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Porous Titania Obtained through Polymer Incorporated Composites

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Mesoporous titania with a large surface area has been prepared by calcination of hybrid composites. The composites were obtained by the incorporation of the biopolymer chitosan in titania networks produced from titanium isopropoxide by a sol−gel process. The resultant titania is of the pure anatase form. The effect of the experimental variables on the product's characteristics are studied.

Introduction

The properties of titania have generated increasing interest in its use as a catalyst in photocatalysis or as a support,[1−6] especially for group VIII metals, where it has a remarkable influence on the surface structure and the catalytic activity of the supported metal.[7−8]

An important limitation to the use as a support of titania obtained by conventional methods is its low surface area. One way of obtaining titania with larger surface areas (>100 m^2/g) has been through the preparation of aerogels[9−11] using the sol−gel process, followed by supercritical drying.

The possibility of preparing materials having a variety of pore structures is one of the main advantages of the sol−gel method based on the controlled hydrolysis of alkoxides. It is known that the pore structure is affected by reaction parameters of hydrolysis and condensation such as water and catalyst concentration, pH, and temperature. Moreover, the aging and drying conditions also affect the pore structure of a xerogel. A somewhat different method for preparing materials with high surface area and controlled pore size is by calcination of hybrid polymer composites prepared by the sol−gel method. This procedure has been used successfully to obtain porous silica gel.[13−16] The preparation of polymer hybrids was achieved by incorporating organic polymers at the level of molecular dispersion into a silica matrix. This was accomplished by the hydrolysis−condensation of tetraalkoxysilane in the presence of the appropriate organic polymer. Kure et al.[13] have found that the molecular weight, the functional groups, and the content of organic polymer segments in the hybrid stage had little influence on the sizes of the pores formed. However, Tomalia[14] was able to control the pore size of porous silica by using the so-called starburst dendrimer as an organic polymer segment. A variation of this method, consisting of the solvent extraction of the polymer-rich phase from the xerogel, has been reported recently.[17]

This paper reports the preparation of high surface area titania by calcination of composites containing the biopolymer chitosan incorporated into the inorganic network precursor of titania prepared by the sol−gel technique.

Because of the remarkable effect of the reaction parameters on the characteristics of the products, the preparation of titania/chitosan composites under a variety of experimental conditions has been investigated in order to study their effect on the surface area and pore structure of the products obtained.

The use of chitosan for preparing hybrid materials is currently being examined in our laboratories.[18,19] Chitosan, or poly-β(1−4)-2-amino-2-deoxy-D-glucose, is the deacetylated product of the alkali treatment of chitin, an abundant biopolymer contained in the shells of crustaceans.

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Table 1. Effect of the Initial Composition Mixture on the Surface Properties of Porous Titania

sample	experiment	mole ratio CHI:TiO_2	BET area (m^2/g)	pore volume (cm^3/g)	pore diameter (Å)	observations
T_0	Ti sol −5% formic acid	0	40	0.083	81.7	blank
T_1	Ti sol with chitosan	0.06	37	0.072	76.3	mesoporous monomodal
T_2	Ti sol with chitosan	0.13	42	0.073	66.1	mesoporous monomodal
T_3	Ti sol with chitosan	0.2	69	0.183	101.4	mesoporous monomodal
T_4	Ti sol with chitosan	0.3	79	0.193	94.5	mesoporous monomodal
T_5	Ti sol with chitosan	0.5	99	0.214	86.8	mesoporous monomodal
T_6	Ti sol with chitosan	0.6	103	0.205	84.4	mesoporous monomodal
T_7	Ti sol with chitosan	0.9	97	0.185	71.9	mesoporous monomodal
T_8	Ti sol with chitosan	1.3	95	0.205	78.8	mesoporous monomodal
T_9	Ti isopropoxide with chitosan	0.5	65	0.149	91.5	excess 2-propanol; mesoporous multimodal
T_{10}	Ti isopropoxide with chitosan	0.5	88	0.163	73.9	mesoporous

Experimental Section

Components of the Composite. *Chitosan*. The chitosan (CHI) (Aldrich, high molecular weight) used as the polymeric component was characterized in our laboratory (MW = $1.2 \cdot 10^6$, 80% deacetylation degree).[20] It was washed with acetone and ethanol and then dried at 65 °C for 24 h, and a 1% solution in dilute (5%) formic acid was made.

