method 2). Blank samples were also prepared under similar conditions without addition of CHI. The composition of all samples are shown in Tables I and II. The resulting xerogels were dried at 70 °C for 20 h and finally calcinated in air in a programmed temperature Nabertherm S27 (Merseburg, Germany) furnace at 550 °C or at the temperature predetermined for a specific experiment. The heating temperature gradient was 10 °C/min.

C. Characterization

Specific surface areas, pore size, and pore-size distribution of the heat-treated powder samples were determined by using a Micrometrics ASAP 2010 apparatus (Norcross, GA).

TABLE I. Effect of precursor xerogel composition on the surface characteristics of silica after 2-h calcination at 550 °C. Xerogel prepared by solvent extraction from the mixed sol.

Sample	Molar ratio CHI/SiO_2	Pore volume cm^3/g	Pore ϕ (Å)	BET area (m^2/g)
S_0	0 (blank)	0.00006	⋯	45
S_1	0.06	0.156	14.2	323
S_2	0.1	0.160	14.6	327
S_3	0.2	0.18	17.9	503
S_4	0.5	0.478	25.0	632
S_5	1.0	0.406	33.8	481
S_6	1.7	1.774	96	273

SiO_2 prepared starting from a SiO_2 sol in HCOOH.

TABLE II. Effect of precursor xerogel composition on the surface characteristics of silica after 2-h calcination at 550 °C. Xerogel prepared by precipitation of mixed sol in 0.5 N NH_4OH.

Sample	Molar ratio CHI/SiO_2	Pore volume cm^3/g	Pore ϕ (Å)	BET area (m^2/g)
P_0	0 (blank)	0.261	32	320
P_1	0.2	0.424	36.2	339
P_2	0.5	0.662	51.3	515
P_3	1.0	0.630	64.5	292
P_4	1.5	0.679	97.3	273
P_5	2.0	0.917	171	147
B_1	1.0	1.12	145.2	262[a]
B_2	1.5	1.267	177	247[a]

[a] Precursor sols prepared with basic (NH_4OH) catalyst.

Morphologies were examined on micrographs obtained by scanning electron microscopy (SEM; Philips EM 300) (Siemens Autoscan, Munchen, Germany). Fourier transform infrared (FTIR) spectra (Bruker Vector 22, Ettlingen, Germany) were taken to verify absence of residual organic compounds.

III. RESULTS AND DISCUSSION

A. Siloxane sols

It is well known that mainly linear polysiloxanes are produced by hydrolyzing TEOS with acid catalysts in the presence of little water.[21] The resulting gel is then only weakly branched. On the other hand, basic catalysts increase the hydrolysis rate and, consequently, the degree of branching of the polysiloxanes in the sol. Thus, base-catalyzed gels are highly branched polysiloxanes containing colloidal aggregates, especially when excess water is used. Because of the different extent of branching and particle size, acid-catalyzed gels contain largely micropores whereas base-catalyzed ones are mesoporous.[22] The porosity of silica produced by sol-gel can be tailored to some extent by using different conditions of hydrolysis. However, controlled porosity can also be produced in an inorganic matrix by elimination of the organic part of an organic–inorganic hybrid xerogel. In this work, we combined both synthetic approaches to better control porosity as well as morphology of the resulting silica. We blended CHI in different ratios with siloxane sols prepared using acidic or basic catalysts. The mixed sols were used to prepare hybrid xerogels with different characteristics to study the effects of these and other reaction conditions on the morphological and porosity properties of silica samples obtained after calcination of the xerogels.

B. Hybrid CHI/SiO$_2$ xerogels

As already described, starting from CHI and siloxane sols prepared under acidic or basic conditions, hybrid xerogels were prepared either by solvent evaporation (method 1) or by precipitation in dilute ammonia (method 2). The method used in each particular preparation leads to important changes in the characteristics of the xerogel and the final silica particles as already explained.

