Synthesis and Characterization of Titania Aerogels

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Titania (TiO_2) aerogels were prepared by the sol–gel synthesis of titanium *n*-butoxide in methanol and the subsequent removal of solvent with supercritical carbon dioxide. The water and nitric acid contents were varied in an attempt to maximize the surface area of the calcined sample. The resulting TiO_2 aerogel, after calcination at 773 K for 2 h, had a BET surface area in excess of 200 m^2/g, contained mesopores in the range 2–10 nm, and was of the pure anatase form. Nitrogen adsorption, X-ray diffraction, and laser Raman spectroscopy were used to characterize the physical properties of this sample as a function of heat treatment up to 1073 K. Titration with *n*-butylamine showed that this TiO_2 aerogel was weakly acidic. Comparisons with a commercial sample, Degussa P-25, were made.

Introduction

Titania (TiO_2) is a material of great catalytic interest. As a support for metals it exhibits the well-known strong metal–support interactions[1] and as a support for oxides such as vanadia it also has many catalytic applications.[2] Titania samples prepared by conventional methods, however, have low-to-moderate surface areas. For example, Degussa P-25, a commonly used TiO_2 prepared by the flame hydrolysis of titanium tetrachloride, has a BET surface area of about 50 m^2/g.[1] The Glidden TiO_2, prepared by the hydrolysis of titanium isopropylate, has a surface area of about 90 m^2/g after heating at 773 K.[3] Ragai et al.[4] prepared a series of TiO_2 by adding ammonia to aqueous titanous chloride at different pH values. After being dried in air at 383–393 K, some of these samples have surface areas that are in excess of 200 m^2/g. However, these authors did not study the thermal stability of their samples under more severe heat treatments that would be typical of catalytic applications. In a later study Ko et al.[5] found that a TiO_2 sample prepared similarly has a surface area of 113 m^2/g after heating at 773 K.

One approach to prepare high-surface-area TiO_2 is by the controlled hydrolysis of titanium alkoxides.[6–10] Barringer and Bowen[7] synthesized TiO_2 powders by hydrolyzing dilute ethanolic solutions of titanium tetraethoxide at room temperature and obtained specific surface areas of water-washed samples ranging from 250 to 320 m^2/g. Kozlowski et al.[6] hydrolyzed titanium butoxide in water at 343 K, and the resulting TiO_2 particles, after calcination at 673 K for 5 h, had a surface area of 180 m^2/g. In these two examples, the high surface areas arise from small particle sizes; the particles themselves are nonporous.

Sol–gel synthesis is another popular approach to prepare TiO_2 because of its many applications as glasses and ceramics.[11,12] Samples thus prepared are usually porous because a gel, after all, represents a three-dimensional polymeric network. However, conventional drying to remove the solvent in a gel often collapses the porous network due to the interfacial tension associated with the liquid–vapor interface. One effective way to bypass this difficulty is to remove the solvent by supercritical drying. This technology, first introduced by Kistler 6 decades ago,[13,14] results in materials known as aerogels.

Because of their porosity and high surface area, the use of aerogels in catalytic applications has been widely explored.[15–17] With respect to TiO_2 in particular, Teichner et al.[15] synthesized TiO_2 aerogels from titanium butylate in butanol and from solutions of titanium butylate or propylate in benzene. These samples have surface areas which are less than 110 m^2/g. More recently Schneider and Baiker[18] used tetrabutoxytitanium as a precursor to prepare an acid-catalyzed TiO_2 aerogel that has a surface area of nearly 200 m^2/g after calcination in flowing air at 623 K. Other authors have reported titania-containing mixed gels such as TiO_2/V_2O_5[19] and TiO_2/SiO_2.[20]

In this paper we report a formulation for synthesizing TiO_2 aerogels from a methanolic solution of titanium *n*-butoxide. After calcination at 773 K for 2 h, this sample has a surface area in excess of 200 m^2/g, contains primarily mesopores in the range 2–10 nm, and is of the pure anatase form. We describe first the preparation variables which we studied in order to optimize the surface area, then the physical characteristics of the TiO_2 aerogel as a function

Table I. Screening of Solvents[a]

solvent	gel time (s)	gel clarity	bounce
methanol	37	clear	good
ethanol	185	clear	fair
1-propanol	1158	clear	fair
2-propanol	126	moderately cloudy	poor
2-butanol	161	very cloudy	poor

[a] Standard conditions: 50 mL of alcohol, 0.625 mmol of TiB (titanium *n*-butoxide)/mL of alcohol, 4 mol of H_2O/mol of TiB, 0.1 mol of HNO_3/mol of TiB.

