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Adsorption of Well-Ordered Zirconium Phosphonate Multilayer Films on High Surface Area Silica

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Multilayer films of zirconium 1,8-octanediylbisphosphonate (ZOBP) were grown on the surface of fumed silica (Cab-O-Sil) via a sequential adsorption technique and were characterized by infrared spectroscopy, X-ray powder diffraction, BET measurements, and elemental analysis. Either an organosilane molecule bearing a phosphonic acid group or a Zr(IV) layer grown from $ZrOCl_2$ solution can be used as an anchoring point for subsequent growth of multilayer films. The structure of multilayer films grown on either support was found to be similar to bulk microcrystalline ZOBP. Surface area measurements, X-ray diffraction line widths, and elemental analyses were consistent with a model in which compact, well-ordered multilayers grown in concentric shells on the silica support. The thickness of the individual ZOBP layers was found to be 13.5 Å by X-ray diffraction.

Introduction

In recent years a number of new processes have been developed for the chemical modification of surfaces. The goal of much of this research is to prepare rationally designed molecular surface microstructures that can impart to bulk materials desirable properties relevant to catalysis,[1] electron-transfer reactions,[2,3] light-induced vectorial electron transport,[2c,4] corrosion inhibition,[5] and solid-state microelectronics.[6] Among the techniques presently available for the construction of such molecular systems are the formation of amphiphilic monolayers via self-assembly[7-9] and the classical Langmuir–Blodgett (LB) technique.[10] While the LB method relies on the transfer of monolayers prepared at an air–water interface to form well-organized, but metastable[11,12] multilayer films, the self-assembly method is based on the spontaneous adsorption from solution of thermodynamically stable surface monolayers.

Recently, new schemes for producing stable *multilayer* structures via spontaneous self-assembly have been described. Netzer and Sagiv[7b] showed that sequential adsorption/chemical activation steps could be used to make multilayer films from 15-hexadecenyltrichlorosilane, $CH_2{=}CH(CH_2)_{14}SiCl_3$. In a similar fashion, Ulman and co-workers[13] used 23-(trichlorosilyl)tricosanoate, $CH_3O_2C(CH_2)_{22}SiCl_3$, to make remarkably well-ordered and durable multilayer films via sequential adsorption and reduction of the ester group with $LiAlH_4$. We have explored another approach to the same kind of multilayer synthesis, namely, the sequential adsorption of the two soluble components of a highly insoluble layered compound. Planar gold and silicon substrates can be functionalized with metal phosphonate films by alternate immersion in aqueous solutions of the appropriate metal ions and alkanediylbisphosphonic acids.[14,15] A number of structural probes, such as ellipsometry, infrared spectroscopy, electrochemistry, and angle-resolved X-ray photoelectron spectroscopy, provide evidence that, on planar surfaces, these multilayer films are well ordered and that their structure resembles that of the parent crystalline metal phosphonate phases. Mixed phosphonate/inorganic phosphate films have also been prepared by adsorbing zirconium ions alternately with a mixture of alkanediylbisphosphonic acid and inorganic phosphoric acid. These films, prepared on electrode surfaces, show an interesting molecular sieving property (again suggesting a structure that is closely related to that of the corresponding bulk phases[16]), binding cations smaller than the interlamellar space defined by the alkanediylbis-

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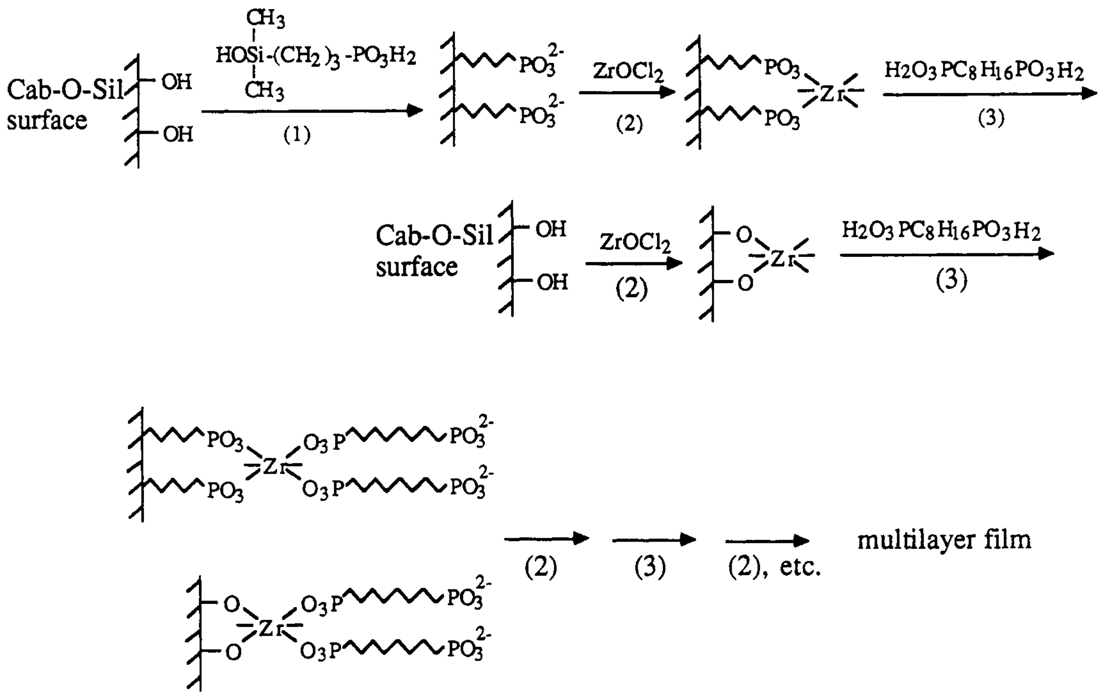
Scheme I. Growth of ZOBP Layers on Cab-O-Sil by Sequential Adsorption of OBPA and Zr(IV)



phosphonate pillaring groups.[17]

