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(71) Applicant(s)
NGK INSULATORS, LTD.

(72) Inventor(s)
Takeno, Shogo;Ichikawa, Akimasa;Nonokawa, Masami

(74) Agent / Attorney
Patent Attorney Services, 26 Ellingworth Parade, Box Hill, VIC, 3128

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(71) **Applicant** *(for all designated States except US)*: **NGK INSULATORS, LTD.** [JP/JP]; 2-56, Suda-cho, Mizuho-ku, Nagoya-shi, Aichi, 4678530 (JP).

(72) **Inventors; and**

(75) **Inventors/Applicants** *(for US only)*: **ICHIKAWA, Akimasa** [JP/JP]; c/o NGK INSULATORS, LTD., 2-56, Suda-cho, Mizuho-ku, Nagoya-shi, Aichi, 4678530 (JP). **TAKENO, Shogo** [JP/JP]; c/o NGK INSULATORS, LTD., 2-56, Suda-cho, Mizuho-ku, Nagoya-shi, Aichi, 4678530 (JP). **NONOKAWA, Masami** [JP/JP]; c/o NGK INSULATORS, LTD., 2-56, Suda-cho, Mizuho-ku, Nagoya-shi, Aichi, 4678530 (JP).

(74) **Agent: WATANABE, Kazuhira**; 3rd Fl., No.8 Kikuboshi Tower Building, 20-18, Asakusabashi 3-chome, Taito-ku, Tokyo, 1110053 (JP).

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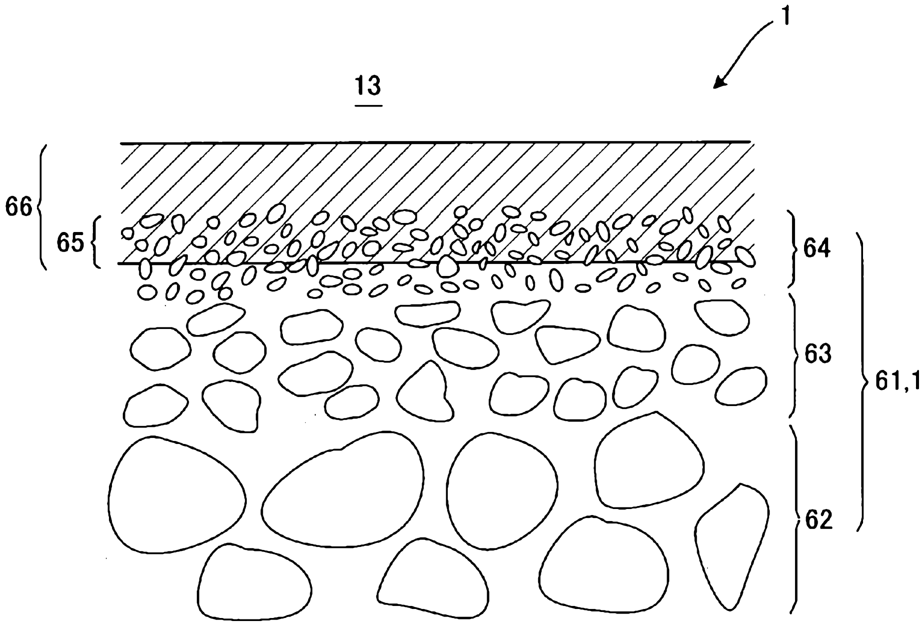

(57) **Abstract:** A separation membrane-porous material composite (1) being improved in flux and selectivity, which comprises a porous ceramic material and a separation membrane formed on the porous material, wherein a composite layer (65) having a thickness of 1 mm or less is provided at the interface between the porous material (61) as a dense layer (64) and the separation membrane (66) being formed as a carbonaceous film while maintaining an increased pressure inside the porous material to avoid penetration of the carbon layer precursor into the pores.

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DESCRIPTION

SEPARATION MEMBRANE-POROUS MATERIAL COMPOSITE AND METHOD FOR MANUFACTURING THE SAME

Technical Field

[0001]

The present invention relates to a separation membrane-porous material composite having a porous material and a separation membrane formed on a surface of the porous material and to a method for manufacturing the separation membrane-porous material composite.

Background Art

[0002]

There is a technical demand for selective separation of a specific substance (e.g., gas) from a mixture of a plurality of substances (e.g., gas) at the molecule level. As filters to meet the demand, there have generally been known filters which employ polysulfone, silicon, polyamide, polyimide, or the like for a separation membrane.

[0003]

However, since separation membranes of these materials are of polymer resins, there is a problem of limited mixture subjected to separation because the film easily changes in quality and deteriorates when an organic solvent is contained in the mixture.