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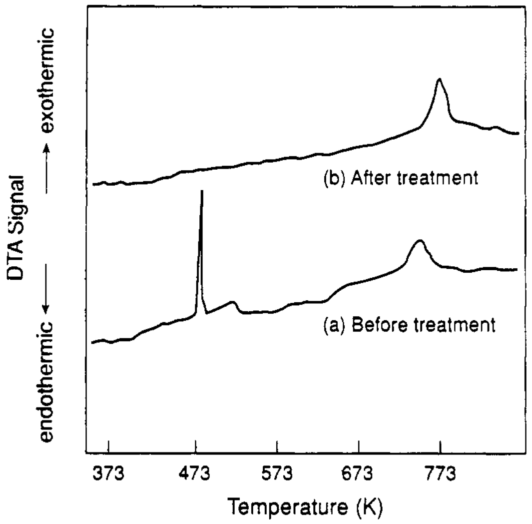

Figure 1. Differential thermal analysis (DTA) data as a TiO_2 aerogel was heated at 10 K/min in flowing helium: (a) sample had not been heat treated in a vacuum oven; (b) sample heat treated in a vacuum oven at 483 K for 3 h.

of heat treatment. Since our intention was to develop this material as a catalyst support, we compared some of its properties to those of Degussa P-25 which is the most widely used TiO_2 for that purpose.

Experimental Section

Sample Preparation. We prepared a titania gel from an alcoholic solution of titanium *n*-butoxide ($Ti(C_4H_9O)_4$, Alfa) and subsequently extracted the solvent with supercritical CO_2 to obtain the aerogel. The first step was to screen five alcohols (methanol, ethanol, 1-propanol, 2-propanol, and 2-butanol) as solvents. In each run titanium *n*-butoxide was added to 40 mL of the alcohol in a dry glovebox. To this we added another solution containing 10 mL of the same alcohol, nitric acid (Fisher, 15.8 N), and deionized water. The concentrations of the titanium *n*-butoxide (denoted as TiB for brevity), water, and acid were kept at 0.625 mmol of TiB/mL of alcohol, 4 mol of H_2O/mol of TiB, and 0.1 mol of HNO_3/mol of TiB, respectively. These concentrations were chosen on the basis of our experience in working with similar metal alkoxides. The time required for the vortex caused by stirring to disappear after the two solutions had been mixed was recorded as the gel time. Two other qualitative guidelines were adopted to evaluate the resulting gel: clarity, which indicated the absence of precipitates, and bounce, which reflected the continuity of the polymeric network. By "bounce" we mean the movement of the gel as the beaker containing it was gently tapped against a hard surface. Physically a bouncy gel is one which gives a large deformation for a given stress and hence has a small shear modulus.[21] As shown in Table I, of the five solvents screened, methanol gave a clear, bouncy gel in the shortest time and was picked as the solvent used in all subsequent runs. We noted that a white precipitate appeared in the methanolic solution of titanium butoxide under stirring due probably to an alcohol exchange reaction, but it could be removed by the addition of 50 μL of deionized water.