Chemically modified inorganic materials have considerable potential as alternatives to conventional heterogeneous catalysts,[18] as stationary phases for chromatography,[19] as supports for immobilized enzymes,[20] and as structurally organized assemblies for photoelectrochemical energy conversion.[21] A key to the realization of these applications is the successful growth and characterization of well-ordered multilayers on high surface area supports. In this paper, we report the characterization of zirconium 1,8-octanediylbisphosphonate (ZOBP) films grown on Cab-O-Sil.[22] Cab-O-Sil is a nonporous fumed silica with a high surface area (150–200 m^2/g) and small average particle diameter (ca. 240 Å). The particle radius of curvature and surface chemical composition are quite similar to those of commonly used support materials, such as chromatographic silica gel, but the nonporous nature of Cab-O-Sil makes it a convenient and easily characterized support for multilayer film growth. ZOBP multilayers were deposited on Cab-O-Sil, following the method used for planar substrates such as silicon, i.e., Scheme I. In this procedure the silica surface, which is terminated by silanol groups, is functionalized via I (3-(hydroxydimethylsilyl)propanephosphonic acid, $HO(CH_3)_2Si(CH_2)_3PO_3H_2$) to yield a phosphonic acid surface. Alternate immersion of the silica in aqueous Zr^{4+} and 1,8-octanediylbisphosphonic acid (OBPA) solutions then produces a solid multilayer film. An alternative to this procedure is to begin with a silica surface pretreated with Zr^{4+} (which presumably forms stable Si–O–Zr linkages), eliminating the need for steps 1 and 2 in Scheme I. Alternate immersion of the zirconated silica in OBPA and Zr(IV) solutions then also produces ZOBP multilayer films on Cab-O-Sil.

Bulk characterization techniques such as elemental analysis, X-ray diffraction, BET surface area measurements, and infrared absorption spectroscopy can be applied to this high surface area material and show that a well-ordered ZOBP phase is formed. Once an "anchoring" monolayer such as Zr(IV) or I is applied to the Cab-O-Sil surface, the growth of subsequent ZOBP films appears to occur in a layer-by-layer fashion, as with planar support materials.

Experimental Section

Materials. Cab-O-Sil (fumed silica) L-90 (nitrogen BET surface area 156 m^2/g, average particle diameter 240 Å) was used as received from Cabot Corp. Zirconyl chloride octahydrate was obtained from Aldrich Chemical Co. Deionized water purified to a resistivity of 18.3 MΩ cm with a Barnstead Nanopure II system (Sybron Corp.) was used in all experiments. Zirconium ion standard solution and arsenazo III, which were used for the spectrophotometric determination of zirconium concentrations, were obtained from Alfa Chemicals. 1,8-Octanediylbisphosphonic acid ($H_2O_3PC_8H_{16}PO_3H_2$, OBPA) and 3-(hydroxydimethylsilyl)propanephosphonic acid (I) were prepared as described below. All other compounds were reagent grade and obtained from commercial sources.

Preparation of 3-(Hydroxydimethylsilyl)propanephosphonic Acid (I) Solution. To an oven-dried three-necked flask equipped with a drying tube were added 5.8 mL (20 mmol) of bis(3-chloropropyl)tetramethyldisiloxane (Petrarch) and 34 mL (200 mmol) of triethyl phosphite (Aldrich). The mixture was heated to 155–160 °C for 10 days, until the reaction was complete. The system was flushed with N_2 prior to and during the reaction. The reaction was monitored periodically by ^1H NMR in order to check for consumption of starting materials. Excess triethyl phosphite was removed by vacuum distillation, leaving crude

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bis(3-diethylphosphonopropyl)tetramethyldisiloxane. The yield was ca. 99%. This oily diethyl phosphonate was identified by ^{13}C and ^{1}H NMR. ^{13}C NMR (GE QE 300, $CDCl_2$) δ 0.3 ($SiCH_3$), 16.5 ($-OCH_2CH_3$), 16.8 ($SiCH_2-$), 19.8 ($-CH_2CH_2CH_2P$, J_{CP} 13.8 Hz), 29.3 ($-CH_2P$, J_{CP} 138.2 Hz), 61.1 ($-OCH_2-$). ^{1}H NMR (Varian EM390, $CDCl_3$) δ 0.1 (s, 12 H, $SiCH_3$), 0.4–0.7 (m, 4 H, $SiCH_2-$), 1.3 (t, 12 H, $-CH_3$), 1.5–1.9 (m, 8 H, $-CH_2CH_2P$), 4.1 (quintet, 8 H, $-OCH_2-$). Concentrated HCl (37%, 20 mL) was added to the bis(3-diethylphosphonopropyl)tetramethyldisiloxane, and the mixture was refluxed at 100 °C for 10 h. Gaseous chloroethane is generated in this acidic hydrolysis, and the resulting bis(3-phosphonopropyl)tetramethyldisiloxane is in equillibrium with monomeric 3-(hydroxydimethylsilyl)- and 3-(chlorodimethylsilyl)propanephosphonic acid. The resulting anchoring agent (I) was not isolated but was diluted with methanol to a volume of 250 mL and stored as a stable solution.

