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Stabilisation of the Secondary Structure of Chitosan Gels during the Preparation of Composites

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Summary: Zeolite-chitosan composites have been prepared by encapsulation of zeolites by a gelling solution of chitosan or by in-situ synthesis of zeolites inside a chitosan gel. The preparation of the composite implies modifications of both components. Zeolites are dealuminated by the acid solution in which chitosan is dissolved and the morphology of the chitosan fibrils is stabilized by iniorganic species issued from the dealumination of the zeolites or from their synthesis medium. Zeolite-bearing chitosan xerogels present surface area and porosity similar to the textural properties of chitosan aerogels.

Keywords: aerogels; chitosan; inorganic-polymer composites; self-assembled systems; textural properties

Introduction

Chitosan (poly-β-(1, 4)-glucosamine) is the deacetylated form of chitin, the main organic component of the exoskeleton of crustacea and insects. Chitosan is widely used as a material for separation membranes due to its good film forming properties, its affinity toward water, and the ease of cross-linking and modification of its functional groups. As a membrane material, chitosan is largely applied in the field of pervaporative dehydration of alcohols and glycols[1–7] and for the separation of heavy metal ions from aqueous solutions.[8–10]

Zeolites are crystalline microporous aluminosilicates with ion exchange properties suitable for a wide range of applications in catalysis and separation of liquid and gaseous mixtures.[11,12] Zeolites with several structures and compositions can be obtained by tuning the synthesis conditions.[13–15] The structure of zeolite A and faujasite, two of the most common zeolites, are represented in Figure 1. An optimal performance of these microporous materials can be achieved by engineering the access of adsorbates or reactants and forming them in shapes and sizes suitable for a given application. The incorporation of zeolites or porous fillers has been proposed to improve the separation performance of membranes[16–20] due to the combined effects of molecular sieving action, selective adsorption and difference in diffusion rates. The interplay of selectivity and permeability in a separation system is quite complex[21,22] and the incorporation of a second adsorbent in the system can extend the field of performance of the membranes.

Incorporation in chitosan membranes is an effective method to control the diffusion outside the zeolite crystals and appropriately designed composite systems can find numerous opportunities for applications in wastewater treatment and solvent recovery. Most of the chitosan-zeolites composites reported in the literature are obtained by inclusion of the zeolites in the gelling polysaccharide. Nevertheless, the chitosan

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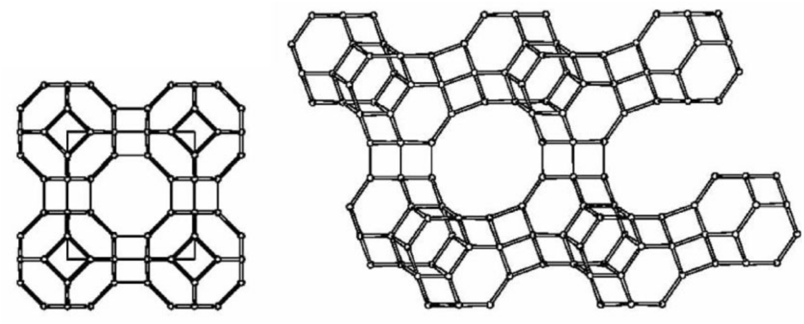

Figure 1.

Structure of zeolite A (lefthand) and faujasite (righthand). The circles represent silicon or oxygen atoms (T-atoms). Oxygen atoms form bridges between two T-atoms. Both structures are formed by arrays of sodalite cages (truncated octahedra formed by 24 T-atoms). The different ordering of the sodalite cages forms windows surrounded by 8 T-atoms (diameter 4.1 Å) in the case of zeolite A and windows surrounded by 12 T-atoms (diameter 7.4 Å) in the case of faujasite.[23]

gel is stable in the basic alkaline solution in which it was prepared (NaOH 4M) and thermogravimetric analysis shows that chitosan is thermally stable until 200 °C.[24] Most zeolites are formed from alkaline solutions at temperature much lower than 200 °C. As a consequence, chitosan is expected to be compatible with the formation domain of zeolites and zeolites are stable in the gelling domain of chitosan. These properties allow to propose others methods of preparation of composites like direct synthesis of zeolites inside the chitosan gel or zeolitisation of a chitosan-silica composite.[25] The textural properties of these composites are presented and discussed in this work.