The absorption bands in the 1330–1750 cm^{-1} region in the FTIR spectrum of a silica xerogel thin film, obtained from a partially hydrolyzed TEOS solution [Fig. 1(a)], can be compared with those of a hybrid xerogel CHI/SiO$_2$ [Fig.1(b)] and CHI films [Fig. 1(c)]. It is seen that the FTIR spectrum of xerogel prepared by method 1 having an SiO$_2$:CHI = 1:0.5 M composition, compared with the FTIR spectrum of pristine CHI, shows the amido II band (–NH bending vibration) of CHI at 1575 cm^{-1} shifted to 1525 cm^{-1} in the hybrid xerogel. Considering that silica xerogel does not present any absorption band in this region [Fig. 1(a)], the observed spectral changes in the hybrid film may be attributed to the interaction between silanol and the amido-carbonyl groups of CHI through hydrogen bonding. With respect to the absorption bands in the 1300–1400 cm^{-1} region, it should be mentioned that Samuels[23] and Urbanczyck[24] have shown that some prominent features observed in the FTIR spectrum of chitosan may be related to the crystalline structure of a particular sample. Indeed, they have identified two main forms of chitosan: an amorphous (β) form and a crystalline (α) form. The β-form shows two absorption bands at 1350 and 1380 cm^{-1}. The α-form, on the other hand, has only the peak at 1380 cm^{-1} making it possible to determine the transformation of the β form into the α form. The bands at 1350 and 1380 cm^{-1} seem to arise from stretching vibrations of the methyl groups present in the approximately 12% residual acetamido groups of the chitosan, due to incomplete deacetylation of the parent chitin. It is well known that the band at 1350 cm^{-1}, assigned to the vibrations of the amide CH$_3$ group, is strongly influenced by groups in its vicinity. Specifically, its degree of freedom can be influenced by intermolecular hydrogen bonding interactions. Thus, in chitosan samples with high crystallinity (α-form) this band practically disappears, similar to what is seen for the hybrid structure in Fig. 1(b). These results can be interpreted on the basis of the compatibility of both phases through hydrogen bonding, presumably between amino and/or residual amido groups of CHI with the silanol (Si–OH) groups of the inorganic matrix.

Moreover, the ultraviolet-visible spectrum of hybrid films with the same composition, prepared by gel casting, shows that the absorption of CHI (213 nm) shifted to 207 nm in the hybrid material, also indicative of interactions between the CHI and silica phases.

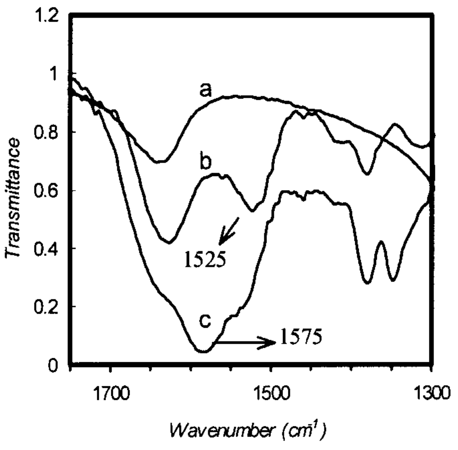

FIG. 1. FTIR spectra of (a) silica xerogel film prepared from a siloxane sol, (b) hybrid film with CHI/SiO$_2$ = 0.6 M, and (c) pristine CHI film with β-crystalline structure.

To obtain reproducible results it is very important to maintain the drying and aging conditions of the xerogels and always use freshly prepared CHI solutions.

C. Effect on morphology: Mixed sol processing routes

1. Method 1: Solvent evaporation

In this case, silica particles with layered morphology were obtained. This fact can be correlated with the previous observation of a self-assembled layered structure found in CHI/siloxane films prepared by gel-casting.[16] The association of both phases occurs through H-bonding as shown by FTIR. The hybrid xerogel structure [Fig. 2(a)] was preserved in the irregularly shaped final silica [Fig. 2(b)].