The gel was allowed to age for 2 h and then extracted in a standard autoclave (Autoclave Engineers, Model 08U-06-60FS) with supercritical CO_2 (Airco) at a flow rate of 24.6 L/h, a temperature of 343 K, and a pressure of 2.07×10^7 Pa (3000 psi). The extraction procedure, which was similar to that used by Cheng et al.,[22] lasted for 2–3 h for the complete removal of solvent. After extraction the sample was heated in a vacuum oven at 3.4 kPa and 383 K for 3 h to remove the residual solvent and at 3.4 kPa and 483 K for 3 h to remove any residual organics. We found this to be a crucial step for attaining a high surface area in the subsequently calcined product. Differential thermal analysis (DTA) results shown in Figure 1 provided a possible explanation of this observation. The main difference between curves (a) and (b) is the absence of the exothermic peak at 479 K after the second vacuum oven treatment (the peak at about 773 K corresponded to the amorphous → anatase transformation). The exothermic peak was apparently due to the decomposition of residual organics such as surface alkoxides. The chemistry of this decomposition step is unknown at present, but it is clear that it has a deleterious effect on the surface area of the heat-treated sample. We thus strongly recommend the second heat-treatment step in the vacuum oven to be done at a minimum temperature of 483 K; in practice we found that temperatures in the range 483–573 K would work. The pretreated sample had a cinnamon brown color and turned white after calcination at 773 K or above.

Characterization. The BET surface area, pore volume, and pore size distribution of the samples were obtained from nitrogen adsorption–desorption data with a commercial Autosorb-1 instrument (Quantachrome Corp.). The Kelvin equation was used to calculate the pore radius as a function of relative pressure and the Barrett–Joyner–Halenda method[23] was used to compute the pore size distribution from a 40-point desorption isotherm. The pore volume was determined from the amount of nitrogen adsorbed at a relative pressure close to unity.

Powder X-ray diffraction patterns were obtained with a Rigaku D/Max diffractometer with Cu Kα radiation; the samples were lightly pressed onto a brass holder for analysis. Differential thermal analysis was done with a Perkin-Elmer DTA Model 1700 high-temperature thermal analyzer. Raman spectra were obtained with the 514.5-nm line of a Spectra Physics Model 2050-5W argon ion laser. Details of the Raman spectrometer and experimental procedure can be found elsewhere.[24]

The acid site distribution of the samples was determined by titration with *n*-butylamine following a procedure similar to the Benesi method.[25] All titrations were done using a digital pipette of 0.01-mL resolution with the sample solution vigorously stirred by a micromagnetic bar. Even though the titration technique has intrinsic limitations,[26,27] we took precautions to handle our samples in a consistent manner to ensure that the results were reproducible and could be confidently compared on a relative basis.[5]

Results and Discussion

Effect of Preparation Variables. Since our goal was to produce a high-surface-area TiO_2 aerogel, we examined the effects of water and acid contents on the surface area of the sample after calcination at 773 K for 2 h. This temperature was picked because it is typically used in catalyst pretreatments. In the first series of experiments, the acid content was kept constant at 0.1 mol of HNO_3/mol of TiB while the water content (expressed as the hydrolysis water ratio) was varied from 1 to 8 mol of H_2O/mol of TiB. Figure 2a shows that the gel time decreased with increasing hydrolysis water ratio up to the stoichiometric amount (4 mol of H_2O/mol of TiB) and was independent of the hydrolysis water ratio afterward. At low hydrolysis water ratios the solution either did not gel within a day (as in the case of 1 mol of H_2O/mol of TiB) or formed soft gels which were indicative of a linear rather than cross-linked polymeric network.[28] At higher ratios the gels became increasingly cloudly as typical for colloidal gels which contain precipitates within the gel network.[11] Our observed dependence of gel time on the hydrolysis water ratio is qualitatively similar to the results reported by Prassas and Hench[29] and by Yoldas;[30] the quantitative