Experimental Part

Preparation of Chitosan Gel

Chitosan (degree of acetylation of 10% as measured by IR spectroscopy, MW = 700 000 g.mol^{-1} determined by viscosimetry) from crab shell was obtained from Aldrich Chemicals. Chitosan (3% w/w) was totally dissolved by stirring 2 hours at room temperature in a 1% acetic acid solution. Gelation was obtained by dropping the chitosan solution into a 4 M NaOH solution through a 0.8 mm gauge needle. The chitosan beads were left in the alkaline solution for 2 hours, filtered and washed with deionised water.

Preparation of Chitosan-Zeolite Composites

Two preparation methods have been used to obtain chitosan-zeolite composites:

1) Micrometric crystals of zeolites X or Y were dispersed in a 3% chitosan solution in 1% aqueous acetic acid (zeolite X and zeolite Y share the faujasite structure but present different Si/Al ratios, about 1.25 for zeolite X and 2.5 for zeolite Y). The chitosan gel was formed as described above and the zeolite crystals were encapsulated during the gelling process.
2) Zeolites have been synthesized inside chitosan gels prepared as described above. The reagents for the zeolite synthesis were introduced in the gel by impregnation with an alkaline sodium aluminosilicate solution with molar ratios 2.5 Na/0.67 Al/SiO_2/52 H_2O. The crystallization of zeolites was obtained by 48 hours of hydrothermal treatment at 80 °C in a sealed Teflon-lined autoclave. In the absence of polysaccharide, zeolite X is expected to crystallize in such a synthesis system.[26]

All solids have been dried by solvent evaporation at 80 °C.

Characterization of Materials

Nitrogen adsorption was performed at −196 °C in a Micromeritics ASAP 2010 volumetric instrument. The samples were outgassed at 80 °C prior to the adsorption measurement until a $3 \cdot 10^{-3}$ Torr static vacuum was reached. The surface area was calculated by the Brunauer-Emmett-Teller (BET) method. Micropore volume and external surface area were evaluated by the alpha-S method using a standard isotherm measured on Aerosil 200 fumed silica.[27] Powder X-ray diffraction (XRD) patterns of samples dried at 80 °C were collected at room temperature on a Bruker AXS D-8 diffractometer with Cu Kα radiation. The thermal stability and the organic contents of the dried solids were determined by thermogravimetric analysis. The samples were heated in air flow at 10 °C min^{-1} up to 900 °C in a Netzsch TG 209 C thermal balance. SEM micrographs were recorded on a Hitachi S4500 microscope.

Results and Discussion

A 30% zeolite Y-chitosan composite was prepared by encapsulation method. The powder X-ray diffractogram of the composite (Figure 2c) presents the characteristic peaks of the encapsulated zeolite.[28] A chitosan-zeolite composite containing 10% of mineral fraction was prepared by in-situ zeolite synthesis. The X-ray powder pattern of the composite (Figure 2b) is typical of faujasite but the peaks are shifted at a lower angle. The size of the cubic cell of faujasite is proportional to its aluminium content[29–31] and it is normal that zeolite X present diffraction peaks at lower angle than aluminium-poorer zeolite Y. The XRD pattern of chitosan is also observable in the composite with the lowest zeolite content. The XRD pattern of the pure chitosan gel cast from the solution is provided in Figure 2a and corresponds mainly to the type II crystal structure.[32]

Whatever the synthesis procedure, Scanning electron microscopy indicated that the zeolite crystals were homogeneously dispersed inside the gel. They present the classical shape expected for the zeolite types, twinned octahedra for faujasite and cubic crystals for zeolite A (Figure 3). The macroporous network of the polymer is still observable. The sample depicted in Figure 3c is the results of an in-situ synthesis in which the chitosan gel beads were extracted from the aluminosilicate solution before the hydrothermal treatment, leading to the formation of zeolite A instead of zeolite X.