SEM micrographs of samples prepared from composites with low chitosan content (S_1) show an irregular surface with folded planes and macropores. However, the corresponding micrographs of sample S_4 (Fig. 3), with a higher Brunauer–Emmett–Teller (BET) area, show flat surfaces with some "craters" or protrusions ($\phi = 2$ to 4 μ). This morphology is completely different from that reported for porous silica, starting from silica/polyacrylic hybrids and followed by calcination, where large numbers of macropores are visible.[7]

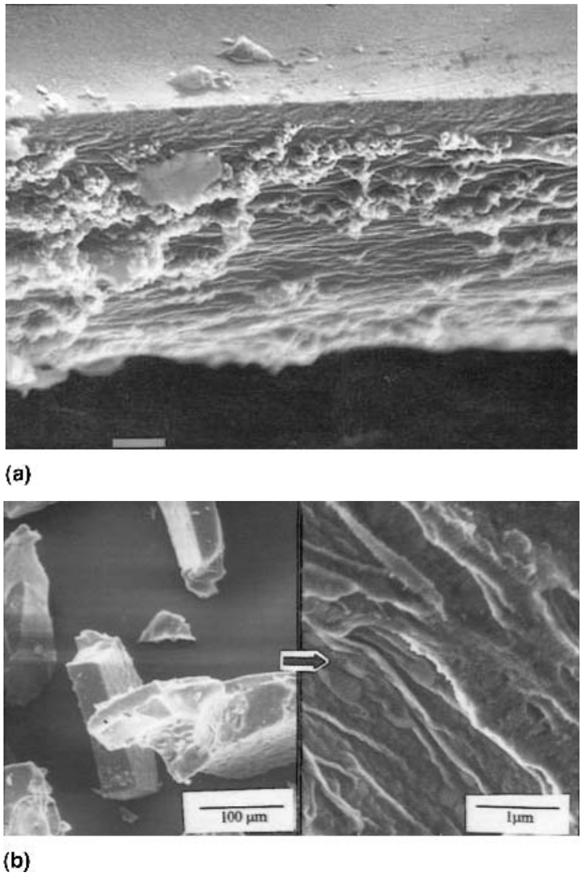

FIG. 2. SEM micrographs of (a) fractured surface of a silica/CHI (1:0.5 M) self-assembled hybrid film, and (b) silica particles after calcination of the hybrid at 550 °C/2 h. The bar size in (a) corresponds to 1 μm.

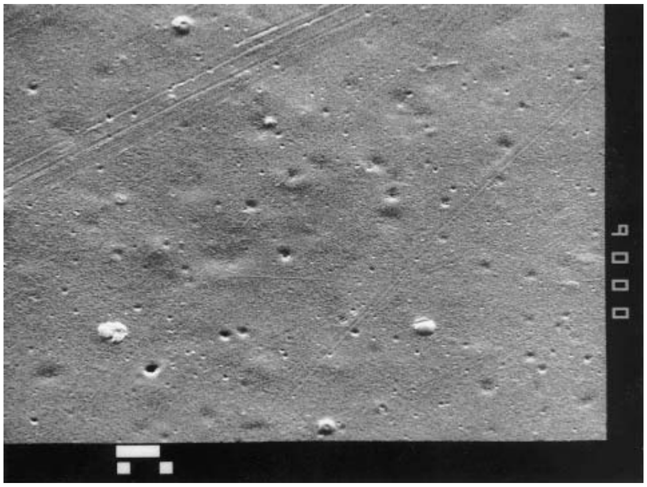

FIG. 3. SEM micrographs of the surface of a silica/CHI (1:0.5 M) self-assembled hybrid film. The bar size corresponds to 10 μm.