Titania Sol. A 14.8 mL portion of titanium(IV) isopropoxide (0.05 mol) was added to a solution of 4.8 mL diethanolamine (DEA) (0.05 mol) in 34.4 mL (0.45 mol) of 2-propanol, and the mixture was hydrolyzed by adding dropwise 0.81 mL (0.045 mol) of water dissolved in 34.4 mL (0.45 mol) of 2-propanol. The solution was stirred mechanically at room temperature for 4 h. The titania sol prepared in this way was stored in a refrigerator to provide the amounts required for each sample.

Gel Preparation. The titania sol was added dropwise to the mechanically stirred CHI solution. The relative amounts of both solutions were predetermined from the CHI/TiO_2 molar ratio desired in the hybrid. As the titania sol was added, gel particles were produced which were later separated and washed twice with ethanol by centrifuging at 10 000 rpm. The product was allowed to stand for 16 h, followed by drying at 80 °C for 24 h, and was finally calcined. In some experiments (samples T_9 and T_{10}, Table 1) the solution of Ti isopropoxide and DEA in ethanol was added directly, without prehydrolysis, to the CHI, but the rest of the procedure was the same.

Heat Treatment. A forced convection, temperature-programmed Nabertherm S27 furnace was used. The samples were calcined in air at the predetermined temperature (500−800 °C) for two or more hours.

Characterization. Specific surface areas were measured by adsorption of nitrogen at 77 K according to the BET method. Pore size distributions of heat-treated powder samples were determined using a Poresizer Micromeritics ASAP 2010 apparatus. Powder X-ray diffraction analyses were carried out with a Siemens D-500 instrument, and morphologies were examined on micrographs obtained by scanning electron microscopy (SEM, Philips EM 300). A Netzch Simultaneous Thermal Analyzer STA 409 was used for the (DTA/TGA) analyses.

Results and Discussion

Table 1 shows the BET areas determined for titania obtained from CHI/TiO_2 hybrids of different composition after calcination at 550 °C for 2 h. Table 1 also shows the results obtained from porosity analysis. Samples T_1−T_8 show that the structures obtained are mesoporous, with a monomodal pore size distribution. On the other hand, the results obtained for the samples with the lower amounts of CHI (T_1 and T_2) indicate that they are very similar in BET area and total pore volume to the blank samples prepared without CHI (T_0). Thereafter it is seen that the surface area increases with the CHI content in the hybrid up to a maximum (103 m^2/g) for a CHI/TiO_2 mole ratio of 0.6 (T_6) and then decreases slightly. A similar tendency is observed for the total pore volume determined in the corresponding samples. This surface area is comparable to the one that has been obtained with titania aerogels (96−107 m^2/g).[10] However, it is smaller than that obtained by Ko[11] (200 m^2/g) by controlling the amount of water and nitric acid used in the formation step of the xerogel precursor of the final aerogel.

As the quantity of CHI increases, the increase in the surface area may be due to an increase of the polymer domains in the interconnected hybrid structure. As already stated, by increasing the proportion of CHI beyond the optimum value determined for the CHI/TiO_2 feed ratio in the mixture, the BET area of the product does not continue increasing. This could be caused either by a segregation of the excess CHI from the composite, giving rise to extensive regions or domains that do not generate porosity upon its elimination, or to local temperature increases caused by the combustion of larger polymer quantities, a process that would neutralize a potentially greater area. It was observed that, for the higher CHI contents in the feed ratio (samples T_7 and T_8), the solution, after precipitation of the hybrid, contains some dissolved chitosan; this fact suggests that an excess of chitosan over the optimum proportion should not be incorporated into the composite or segregated from it. Moreover, we think that the similar values of BET area, total volume, and pore diameter determined in these last samples, showing a small influence of the quantity of CHI in this range of composition (CHI/TiO_2 = 0.5−1.3), could be related to the formation of hybrid networks with some degree of order among the phases for an optimum ratio (CHI/TiO_2 = 0.5−0.6), similarly to what has been shown to occur in CHI/SiO_2 hybrids, in which a complex with nanocomposite structure is formed for the molar ratio CHI/SiO_2 = 0.6.[19] Similarly, silica with the higher BET area has been obtained by Wilkes et al. for an optimum polymer/SiO_2 feed ratio (30−50% weight ratio) after calcination of the hybrid material.[16]

Heat Treatment. The decrease of the BET area with heat treatment time is shown in Figure 1. It is seen that during the first hours at 550 °C there is a rapid decrease of the area of sample T_6, which tends to remain rather constant for a long time, implying a stabilization of the porous structure. The rapid initial decrease may be due to the formation of crystalline microdomains and/or the

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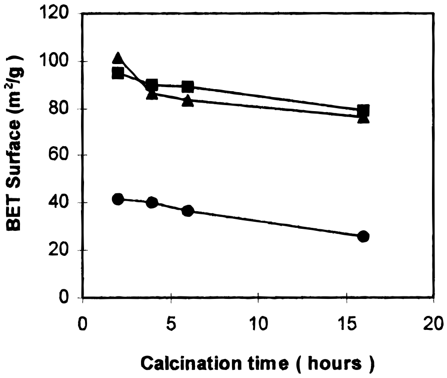

Figure 1. Effect of calcination time at 550 °C on the surface area of titania: ▲, sample T_6; ■, sample T_8; ●, sample T_2.

