MICROPOROUS STRUCTURE WITH LAYERED INTERSTITIAL SURFACE TREATMENT, AND METHOD AND APPARATUS FOR PREPARATION THEREOF

Inventor: Steven L. Koontz, League City, Tex.
Assignee: The United States of America as represented by the Administrator of the National Aeronautics and Space Administration, Washington, D.C.

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Primary Examiner—Peter Hruskoci
Assistant Examiner—Neil M. McCarthy
Attorney, Agent, or Firm—Hardie R. Barr: Guy M. Miller: Edward K. Fein

ABSTRACT
A microporous structure with layered interstitial surface treatments, and method and apparatus for preparation thereof. The structure is prepared by sequentially subjecting a uniformly surface-treated structure (10a) to atomic oxygen treatment to remove an outer layer (16) of surface treatment to a generally uniform depth, and then surface treating the so exposed layer with another surface treating agent. The atomic oxygen/surface treatment steps may optionally be repeated, each successive time to a lesser depth, to produce a microporous structure having multilayered surface treatments. The apparatus (200) employs at least one side arm (228) from a main atomic oxygen-containing chamber (202). The side arm (228) has characteristic relaxation times such that a uniform atomic oxygen dose rate is delivered to a specimen (239) positioned transversely in the side arm (228) spaced from the main gas chamber (202).

16 Claims, 2 Drawing Sheets
MICROPOROUS STRUCTURE WITH LAYERED INTERSTITIAL SURFACE TREATMENT, AND METHOD AND APPARATUS FOR PREPARATION THEREOF

ORIGIN OF THE INVENTION

The invention described herein was made by employee(s) of the United States Government and may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

TECHNICAL FIELD OF THE INVENTION

This invention relates to microporous structures with layered interstitial surface treatments, and particularly to microporous silica with such layered surface treatments having utility in chromatographic separation techniques. The invention also relates to methods of preparing such microporous structures employing atomic oxygen, and the design of atomic oxygen reactors. The invention further relates to the activation of aerogel catalysts with atomic oxygen.

BACKGROUND ART

Chromatography involves the flow of a mobile phase over a stationary phase. Liquid chromatography is used for soluble substances, and gas chromatography for volatile substances. As the mobile phase moves past the stationary phase, repeated adsorption and desorption of the solute occurs at a rate determined chiefly by its distribution ratio between the two phases. If the ratio is large enough, the components of the mixture will move at different rates, producing a series of bands or chromatographs by which their identity can be determined. The analysis of many biological samples is commonly performed using a chromatographic technique known as high performance liquid chromatography (HPLC). Typical packing materials employed in HPLC and other chromatographic columns of various lengths include silica gel, alumina, glass beads, polystyrene gel and ion exchange resins. Separation of materials in a sample is effected by the affinity of a sample component or isolate towards the packing material. For example, hydrophobic substances can generally be separated by using hydrophobic octadecylsilane columns or another alkyl-bonded silica column. However, one problem encountered in the analysis of biological samples with such packing material, is that proteins in many biological samples denature on the hydrophobic surfaces of packing material, adsorb onto the support particulates and accumulate inside the chromatographic column to eventually damage the column. One approach to overcome this problem has been to pretreat the biological sample, such as, for example, by protein precipitation followed by organic extraction, or the removal of proteins and anionics on large particulate silica bonded materials, either off-line or as a precolumn. Various solid-phase extraction techniques for sample preparation are reviewed in Tippins, American Laboratory, p. 107 (February 1987). These techniques are undesirable, however, because of the additional sample processing and time required.