Micrographs obtained by SEM show that the morphological characteristics present in the hybrid xerogels are preserved in the silica particles after elimination of the organic component. In this way we found that layered and irregular shaped silica particles were obtained when the precursor xerogel was prepared by method 1, i.e., by solvent evaporation. This result can be correlated with the previous observation of a self-assembled layered structure present in CHI/siloxane films prepared by gel-casting.[18]

2. Method 2: Precipitation in NH_4OH

In this case spherical xerogel [Fig. 4(a)] and spherical porous silica particles [Fig. 4(b)] were obtained. Considering that both components, CHI and siloxanes, can form spherical particles by precipitation in ammonia, it is possible for a mixture of particles of both phases to be formed. However, silica particles obtained after calcination of the xerogel [Fig. 4(b)] have considerable BET areas and pore volumes, and these characteristics depend on the particular CHI/siloxane composition in the precursor mixed sols. The micrograph shows that closely packed smaller spheres of about 0.05 μm constitute the surface of the main spherical silica particles. These results indicate that the precipitated xerogel particles are hybrid composites in which the phases are associated.

To verify the existence of a strong tendency for association between CHI and siloxanes, a sol of siloxanes prepared with an acid catalyst was added to a suspension of microspherical particles of CHI prepared previously by forming an emulsion with a surface active agent (Span 20) in trichloroethylene in the presence of glutaraldehyde as a crosslinker. In this case, the SEM micrographs of the silica show fragmented and very thin spheroidal shells (Fig. 5).

This morphology indicates that the siloxanes present in the sol formed a coating over the surface of the chitosan particles prior to calcination. Moreover, when the CHI part of the hybrid spherical particles is partially extracted before calcination, hollow spheres of silica could be prepared.[25] These results support the templating action of CHI macromolecules towards the inorganic phase, and furthermore, it is possible that both phases were already associated in the mixed precursor solution. Figure 6 shows a schematic diagram to explain the templating role of chitosan in the formation of silica particles with different morphologies.

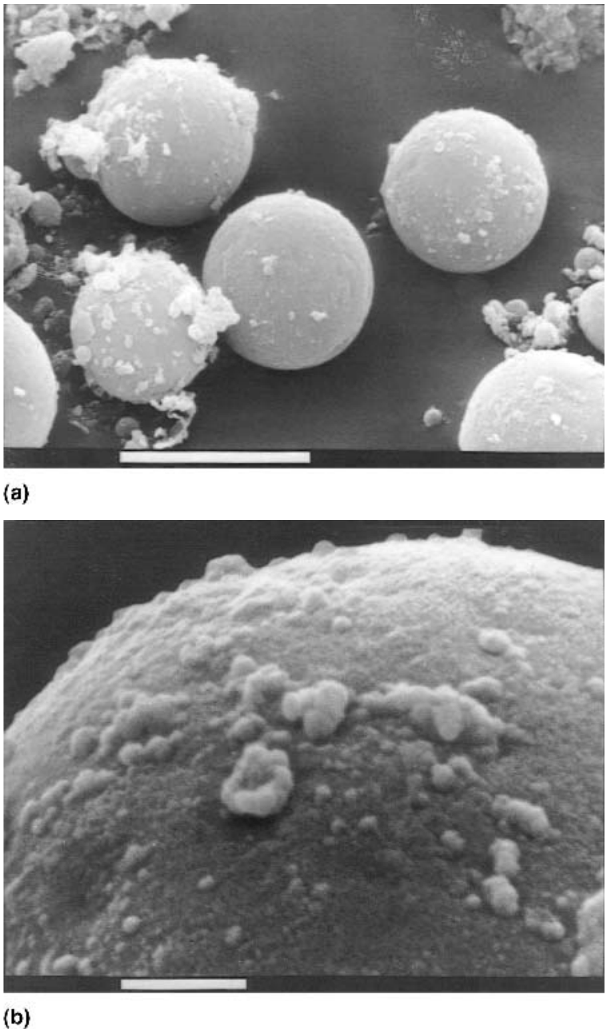

FIG. 4. SEM micrographs of (a) particles of a silica/CHI (1:0.5 M) hybrid xerogel precipitated in ammonia, and (b) particle of porous silica prepared by calcination of the hybrid particles at 550 °C for 2 h. The bar size in (a) corresponds to 10 μm and in (b) to 1 μm.