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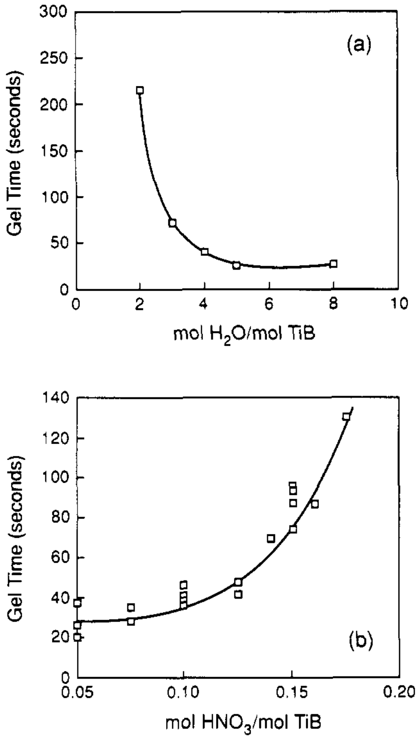

Figure 2. Effect of (a) water content and (b) acid content on the gel time of TiO_2.

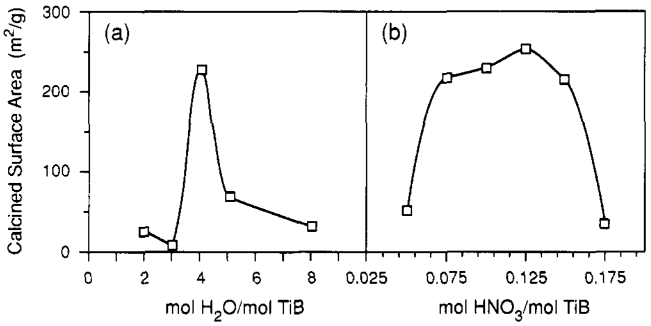

Figure 3. Effect of (a) water content and (b) acid content on the surface area of TiO_2 aerogels after calcination at 773 K for 2 h.

time scales are different because of the different titanium precursors used in these studies.

The gel quality, which was affected by the hydrolysis water ratio as noted above, impacted strongly on the surface area of the calcined TiO_2 aerogel. The gel obtained with 4 mol of H_2O/mol of TiB was clear and had a good bounce and led to a calcined product with a surface area of 227 m^2/g. As shown in Figure 3a, the surface area dropped off precipitously on either side of the optimum hydrolysis water ratio, apparently due to the collapse of weaker structures in these gels.

We next varied the amount of HNO_3 at a constant water ratio of 4 mol of H_2O/mol of TiB. As shown in Figures 2b and 3b, both the gel time and the surface area of the calcined product were also sensitive to the acid content. On the other hand, there was a wider range of acid content (from 0.075 to 0.15 mol of HNO_3/mol of TiB) over which a high-surface-area aerogel could be made. This was the same range over which Schneider and Baiker found no effect of acid content on the surface area of their calcined TiO_2 aerogel.[18] However, we found a significant effect for acid contents that are outside of this range. Qualitatively increasing the acid content had the same effect as decreasing the water content. Too high an acid ratio produced a soft gel and too low, a colloidal gel.

Table II. Recommended Formulation for Producing High-Surface-Area TiO_2 Aerogels

material	volume (mL)	ratio
methanol	50	
titanium *n*-butoxide	10.69	0.625 mmol/mL of methanol
water	2.26	4 mol/mol of TiB[a]
nitric acid	0.164	0.125 mol/mol of TiB[a]

[a] TiB denotes titanium *n*-butoxide.

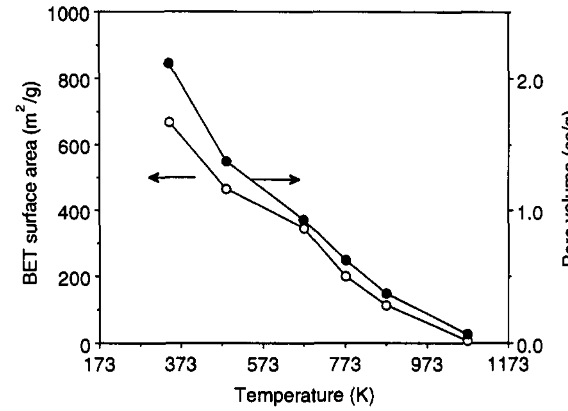

Figure 4. Effect of heat treatment on the surface area and pore volume of TiO_2 aerogels.