An alternative approach for avoiding protein denaturation in HPLC analysis of biological samples has been the use of silica packing materials wherein the hydrophobic partitioning phase is confined exclusively to the internal particulate region of a porous silica support, while keeping the external surface of the support hydrophilic and non-adsorptive to proteins. Such chromatographic support material is also known as an internal surface reversed-phase (ISRP) support. It has been known to prepare such ISRP packings using an elaborate procedure. In the conventional ISRP preparation procedure, small-pore-diameter silica is first modified with a glycerylpropyl bonded phase. Poly-peptides with hydrophobic moieties which are susceptible to enzyme cleavage are then covalently bound to the glycerylpropyl phase. The derivitized packing is then treated with enzymes to remove the hydrophobic species from only the external surface by selecting enzymes which are too large to enter the internal surface region. Such ISRP supports are described, for example, in Hagestam et al, Analytical Chemistry, vol. 57, pp. 1757-1763 (1985); Pinkerton et al, BioChromatography, vol. 1, pp. 96-105 (1986); and Pinkerton, American Laboratory, pp. 70-76 (April 1988). Pinkerton ISRP columns are commercially available from Regis Chemical Co. ISRP supports having a phase bonded with propylamine-coupled lecithin-imidazolide are described in Pidgeon, Chemical & Engineering News, pp. 23-24 Dec. 12, 1988.

The use of particulate materials similar to chromatographic column supports is common in other applications as well. For example, the use as catalysts of aerogels containing minor impurities is well known. Such catalysts have been used, for example, in the conversion by nitric oxide of paraffins, olefins, and alkylaromatics into nitriles. Such catalysts are typically activated by exposing the catalyst to oxygen or an oxygen-containing gas at extremely elevated temperatures, such as, for example, 400° C. and above for 24-48 hours, or about the time required for spinel formation. Such catalysts have been investigated in, for example, Rahman et al, Applied Catalysis, Vol. 36, pp. 209-220 (1988). However, exposure of the aerogel catalysts to high temperature during activation can have an undesired effect on other properties of the catalyst, such as the textural and structural aspects thereof, and has given rise to attempts to avoid high temperature activation. From U.S. Pat. No. 3,963,646 to Teichner et al, for example, it is known to form hydrogenation or controlled oxidation catalysts by coprecipitation of mixtures of hydrolyzable salts of a transition metal and a refractory metal oxide in a non-aqueous solvent with the simultaneous addition of a stoichiometric amount of water, followed by drying of the coprecipitate under hypcrnritical conditions.

Membranes have a significant role in industrial processing, especially in the biotechnology, industrial gas separation and drug delivery device areas. The preparation of membranes having a symmetrical physical and surface-chemical properties has been described, for example, in Haggin, Chemical and Engineering News, p. 25-32 Jul. 11, 1988). Such membranes have been used in membrane reactors which combine catalytic reaction with product separation. Successful membrane reactors require surface chemistry which varies with location in the cross-section of the membrane. However, the layering of different materials to form such composite membranes involves a difficult fabrication and results in the deposition of inherently thick layers.

Various techniques are known for the plasma activated chemical vapor deposition onto a substrate. For example, from U.S. Pat. No. 3,826,226 to Clark, it is known to deposit a controlled thickness metallic coat-

