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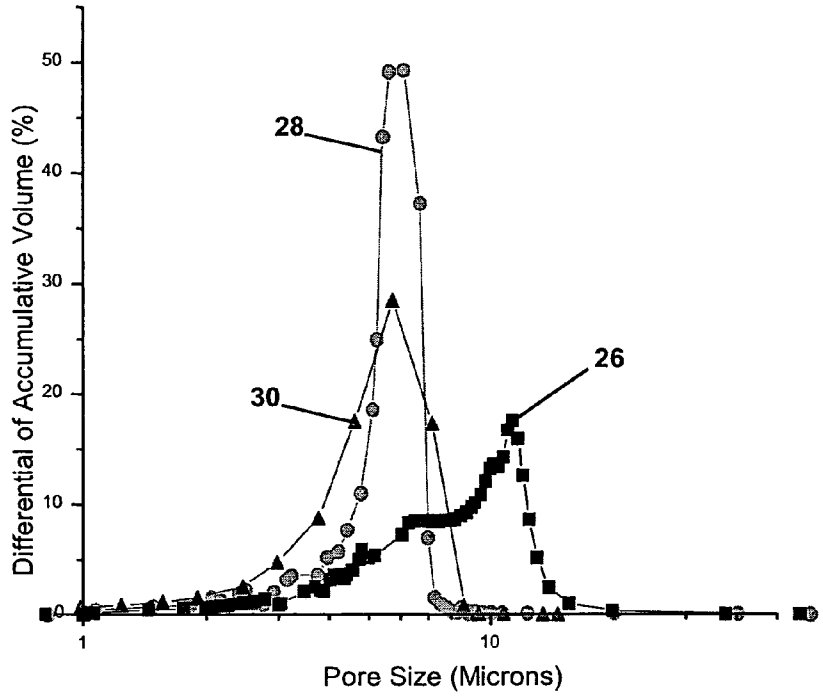
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[Continued on next page]

(54) Title: ALPHA-ALUMINA INORGANIC MEMBRANE SUPPORT AND METHOD OF MAKING THE SAME



(57) Abstract: Compositions for making alpha-alumina supports for, for example, inorganic membranes are described. Methods for controlling the alumina and pore former particle sizes and other process variables are described which facilitate desirable porosity, pore distribution and strength characteristics of the resulting alpha-alumina inorganic membrane supports.

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ABSTRACT

Compositions for making alpha-alumina supports for, for example, inorganic membranes are described. Methods for controlling the alumina and pore former particle sizes and other process variables are described which facilitate desirable porosity, pore distribution and strength characteristics of the resulting alpha-alumina inorganic membrane supports.

ALPHA-ALUMINA INORGANIC MEMBRANE SUPPORT AND METHOD OF MAKING THE SAME

BACKGROUND

[0001] This application claims the benefit of priority to provisional application no. 60/874070, titled "Alpha-Alumina Inorganic Membrane Support and Method of Making the Same," filed on December 11, 2006 attorney docket no. SP06-172P, the contents of which are incorporated by reference herein in their entirety.

Field of the Invention

[0002] The invention relates generally to alpha-alumina inorganic membrane supports and more particularly to controlling porosity, pore distribution and strength characteristics of alpha-alumina inorganic membrane supports via control of alumina and/or pore former particle sizes and other process variables.

Technical Background

[0003] In the field of membrane separations, thin porous materials deposited on porous supports are widely used for micro-filtration or ultra-filtration of liquid media and for gas separation. The porous support functions to provide mechanical strength for the thin porous materials.

[0004] Porous ceramic supports can be deposited with inorganic coatings to form a membrane structure for use in, for example, filtration and separation applications in, for example, the environmental, biological, food and drink, semiconductor, chemical, petrochemical, gas and energy industries. These industries often require purified gas/vapor or purified liquid whose source is a mixed feed stream composed of different gas and/or liquid/particulate combinations. Specific examples include purification and separation of hydrogen gas,

sequestration of carbon dioxide gas, filtration of oil/water mixtures, wastewater treatment, filtration of wines and juices, filtration of bacteria and viruses from fluid streams, separation of ethanol from biomass, production of high purity gas and water for the semiconductor and microelectronics industry.

[0005] The membrane support functions to provide a high geometric surface area packing density for film/coating deposition and, at the same time, it is advantageous if the support has high permeability, strength, chemical stability, thermal stability and structural uniformity.

[0006] A monolithic inorganic membrane product concept and macroscopic design parameters are described in detail in commonly owned US Patent Application Publication 2006/0090649. This design has the advantage of high surface area packing density and geometric simplicity for easy engineering as compared to conventional designs. In this design configuration, it is advantageous that the support have high permeability and high strength.

[0007] Commonly owned EP Patent No. 0,787,524 relates to a mullite membrane support design. The mullite membrane support is configured as a honeycomb of 0.2 μm average pore size and is used to fabricate a membrane module.

[0008] Commonly owned US Patent No. 5,223,318 relates to the making of titania substrates for membrane supports.

[0009] High purity α-alumina is known to have high chemical stability in acid, base and other reactive environments and also has high thermal and hydrothermal stability. High purity α-alumina is used in research on various inorganic membranes, and is a preferred material from which to make membrane supports. Alumina membranes, generally in a single tube form, have been developed and used for isotopic separation of uranium for nuclear reactor applications. Abe, Fumio; Mori, Hiroshi. "Inorganic porous membranes" (NGK Insulators, Ltd.,

Japan) Jpn. Kokai Tokkyo Koho (1990), relates to a method of using a glass binder to make an α-alumina support of a multi-channel structure. Pall Corporation provides alumina supports in single tube and multi-channel form under the product name Membralox®. However, these existing multi-channel products have large channel sizes (> 2 mm) and thus provide low surface area packing density as well as low porosity (< 36%).