Synthesis of 1,8-Octanediylbisphosphonic Acid (OBPA). OBPA was prepared by the Michaelis–Arbuzov reaction of 1,8-dibromooctane with triethyl phosphite. 1,8-Dibromooctane (0.1 mol) and $P(OC_2H_5)_3$ (0.25 mol) were refluxed at 150 °C for 6 h, with evolution of ethyl bromide; the solution was cooled to room temperature and the excess triethyl phosphite was removed by vacuum distillation. Concentrated (37%, 150 mL) aqueous HCl solution was then added, and heating was resumed at 100 °C for 10 h; the aqueous layer was then separated and evaporated at room temperature. The white crystalline OBPA that precipitated was washed several times with HPLC grade CH_3CN and dried in vacuo. The yield was ca. 80%.

Preparation of Crystalline Bulk ZOBP. The method used to obtain microcrystalline zirconium 1,8-octanediylbisphosphonate ($Zr(O_3PC_8H_{16}PO_3)$, ZOBP) was similar to that reported by Alberti and Torraca[24] for the preparation of well-crystallized α-ZR-$(HPO_4)_2 \cdot H_2O$. In a 500-mL polypropylene bottle, 0.28 g of OBPA was dissolved in 200 mL of water. An aqueous solution of 0.33 g of $ZrOCl_2 \cdot 8H_2O$ (1 mmol) dissolved in 20 mL of water was added dropwise to the solution of OBPA while the solution was stirred. A white gelatinous precipitated formed immediately. Aqueous HF (48%) was added dropwise to the mixture with stirring until a clear solution was again obtained. This solution was kept at 70 °C, and nitrogen gas was bubbled slowly through the solution. Water was periodically added to maintain the solution volume at 150–200 mL. After 2 days a white precipitate began to appear, and precipitation was complete in about 2 weeks. The solution was decanted away from the solid, which was filtered and washed with water, and then with ethanol, and dried at 90 °C in air. The yield was ca. 75%.

Preparation of ZOBP Multilayer Films on Cab-O-Sil Modified with I. In a typical preparation, 3.0 g of Cab-O-Sil was suspended by sonication in 250 mL of a 160 mM methanol solution of I in a polypropylene bottle. The suspension was heated and stirred at 60 °C for 3 days, and the solid was separated by centrifugation at 12000 rpm for 20 min in a Sorvall Superspeed centrifuge. The solid was resuspended in 1 L of deionized water and then stirred to break up agglomerates that had formed during the centrifugation step. The aqueous suspension was centrifuged again, and the resuspension/centrifugation steps were repeated, typically seven times to remove any unbound I. The supernatant solutions were assayed for unbound I by precipitation with aqueous 5 mM $ZrOCl_2$. Typically, no more clouding of the solution was seen after the third resuspension/centrifugation step. The growth of ZOBP layers proceeded by alternate adsorption of zirconyl chloride and OBPA. The resuspended Cab-O-Sil that had been reacted with I was slowly added to the 500 mL of 40 mM aqueous $ZrOCl_2 \cdot 8H_2O$ with vigorous stirring for 10 h at room temperature. The solid was separated from the solution by centrifigation and resuspended/centrifuged with deionized water as before seven times.

The supernatant solutions were assayed for zirconium ion spectrophotometrically by using arsenazo III in 6 M HCl. This is a sensitive test,[24] since uncomplexed arsenazo III does not absorb in the visible region. Typically, no zirconium was detected in the supernatant after the fourth wash by this method. The resuspended Cab-O-Sil which was modified with I and Zr(IV) was slowly added to 1.7 L of 2.2 mM aqueous OBPA with stirring at room temperature for 36–48 h. The solid was separated from the solution by centrifugation and resuspended/centrifuged with deionized water as before, typically seven times. The supernatant solution was assayed for unreacted OBPA by precipitation with aqueous 5 mM $ZrOCl_2$ again. Typically, no more clouding of the solution was observed after the second resuspension/centrifugation step.

The Cab-O-Sil modified with I, Zr(IV), and OBPA was resuspended in 400 mL of deionized water. The aqueous Cab-O-Sil suspension was then divided into seven centrifuge cells. One of them was set aside as Cab-O-Sil containing a single OBPA layer. The other suspensions were added to 500 mL of 40 mM aqueous $ZrOCl_2 \cdot 8H_2O$ with stirring for 10 h at room temperature in order to deposit the second Zr layer onto the Cab-O-Sil/OBPA. Multilayer films on Cab-O-Sil were prepared by repeating these adsorption steps in the manner described above. All of the multilayer deposition sequences ended with adsorption of an OBPA layer.

Interestingly, precipitation of the surface-modified Cab-O-Sil particles was always very slow following addition of a Zr(IV) layer, whereas flocculation and precipitation was rapid following the application of an OBPA layer. this suggests that the particles acquire a positive surface charge when the films are terminated with Zr(IV), inhibiting flocculation. Following adsorption of (weak acid) OBPA layers, the films are terminated with un-ionized phosphonic acid groups which can hydrogen bond with similar groups on other particles; therefore flocculation and precipitation are rapid.