5,141,806
The invention provides a method of preparing a porous inorganic material with layered surface treatments. The method includes the sequential treatment of a solid porous structure of the material which has an exterior and an interior, wherein the interior comprises a substantially uniform wall of a material, the composition of which is substantially the same as that of the exterior. The method also includes the step of exposing the interior to a first oxidizing gas. The oxidizing gas contains an oxidizing species such as oxygen or hydroxyl radicals at a low temperature. The oxidizing gas is in fluid communication with the interior of the material, and the oxidizing gas is provided therethrough in an axial direction thereof. The oxidizing gas contains oxidizing species selected from, for example, atomic oxygen and hydroxyl radicals, for introduction into the gas chamber. Each sidearm conduit is in fluid communication with the gas chamber and extends transversely therefrom. The positioning means for positioning in the sidearm conduit a plurality of intermediate layers disposed between the exterior and the interior of the material. The gas source contains oxidizing species selected from, for example, atomic oxygen, and hydroxyl radicals, for introduction into the gas chamber. Each sidearm conduit is in fluid communication with the gas chamber and extends transversely therefrom. The positioning means for positioning in the sidearm conduit a plurality of intermediate layers disposed between the exterior and the interior of the material. The gas source contains oxidizing species selected from, for example, atomic oxygen, and hydroxyl radicals, for introduction into the gas chamber. Each sidearm conduit is in fluid communication with the gas chamber and extends transversely therefrom. The positioning means for positioning in the sidearm conduit a plurality of intermediate layers disposed between the exterior and the interior of the material. 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The specific design of this sidearm atomic oxygen reactor eliminates any significant radial concentration gradients of atomic oxygen, hydroxyl radicals or other oxidizing species in the sidearm conduit, and provides a uniform atomic oxygen and/or hydroxyl radical dose delivered to the specimen surface. The method includes the steps of exposing the aerogel catalyst to an oxidizing gas containing atomic oxygen or hydroxyl radicals at a low temperature below about 100°C, for example, and recovering at a higher temperature. The aerogel catalyst may comprise silica or alumina and minor amounts of transition metals such as, for example, nickel. Still further, the invention provides aerogel catalysts activated by atomic oxygen at a low temperature.
BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1A-C schematically represent the consecutive reaction of a porous solid spherical structure with a first surface treating agent (FIG. 1A), atomic oxygen (FIG. 1B) and a second surface treating agent (FIG. 1C), according to the present invention.

FIG. 2 is a schematic representation of a drop tower designed for the oxidation of porous solids wherein the porous solid descends through an atomic oxygen treatment section, according to the present invention.

FIG. 3 is an alternative embodiment of the drop tower of FIG. 2 wherein atomic oxygen is provided as an afterglow from a microwave discharge cell or other source of atomic oxygen-containing gas.

FIG. 4 is a schematic cross-sectional view of a sidearm atomic oxygen reactor according to the present invention.

FIG. 5 is a cross-sectional view of the sidearm atomic oxygen reactor of FIG. 4 as seen along the lines 5—5.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

A porous structure of layered interstitial surface treatments can be obtained by sequentially treating the structure with a surface treating agent, removing an outer layer of the surface treating agent using an oxidizing plasma and treating the structure with a second surface treating agent. Porous structures suitable in the present invention include any porous solid material which is essentially inert in an oxidizing plasma or atomic oxygen-containing atmosphere. Inorganic materials such as refractory metal oxides are well suited as the base structure in the present invention, preferably alumina, and especially silica. Microporous silica particles or beads are generally composed of agglomerated silica microspheres and have effective pore diameters in the range of from about 1 to about 10,000 Å, preferably from 10 to 1000 Å and especially for silica supports used in chromatography, from about 30 to about 500 Å.

The porous structure may be in the form of a sphere or other particulate, tube, rod, sheet or membrane, or the like, depending upon the desired use for the multilayered structure. For convenience, clarity and the purpose of illustration only, reference is made herein to microporous spherical silica particles with the understanding that other microporous structures may also be suitably employed in the present invention.

The preparation of the plural-layered porous structure involves the treatment of the interstitial surface of the internal pores or voids in the microporous structure. Any surface treating agent capable of bonding with the material of the structure is generally suitable. It will be readily appreciated that the surface treating agent will also be capable of diffusing into the interstices or pores of the structure, i.e. it should be smaller than the effective pore size. A surface treating agent, other than the final surface treating agent, is also desirably reactive with atomic oxygen and/or hydroxyl radicals so that it can be removed from the internal surfaces by reaction therewith. The surface treating agent may be hydrophilic, hydrophobic, amphiphilic, ionic, or capable of covalently adsorbing an isolate, as desired. The surface treating agent itself may have functional groups which are in turn reactive with additional modifying agents.