Table II summarizes the parameters which are optimal for synthesizing a high-surface-area TiO_2 aerogel. Under these conditions the gel time was about 1 min. The average BET surface area for the first seven samples prepared with the same formulation was 220 ± 20 m^2/g with a batch-to-batch variation of approximately 10%. The variation may have to do with the different times the samples in this series were allowed to age before and after supercritical extraction. We have since obtained even more consistent results by extracting the alcogel 2–3 h after it is prepared and heating the sample in the vacuum oven immediately after extraction.

Effect of Heat Treatment. Figure 4 shows the effect of heat treatment on the surface area and pore volume of TiO_2 aerogels. The two lowest temperatures correspond to the extraction condition (343 K) and treatment in the vacuum oven (483 K), respectively. The sample was heated at the next four higher temperatures (673, 773, 873, and 1073 K) for 2 h in flowing oxygen (300 cm^3/min). Clearly the surface area decreased dramatically with increasing temperature due to the collapse of the porous network. At a temperature above 873 K, the surface area decreased to a value which would be characteristic of a xerogel. Still we refer to these samples as aerogels to highlight the fact that the original solvent removal was done by supercritical drying.

Figure 4 shows that the pore volume also decreased markedly with increasing temperature. Assuming a cylindrical pore model, we further infer from the near parallel decline in surface area and pore volume that the average pore radius probably did not vary much as the sample was heated. This is confirmed by data in Figure 5, which shows that the pore size distribution was basically the same until 1073 K, at which point most of the mesopores had disappeared. We also note from this figure that our TiO_2 aerogels contain mostly mesopores in the range 2–10 nm and

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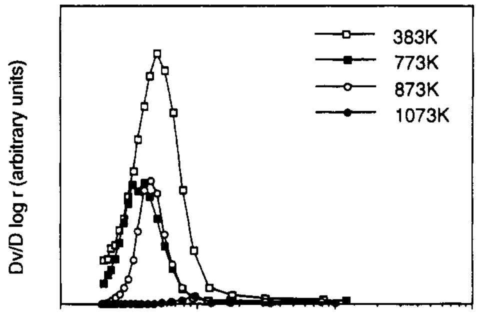

Figure 5. Effect of heat treatment on the pore size distribution of TiO_2 aerogels.

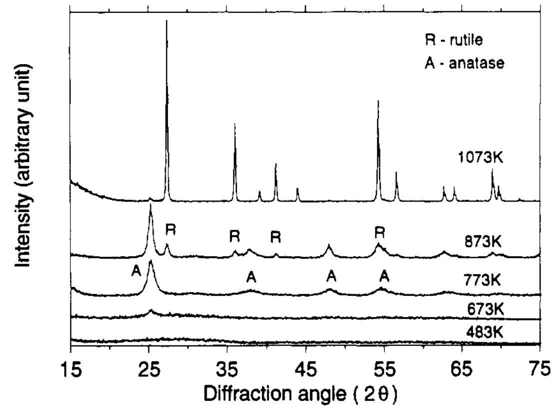

Figure 6. Effect of heat treatment on the structure of TiO_2 aerogels as determined by X-ray diffraction.

have a relatively narrow pore size distribution.

Figure 6 shows the X-ray diffraction results of the TiO_2 aerogels heat treated at the indicated temperatures. The sample remained X-ray amorphous up to 673 K, which suggested that crystallization was kinetically hindered due presumably to the integrity of the porous network arising from supercritical drying. It is also significant that a pure anatase phase was obtained at 773 K, as it would be desirable to have a single-phase support for establishing a structure–reactivity relationship in catalytic applications. With increasing temperature, rutile TiO_2 began to form at 873 K and was the dominant phase at 1073 K. The anatase to rutile transformation has been extensively reported in the literature and the transformation temperature is a strong function of the preparation method. Vejux and Courtine[31] noted that pure or doped TiO_2 transforms from anatase to rutile at or above 1123 K.[32] Shastri et al.[3] found that as a Glidden TiO_2 is heated, the sample shows a collapse in surface area at 873 K but remains as anatase; transformation to the rutile phase begins at 973 K. El-Akkad[33] showed that a titanium hydroxide gel, prepared by adding ammonium hydroxide to titanium chloride, remains in the anatase form up to 873 K. For our aerogel, the transformation into rutile was almost complete at 1073 K, along with a collapse in the pore structure (see Figures 4 and 5).