[0010] There is a need for an α-alumina support in a monolith structured form having high purity, large pore size, high porosity and uniform pore distribution facilitating a membrane support capable of being used for a variety of membrane filtration applications. The high purity of the α-alumina support would be useful in maintaining chemical stability, since impurities generally make the alumina more reactive. The large pore size and the high porosity would be useful in, for example, providing high permeability and high thermal stability. At the same time, the pore structure and distribution should be well balanced in order to maintain mechanical strength and structural uniformity.

SUMMARY OF THE INVENTION

[0011] The invention discloses compositions and methods useful for making high purity α-alumina monolith supports having large pore sizes and high porosity which can be used as, for example, inorganic membrane supports as well as for other applications.

[0012] One embodiment of the invention is a composition comprising from 50 weight% to 90 weight% of α-alumina particles, from 10 weight% to 30 weight% of organic pore former particles, and from 1 weight% to 15 weight% of a sintering aid.

[0013] Another embodiment of the invention is a method of forming an α-alumina support. The method comprises providing a batch composition comprising 50 weight% to 90 weight% α-alumina particles, 10 weight% to 30 weight% of organic pore former particles and 1 weight% to 15 weight% of a sintering aid, shaping the batch to form a green body, and sintering the green body to form the α-alumina support.

[0014] Another embodiment of the invention is an α-alumina support comprising a mean pore size of from 6 microns to 15 microns and having a pore size distribution of from 0.50 to 1.70 as described by the formula:

$$d_{ps} = (dp_{90}-dp_{10})/dp_{50};$$

wherein dp_{10} is a pore size wherein 10% of the pore volume has a smaller pore size;

dp_{50} is a median pore size wherein 50% of the pore volume has a smaller pore size; and

dp_{90} is a pore size wherein 90% of the pore volume has a smaller pore size.

[0015] The α-alumina supports, according to the invention, have one or more desirable properties, such as high geometric surface area packing density for membrane deposition, high porosity, high permeability, high strength, chemical stability, thermal stability, structural uniformity, narrow pore size distribution, etc. into a single support structure.

[0016] Additional features and advantages of the invention will be set forth in the detailed description which follows, and in part will be readily apparent to those skilled in the art from that description or recognized by practicing the invention as described herein, including the detailed description which follows, the claims, as well as the appended drawings.

[0017] It is to be understood that both the foregoing general description and the following detailed description embodiments

of the invention, and are intended to provide an overview or framework for understanding the nature and character of the invention as it is claimed. The accompanying drawings are included to provide a further understanding of the invention, and are incorporated into and constitute a part of this specification. The drawings illustrate various embodiments of the invention and together with the description serve to explain the principles and operations of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] The invention can be understood from the following detailed description either alone or together with the accompanying drawing figures.

[0019] **Figure 1** is a graph showing permeability of exemplary α-alumina supports as a function of mean pore size and narrow pore distribution.

[0020] **Figure 2** is a graph showing the impact of alumina particle size on final pore size and pore size distribution in the resulting α-alumina support, according to some embodiments.

[0021] **Figure 3** is a graph showing the impact of the organic pore former particle size on final pore size and pore size distribution in the resulting α-alumina support, according to some embodiments.

[0022] **Figure 4** is a graph showing the impact of sintering temperature on pore size and pore size distribution in the resulting α-alumina support, according to some embodiments.

[0023] **Figure 5** is a graph showing the porosity results for two compositions, according to the invention, as compared to the porosity results for various conventional control materials.

DETAILED DESCRIPTION

[0024] Reference will now be made in detail to various embodiments of the invention, examples of which are illustrated in the accompanying drawings. Wherever possible, the same reference numbers will be used throughout the drawings to refer to the same or like parts.

[0025] One embodiment of the invention is a composition comprising from 50 weight% to 90 weight% of α-alumina particles, from 10 weight% to 30 weight% of organic pore former particles, and from 1 weight% to 15 weight% of a sintering aid. In one embodiment, the composition further comprises fluid components, for example, water, one or more oils and combinations thereof. Other components, according to one embodiment, can be binder materials, for example methylcellulose or the like. These materials can be used alone or in combination to provide a remaining weight % for a total weight % of 100 weight %.

[0026] Another embodiment is a method for forming an α-alumina support that comprises providing a batch composition comprising 50 weight% to 90 weight% α-alumina particles, 10 weight% to 30 weight% of organic pore former particles and 1 weight% to 15 weight% of a sintering aid, shaping the batch to form a green body, and sintering the green body to form the α-alumina support.

[0027] According to the invention, the α-alumina monolith support comprises one or more of the following properties;

a) Pore size in the range of from 6μm to 15μm;

b) Pore size distribution (d_{ps}), as measured by $d_f = (dp_{50} - dp_{10})/dp_{50}$, of 0.30 or less;

c) Strength, as measured by modulus of rupture (MOR), of 2000 psi or greater, for example, greater than around 5000 psi;

d) Water permeability of 50000 L/h/m^2/bar or greater; and/or

e) N_2 permeability of 10000 sccm/cm^2/bar or greater.

[0028] Particle size distribution (PSD) in alpha-alumina inorganic supports, according to the invention, may be described by the following formula:

$$PSD = (PD_{90}-PD_{10})/PD_{50};$$

wherein PD_{10} is a particle size wherein 10% of the particle volume has a smaller particle size;

PD_{50} is a median particle size wherein 50% of the particle volume has a smaller particle size; and

PD_{90} is a particle size wherein 90% of the particle volume has a smaller particle size. Particle size can be measured by a laser diffraction technique, using, for example, a Microtrac particle size analyzer.