Thus, the surface treatment step may include an intermediate step wherein a modifying agent is used to derivatize, or couple with, the surface treating agent by reaction with functional groups thereof. For silica structures, a suitable surface treating agent is a silylating agent, such as, for example, hexamethyldisilazane, dimethyldichlorosilane, octadecyl dimethylchlorosilane, and the like. Surface treating agents, such as silylating agents, are well known in the art and are used commercially to manufacture various silica separation media. Silica particles treated with various surface treating agents are also commercially available and widely used in the chromatographic separation arts.

The method of the invention is described in reference to FIGS. 1A, 1B and 1C. The initial surface treating step of a silica bead or spherical particle 10 is illustrated schematically in FIG. 1A. The silica particle 10 has an exterior 12 and internal interstitial surface 14. The surface 14 comprises the walls of the interstitial pores, voids, spaces or channels in the microporous particle 10. When the particle 10 is treated with the first surface treating agent, both the exterior 12 and the internal surface 14 are treated with the surface treating agent which bonds thereto. The uniformly surface-treated particle 10a is then subjected to oxidation with atomic oxygen and/or hydroxyl radicals as illustrated schematically in FIG. 1B. The oxidation serves to remove the surface treating agent from an outer layer 16 of the internal interstitial surface while leaving an inner region or layer 18 modified with the first treating agent. The depth of outer layer 16 is determined primarily by the amount of oxidizing agent with which the particle 10a is reacted, i.e. more atomic oxygen reaction with the particle results in a greater depth of the layer 16. Then, as depicted in FIG. 1C, a second treating agent is used to modify the outer layer 16, but the inner layer 18 is generally unaffected since its bonding sites are occupied or blocked by the first surface treatment. Thus, in the particle 10c, the outer layer 16 is modified with a second surface treating agent and the inner layer 18 remains modified with the first surface treating agent in a bilayer configuration.

If desired, the foregoing alternating surface treatments and oxidations may be repeated a plurality of times, with each subsequent oxidation proceeding to a lesser depth than the preceding oxidation step, and with each successive surface treating agent being different than the surface treating agent in the immediately preceding step. The particle thus produced has a multi-layered interstitial internal surface wherein the depth of each layer is controlled by the subsequent amount of oxidation effected in the oxidizing plasma.

As mentioned above, each surface treatment step may include a derivitization step. Thus, for example, a derivitizable treating agent may be employed in a surface treatment step. Then following the subsequent oxidation step to strip away an outer layer of the derivitizable treating agent treatment, the remaining layer is derivitized to yield the desired surface treatment. This has the advantage of conserving the derivitizing agent which can in some instances be quite valuable, and also conserving atomic oxygen where the initial derivitizable surface treatment has a lower molecular weight than the corresponding derivitized surface treatment. As one example, the initial surface treating agent may comprise an aminosilane silating agent, and the derivitizing agent may comprise a peptide having blocked functionalities except for a C-terminus carboxyl group which has been converted to a corresponding acid anhydride, acid halide (e.g. chloride), carboxyldimidazole, or a similar functional group capable of binding the peptide...
to the primary amine of the aminooalkyl bonded silica surface. In this embodiment, the remaining untreated outer layer may be subsequently treated with a surface treating agent which can be the same as or different than the preceding derivitizable aminooalkyl silylating agent, and if desired, similarly derivitized.

The oxidization of the outer layer of porous internal surface area may be effected using conventional atomic oxygen reactors, including commercially available plasma ashers, or other suitable sources of atomic oxygen, such as, for example, ram flow in low earth orbit, laser photodissociation of parent molecules, and the like. Oxidization of the surface-treated microporous structure with highly reactive atomic oxygen has the advantage of obtaining a distinct oxidation reaction front, generally on the order of one effective pore diameter of the structure, a result not possible with less reactive molecular oxygen which does not obtain a sharp reaction front. In addition, atomic oxygen does not require the high temperatures that thermal, molecular oxygen requires, so there are no thermally induced changes in the physical or structural characteristics of the microporous structure when the atomic oxygen is used at a low temperature, preferably below about 100° C, and more preferably below about 40° C.