To confirm the structural assignments of X-ray diffraction, we obtained Raman spectra for the two samples after calcination at 773 and 1073 K. As shown in Figure 7, the sample calcined at 773 K had the three most intense Raman bands at 398, 518, and 634 cm^{-1}, whereas the sample calcined at 1073 K had main bands at 441 and 607 cm^{-1}. These vibrational features have been assigned to the anatase and rutile phase of TiO_2,[34] respectively, consistent with the X-ray diffraction results.

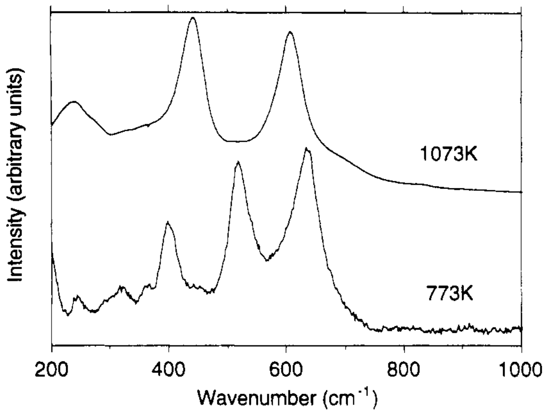

Figure 7. Effect of heat treatment on the structure of TiO_2 aerogels as determined by laser Raman spectroscopy.

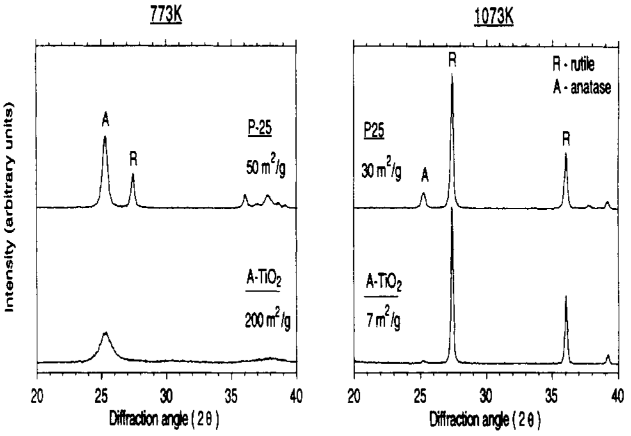

Figure 8. Comparison of the surface area and structure between TiO_2 aerogel and Degussa P-25 after heat treatment at 773 and 1073 K.

Our TiO_2 aerogel, after calcination at 773 K, has physical characteristics similar to the sample of Schneider and Baiker.[18] Both materials have surface area of about 200 m^2/g, are in the anatase form, and contain mostly mesopores. These similarities are not surprising in view of the comparable synthetic conditions in the two studies. There is, however, one important difference. The sample of Schneider and Baiker was calcined at 623 K, 150 K lower than our calcination temperature of 773 K. After a calcination temperature of 673 K, our TiO_2 aerogel has a surface area of about 350 m^2/g (see Figure 4) and remains X-ray amorphous (see Figure 5). These results suggest that our synthesis leads to a more rigid porous network that better resists sintering and crystallization. As a possible explanation of this observation, we note that the extraction conditions in the two studies were different. We extracted with flowing CO_2 at 343 K and 21 MPa in a continuous system, whereas Schneider and Baiker extracted with added methanol at 538 K and a final pressure of 19 MPa in presumably a batch operation.[18]

Comparison with Degussa P-25. In anticipation of the use of our TiO_2 aerogel as a catalyst support, we compared its properties with those of Degussa P-25 which has been widely studied for strong metal–support interactions. As shown in Figure 8, after calcination at 773 K, the TiO_2 aerogel had a surface area which was 4 times as large and was of the pure anatase form. In contrast, Degussa P-25 was a mixture of anatase and rutile, as confirmed by X-ray