[0029] In another embodiment, the α-alumina support comprises a mean pore size of from 6 microns to 15 microns and has a pore size distribution of from 0.50 to 1.70 as described by the formula:

$$d_{ps} = (dp_{90}-dp_{10})/dp_{50};$$

wherein dp_{10} is a pore size wherein 10% of the pore volume has a smaller pore size;

dp_{50} is a median pore size wherein 50% of the pore volume has a smaller pore size; and

dp_{90} is a pore size wherein 90% of the pore volume has a smaller pore size.

[0030] It is advantageous if the smaller pore size portion of the pore size distribution (that portion of the distribution equal to and below dp_{50}) is controlled to be relatively narrow. This so-called "d-factor" (d_f), is utilized herein to measure and characterize the narrowness of the smaller pore size portion of the pore size distribution. The d-factor is described by the following formula:

$$d_f = (dp_{50} - dp_{10}) / dp_{50};$$

wherein dp_{10} and dp_{50} are as defined above.

In one embodiment, the α-alumina support has a d-factor of from 0.20 to 0.60.

[0031] The α-alumina support, according to one embodiment, comprise a first end, a second end, and an inner channel having surfaces defined by porous walls and extending through the support from the first end to the second end. According to another embodiment, the α-alumina support is in the form of a honeycomb monolith. An α-alumina support comprising "an inner channel" includes a support comprising one inner channel as well as a support comprising a plurality of inner channels, such as a plurality of parallel inner channels extending through the support from the first end to the second end.

[0032] Total volume percent porosity (P) is the porosity in the α-alumina monolith support and can be measured by a mercury porosimetry method, which is well known in the art. The α-alumina monolith supports of the invention may be characterized by $P \geq 35\%$, for example, $35\% \leq P \leq 65\%$; or $40\% \leq P \leq 65\%$, for example, $40\% \leq P \leq 55\%$.

[0033] As illustrated in **Figure 1**, in order to gain increased permeability, the high purity α-alumina monolith supports should have a larger mean pore size and a narrower pore distribution with respect to their final target microstructures **10**, for example, desired pore size distribution for increased permeability for fluid transport within a porous medium. The target microstructures **10** are achieved through reducing the bi-modal distribution typically found in experimental batch compositions, for example, as shown in **Figure 1**, batch composition **12**, which has a composition comprising 15 weight% Canna starch and alpha-alumina comprising a mean particle size of 5.8μm (processed at a sintering temperature of 1600^{0}C) and also by increasing the

mean pore size. The resulting α-alumina monolith support made from the batch composition **12** is characterized as follows: P=45.28%, dp_{50}=3.39μm, dp_{10}=0.95μm, dp_{90}=5.45μm and d_f=0.72.

[0034] The reduction or elimination of the bi-modal distribution and the increase in the mean pore size of the resulting α-alumina monolith support can be realized through controlling the batch composition properties, for example, the size and shape of the alumina, the size and volume of the pore former, additional batch components (i.e. crosslinkers) and the temperature and time of the sintering process.

[0035] The compositions and the methods of processing the compositions in order to form high purity α-alumina monolith supports, according to the invention, are demonstrated by the following examples.

Exemplary Compositions

[0036] The composition, according to some embodiments, comprises the following components:

1) 50 weight% to 90 weight% of α-alumina particles;
2) from 10 weight% to 30 weight% of organic pore former particles; and
3) from 1 weight% to 15 weight% of a sintering aid is described.

[0037] Regarding component 1), according to one embodiment, the α-alumina comprises from 50 weight% to 90 weight%, for example from 60 weight% to 70 weight% of the total composition. The impact of alumina particle size on final pore size and pore size distribution in the resulting α-alumina support is shown by the graph in **Figure 2**. In this example, 15 weight% Canna starch pore former was used in two batch compositions. In the first composition **16**, the mean alumina particle size was 5.8 μm, while in the second

composition **14**, the mean alumina particle size was 20μm. When the starch and other variables are held constant, an increase in mean alumina particle size causes an increase in mean pore size. As evident in the graph shown in **Figure 2**, an alumina precursor material having a larger mean particle size is advantageous for producing a larger mean pore size (7μm to 10 μm) alumina in the resulting α-alumina support.

[0038] According to one embodiment, the α-alumina has a mean particle size of 15 microns or more. According to another embodiment, the α-alumina has a mean particle size of from 15 microns to 50 microns.

[0039] Regarding component 2), according to one embodiment, the organic pore former comprises 10 weight% to 30 weight%, for example, 20 weight% to 30 weight% of the total composition. According to one embodiment, the organic pore former is a starch. In another embodiment, the starch is selected from the group consisting of Canna starch, potato starch, green bean starch, corn starch, rice starch, and Sago starch. In one embodiment, the organic pore former has a mean particle size of from 7μm to 45μm, for example, from 10μm to 25μm.

[0040] The impact of the organic pore former mean particle size on final pore size and pore size distribution in batch compositions **18**, **20** which have organic pore former particle sizes larger than their alumina particle sizes is shown by the graph in **Figure 3**. Batch composition **18** comprises alumina having particles 6.8μm in size and Canna starch having particles 47μm in size. Batch composition **20** comprises alumina having particles 6.8μm in size and sago starch having particles 32μm in size. The resulting α-alumina monolith support made from the batch composition **18** is characterized as follows: Porosity=45.28%, dp_{50}=3.39μm, dp_{10}=0.95μm, dp_{90}=5.45μm

and d_f=0.72. The resulting α-alumina monolith support made from the batch composition **20** is characterized as follows: Porosity=45.95%, dp_{50}=4.47μm, dp_{10}=1.03μm, dp_{90}=5.92μm and d_f=0.77.