In one preferred embodiment a drop tower is used to effect plasma oxidation of silica particles to the desired depth. In FIG. 2 there is shown a drop tower 100 having a vertical section 102 connected to a vacuum pump 104 at the bottom thereof and a product receiver 106 at the top thereof and a product receiver 106 at the bottom thereof. A chute 108 is provided adjacent the top of the vertical section 102 for the introduction of the silica or aerogel particles, or other porous solid material to be treated in the oxidizing plasma, from silica particle source 109. A gas inlet 110 is provided in the lower portion of the vertical section 102 adjacent the product receiver 106, for introducing a gas from gas supply 112 via flow controller 114 and metering valve 116. An inductive coil 118 is provided around the vertical section 102 in an atomic oxygen treatment section 120. The inductive coil 118 is part of a circuit including a matching network 122 and an RF generator 124 for producing an RF field in the treatment portion section 120 to generate oxidizing species in the gas.

When uniform treatment of a flat surface or thin porous membrane is desired, a sidearm atomic oxygen reactor 200 which is best seen in FIGS. 4 and 5 is preferred for the oxidation step. The device 200 is more practical when it is desired to uniformly treat structures having relatively large flat surfaces which are not practically treated using the drop tower devices of FIGS. 2 and 3, but where it is still necessary to obtain a uniform depth of reaction with atomic oxygen across the specimen surface. The sidearm atomic oxygen reactor 200 has a longitudinally oriented flow chamber 202 which may be appropriately constructed of glass or another suitable material in sections, e.g., inlet section 204, mid section 206 and discharge section 208, which are conveniently secured together using conventional coupling flanges 210, 212, 214 and 216. A gas flow source 218 supplies gas through inlet line 220 into the inlet section 204 of the chamber 202. A discharge generating apparatus 222 is positioned in the line 220 to generate a discharge in the section 202 through which the power supply operating at 2450 MHz, such as that obtained under the trade designation Raytheon PGM-10, used with an Evanson-type discharge cavity, has been found to be suitable for this purpose. The gas entering the chamber 202 in the inlet section 204 flows axially...
thethrough and is discharged from discharge end 208 to a vacuum pump 224 via line 226 in fluid communication therebetween. A plurality of sidearms 228 are positioned on the mid section 206 transversely to the longitudinal axis thereof. The sidearms 228 are preferably radially symmetrical and six sidearms 228 are illustrated here for the purposes of an example, but any number more or less than six may be suitably used. A specimen holder 230 is positioned at a distal end of each sidearm conduit 232. The specimen holder 230 may be made, for example, by modifying a conventional union fitting, such as a Cajon brand union, drilled through to remove internal lips and to include the O-ring vacuum seals 234, 236 at either end of a sleeve member 238 adjacent the conduit 232, so that disk-shaped specimen 239 can be held therein. If desired, each specimen holder 230 may also include specimen heater well 240 and thermocouple well 242. Alternatively, the specimen holder 230 may be provided with an adjusting mechanism to vary the distance of the specimen from the sidearm entrance, for example, using an inert (not shown) slidably engaged in the conduit 232. The chamber 202 may further optionally include conventional sampling and probing means and apparatus, such as, for example, an NO sub3; supply and metering valve connected at 244 onto inlet section 204 of the chamber 202, a capacitance monometer connection 246 on connection 246 on discharge section 204, catalytic atomic oxygen probe 248 positioned adjacent the sidearms 228, and the like.

