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Titanium oxide aerogels prepared from titanium metal and hydrogen peroxide

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Abstract

The reaction of hydrogen peroxide with excess titanium metal produces rigid titanium oxide aquagels. Subsequent solvent exchanges with ethanol and carbon dioxide, and supercritical drying produces the corresponding aerogels. The aerogels are translucent yellow in appearance, are amorphous to X-rays, and have a BET surface area of 350 m^2/g. The empirical formula of the material, as prepared, is $TiO_3H_{2.7}C_{0.35}$. Infrared spectroscopy indicates the presence of peroxide and carbonate groups. The microstructure of the aerogel consists of a network of elongated particles 2–5 nm in diameter and tens of nm in length. Thermal treatment under argon at 473 K causes rapid decomposition of the aerogel, forming a blue-gray powder consisting of a mixture of rutile and anatase with a surface area of 80 m^2/g. Additional thermal treatment at 973 K under air forms predominantly rutile, with a surface area of 20 m^2/g. © 1998 Elsevier Science B.V.

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1. Introduction

Aerogels of various titanium oxides are potentially valuable catalysts, or precursors to catalysts, for various photochemical reactions. Photochemical water treatment using the semiconductor titanium dioxide has been successfully developed [1–7]. A desirable photocatalyst based on TiO_2 would possess a ultrafine primary particle size and a correspondingly high surface area. This would shift the band-gap absorbance from the near UV region towards the visible spectrum, increasing the effectiveness of solar radiation in the catalytic process. Small particle size and high surface area are two properties common to most aerogel materials.

Aerogels of TiO_2 are most commonly prepared by supercritical drying of alcogels formed by the hydrolysis and condensation of titanium(IV)isopropoxide or other titanium alkoxides [7–13]. However, aerogels prepared in this way invariably contain a large number of residual alkoxide groups. These organic groups typically begin to char at temperatures above 473 K and burn off above 673 K. Considerable shrinkage and cracking accompany this process. At this time, there have been no reports of aerogels of other oxides of titanium.

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Aqueous titanium peroxide gels derived from titanium metal have been prepared and extensively studied by Tengvall and coworkers [14–20]. These gels acted as oxidizers and contained both peroxide and superoxide groups, as determined spectroscopically. Over time, the wet gels, as well as those dried thermally or by freeze-drying, formed TiO_2 in either the anatase or rutile forms, depending on the conditions used. Previous studies on silica aerogels have shown that exposure of a material to supercritical solvent removal can completely alter the surface chemistry of the material [21]. This can affect the reactivity, stability, and physical properties of the material. To obtain a low-organic titanium oxide aerogel, and as part of an ongoing investigation into alternate routes to aerogel materials, we have prepared titanium oxide aerogels from metallic titanium and hydrogen peroxide.

2. Experimental section

Gels were prepared using the general method described by Tengvall, and associates, with the modification that 50% (w/w) H_2O_2 was used as the peroxide source [19]. Titanium sponge-2N5 was obtained from Strem Chemical, and hydrogen peroxide (50% w/w) was obtained from EM Scientific. Titanium sponge (2.0 g) was combined with 50 ml of 50% H_2O_2 and the mixture was held at 10°C. Cooling the reaction is essential as the process is exothermic and can become extremely vigorous at higher temperatures. Over a period of 7 days the solution evolved oxygen and changed from pale yellow to deep orange. When oxygen evolution had slowed, the solution was decanted from the remaining Ti sponge into a glass petri dish. After an additional 5 days at 10°C, a rigid yellow gel had formed. Water and H_2O_2 in the gel were then exchanged for ethanol over 7 days by soaking the gel in 100% EtOH at 25°C. Soakings were exchanged with fresh ethanol several times. During this process the gel shrank considerably and fragmented into several pieces.

The gel was dried in a 300 ml autoclave (Polaron critical point dryer, Ted Pella) 100 ml of EtOH was placed in the autoclave with the gel, and the remaining volume was filled with CO_2 at 5°C and 870 psi. The vessel was purged several times with CO_2, until the effluents were ethanol dry. The vessel was then heated to 45°C and CO_2 was vented to maintain a constant pressure of 1400 psi. The system was held at these conditions for 30 m, and then vented to ambient pressure over 1 h. The aerogels prepared in this way were monolithic, yellow colored, and slightly translucent. The apparent bulk density was estimated to be approximately 0.05 g/cm^3.