[0041] When the organic pore former particle size (PS) is larger than the alumina particle size (PS), a bimodal pore size distribution is observed in the α-alumina support. The total mean pore size is not determined by the organic pore former size, but rather by the alumina/organic pore former particle packing characteristics. To minimize an undesirable bimodal pore size distribution (d_{ps}) it is best to select $PS_{alumina} > PS_{pore\ former}$. Due to improved particle packing, both the total porosity and pore size increase as the volume of the pore former is increased, while the pore size distribution becomes narrower.

[0042] Plate-like alumina particles tend to aggregate together during the extrusion process causing a bimodal pore size distribution when mixed with the organic pore former. This can be minimized by mixing plate alumina with spheroidal organic pore former. Alumina and organic pore former particle shape similarity contribute to a narrower pore size distribution.

[0043] Regarding component 3), according to one embodiment, the sintering aid comprises from 1 weight% to 15 weight%, for example 5 weight% to 10 weight% of the total composition. According to one embodiment, the sintering aid is selected from the group consisting of boehmite sol, alumina organic compounds, TiO_2, CuO, MnO_2, MgO, ZrO_2, Y_2O_3, colloidal alumina, SiO_2, AlO(OH) slurry and sodium alumina($Al_2O_3 \cdot Na_2O$). Examples of sources of exemplary sintering aids are as follows: colloidal alumina from AL20, TiO_2 from tetra-isopropyl titanate (TPT), CuO from copper acetate or copper nitrate, MnO_2 from manganese acetate, manganese nitrate or manganese oxalate, MgO from magnesium acetate or magnesium nitrate, ZrO_2 from

colloidal zirconia, Y_2O_3 from yttrium salts, and colloidal alumina from AL20. The sintering aid can function to reduce the melting point of the α-alumina.

[0044] The use of a sintering aid can narrow the pore size distribution and increase the resulting α-alumina support strength. However, introduction of non-Al additives into the extrusion batch lowers purity of the resulted honeycomb monolith and may decrease chemical stability. Thus, a sintering aid containing an Al metal element is advantageous, in part, because the Al in such additives is converted into alpha-alumina crystal phase after the sintering the shaped green body, which does not affect the chemical purity of the final α-alumina support.

[0045] According to one embodiment, the composition further comprises an organic crosslinker. According to one embodiment, the organic crosslinker is selected from the group consisting of an organic agent, epichlorohydrin, cyclopolyamine oligomer and ionene. The organic crosslinker, for example, epichlorohydrin, cyclopolyamine oligomer, ionene, BERSET® 2700 manufactured by Bercen, Inc. or the like can function to crosslink the organic pore former.

[0046] According to another embodiment, the composition comprises forming aids that may include a lubricant, a binder, and/or a solvent vehicle. Methocel is an exemplary binder. Water is an exemplary solvent vehicle.

[0047] Exemplary compositions useful for, for example, batch compositions for the α-alumina supports of the invention are shown in Table 1.

Exemplary Alumina Membrane Support Compositions							
Example No.	1	2	3	4	5	6	7
Composition Code	XFN167	WIJ167	JCK166	WIS167	WII167	WJE167	WKS167
Pore Former							
Starch Type	Corn	Green Bean	Canna	Canna	Rice	Green Bean	Rice
Wt% Starch	18.2	25	15	15	15	25	5
Starch Mean Particle size (μ)	15	23	48	48	7	23	7
Inorganic Raw Materials							
Alumina type	Alcan C701	Sumicorundum AA18	Norton 7921	Norton 7921	Sumicorundum AA18	Sumicorundum AA18 +625mesh	Sumicorundum AA18
Alumina (Wt%)	91.06	100	100	100	100	100	100
Alumina Mean Particle Size (μ)	5.8	20	18	18	20	23	20
Boehmite gamma alumina (Wt%)	9.1	-	-	-	-	-	-
Colloidal Gamma Alumina Solution (AL20) Wt%	25	31	0	33	0	25	0
Organic Materials							
Methyl Cellulose	5	4.5	4	4	4	4.5	4
Liga	0.8	1	0.5	0.5	0	1	0
Emulsia T (Tall oil, TEA, Water)	0	0	0	0	10	0	10
Bereset 2700	0	0	0	0	12	0	12

Table 1.

Exemplary Methods of Making α-alumina Supports

[0048] A method of synthesizing an α-alumina support, according to some embodiments, comprises the following steps:

1) providing a batch composition comprising 50 weight% to 90 weight% α-alumina particles, 10 weight% to 30 weight% of an organic pore former particles and 1 weight% to 15 weight% of a sintering aid;
2) shaping the batch to form a green body; and
3) sintering the green body to form the α-alumina support.

[0049] Regarding step 1), according to one embodiment, the method further comprises providing the batch composition by combining the 50 weight% to 90 weight% α-alumina particles, 10 weight% to 30 weight% of the organic pore former particles and

1 weight% to 15 weight% of the sintering aid and mixing the α-alumina particles, the organic pore former particles and the sintering aid to provide a homogeneous mixture.

[0050] Regarding step 2), according to one embodiment, the method comprises extruding the batch through an extrusion die. The shaping can be accomplished by an extrusion process by several methods commonly know in the art, for example, by extruding the mixture from a twin screw or ram extruder through an extrusion die, as described in US Pat. No. 6,080,348.

[0051] Batch compositions of the invention can be extruded in several geometries producing useful alpha-alumina supports for several applications (water filtration, air filtration, liquid separation, etc). Useful geometries, for example, include honeycomb monolith structures comprising 1mm rounded channels or cells, a cell density of 100 cells per square inch (cpsi) to 600cpsi, where the channels are substantially parallel with respect to each other and may be produced within a wide range of thicknesses.