The sidearms 228 are constructed and operated so that no significant radial concentration gradients exist in the specimen holder 230 and an uniform atomic oxygen dose is thereby delivered to the specimen surface 239 which is held or secured transversely in the specimen holder 230. The elimination of radial concentration gradients in the sidearms 228 is determined by the relative magnitude of two characteristic relaxation times. Tdiff and Trem wherein Tdiff is the characteristic diffusional relaxation time for the sidearm conduit from all first order processes, C is the atomic oxygen concentration, r is radial position from the longitudinal axis of the sidearm conduit, and z is an axial position (distance from the sidearm conduit entrance from the main gas chamber), with the boundary conditions:

\[
\frac{-D}{r^2} \frac{\partial^2 C(r,z)}{\partial z^2} = k_1 C(r,z) \text{ at } z = \pm \frac{L}{2} (the specimen surface);
\]

wherein k1 is the rate constant for atomic oxygen loss at the specimen surface. If Tdiff < < Trem, the partial differential equation simplifies to:

\[
\frac{k_1 C(r,z)}{D} = \frac{1}{v^2} \frac{\partial^2 C(r,z)}{\partial t^2}.
\]

A general solution to this has the form:

\[
C(r,z) = Ae^{x (- (k_1/D)^{0.5} z^2 + Bexp(\kappa r/D^{0.5} z))}
\]

wherein A and B are constants determined by application of the boundary conditions as follows:

\[
A = \frac{G_B C_0}{G_A - G_B}; \quad B = \frac{G_A C_0}{G_A - G_B};
\]

wherein:

\[
G_A = [D(k_1/D)^{0.5} - k_1]exp(-k_1/D^{0.5} z_2);
\]

and

\[
G_B = [D(k_1/D)^{0.5} - k_1]exp(k_1/D^{0.5} z_2).
\]

The complete analytical solution for the case of no radial concentration dependence and first order atomic oxygen loss processes is as follows:

\[
C(z) = \frac{C_0}{(G_A - G_B)} [G_B exp(-k_1/D^{0.5} z^2) - G_A exp(k_1/D^{0.5} z_2)]
\]

The atomic oxygen dose rate can thus be estimated.
and altered by the material of the sidearm conduit and the specimen material. Total atomic oxygen doses of about $10^{4}$-$10^{6}$ cm$^{-2}$ day$^{-1}$ or more can be obtained with this apparatus.

The foregoing oxygen reactors, as well as other more conventional atomic oxygen sources, also find application in the activation of silica and alumina aerogel catalysts therewith. Such catalysts have heretofore been activated by thermal molecular oxygen at elevated temperatures for extended periods of time, e.g. 410° C. for 48 hours. According to the present invention such catalysts are activated by exposing them to atomic oxygen at a relatively low temperature, preferably below about 100° C. and more preferably below about 40° C., for a period of time effective to activate the aerogel for catalytic purposes, preferably for about 24-48 hours.

Aerogels suitably employed herein include silica oxide on alumina aerogel catalysts described, for example, in Rahman et al., supra, which is hereby incorporated herein by reference. Briefly, the aerogel comprises a transition metal oxide dispersed or supported on a highly porous refractory oxide. Suitable transition metals are, for example, iron, cobalt and especially nickel. Suitable refractory oxides include silica, and especially alumina. The preparation and use of such supported catalysts is well known by the artisan. The present method for activating such catalysts with atomic oxygen, however, has the advantage that a novel low-temperature activated aerogel catalyst is obtained which is essentially free of the physical and textural changes occasioned by high temperature activation, and further, the activated catalyst is more specific toward certain reactions than the corresponding thermally activated aerogels when used in conventional catalytic processes.

The invention is illustrated by way of the examples which follow.