Preparation of ZOBP Multilayer Films on Zr(IV)-Treated Cab-O-Sil. All solutions were prepared by using deionized water and filtered through 0.22-μm filter paper prior to use. $ZrOCl_2 \cdot 8H_2O$ (18.8 g, 60 mmol) was dissolved in 1 L of H_2O. Cab-O-Sil (3.5 g) was added to 200 mL of H_2O and was suspended by sonication. This suspension was added to the filtered zirconium(IV) solution and heated to 60 °C with stirring for 2 days. The suspension was then centrifuged (12000 rpm) for 20 min, and the supernatant decanted off. The solid was crushed with a rubber bar in 100 mL of H_2O, and then the solution was shaken vigorously to break up agglomerates that had formed during the centrifugation step. The suspension was added to 1000 mL of water and then stirred for 2 h. The aqueous suspension was centrifuged again, and the resuspension/centrifugation steps were repeated, typically seven times, to remove excess Zr(IV). The supernatant solutions were assayed for Zr(IV) spectrophotometrically by using arsenazo III in 6 M HCl. No Zr(IV) was detected in the supernatant after the fourth washing step. After seven washes of the Zr(IV)-treated Cab-O-Sil, this solid was resuspended in 400 mL of water. This resuspended solution was divided into seven equal volumes. One sample was set aside, and the other six were slowly added to 1400 mL of 3 mM aqueous OBPA with stirring. This solution was allowed to stir for 36–48 h at room temperature. The Cab-O-Sil modified with Zr(IV) and OBPA was separated in the same way and under the same conditions as before to remove excess OBPA. The supernatant solutions were tested for OBPA as described above. All of the multilayer films prepared on Zr(IV)-treated Cab-O-Sil were again terminated with an OBPA layer.

Instrumentation. X-ray powder diffraction patterns were obtained with a Philips diffractometer using monochromatized Cu Kα radiation. A Nicolet 730 FT-IR spectrometer (Nicolet Analytical Instruments) purged with dry nitrogen and equipped with a liquid nitrogen cooled (wide band) MCT-A detector was used to obtain infrared spectra. Spectra were acquired by signal averaging 1024 scans at a normal resolution of 4 cm^{-1} using a Happ-Genzel apodization function. Elemental analyses of Cab-O-Sil modified with OBPA, Zr(IV), and/or I were done by Galbraith Laboratories, Inc. Surface areas were measured by nitrogen adsorption on a Micromeritics AccuSorb 2100E physical adsorption analyzer (Micrometrics Instrument Corp.). Surface areas reported represent the average of three independent measurements per sample.

Preparation of Samples for Infrared Spectroscopy. All of the samples used to obtain IR spectra (except bulk ZOBP) were prepared by pressing the modified Cab-O-Sil powder into a

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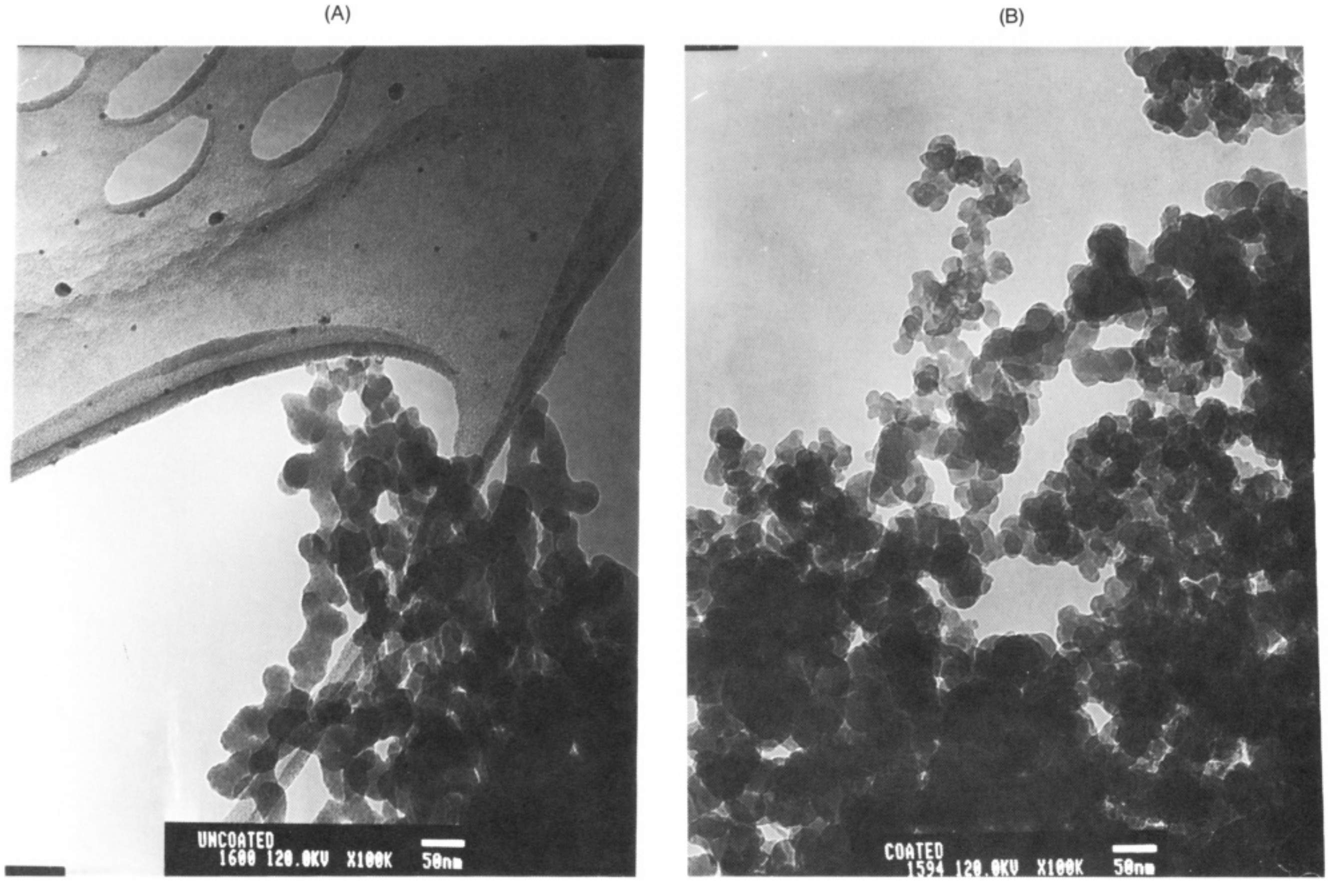

Figure 1. Transmission electron micrograph of (A) Cab-O-Sil aggregates (bar = 50 nm) and (B) Cab-O-Sil with 6 ZODP layers. The object at the top of the figure in A is the holey carbon grid.

tantalum mesh. The bulk ZOBP sample was prepared by dispersion in a KBr pellet. All of the samples of modified Cab-O-Sil were dried overnight at 100 °C in the air prior to the IR measurements.