[0052] Regarding step 3), according to one embodiment, the method comprises sintering the green body, wherein the sintering comprises heating or soaking the green body at a temperature of from 1500 degrees Celcius to 2000 degrees Celcius for from 1 hour to 16 hours, for example from 8 hours to 16 hours. Although the sintering temperature, in this example, is 1600^{0}C, sintering temperature can be in the range of from 1500^{0}C to 2000^{0}C, for example, from 1550^{0}C to 1780^{0}C depending on the application. Typically, higher sintering temperatures result in higher strength, lower porosity and more uniform pore distribution.

[0053] According to another embodiment, sintering the green body comprises heating the green body at a temperature of from 1600 degrees Celcius to 1775 degrees Celcius for from 8 hours to 16 hours.

[0054] The impact of sintering temperature on pore size and pore size distribution is shown in **Figure 4**. An increase in the sintering temperature will reduce the porosity and mean pore size, but will also significantly increase strength. A long hold time at the soaking temperature will reduce the porosity and mean pore size while increasing the pore size distribution. Therefore, a shorter hold time at the soaking temperature is preferred. Batch composition **24** comprises alumina having particles 20μm in size and 15 weight percent Canna starch. The extruded alpha-alumina support was dried and then fired at 1600°C. Batch composition **22** comprises alumina having particles 20μm in size and 15 weight percent Canna starch. The extruded alpha-alumina support was dried and then fired at 1750°C. The resulting α-alumina monolith support made from the batch composition **24** is characterized as follows: P=64.6%, dp_{50}=10.07μm, dp_{10}=5.13μm, dp_{90}=14.02μm and d_f=0.49. The resulting α-alumina monolith support made from the batch composition **22** is characterized as follows: P=55.2%, dp_{50}=9.94μm, dp_{10}=5.40μm, dp_{90}=13.10μm and d_f=0.46.

[0055] The data in **Figure 5** shows the porosity results for two compositions (composition 3 **26** and composition 7 **28** shown in Table 1) prepared using a method described by the invention as compared to the porosity results for the control **30**, Corning Mullite.

[0056] The ideal pore structure (dp_{50} = 7μm-15μm, porosity = 43%-50%, $(dp_{50}-dp_{10})/dp_{50} < 0.25$) for the α-alumina supports was achieved using larger alumina particles (> 20 μm), a smaller particle size starch pore former (< 10 μm), similar alumina and starch particle shapes, a maximal volume of starch (5-15 wt. %), and sintering at higher temperature (1775°C) for 8-16h in the presence of a crosslinker such as ionene or a sintering aid as described above.

[0057] Table 2 shows water and N_2 permeability data for α-alumina supports prepared using the methods described by the invention as compared to control materials.

Batch Composition	3	3	Control	Control
Extrusion batch	Canna Starch	Canna Starch	Canna starch	Sago starch
	18μm alumina	18μm alumina	Al15 alumina	Al15 alumina
Firing temperature	1600°C	1750°C	1600°C	1600°C
Porosity %	64.6	55.2	50.3	46.0
Intrusion pore volume, cc/g	0.41	0.32	0.22	0.22
Median Diameter (dp50), μm	10.1	9.9	3.7	4.5
dp10μm	5.1	5.4	1.0	1.0
dp90μm	14.0	13.1	6.2	5.9
(dp50-dp10)/dp50	0.5	0.5	0.7	0.8
Pure water permeability at 22°C				
Permeance, L/h/m2/bar	122,137	128,200	11,545	16,181
Pure N_2 gas permeability at 22°C				
Permeance, sccm/cm2/bar	12,934	13,130	2,556	2,792

Table 2.

[0058] The batch compositions described in Table 2 were extruded into single-channel form to measure intrinsic permeability. Table 2 also shows that α-alumina supports having the desirable properties (i.e. high porosity, large mean pore size, lower pore size distribution) resulting from their preparation according to the methods of the invention are found to have substantially increased water and nitrogen gas permeability - by nearly one order of magnitude over the control materials having less desirable properties.

[0059] The characteristic properties of the α-alumina and the pore former in the batch composition, particularly particle size and shape, together with the sintering process parameters, contribute to the overall pore distribution of the

α-alumina inorganic membrane support. Examples are shown in Table 3.

Exemplary Membrane Support - Properties							
Example No.	1	2	3	4	5	6	7
Composition Code	XFN167	WIJ167	JCK166	WIS167	WII167	WJE167	WKS167
Soak Temperature (°C)	1600	1775	1750	1750	1750	1750	1775
Soak Time (hours)	8	8	16	16	8	8	8
Fired Properties							
MOR rod (psi)	7930.5	2724.5	2174	6636	1945.7	2441.2	2443.2
Predominant Phase	Corundum	Corundum	Corundum	Corundum	Corundum	Corundum	Corundum
Porosity (%)	47.16	50.49	55.12	48.5	48.3	50.6	43.98
d1 (μ)	0.4	2.54		1.56	2.78	2.61	
dp10 (m)	1.06	5.78	5.31	3.21	5.43	5.9	4.69
dp50 (m)	2.31	9.5	10.52	6.43	6.91	9.66	6.07
dp90 (m)	2.78	11.1	13.46	8.62	16.39	11.55	6.71
df = (dp50-dp10)/dp50	0.54	0.39	0.50	0.50	0.21	0.39	0.23
db = (dp90-dp10)/dp50	0.74	0.56	0.77	0.84	1.59	0.58	0.33

Table 3.

[0060] The extrusion batch composition is designed to optimize pore size distribution using a rationale based on an understanding of the role that particle packing plays in pore formation. Two Gaussian functions can be used to describe the final pore distribution. A broad Gaussian distribution with a fine mean pore size is a result of, and is mainly influenced by, α-alumina particle packing, while a narrow Gaussian distribution is favored and influenced by the starch pore former particle size and distribution. An alumina support with narrow pore distribution and larger mean pore size can be prepared by both careful material selection (alumina and starch particle size, size distribution, shape, and volume, as well as selection of sintering agents) and process optimization (soaking time and sintering temperature) which can control particle packing by influencing boundary diffusion.