**EXAMPLE 1**

Cubes of waterproofed silica were exposed to atomic oxygen to demonstrate the stripping away of an outer layer of a porous structure. The cubes measured 2.54 cm on each side and were obtained from Lockheed Missile and Space Corporation as L1 900 space shuttle orbiter thermal protection tile material believed to contain silica fibers suspended in silica gel material fired to remove water. The cubes were cut from the tile material with a band saw and water-proofed with dimethylethoxysilane. The cubes were placed in the bottom of a cylindrical treatment chamber of an LFE Corporation model LTA-302 low temperature plasma asher. The longitudinal axis of the treatment chamber was horizontal so that only opposite lower edges of the cubes were in contact with the chamber wall. The plasma asher was operated at 13.56 MHz using 100 watts of forward RF power with a working gas pressure of about 3500 Pa (267 Torr). The working gas was Liquid Air Corporation (analyzed >99.5% pure) aviator's breathing oxygen containing 12 ppm total hydrocarbon and less than 4 ppm water vapor. The cubes were subjected to treatment in the plasma asher for a period of time from about 2 minutes to about 2 hours. The cubes were removed from the asher and immersed in an aqueous solution containing methylene blue dye for a few minutes. The cubes were then cross-sectioned with a hack saw. The outer portion of the cubes which were treated in the plasma asher for a period of time of 30 minutes or less were seen to be blue and were easily wetted with water, but the inner portion was still white, fully hydrophobic and appeared cubical in shape. The size of the hydrophobic core region depended on the duration of exposure to the oxygen plasma, and the cubes absorbed the aqueous blue dye to a depth determined by the progress of the atomic oxygen reaction front. Cubes exposed to the oxygen plasma for a period of time greater than 30 minutes did not contain an inner hydrophobic core and absorbed blue dye to the center of the cube.

**EXAMPLE 2**

Chromatographic packing material was treated with a hydrophobic surface agent and exposed to oxygen plasma to demonstrate the partial removal of a hydrophobic surface treatment. Porous silica spheres having a size distribution between 80 and 100 mesh were obtained under the trade designation PORASIL. The spheres were treated with dimethylethoxysilane as described in Example 1. The resulting spheres were fully hydrophobic and floated on deionized water. The treated spheres were placed in the oxygen plasma asher described in Example 1 in a monolayer arrangement. Exposure of the silica spheres to oxygen plasma for 30 seconds produced silica spheres which still floated but were wet by the water, indicating that the outer region of the porous silica spheres had become hydrophilic while the inner region remained hydrophobic from the dimethylethoxysilane treatment. Prolonged treatment of the silica spheres in the oxygen plasma asher resulted in progressive loss of hydrophobic properties until the spheres behaved like the starting PORASIL material before treatment with dimethylethoxysilane.

**EXAMPLE 3**

Chromatographic separation of the octapeptide Angiotensin II from serum or plasma is effected with silica particles having an inner internal layer surface treated with phenyl groups, and an outer internal layer and exterior surface-treated with phosphorylcholine groups. Silica particles are treated with phenyl dimethyldichlorosilane (product PO160 from Petrarch) to obtain uniform surface treatment of the particle surfaces with pendant phenyl groups. The particles are then briefly exposed to remove the phenyl groups from the particle exterior and in a layer of relatively small depth adjacent the exterior. The particles are then treated with dimethyldichlorosilane (product D5550 from Petrarch) and a phosphorylcholine (see Durrani, et al., "Modification of Polymer Surfaces for Biomedical Application," in chapter 10 of *Polymer Surfaces and Interfaces*, Feast et al. (ed.), pp. 189-200 (John Wiley & Sons, Ltd. 1987) of the formula:

\[
\text{OH} \cdots \text{CH}_2 \cdots \text{CH}_2 \cdots \text{O} \cdots \text{P} \cdots \text{O} \cdots \text{CH}_2 \cdots \text{CH}_2 \cdots \text{N} \cdots \text{CH}_3.
\]

This is done according to well known techniques for treating silica particles therewith, except that the interior layer of phenyl-treated surface is "blocked" against the phosphorylcholine treatment. The resulting particles have an innermost layer with phenyl groups on its surface and an outer layer and exterior with pendant phosphoryl choline groups. In HPLC, the octapeptide is adsorbed and thereby separated by the interior phenyl groups, while the serum or plasma proteins are ex-
cluded by the phosphorylcholine-treated hydrophilic outer layer.