Textural Properties of the Chitosan-Zeolite Composites

The neutralisation of acid chitosan solutions forms entangled hydrogels by aggregation of the polymer chains in fibrillar secondary structures. The drying method of the hydrogel strongly affects its morphology, as evidenced by the N_2 adsorption-

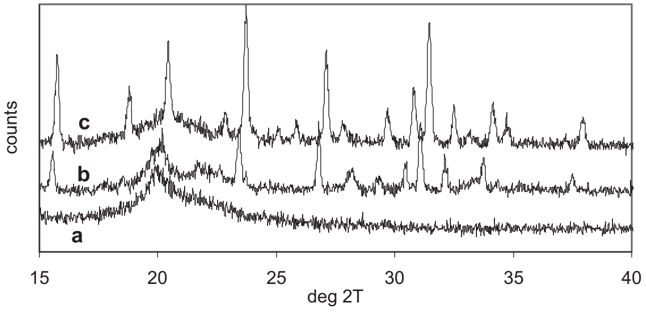

Figure 2.

X-ray power diffraction patterns for xerogels of (a) pure chitosan gel, (b) 10% zeolite X synthesized in chitosan gel, (c) 30% zeolite Y encapsulated in chitosan.

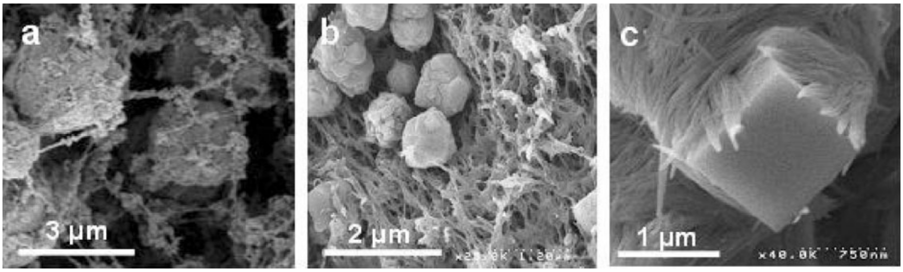

Figure 3.
Scanning electron micrographs for (a) zeolite X encapsulated in chitosan gel, (b) encapsulated zeolite Y, (c) in-situ synthesized zeolite A crystal.

desorption isotherms of chitosan xerogel and aerogel reported in Figure 4.

If the hydrogel is dried by evaporation, the surface tension of the receding menisci draw together the secondary structures of the polymer and a compact xerogel with surface area lower than 5 $m^2 \cdot g^{-1}$ is formed with virtually no porosity. A method to preserved the tridimensional network of the hydrogels is to dry the gels under supercritical CO_2 conditions.[33,34] Aerogels are formed which develop surface areas as high as 300 $m^2 \cdot g^{-1}$ and provide an excellent accessibility to reacting molecules.[35]

The zeolite-chitosan composite xerogels present a completely different isotherm than chitosan xerogel. The shape of the isotherm, intermediate between type 2 and type 4 in the IUPAC classification, indicates the presence of large mesopores (pore diameter between 2 and 50 nm) at the borderline with macroporosity (pores larger than 50 nm). The isotherms of composites of different compositions are reported in Figure 5.

The isotherms observed, except the limited contribution of microporosity, does not correspond to zeolitic systems but are very similar to the isotherms measured on supercritically-dried polysaccharide aerogels (Figure 5). It is clear that the presence of inorganic matter has prevented the shrinkage of the polymer fibrils which is usually brought about by thermal drying. The textural properties deduced from the nitrogen isotherms are reported in Table 1.

The surface area of the zeolite A-chitosan composite obtained by in-situ

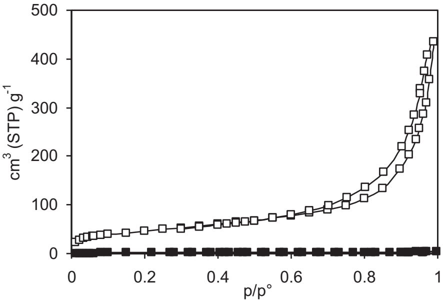

Figure 4.
Adsorption-desorption isotherms of N_2 at −196 °C for chitosan xerogel (filled squares), chitosan aerogel (empty squares).