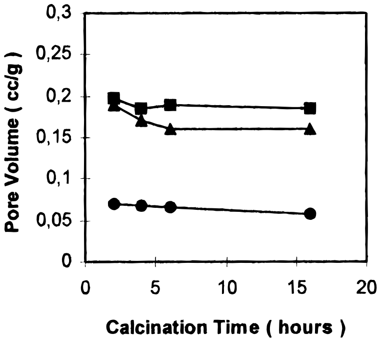

Figure 2. Variation of pore volume with calcination time at 550 °C: ▲, sample T_6; ■, sample T_8; ●, sample T_2.

continuation of the titania matrix densification through condensation reactions between Ti−OH groups. To study this point, DTA/TGA simultaneous thermal analyses were carried out on sample T_6 ($CHI/TiO_2 = 0.6$) previously calcined at 550 °C for 2 h. This was done by first heating at a rate of 10 °C/min up to 600 °C, maintaining this temperature for 12 h, and finally heating to 900 °C at 10 °C/min. No weight loss was detected after 350 °C, but a notorious endothermic peak during the period around 600 °C should indicate the crystallization of amorphous titania to anatase. On the other hand, if the thermal analysis is carried out from 20 to 900 °C at a heating rate of 10 °C/min, defined peaks due to crystallization are not observed. Under those conditions this process take place over a wider temperature range and is faster at higher temperatures. The slow crystallization at constant moderate temperatures (550−600 °C) should be mainly responsible for the decrease in BET area shown in Figure 1.

It is well-known that during the heat treatment, sintering of gel networks eliminates small pores and makes total pore volume low and average pore size large. In the case of TiO_2, the tendency of the titania networks to crystallize should increase this process considerably with respect to silica networks. The effect of calcination time at 550 °C in samples T_2 and T_8 with different CHI/TiO_2 feed ratios (namely 0.13 and 1.3, respectively) was determined and included in Figure 1. In these cases the BET area of the samples decreased less markedly with calcination time. The decreases of pore volume as well as the increases of pore diameter are shown in Figures 2 and 3.

The decrease in the BET area with calcination temperature for composites prepared with the $CHI/TiO_2 =$ 0.6 ratio is shown in Figure 4. It was found that at the lowest usable calcination temperature (500 °C), a maximum BET area of 120 m^2/g was obtained. Complete elimination of CHI was not achieved at lower temperatures (<500 °C), leading to colored samples whose FTIR spectrum shows organic group residues. Moreover, it is seen that the surface area of our titania after heating at 800 °C for 2 h was 11 m^2/g, a value higher than that reported for previous aerogels[11] in which it was reduced to only 7 m^2/g after a similar heat treatment.

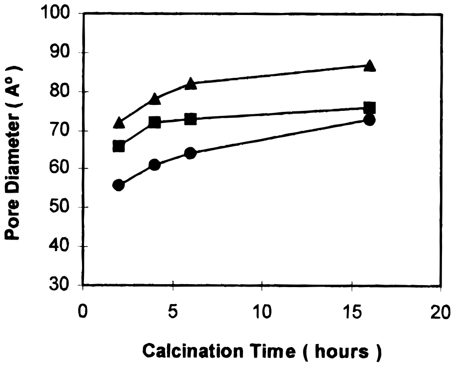

Figure 3. Variation of pore diameter with calcination time at 550 °C: ▲, sample T_6; ■, sample T_8; ●, sample T_2.

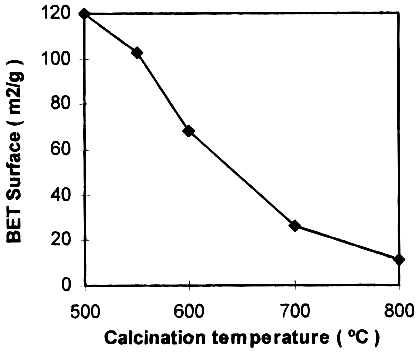

Figure 4. Effect of calcination temperature for 2 h on the surface area of sample T_6.