D. Effect of hybrid composition

Tables I and II summarize results on the porosity of silica samples prepared from xerogels. These xerogels were prepared with siloxane sols formed under linear polymerization conditions and by varying the amount of chitosan incorporated in them. The properties characterizing sample porosity after heat treatment at 550 °C for 2 h are also shown in Tables I and II. Data shown in Table I correspond to silica samples obtained from mixed xerogels prepared by solvent extraction. In sample S_0, silica obtained from a precursor gel without CHI shows a low surface area and is nonporous in the measured range. Here, the siloxane sol was mixed with HCOOH, which had been used as the solvent for CHI to use the resulting silica as a control to show that formic acid does not affect sample porosity. The result agrees with the formation of nonporous films in samples obtained from "linear" sols.

On the other hand, surface area, as well as pore volume and average pore size, increases with the amount of CHI in the precursor solution up to a CHI/SiO_2 molar ratio = 0.5. The pore-size distribution is narrow and monomodal

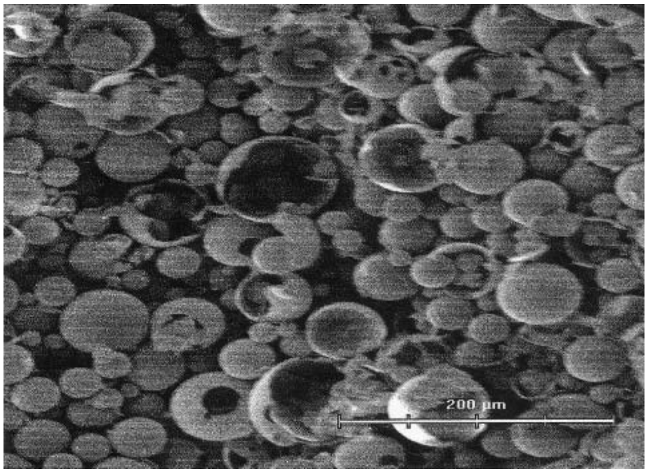

FIG. 5. SEM micrograph of fractured shells of silica initially coated over CHI microspheres. The bar size corresponds to 200 μm.

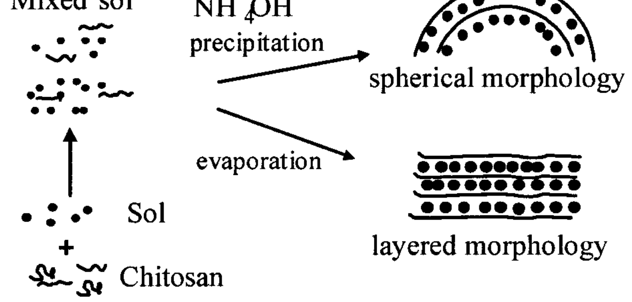

FIG. 6. Schematic representation proposed for the formation of silica with different morphologies.

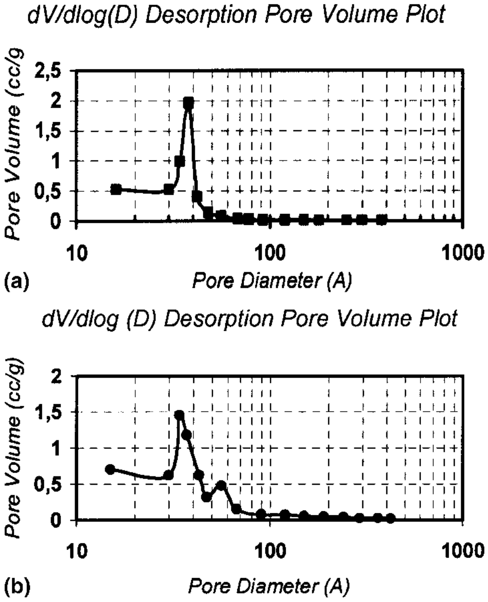

FIG. 7. Differential desorption pore volume plots showing pore-size distribution of silica samples S_4 and S_5 prepared from hybrid xerogels with CHI/SiO_2 (a) 0.5 M and (b) 1.0 M, respectively.