[0061] Making use of this understanding of the factors influencing microstructure optimization in a single inorganic

component (alumina) system, the α-alumina supports of the invention exhibit a very narrow pore distribution ($(dp_{50} - dp_{10}/dp_{50} = 0.21)$, which is much less than the control material) efficiently filling alumina particle packing gaps with starch pore former and firing at a temperature close to the melting temperature of the alumina in the presence of an included sintering aid such as AL20, a 50 nanometer alumina. This high permeability α-alumina support has a mean pore size greater than 6 μm, a porosity of greater than 43%, and high strength (MOR or modulus of rupture greater than 5000 psi).

[0062] The invention provides suitable membrane supports to facilitate the product concept described in US Patent Application Publication 2006/0090649 (referenced above) and also is suitable for supporting the nano-sized needle crystal mullite films to form an inorganic membrane as described in commonly owned US Patent Application No. 11/585,477. As compared to mullite based inorganic membrane support materials the α-alumina supports of the invention possess higher porosity, larger mean pore size, a more narrow pore size distribution, higher mechanical strength, and higher chemical resistance. The structural uniformity (in terms of narrow pore size distribution) of the α-alumina of this invention is better than that of the control materials.

[0063] It will be apparent to those skilled in the art that various modifications and variations can be made to the invention without departing from the spirit or scope of the invention. Thus, it is intended that the invention cover the modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.

CLAIMS

What is claimed is:

1. A composition comprising;

from 50 weight% to 90 weight% of α-alumina particles;

from 10 weight% to 30 weight% of organic pore former particles; and

from 1 weight% to 15 weight% of a sintering aid.

2. The composition according to claim 1, wherein the α-alumina has a mean particle size of 15 microns or more.

3. The compostion according to claim 2, wherein the α-alumina has a mean particle size of from 15 microns to 50 microns.

4. The composition according to claim 1, further comprising an organic crosslinker.

5. The composition according to claim 4, wherein the organic crosslinker is selected from the group consisting of an organic agent, epichlorohydrin, cyclopolyamine oligomer and ionene.

6. The composition according to claim 1, wherein the sintering aid is selected from the group consisting of boehmite sol, alumina organic compounds, TiO_2, CuO, MnO_2, MgO, ZrO_2, Y_2O_3, colloidal alumina, SiO_2, AlO(OH) slurry, and sodium alumina.

7. The composition according to claim 1, wherein the organic pore former is a starch.

8. The composition according to claim 7, wherein the starch is selected from the group consisting of Canna starch, potato starch, green bean starch, corn starch, rice starch, and Sago starch.

9. The composition according to claim 1, wherein the organic pore former has a mean particle size of from 7μm to 45μm.

10. A method of forming an α-alumina support, the method comprising;

providing a batch composition comprising 50 weight% to 90 weight% α-alumina particles, 10 weight% to 30 weight% of organic pore former particles and 1 weight% to 15 weight% of a sintering aid;

shaping the batch to form a green body; and

sintering the green body to form the α-alumina support.

11. The method according to claim 10, comprising providing the batch composition by combining the 50 weight% to 90 weight% α-alumina particles, 10 weight% to 30 weight% of the organic pore former particles and 1 weight% to 15 weight% of the sintering aid and mixing the α-alumina particles, the organic pore former particles and the sintering aid to provide a homogeneous mixture.

12. The method according to claim 10, wherein the sintering the green body comprises heating the green body at a temperature of from 1500 degrees Celcius to 2000 degrees Celcius for from 1 hour to 16 hours.

13. The method according to claim 10, wherein the sintering the green body comprises heating the green body at a

temperature of from 1600 degrees Celcius to 1775 degrees Celcius for from 8 hours to 16 hours.

14. The method according to claim 10, wherein the organic pore former is a starch.

15. The method according to claim 14, wherein the starch is selected from the group consisting of Canna starch, potato starch, green bean starch, corn starch, rice starch, and Sago starch.

16. The method according to claim 10, wherein the shaping the batch comprises extruding the batch through an extrusion die.

17. An α-alumina support comprising a mean pore size of from 6 microns to 15 microns and having a pore size distribution (d_{ps}) of from 0.50 to 1.70 as described by the formula:

$$d_{ps} = (dp_{90}-dp_{10})/dp_{50};$$

wherein dp_{10} is a pore size wherein 10% of the pore volume has a smaller pore size;

dp_{50} is a median pore size wherein 50% of the pore volume has a smaller pore size; and

dp_{90} is a pore size wherein 90% of the pore volume has a smaller pore size.

18. The α-alumina support according to claim 17, having a d_f of from 0.20 to 0.60 as described by the formula:

$$d_f = (dp_{50} - dp_{10}) / dp_{50}.$$

19. The α-alumina support according to claim 17, comprising a first end, a second end, and an inner channel having surfaces defined by porous walls and extending through the support from the first end to the second end.