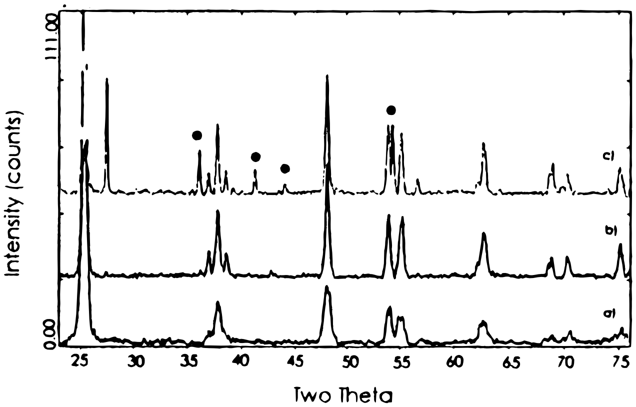

Figure 5. X-ray diffraction patterns of samples prepared from mixtures with a $CHI/TiO_2 = 0.6$ mole ratio after calcination: (a) 550 °C for 2 h; (b) 550 °C for 16 h; and (c) 800 °C for 2 h. ● denotes rutile phase peaks. The other peaks belong to the anatase phase.

The X-ray diffraction pattern (Figure 5) show that already in samples calcined at 550 °C for 2 h, crystallization as anatase is evident. The anatase form still remains as the only phase after 16 h at 550 °C and even