Results and Discussion

Cab-O-Sil is a fumed silica, a material that is generally regarded as unique in industry because of its unusual particle characteristics. The fine, particulate nature of Cab-O-Sil can be seen in high magnification electron micrographs of the material. Figure 1A is a typical electron micrograph of Cab-O-Sil showing a single aggregate.[22] It shows that the aggregate chain is in fact composed of many primary particles that have been fused together. Figure 1B shows the Cab-O-Sil at the same magnification after coating with six ZODP layers. The particles appear somewhat more faceted in B, which indicates that ZOBP crystallites with dimensions on the order of a few nanometers have grown on the surface of the Cab-O-Sil particles. The layer-by-layer mode of growth of these ZOBP crystallites is revealed by infrared spectroscopy, X-ray diffraction, surface area measurements, and elemental analysis, as discussed below.

Infrared Spectra of Monolayer Films. Figure 2a is a typical infrared spectrum of Cab-O-Sil with normal adsorbed surface moisture removed by dehydration at 100 °C. The isolated free hydroxyl groups bound to a surface Si atom, surrounded by siloxane (Si–O–Si) groups, shows a sharp O–H stretching peak at 3747 cm^{-1},[26,35] even though there may be some weakly coupled geminal pairs of silanol groups present.[27] Chemical and thermogravimetric analyses indicate that there are an average of approximately 3.5–4.5 hydroxyl groups/100 Å^2 of silica surface.[22] The Si–O–Si combination band of the Cab-O-Sil substrate appears at around 1864 cm^{-1}.[28] The band at 1635 cm^{-1}

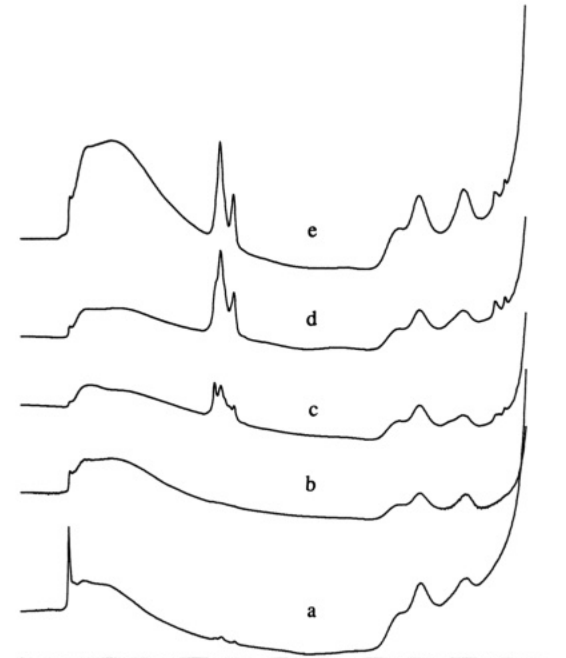

Figure 2. Infrared spectra of modified Cab-O-Sil: (a) pure Cab-O-Sil; (b) zirconated Cab-O-Sil; (c) Cab-O-Sil reacted with I; (d) 1 layer of ZOBP adsorbed on Cab-O-Sil/I; (e) 1 layer of ZOBP adsorbed on Cab-O-Sil/Zr(IV).

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Table I. Peak Assignments for Infrared Spectra of Modified Cab-O-Sil

a	*b*	*c*	*d*	*e*	*f,g*	*h*	mode	ref
3747							free SiOH group	22, 26, 35
		2962					$SiCH_3$, C–H asym str	29, 35
						2941		
		2929	2929	2929	2927	2923	$-CH_2-$, C–H asym str	31, 32, 34
						2911		
		2858	2858	2858	2854	2848	$-CH_2-$, C–H sym str	31, 32, 34
1864	1867	1867	1866	1867	1865		Si–O–Si combination band	22, 26
1635	1635	1635	1635	1635	1634		Si–O str overtone band	22, 36
		1459	1463	1466	1465	1466	$-CH_2-$, sym bending def	31, 33, 34
		1410	1410	1410	1409	1410	$-CH_2-$, scissors def	33, 34

[a] Pure Cab-O-Sil. [b] Zirconated Cab-O-Sil. [c] I/Cab-O-Sil. [d] 1 layer of ZOBP/I/Cab-O-Sil. [e] 1 layer of ZOBP/zirconated Cab-O-Sil. [f] 6 layers of ZOBP/I/Cab-O-Sil. [g] 6 layers of ZOBP/zirconated Cab-O-Sil. [h] Bulk ZOBP with KBr.

is due to the overtone of a Si–O lattice vibration at lower frequency.[22,36]

The infrared spectra of Cab-O-Sil reacted with Zr(IV) and I are shown in Figure 2b,c, respectively. The strong free hydroxyl peak at 3747 cm^{-1} is completely attenuated. This indicates that the silanol (Si–OH) groups have reacted with the silanol functional group of I (in Figure 2c) or with Zr–OH groups (in Figure 2b), by condensation and dehydration. The peak assignments of the infrared spectra of surface-modified Cab-O-Sil are given in the Table I. The strong peaks at 2962 and 2929 cm^{-1} in Figure 2c are assigned to the C–H asymmetric stretching vibration in $Si-CH_3$ and $-CH_2-$ of I. A weak C–H symmetric stretching vibration from the $-CH_2-$ groups of I is observed at 2858 cm^{-1}.