20. The α-alumina support according to claim 19, wherein the α-alumina support is in the form of a honeycomb monolith.

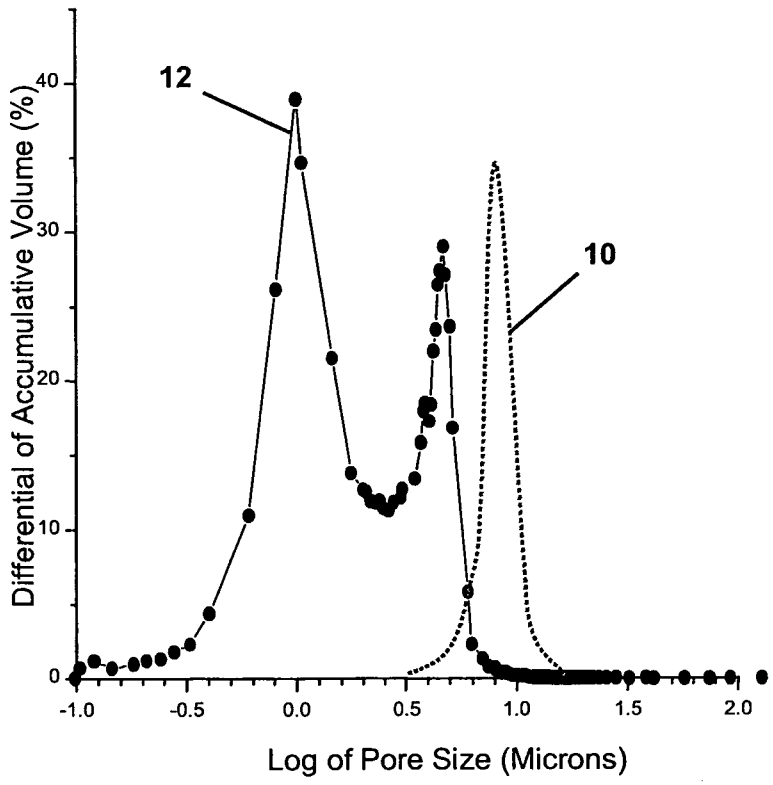

12
10
Differential of Accumulative Volume (%)
0
10
20
30
40
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
Log of Pore Size (Microns)

Figure 1

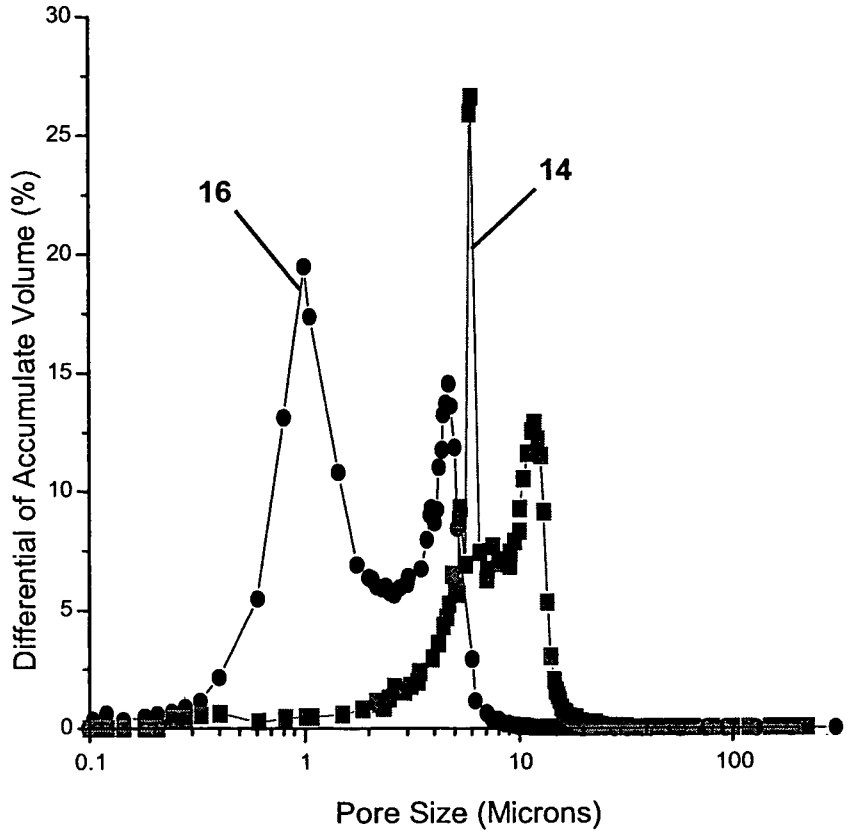

30
25
20
15
10
5
0
Differential of Accumulate Volume (%)
16
14
0.1
1
10
100
Pore Size (Microns)