[Fig. 7(a)], which can be explained on the basis of a homogeneous distribution of the growing polymer domains inside the inorganic network. By studying hybrid CHI/SiO_2 films with molar ratios of 0.5:0.6 (1:1 by weight), we found that a hybrid complex with a nanocomposite structure is formed.[16] This fact can be related to the porous characteristics of silica particles obtained from these hybrids. Homogeneously distributed organic polymer inside the inorganic network is probably present in composites with lower amounts of CHI in relation to the molar composition of the complex (silica: CHI = 1:0.5). Moreover, the higher BET area was obtained for the composite with the composition of the above-cited complex (Table I, sample S_4).

For higher relative amounts of CHI (samples S_5 and S_6), surface area decreases but average pore size increases, and the pore-size distribution becomes bimodal in sample S_5 [Fig. 7(b)]. By increasing the initial amount of chitosan (sample S_6), the differential plot for pore volume shows a multimodal and broad distribution of pore size.

We think that chitosan in excess over the molar composition of the complex should induce phase separation and formation of heterogeneous domains in composite samples. As expected, after elimination of the organic component, pore size could be related with the size of the polymer domains present in the xerogel precursor.

Table II shows the results for silica samples from xerogels prepared by precipitating mixed sols in ammonia. As mentioned above, the silica particles prepared in this way are spherical (1–10 μm). The control (sample P_0), prepared from siloxane sols, mixed with 5% formic acid and then precipitated in 0.5 N ammonia, forms a gel which, after calcination at 550 °C for 2 h, produces mesoporous silica with high BET surface area (320 m^2/g) and pore volume (0.258 cm^3/g). Mean pore diameter is ϕ_p = 32 Å. As shown in Fig. 6, it is possible that the low-branched polysiloxanes produced during sol formation tend to associate and form spheres in the presence of ammonia. This effect is similar to that observed in the classical method of Stöber,[26] in which sols are produced and precipitated in methanol saturated with ammonia, thereby generating monodisperse and nonporous microspheres of silica.

There is a large difference in the BET area and porosity characteristics between both controls, i.e., samples P_0 (Table II) and S_0 (Table I). The porosity of S_0 could be due to a porogenic effect of HCOOH in the xerogel precursor of P_0 caused by rapid precipitation. Here, HCOOH present in the sol should be retained in the network of the xerogel, unlike xerogels produced by evaporation, as in sample S_0.

Results obtained from the samples presented in Table II, as well as with those in Table I, show a marked effect of composition on porosity, especially on mean pore diameter and surface area of the resulting silica. In both cases, as already discussed, maximum area was found for samples obtained from xerogels with a 1:0.5 silica:CHI molar composition. This composition corresponds to a nanocomposite with the structure of a complex,[15] i.e., both phases homogeneously associated on a nanoscale. However, there is substantial increase in the pore sizes of the samples in Table II compared to those in Table I, obtained from xerogels with similar composition. For example, for the complex composition in sample S_4 (Table I) ϕ_p = 32 Å, while for the equivalent sample in Table II (P_2) the pores are considerably larger (ϕ_p = 51 Å). By increasing the CHI content in the hybrid, pore sizes increase considerably until ϕ_p = 171 Å for a silica:CHI molar ratio of 1:0.5. The explanation for this trend is given above for the samples shown in Table I. However, the greater pore size of samples obtained from xerogels precipitated in ammonia can be the result of the rapid aggregation of the siloxanes contained in the sol produced in this stage through a process of extensive branching of pristine linear or lightly branched siloxanes.

Samples B1 and B2 (Table II) correspond to silica samples from xerogels prepared from siloxane sols obtained with a basic catalyst and precipitated in ammonia.

As indicated above, the resulting sol from basic catalysis of TEOS hydrolysis contains branched siloxanes leading to the formation of colloidal aggregates.[16] Therefore, silica obtained from xerogels prepared starting from base catalyzed sols has considerably larger pore size and pore volume, as shown by comparing the data for sample B_1 with that for samples P_3 and S_5. These samples were obtained from xerogels with silica:CHI molar ratio of 1.