EXAMPLE 4

Chromatographic separation of natriuretic peptide (ANP) from whole serum, or of β-endorphins from tissue preparations, is effected with silica particles having an inner region of octadecyl surface treatment and an exterior region of phosphorylcholine treatment. The silica particles are treated as in Example 3, except that octadecyl-bonded porous silica (obtained commercially, e.g., from Analytchem International) is used instead of phenyl dimethyldichlorosilane-treated silica. In HPLC, the ANP and/or β-endorphins are adsorbed and thereby separated by the interior octadecyl groups, while the serum and tissue proteins are excluded by the phosphorylcholine groups in the outer layer.

EXAMPLE 5

Chromatographic separation of catecholamines from plasma or urine is effected with silica particles having an interior layer surface treated to have pendant vicinal diol groups and an exterior layer surface treated to have pendant phosphorylcholine groups. Silica particles are treated with a phenylboronic acid silylating agent, e.g., pendant phosphorylcholine groups. Silica particles are treated with a phenylboronic acid silylating agent, e.g., 4-aminobutyl dimethyl methoxysilane obtained as product A0695 from Petrarch. The surface is activated in the plasma asher as described in Example 1 using a pressure of 26 Pa. A sample of 100 mg was spread evenly over the bottom of a glass boat placed in the bottom of the plasma chamber. The sample was stirred once at 8 hours, and removed after 23 hours. The catalytic bead was active and had better selectivity for acrylonitrile production in the nitroxidation of propylene than the same catalyst activated in air at 410° C for 48 hours.

The invention is described hereinabove by way of illustration, and various modifications in the details thereof will become apparent to those skilled in the art in view thereof. All such variations within the scope and spirit of the appended claims are intended to be embraced thereby.

I claim:

1. A microporous structure having a plurality of layers of interstitial surface treatments, comprising:
   a solid microporous structure having an exterior and an interior, said interior comprising an interstitial surface extending from said exterior;
   an outer layer of said interstitial surface adjacent to said exterior surface treated with a first surface treating agent;
   and an inner layer of said interstitial surface disposed from said exterior and treated with a second surface treating agent.

2. The structure of claim 1, wherein said structure comprises silica or alumina.

3. The structure of claim 1, wherein said structure is non-particulated.

4. The structure of claim 3, wherein said structure has the physical form of a cube, sheet, membrane, rod or tube.

5. The structure of claim 1, wherein said inner layer is disposed adjacent said outer layer in a bilayer configuration and said first and second surface treating agents are dissimilar.

6. The structure of claim 1, further comprising one or more layers intermediate said inner and outer layers wherein each layer has a different surface treatment than each layer adjacent thereto.

7. The structure of claim 6, wherein said microporous structure has an effective pore diameter of from about 1 to about 10,000 Å.

8. A porous silica structure with layered interstitial surface treatment, comprising:
   a solid microporous silica structure having an exterior and an interior, said interior comprising an interstitial surface underneath said exterior;
   an inner layer of said interstitial surface disposed from said exterior and treated with a first treating agent;
   an outer layer extending from adjacent said exterior toward said inner layer and treated with a second treating agent, said first and second treating agents being different than the surface treating agent in a layer adjacent thereto.
9. The silica structure of claim 8, wherein the silica is particulated.

10. The silica structure of claim 8, wherein the silica has an effective pore diameter of from about 1 to about 10,000 Å.

11. The silica structure of claim 9, wherein the silica has an effective pore diameter of from about 10 to about 1000 Å.

12. The silica structure of claim 9, wherein the silica has an effective pore diameter of from about 30 to 500 Å.

13. The silica structure of claim 8, wherein the structure includes one or more layers intermediate said inner and outer layers, each said intermediate layer having a different surface treatment than each layer adjacent thereto.

14. The silica structure of claim 8, wherein the silica is adapted for chromatographic separation column packing material.

15. The silica structure of claim 14, wherein said outer layer is surface treated to inhibit protein adsorption thereon, and said inner layer has an isolate-selective surface treatment.

16. The silica structure of claim 8, wherein the structure includes a transition zone between said layers, said transition zone having a thickness of about one effective pore diameter.