Figure 2

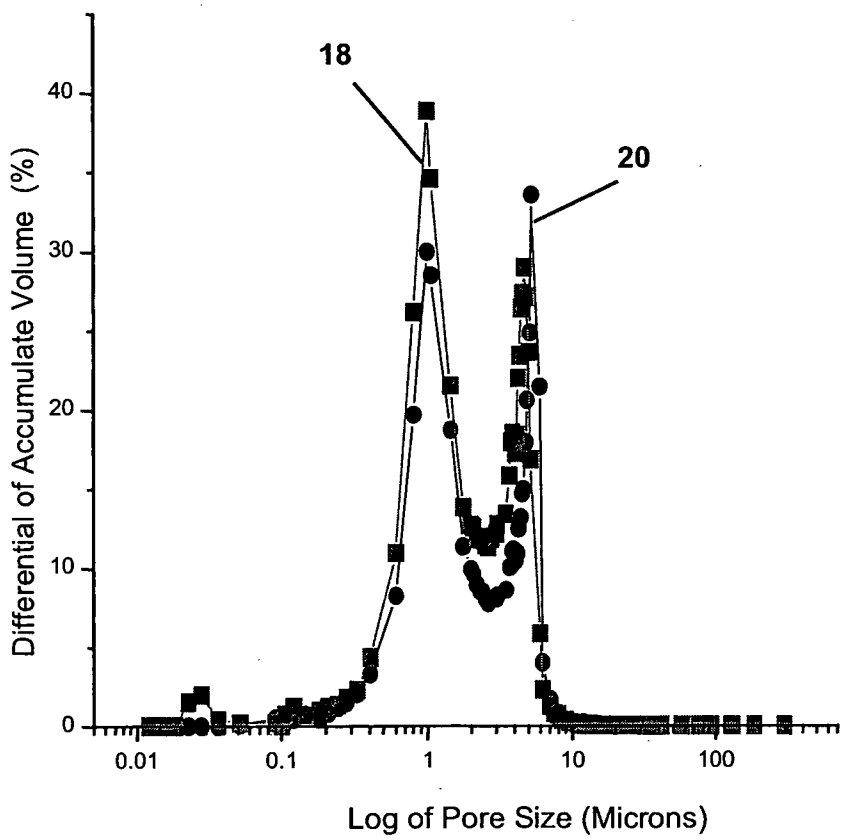

18
20
40
30
20
10
0
Differential of Accumulate Volume (%)
0.01
0.1
1
10
100
Log of Pore Size (Microns)

Figure 3

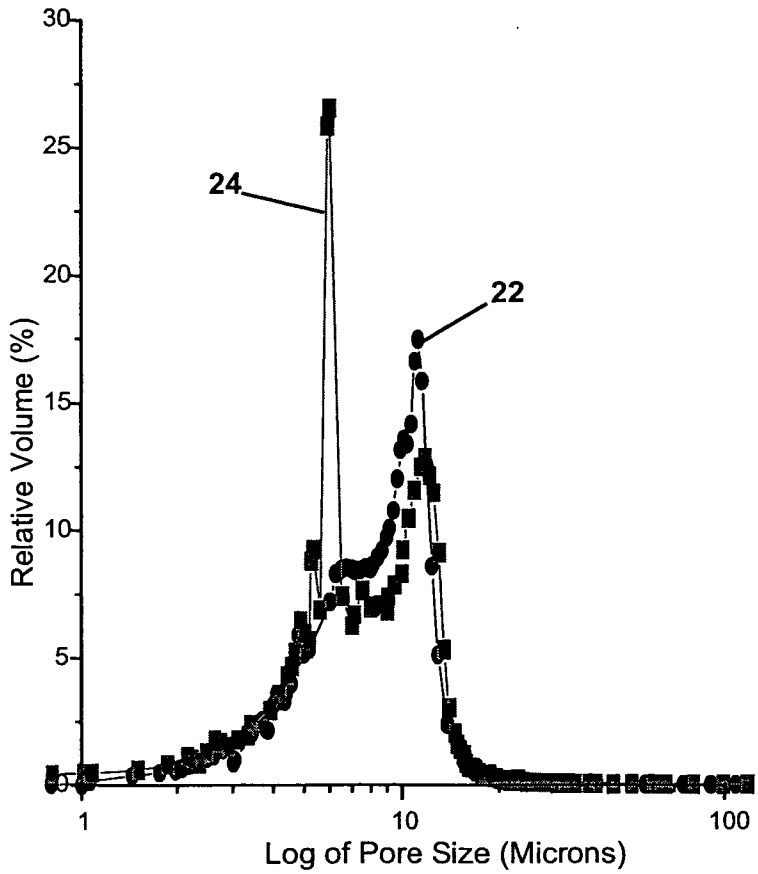

30
25
20
15
10
5
0
Relative Volume (%)
24
22
1
10
100
Log of Pore Size (Microns)

Figure 4

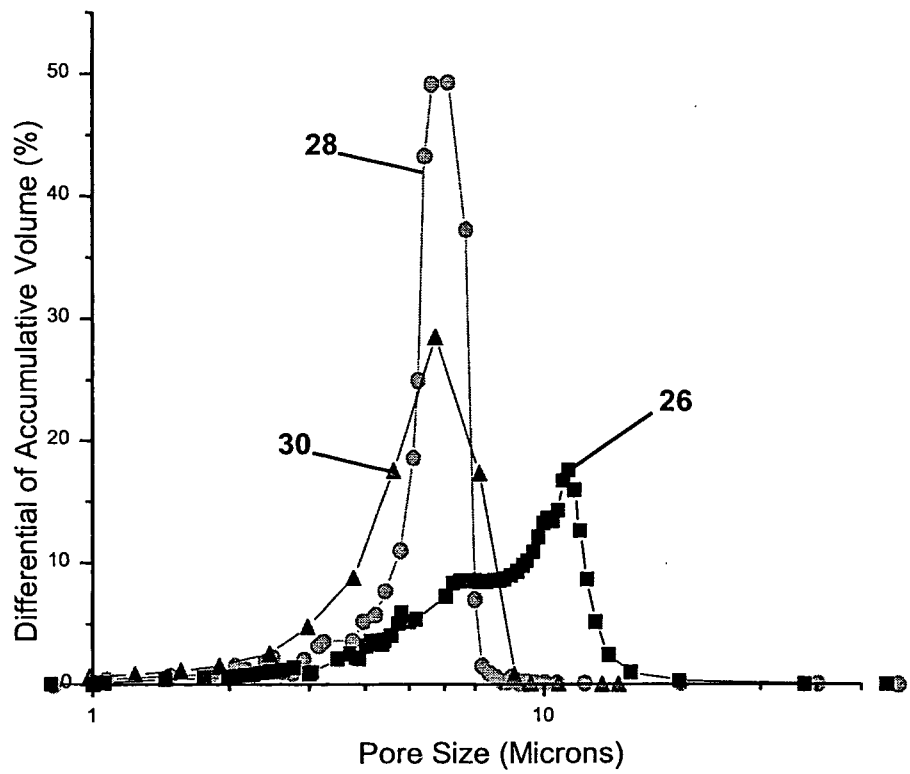

Differential of Accumulative Volume (%)
50
40
30
20
10
0
28
30
26
1
10
Pore Size (Microns)

Figure 5