The results of varying the amount of water used for the hydrolysis of TEOS samples with CHI: SiO_2 = 0.5:1 are shown in Table III. An increase in the amount of water systematically increases the mean pore size and pore volume of the resulting silica. The BET area decreases in the same sequence due to a lower pore–matrix interphase area. Increasing water content presumably affects not only the nature of the phase separation by changing domain sizes but also increases branching in the siloxanes contained in the sol.

E. Heat treatment

The effect of temperature in the 2-h heat treatment on the surface area of a silica sample (S_2) is shown in Fig. 8(a). Surface area decreases with increasing calcination temperature, probably due to sintering of the silica network. As expected, the micropore area and volume diminish even faster than total BET area, from 73 to 6.7 m^2/g and from 0.041 to 0.007 cm^3/g, respectively. On the other hand, the effect of calcination time on the BET area of a similar sample was checked by keeping it at a constant 550 °C [Fig. 8(b)].

TABLE III. Influence of the amount of water used for the hydrolysis of TEOS on the surface characteristics of silica after 2-h calcination at 550 °C.[a]

Sample	H_2O/SiO_2 molar ratio	Pore volume cm^3/g	Pore ϕ (Å)	BET area (m^2/g)
W_1	1	0.662	51.3	515
W_2	2	0.824	61.8	506
W_3	4	0.831	68.9	445
W_4	8	0.989	85.0	432

[a]Acid catalysts and precipitation in 0.5 N NH_4OH.

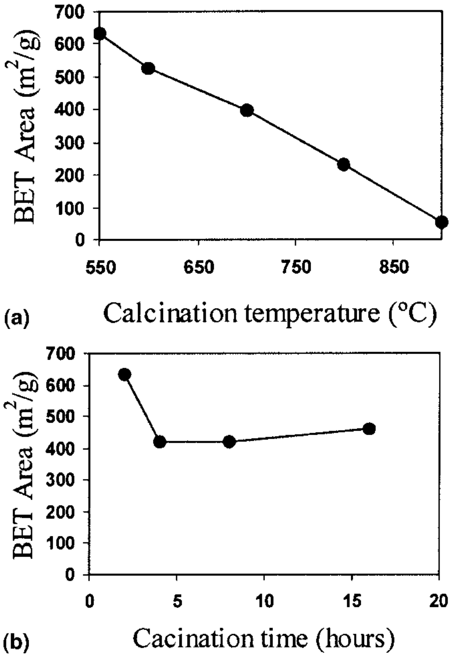

FIG. 8. Influence on BET area of silica (sample S_4) of (a) calcination temperature with 2-h heating time, and (b) calcination time at 550 °C.

In this case, during the first three hours there is a considerable decrease of the BET area, which becomes almost constant for longer periods of calcination. Considering that the BET area of a commercial silica with high area and porosity (e.g., Crossfield ES-70, Crossfield Catalysts, Warrington, Cheshire, England) is stable until about 700 °C, the results in Fig. 8(a) mean that the inorganic network of silica samples synthesized in this work is not well consolidated after 2 h of calcination at 550 °C. It is probable that siloxane chains or chain segments with numerous Si–OH groups are still present, allowing further condensation reactions leading to pore collapse and densification of the matrix.

IV. CONCLUSIONS

The combination of chitosan, a biopolymer with cationic polyelectrolytic properties, with siloxane oligomers produced via sol-gel generates hybrid xerogels. These xerogels can be used to produce silica samples with high surface area and controlled porosity. Surface characteristics of the silica samples can be easily tailored by choosing a convenient siloxane/CHI ratio for the hybrid precursor. Moreover, the morphology of the hybrid xerogels and the final silica after elimination of the organic residue depends on the method of preparation, giving either flat irregular shaped silica particles with a layered morphology or porous spherical silica particles. The results show that chitosan readily associates with siloxane oligomers, precursors of silica via sol-gel, to form nanocomposites acting as templating agents for the morphology of the inorganic network. Although the surface characteristics of the silica samples reported here are in the same range as those of most sol-gel-derived silica gels, this simple method provides a wide range of textural properties and morphologies.

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