Chemical analyses were performed by the Microchemical Laboratory, University of California at Berkeley, Berkeley, California. Single point BET surface areas were measured using a Quantachrome Corp. Quantasorb instrument from the desorption isotherm of 30% N_2/He. Thermal treatments were performed in a fused silica-tube furnace under an atmosphere of flowing (100 cm^3/min) argon or air. Thermal gravimetric analysis (TGA) was obtained on a Dupont Thermal analysis system operated at 10°C/min under an atmosphere of dry nitrogen. High resolution transmission electron microscopy (HRTEM) utilized a JEOL JEM 200 CX microscope operating at 200 kV. Samples for HRTEM were prepared by pulverizing the aerogel with acetone and evaporating the mixture onto copper grids coated with holey carbon. X-ray diffraction analyses were obtained using a Siemens Kristalloflex diffractometer with Cu Kα radiation. Infrared spectra were recorded from samples pressed into KBr pellets using a Mattson Research Series FTIR.

3. Results and discussion

The aerogels produced by the above procedure consisted of monolithic pieces less than 2 cm^3 in size. Macroscopic damage to the monolithic gels occurred primarily during gelation and water–ethanol solvent exchange. Rapid gelation occasionally resulted in the entrapment of oxygen bubbles within the gel. Significant shrinkage and cracking occurred as ethanol replaced the water within the gel pores. The CO_2 drying process did not visibly affect the aerogel.

The microstructure of the aerogel, as revealed by HRTEM, consists of a three-dimensional network of elongated platelets (Fig. 1). The diameters of the particles are typically 2–5 nm, while their lengths range from 10–30 nm. The electron beam of the

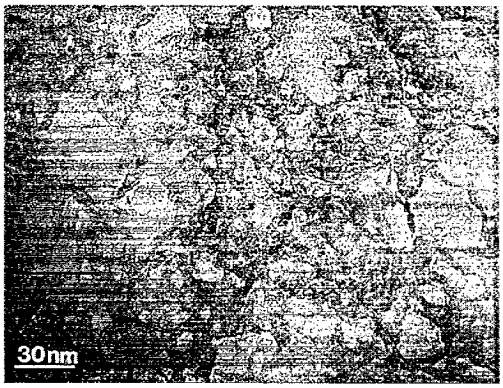

Fig. 1. HRTEM image of titanium peroxide aerogel.

HRTEM did not appear to cause sintering or other damage to the aerogel. However, the carbon coating on the sample holder appeared damaged in several locations, possibly indicating a reaction of the aerogel with the holder. Images of the aerogel were, therefore, obtained from the center of large agglomerated particles to avoid interferences from this effect.

Chemical analyses revealed a composition of 46% Ti, 4.12% C and 2.6% H. Assuming oxygen comprises the balance of the material, the aerogel would have an empirical formula of $TiO_{3.1}H_{2.7}C_{0.35}$. TGA of the aerogel revealed an initial mass loss below 373 K, and further decomposition at ~473 K (Fig. 2). The final mass loss was 29%. This is roughly consistent with the decomposition of $TiO_{3.1}H_{2.7}C_{0.35}$, initially by the loss of adsorbed water, followed by loss of O_2 and CO_2 producing TiO_2.

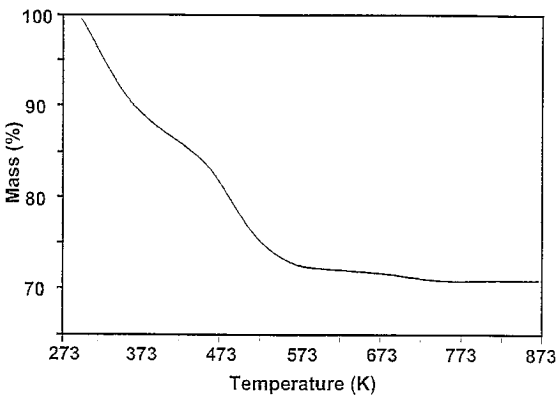

Fig. 2. TGA analysis of titanium peroxide aerogel.