The density of reactive Si–OH groups on Cab-O-Sil (roughly one per 25 $Å^2$) is almost exactly that required to allow a compact monolayer of I (and zirconium phosphonate layers derived from it) to form on the surface. In α-zirconium phosphate and related phosphonate structures,[16,23] the cross-sectional area per phosphate or phosphonate group is 24 $Å^2$. Incubation of untreated Cab-O-Sil with I therefore gives a modified surface containing reactive phosphonic acid groups at approximately monolayer coverage. Covalent binding of the monofunctional silanol to the native oxide layer of Si completes with dimerization to form the corresponding siloxane.[25] Treatment of Cab-O-Sil with Zr(IV) also results in complete reaction of the free silanol groups, to give a zirconated surface. We will show (below) that this Zr-containing layer can also serve as an anchoring point for subsequent growth of compact ZOBP multilayer films.

Figure 2d,e shows the result of adsorption of a single layer of OBPA onto the modified Cab-O-Sil surface. The peak at 2962 cm^{-1} (which was attributed in Figure 2c to CH_2 stretching of I) appears as a shoulder in Figure 2d after one layer of ZOBP has been coated onto the Cab-O-Sil/I surface. Peaks in the C–H stretching region, and especially those at 2929 and 2858 cm^{-1}, which are attributed to the C–H asymmetric and symmetric stretching modes in the $(-CH_2-)_8$ chain of OBPA, become more prominent as an OBPA layer is grown on Cab-O-Sil modified with Zr(IV) or I. The broad peak around 3500 cm^{-1} in Figure 2e is due to adsorbed molecular water in the incompletely dried sample. The cutoff of the observable infrared spectral region near 1300 cm^{-1} arises from Si–O stretching vibrations of the bulk of the Cab-O-Sil.[37] Peaks at 1459–1466 and 1410 cm^{-1} in spectra 2d and 2e are attributed to the CH_2 bending and scissors deformations of the OBPA molecule.

Growth and Characterization of ZOBP Multilayers on Cab-O-Sil. Infrared spectra: In Figure 3 the infrared spectra of samples that contain ZOBP multilayers grown on Cab-O-Sil are compared to the spectrum of microcrystalline bulk ZOBP. Figure 3f shows the spectrum of six ZOBP layers grown on Cab-O-Sil modified with I and Figure 3g shows the spectrum of six ZOBP layers grown on zirconated Cab-O-Sil. These IR spectra are almost identical with each other, suggesting that the structure of the multilayer film is essentially independent of the anchoring step.

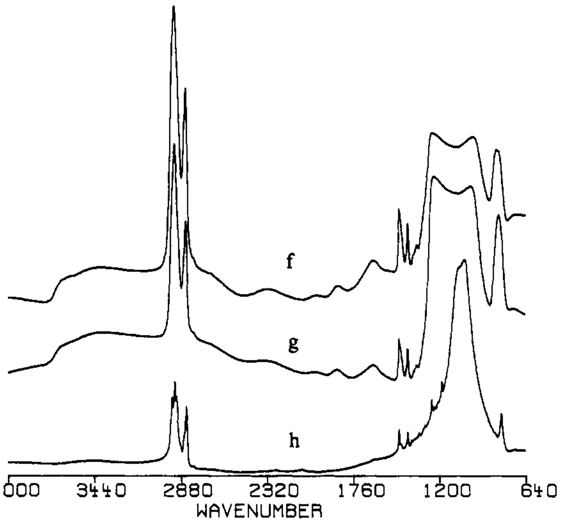

Figure 3. Infrared spectra of modified Cab-O-Sil: (f) 6 layers of ZOBP on Cab-O-Sil/I; (g) 6 layers of ZOBP on Cab-O-Sil/Zr(IV); (h) bulk ZOBP (KBr pellet).

Figure 3h shows the spectrum of bulk microcrystalline ZOBP prepared by the method of Alberti and Torracca.[23] Two strong absorbance peaks which are observed in the spectrum of the six-layer ZOBP/Cab-O-Sil sample are also found in the spectrum of bulk ZOBP. These peaks at 2923 and 2848 cm^{-1} are assigned to the asymmetric and symmetric C–H stretching vibrations of the polymethylene chain in bulk ZOBP. The origin of the other two peaks at 2941 and 2911 cm^{-1} in the spectrum of bulk ZOBP is not clear. These two peaks are also weakly observed in the spectrum of bulk zirconium 1,10-decanediylbisphosphonate (ZDBP). Two sharp bands at 1466 and 1410 cm^{-1}, attributed to CH_2 bending and scissors deformation, are prominent in all three spectra.

The peak widths of the asymmetric and symmetric C–H stretching vibrations can be used as an indicator of packing density, order, and crystallinity of polymethylene chains in organic crystals and self-assembled organic monolayers.[13b] To compare the compactness of the ZOBP multilayer structure on Cab-O-Sil to that of microcrystalline ZOBP, the peak widths at half-height (fwhm) for the asymmetric and symmetric C–H stretching modes were measured. Values obtained were 52 and 30 cm^{-1}, respectively, for six ZOBP layers on Cab-O-Sil modified with I,

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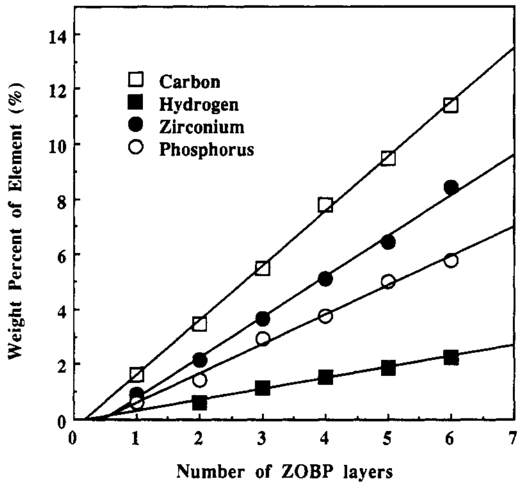

Figure 4. Elemental analysis of Cab-O-Sil modified with ZOBP multilayers.