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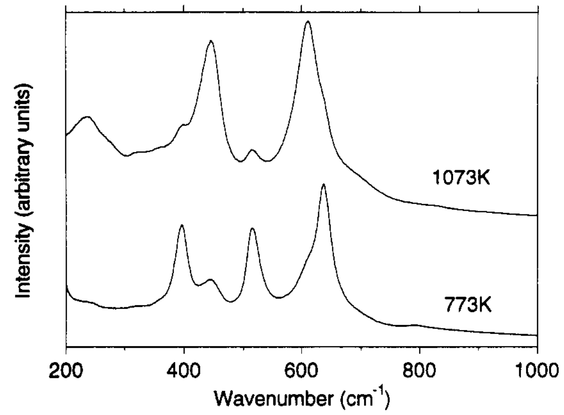

Figure 9. Raman spectra of Degussa P-25 after heat treatment at 773 and 1073 K.

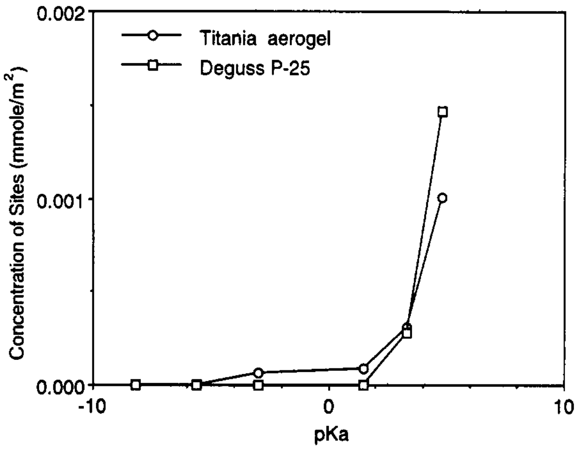

Figure 10. Comparison of the acid site distribution between TiO_2 aerogel and Degussa P-25.

diffraction and laser Raman spectroscopy (see Figure 9). Both materials transformed into rutile upon calcination at 1073 K. But again, Degussa P-25 contained a small amount of anatase as shown in Figures 8 and 9. The rutile form of the TiO_2 aerogel would be of lesser catalytic interest than the anatase form because of its significantly lower surface area (7 vs 200 m^2/g). Note that Degussa P-25 did not undergo as drastic a decrease in surface area because it is a nonporous support.

We also determined the acid site distributions of the two samples by *n*-butylamine titration with Hammett indicators. As shown in Figure 10, neither of the TiO_2 samples had appreciable amounts of acid sites at or below a pK_a value of +1.5. In general, the acid site distributions of the two samples were similar after the difference in surface area had been corrected. From the viewpoint of total acidity, we can thus conclude that both TiO_2 supports are weakly acidic and that the synthesis of an aerogel does not introduce additional acid sites on a per-surface-area basis.

Conclusions

We have synthesized a high-surface-area TiO_2 aerogel by optimizing the water and acid contents in the sol–gel synthesis using a methanolic solution of titanium *n*-butoxide. After calcination at 773 K for 2 h, this TiO_2 aerogel offers two distinct advantages as a potential catalyst support. The first one is its high surface area. In supported oxides, the monolayer coverage (and correspondingly the weight loading) of the supported phase is directly proportional to the surface area of the underlying support. There are numerous examples which show that the supported oxide remains atomically dispersed up to a monolayer but crystallizes beyond that coverage. Our TiO_2 aerogel should thus be able to stabilize a larger amount of supported oxide than a low-surface-area support and, assuming that the dispersed phase is active, to provide more catalytic sites per mass. The second advantage is that the TiO_2 aerogel is of the pure anatase form. Along with the fact that the sample is X-ray amorphous after calcination at 673 K, we can use these materials to probe the reactivity–structure relationship of TiO_2 supports. Work along these lines is underway in our laboratory.

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Registry No. TiO_2, 13463-67-7.