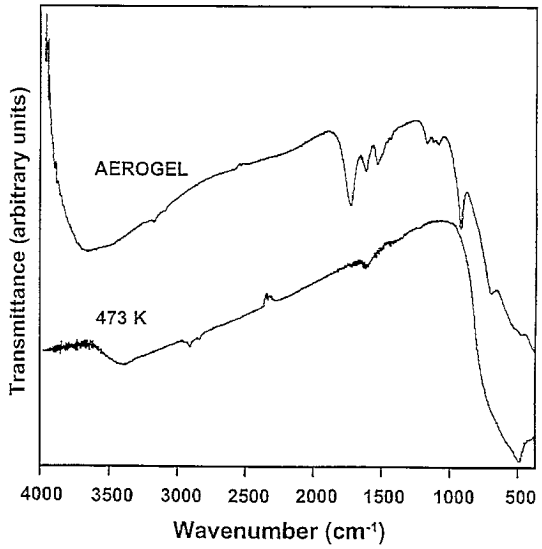

Fig. 3. FTIR spectra of freshly prepared aerogel and aerogel thermally treated at 473 K.

The freshly prepared aerogel possessed a BET surface area of 350 m^2/g. A sample of the aerogel treated to 373 K under argon rapidly decomposed with the evolution of a gas. The powdered product appeared blue-gray in color and possessed a BET surface area of 80 m^2/g. Treatment of this powder with air at 973 K for 1 h followed by cooling to ambient over 6 h gave a fine white powder with a BET surface area of 20 m^2/g.

The Infrared spectra of the fresh aerogel and the thermally treated powders appear in Fig. 3. The fresh aerogel exhibits vibrations at 500 (vs), 693 (s), 898 (s), 1044 (w), 1110 (w), 1446 (m), 1526 (m), and 1634 (m) cm^{-1}, as well as a broad band at 3400 cm^{-1}. The 3400 and 1634 cm^{-1} bands result from –OH vibrations. Tengvall, and associates, have assigned bands from 870–910 cm^{-1} as free or complexed –O–O– vibrations [17]. They did not observe vibrations in the region from 1400–1600 cm^{-1} in freshly dried samples. However, upon aging, their powders exhibited a band at 1400 cm^{-1}, that was attributed to reactions with atmospheric CO_2 or NO_x. The appearance of vibrations at 1446 and 1526 cm^{-1} in the fresh aerogels prepared here suggests a substantial surface coverage of $-CO_3^{2-}$ and/or $-HCO_3^{1-}$, resulting from reaction of the gel with CO_2 during the supercritical drying process. These

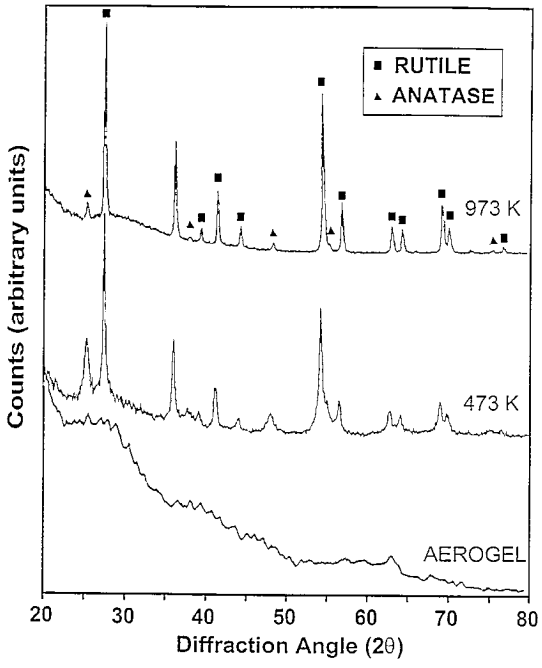

Fig. 4. X-ray powder patterns of freshly prepared and thermally treated aerogels.

surface species most likely account for the 4.12% residual carbon found in this material. How this surface property affects the chemical or thermal reactivity of this material is not yet clear. The FTIR spectrum of the aerogel thermally treated at 473 K shows only trace vibrations in the region from 800–1700 cm^{-1}, and a very strong band at 500 cm^{-1} resulting from titanium oxide.

The results of X-ray diffraction analyses of the fresh and thermally treated aerogels appear in Fig. 4. The diffractogram of the fresh aerogel shows a featureless shape typically observed for aerogels. The aerogel sample thermally treated at 473 K predominantly gives a pattern due to rutile, with a smaller amount of anatase. Conversion to rutile is essentially complete in the sample treated at 973 K.

The loss of surface area during thermal treatment suggests that this material will not serve as an effective precursor to TiO_2. However, this aerogel's initially high surface area, coupled with the reactive nature of peroxide-containing species may prove useful in catalyzing reactions other than those normally associated with TiO_2. This material represents an entry into a class of aerogels that are not prepared using standard sol–gel reactions. Investigations into the properties of this aerogel and the preparation of other aerogels in this class are currently underway.

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