41 and 29 cm^{-1} for six ZOBP layers on zirconated Cab-O-Sil, and 36 and 26 cm^{-1} for bulk polycrystalline ZOBP. These data qualitatively indicate that the crystallinity of ZOBP multilayers on zirconated Cab-O-Sil is quite similar to that of bulk ZOBP and that the structure on zirconated Cab-O-Sil is less defective than it is on Cab-O-Sil/I. These differences are slight, and the spectra qualitatively indicate a similar environment for the polymethylene chains in all three samples, underscoring the viability of multilayer growth on the modified Cab-O-Sil surface.

Elemental analysis: Figure 4 shows the results of elemental analysis for carbon, hydrogen, zirconium, and phosphorus from samples containing different numbers of ZOBP layers on zirconated Cab-O-Sil. Elemental analyses of ZOBP/I/Cab-O-Sil samples show the same trends (data not shown). In these samples, the percent by weight of elements present in the film is linearly proportional to the number of ZOBP layers, consistent with our model of sequential layer growth. We can calculate quantitatively the expected elemental composition of a sample containing a spherical silica core (diameter ca. 240 Å) and six concentric shells of ZOBP, assuming that the first layer of adsorbed Zr(IV) contains one Zr per 24 Å^2. From the density of bulk silica (2.6 g cm^{-3}) and the formula unit volume of crystalline ZOBP (325 Å^3), we should expect a six-layer shell with an outer diameter of ca. 400 Å and a density of 1.8 g cm^{-3}. Such a shell-core structure should contain about 18% Zr, 12% P, 19% C, and 3% H by weight. The data presented in Figure 4 show that the observed contents of Zr, P, C, and H are about half the expected values. Nevertheless, the infrared data (above) support the idea of complete reaction of surface Si–OH groups and subsequent growth of a well-ordered ZOBP structure. This indicates that only about half of the Cab-O-Sil surface is available for layer growth. Characteristic TEM pictures of samples before and after ZOBP layer growth are shown in Figure 1. It appears from these micrographs that a substantial fraction of the geometrical area of each individual Cab-O-Sil particle is unavailable for layer growth because of agglomeration of particles, which probably occurs through Si–O–Si and Si–OH--H_2O--HO–Si contacts.[22]

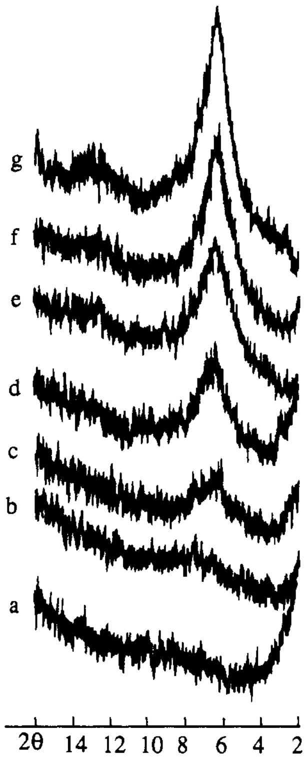

Figure 5. X-ray powder diffraction patterns of ZOBP multilayer films on Cab-O-Sil: (a) untreated Cab-O-Sil; (b–f) 1–6 layers of ZOBP/Cab-O-Sil/I samples.

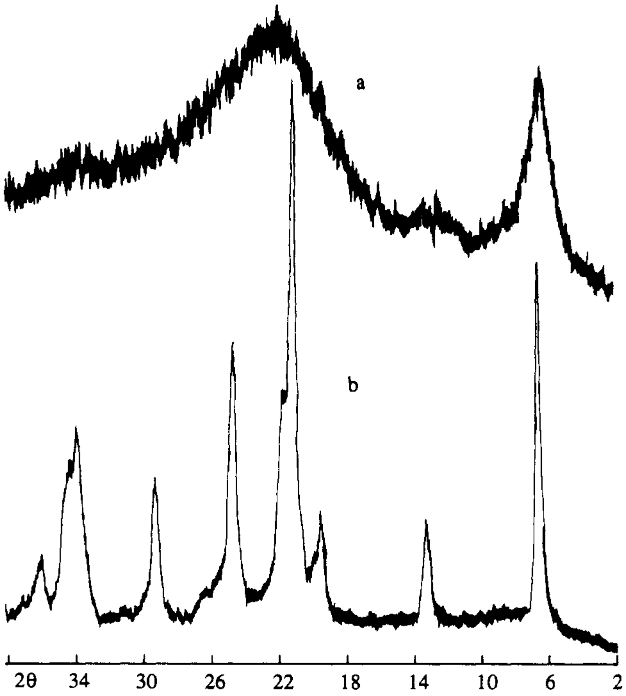

Figure 6. X-ray powder diffraction patterns of (a) 6 layers of ZOBP on Cab-O-Sil/I; (b) bulk microcrystalline ZOBP powder.