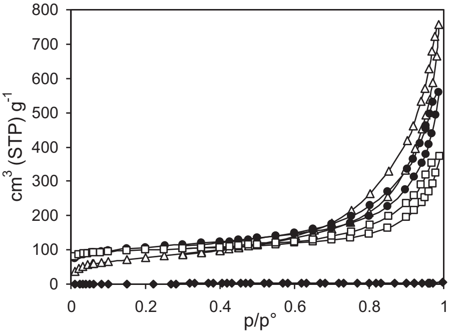

Figure 5.
N_2 adsorption isotherms at 77 K for xerogels of chitosan (filled lozenges), 60% zeolite Y encapsulated in chitosan (void squares), 30% zeolite Y encapsulated in chitosan (filled circles), 10% zeolite A synthesized in chitosan gel (void triangles).

Table 1.
Composition and textural properties (surface area, microporous and mesoporous volume) of chitosan aerogel and xerogel and chitosan-zeolite composite xerogels.

sample	% zeolite	S ($m^2 \cdot g^{-1}$)	Vμ ($cm^2 \cdot g^{-1}$)	Vmeso ($cm^2 \cdot g^{-1}$)
chitosan xerogel	0	3	0.00	0.00
chitosan aerogel	0	185	−0.01	0.21
Y-encapsulated	0.31	238	0.07	0.34
Y-encapsulated	0.61	125	0.10	0.18
A-in situ synthesis	0.11	287	0.00	0.49
X-encapsulated	0.65	133	0.08	0.18

synthesis of the zeolite is 287 $m^2 \cdot g^{-1}$. The α-S treatment of the isotherm indicates that no microporosity (pores smaller than 2 nm) is present. This is quite logical if it is considered that the water occupying the microporosity of zeolite A cannot be outgassed at a temperature as low as 80 °C. In the case of the faujasite-chitosan composites, the step of adsorbed volume at low pressure indicates that some microporosity is present, corresponding to the volume let free by evaporation of the water molecules less tightly bound to the sodium cations in the zeolite.[36]

The stabilisation of the dispersion of the chitosan fibrils by inorganic impregnation seems an acceptable hypothesis in the case of composites formed by in-situ synthesis of the zeolite. In this case, silicate and aluminate solutions are easily conceived to interact with the secondary structures of the chitosan gel. It is more surprising that the same effect is observed for composites prepared by encapsulation of crystalline zeolites. However, modification of the zeolites in the gelling system of chitosan can account for the phenomenon.

In Figure 6, the X-ray diffraction patterns of zeolite X before and after encapsulation in a chitosan gel are reported. A significant high-angle shift of the peaks is observed, which corresponds to a decrease of the cell parameter with encapsulation. The cell parameter of faujasite is a function of its aluminium content and the observed shift corresponds to a change of the Si/Al ratio from the original 1.3 to 2.6. Aluminium-rich zeolites can be easily dealuminated by acid solutions[37,38] and the loss of aluminium can be easily accounted for by the action of the acetic acid solution in which chitosan was dissolved. Once the zeolite-bearing acid solution is brought to basic pH during chitosan gelling, the dissolved aluminium reacts with silicate species dissolved by the added NaOH solution and form small crystals of gismondine, a more aluminium-rich zeolite which can be observed in the X-ray diffraction pattern b of Figure 6.

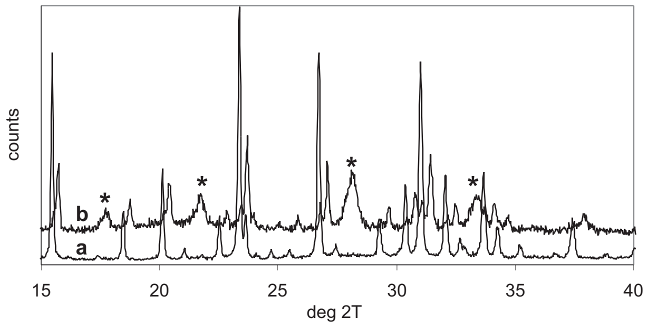

Figure 6.
X-ray powder patterns of (a) zeolite X and (b) 65% zeolite X encapsulated in chitosan. Stars indicate diffraction bands of gismondine.

Dissolved aluminium species are present in the systems from which zeolite-chitosan composites are formed both by encapsulation of the zeolite and by in-situ synthesis. It seems likely that the interaction of such species with chitosan accounts for the stabilization of the texture of the polymer gel, which shows an unusual resistance to evaporative drying.

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