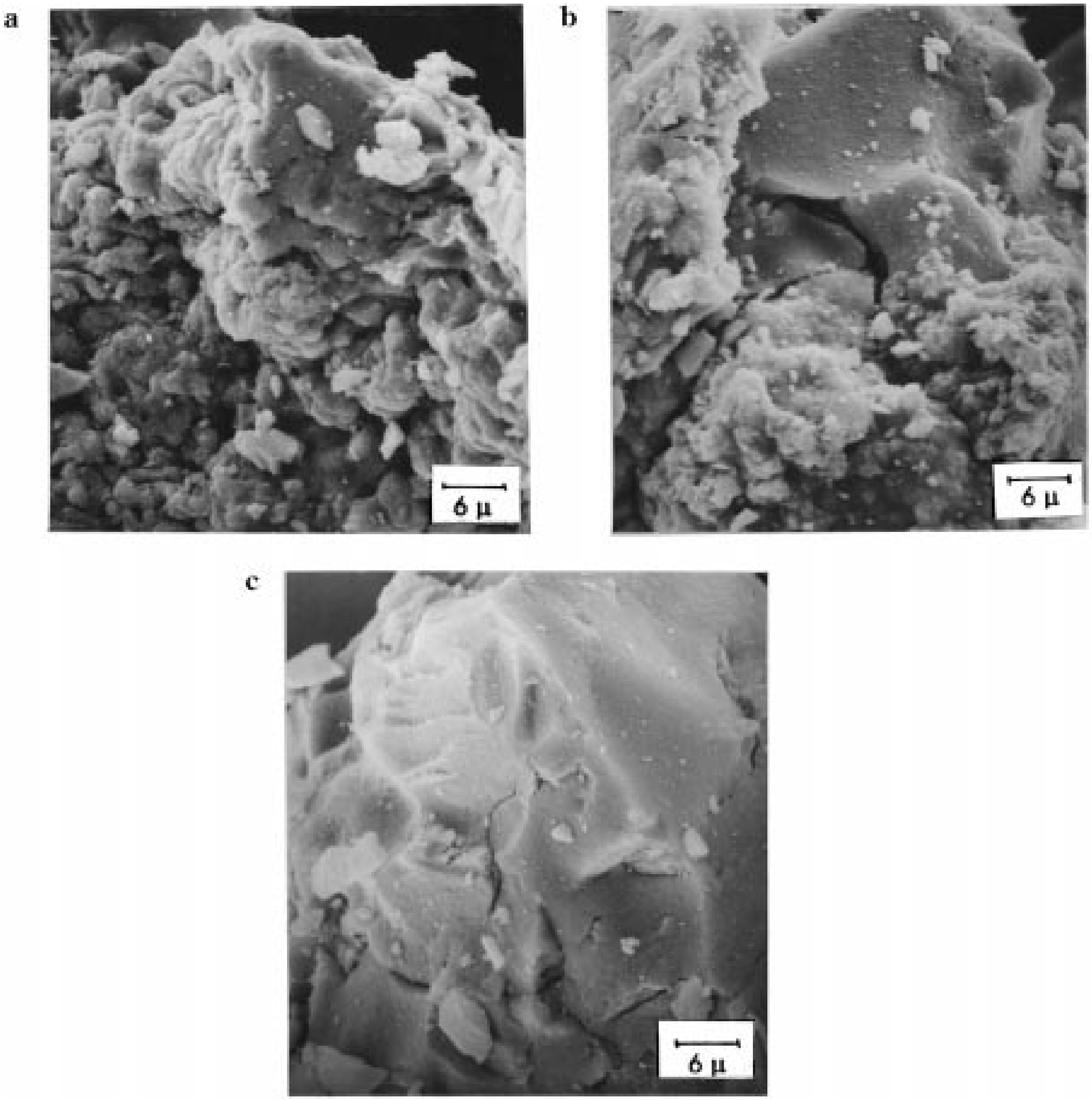

Figure 6. Scanning electron micrographs of samples prepared from mixtures with different CHI/TiO_2 mole ratios after calcination at 550 °C for 2 h: (a) CHI/TiO_2 = 0.13 (BET 42 m^2/g); (b) CHI/TiO_2 = 0.3 (BET 79 m^2/g); and (c) CHI/TiO_2 = 0.9 (BET 97 m^2/g).

at 700 °C for samples heated for 2 h. Only at 800 °C does rutile appear as a second crystalline phase, although in considerably smaller amounts relative to those of the aerogels prepared by Ko[11] under the same heating conditions.

Morphology. Figure 6 shows scanning electron micrographs of titania samples T_2, T_3, and T_9 prepared from mixtures having different CHI/TiO_2 ratios. The appearance is the opposite of what could be expected considering the BET areas of these samples. While the surface area of titania having lower BET areas shows a structure made by agglomeration of very fine particles, as the BET surface increases, there is a flattening of surface details with a loss of the particulate appearance. This morphological change could be due to interaction, through hydrogen bonds, between the two macromolecular systems, CHI and the inorganic network that is being formed.

Preparation of Hybrids with Titanium Isopropoxide. In the experiments described above, a titania sol was mixed with CHI. The oligomers contained in the sol can be expected to be more stable to hydrolysis than the titanium isopropoxide, and they may form composites with the CHI, decreasing the tendency of TiO_2 to precipitate and separate from the organic polymer. However, the usual method for obtaining the organic–inorganic polymeric hybrids is by hydrolyzing the inorganic alkoxide in the presence of the organic polymer, so two experiments were performed following that route, using in both of them the molar ratio of CHI/TiO_2 = 0.6 in order to compare the results with those obtained using titania sol as was previously described. In one experiment the solution of titanium isopropoxide and DEA in 2-propanol was added dropwise to the CHI solution (sample T_{10}, Table 1), while in the other the same procedure was applied to a CHI solution mixed with 2-propanol in a 1:1 ratio to decrease the rate of hydrolysis (sample T_9, Table 1).

It is seen that in both cases the BET areas determined are smaller than those obtained with a titania sol for

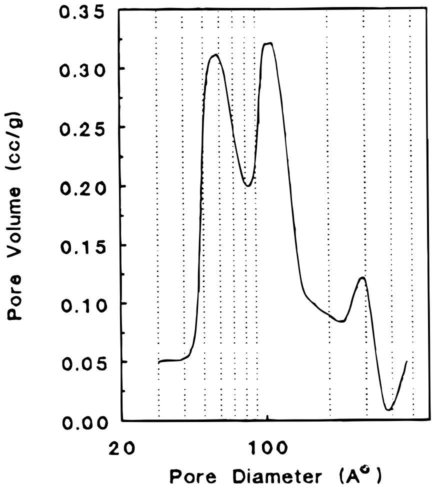

Figure 7. Differential desorption pore volume plot showing the multimodal pore size distribution of a titania sample prepared by mixing a titanium isopropoxide/2-propanol solution with a 5% CHI/HCOOH solution, to obtain a CHI/TiO_2 = 0.5 mole ratio.

similar compositions, but the porosity analysis of sample T_9 points to a multimodal size distribution of the mesopores (Figure 7). The reason for this is not clear, but it opens up a way of controlling the porosity of these materials.

Experiments with Chitosan Samples of Different Molecular Weight. Hybrids with a ratio of CHI/TiO_2 = 0.6 were prepared using samples of chitosan (Fluka) of average molecular weight MW = 70 000, 400 000, and 600 000. After calcination of the hybrids (550 °C for 2 h), similar BET areas (ca. 80 m^2/g) were obtained in all cases. The low effect of the molecular size of the chitosan contained in the hybrid on the surface area of the final product is similar to what has been reported by Kure et al. for the preparation of silica using other organic polymers.[13] However, these values are lower than those achieved using high molecular weight CHI (MW = $1.2 \cdot 10^6$), where, as mentioned above, an area of 103 m^2/g was achieved.

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