X-ray powder diffraction: Figure 5 shows X-ray diffraction (XRD) patterns of samples containing 0–6 layers of ZOBP grown on Cab-O-Sil/I. At low Bragg angle, no diffraction peaks are observed from either Cab-O-Sil itself or from a sample containing a single ZOBP layer. Beginning with the two-layer sample, however, a diffraction peak begins to emerge from the baseline at 6.5° 2*θ*. The height of this peak increases with increasing number of layers, and for the 4–6-layer samples, a second peak begins to appear at 13° 2*θ*. The position of these peaks corresponds closely to the (001) and (002) reflections in the XRD pattern of microcrystalline ZOBP, as shown in Figure 6. The broad maximum centered at 22° 2*θ* in the XRD pattern of 6ZOBP/I/Cab-O-Sil comes from the Cab-O-Sil support. From the position of the 001 reflections a layer spacing of 13.53 Å is calculated for the bulk ZOBP sample and for the thin films.

Table II. X-ray Diffraction Peak Widths and Calculated Crystalline Domain Sizes for ZOBP Multilayer Films Grown on Cab-O-Sil

no. of layers of ZOBP	fwhm, $\Delta(2\theta)$	size,[a] Å	no. of layers of ZOBP	fwhm, $\Delta(2\theta)$	size,[a] Å
1			4	1.9	83.7 (54.1)
2	2.7	58.9 (27.1)	5	1.7	93.6 (67.7)
3	2.3	69.2 (40.6)	6	1.5	106.0 (81.2)

[a] Theoretical values in parentheses, 13.53 Å/layer.

Table III. Nitrogen BET Measurements of Cab-O-Sil Modified with ZOBP Multilayer Films

	surf. area, m^2/g
pure Cab-O-Sil	156 ± 5
2ZOBP/Cab-O-Sil	140 ± 3
4ZOBP/Cab-O-Sil	129 ± 4
6ZOBP/Cab-O-Sil	109 ± 6

It should be noted that the diffraction line at 6.5° 2θ decreases in width with increasing number of ZOBP layers. With use of the Scherrer formula,[30] it is possible to calculate the size of the crystalline domains from which this diffraction peak originates:

$$t = 0.9\lambda/(B \cos \theta_B)$$

This formula is used to estimate the grain size of small crystals from the measured width of the diffraction peaks. The line width B, corrected for instrumental line broadening, is usually measured in radians at half-maximum intensity, and θ_B is the Bragg angle for the reflection; t is the crystal size, and λ is the wavelength of the X-ray. If we take the crystallite size as the layer thickness, we can compare calculated (13.53 Å × number of layers) and observed (calculated from the line width of the (001) reflection) film thicknesses, as shown in Table II. The calculated film thicknesses are systematically smaller than those determined from the line widths; nevertheless, the agreement is surprisingly good considering difficulties in baseline correction and the fact that no correction has been made for X-ray absorption by the sample. The average difference (11.8 Å) in domain size between the n and $(n + 1)$ layer samples is very close to the thickness of a single ZOBP layer (13.5 Å). The observation of 001 diffraction peaks with the same spacings as those of bulk ZOBP and this trend in diffraction line widths together lend further support to the model of well-ordered, compact layers growing as concentric shells on the available surface of the Cab-O-Sil particles. It should be noted that while X-ray diffraction patterns show that there is a periodic repeat of electron density along the stacking axis, there is some conformational flexibility in the alkyl chains, as indicated by infrared spectra, for both the bulk and multilayer ZOBP samples.

Surface area measurements: Table III shows the results of nitrogen adsorption (BET) measurements from Cab-O-Sil/I/ZOBP samples. The surface area per gram of a nonporous powder is proportional to the reciprocal of the average radius and density of particles according to $S/m = 3/r\rho$, where S is surface area, m is the mass, r is the average radius, and ρ is the density of the particle. Using the concentric shell model described above, we calculate an average density of 2.0 g cm^{-3} and a radius of 200 Å for the Cab-O-Sil/6-layer ZOBP particles, compared to a density of 2.6 g cm^{-3} and an average particle radius of 120 Å for pure Cab-O-Sil. The surface area of pure Cab-O-Sil was found to be 156 m^2/g, somewhat higher than that calculated (96 m^2/g) on the basis of a 120-Å particle radius. Since N_2 is a small molecule, the surface area measured by its adsorption is expected to reflect the geometrical area of the particle plus any available micropore area. As each ZOBP layer is adsorbed onto the Cab-O-Sil/I surface, the surface area per gram *decreases*. The surface area per gram of the 6-layer sample is 109 m^2/g. The concentric shell model predicts a decrease in surface area of roughly 22%, and a 30% decrease is observed. If the ZOBP layers were to grow separately as small particles, or as patchy deposits on the Cab-O-Sil surface, the surface area per gram would be expected to increase. The observed *decrease* in surface area per gram with sequential layer deposition provides good evidence for the formation of compact layers that cover the available Cab-O-Sil surface.

Conclusion

This study has shown that multilayer zirconium octanediylbisphosphonate (ZOBP) films can be prepared on a high surface area (fumed silica) support via sequential adsorption of their zirconium(IV) and 1,8-octanediylbisphosphonic acid components. Infrared spectra show that there are only slight differences between Cab-O-Sil silylated with I and Cab-O-Sil treated with Zr(IV) as supporting substrates for the growth of multilayer films. Elemental analysis, BET surface area measurements, and X-ray diffraction patterns are all consistent with the growth of well-ordered, compact multilayer films on the surface of the silica support. The driving force for this ordering is the thermodynamic stability of bulk ZOBP, which crystallizes spontaneously as a layered solid when solutions of its Zr(IV) and OBPA components are mixed. This sequential adsorption procedure, unlike other film deposition techniques such as the Langmuir–Blodgett method, appears to be equally effective in producing well-ordered films on both planar and nonplanar surfaces.

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