[0004]

Therefore, in recent years, there has been proposed a filter having a carbon film as a separation membrane formed on a porous material (porous substrate) as a filter excellent in chemical stability and thermal resistance (see Japanese Patent No. 3647985).

[0005]

However, a filter actually manufactured by forming a carbon film on a surface of a porous material is not satisfactory with regard to a flux and selectivity (separation factor α), showing the necessity of improvement.

[0006]

Generally, improving the selectivity with maintaining the flux, improving the flux with maintaining the selectivity, and improving both the flux and selectivity are always aims. It was found that, particularly when a carbon film is formed on a porous material by an immersion method, the carbon film is formed thick, and thereby a flux tends to decrease.

[0007]

In addition, as disclosed in Japanese Patent No. 3647985, in a method of impregnating the surface of the porous material (porous substrate) with silica sol and forming a carbon film thereon, a pore diameter of the carbon film increases due to formation of a sol layer. Therefore, selectivity is improved with respect to some substances (e.g., gas) having a molecular diameter of 0.43 nm or more and a relatively high molecular weight such as C_3H_8/C_3H_6. However, it has been found that selectivity easily deteriorates with respect to a substance having a relatively small molecular weight such as CO_2/CH_4, N_2/O_2, and water/EtOH, which are industrially useful. In addition, a low flux by the influence of pressure loss due to silica sol has been recognized.

When used in this specification and claims, the terms "comprises" and "comprising" and variations thereof mean that the specified features, steps or integers are included. The terms are not to be interpreted to exclude the presence of other features, steps or components.

The above references to and descriptions of prior proposals or products are not intended to be, and are not to be construed as, statements or admissions of common general knowledge in the art in Australia.

Disclosure of the Invention

[0008]

The present invention has been made in view of the aforementioned circumstances and aims to provide a means for obtaining a filter having porous material and a separation membrane (e.g., carbon film) thereon and having an improved flux and selectivity in comparison with conventional filters. As a result of repeated study, it has been found out that the above problem can be solved by forming a separation membrane on a surface of a porous material under specific conditions in a production process of a separation membrane-porous material composite (applicable to a filter), which led to the completion of the present invention.

According to an aspect of the invention, there is provided a method for manufacturing a composite comprising a porous material and a separation membrane formed on a surface of the porous material, wherein, after preparing a porous material, the prepared porous material is subjected to a step of bringing a solution of a separation membrane or a precursor solution which becomes a separation membrane later into contact at least once with a surface of the porous material when pressure is applied at least once to the inside of pores of the porous material from a face of the porous material opposite to said surface to which the solution is applied.

According to a further aspect of the present invention, there is provided a method for forming a separation membrane on a surface of a porous material, wherein the method includes a step of bringing a solution of a separation membrane or a precursor solution which becomes a separation membrane later into contact at least once with a surface of the porous material when applying pressure of 1 to 1000 kPa, in terms of gauge pressure, at least once to the inside of pores of the porous material by supplying pressurized gas into the pores from a face of the porous material opposite to said surface to which the solution is applied.

[0009]

According to an embodiment of the present invention, there is provided a separation membrane-porous material composite comprising a porous material and a separation membrane formed on a surface of the porous material, wherein a composite layer having a thickness of 1 mm or less is provided as an under layer for the separation layer at an interface between the porous material and the separation membrane, and at least a part of the composite layer is made of same material as a material for the separation layer.

[0010]

The composite layer in the present specification means a layer formed in such a manner that a solution of a precursor for a separation membrane is made to be penetrated into a part of the porous material, especially a part of the dense layer while applying pressure to the inside of pores in the porous material so as to form a layer wherein a material for a separation membrane layer is mingled, desirably in a homogeneous state as much as possible, with the material for the porous material at the interface between the porous material and the separation membrane when the separation membrane is finally formed on the porous material. That is, the composite layer means a portion where both the material constituting a porous material and the material for the separation membrane are present in a mingled state at the interface between the porous material and the separation membrane.

[0011]

In a separation membrane-porous material composite of the present invention, the composite layer has a thickness of preferably 500 μm or less, more preferably 0.01 to 500 μm , furthermore preferably 100 μm or less, and particularly preferably 0.01 to 10 μm.

[0012]

In a separation membrane-porous material composite of the present invention, the porous material preferably has a monolithic shape.

[0013]

In a separation membrane-porous material composite of the present invention, the separation membrane is preferably a molecular sieve carbon film.

[0014]

According to the present invention, there is further provided a ceramic filter constituted by one of the aforementioned separation membrane-porous material composite bodies and capable of separating water from ethanol. In addition, there is provided a ceramic filter constituted by one of the aforementioned separation membrane-porous material composite bodies and capable of separating a gas mixture of, for example, oxygen and nitrogen, or the like, besides a liquid mixture of water and ethanol, or the like, at the molecule level.

[0015]

According to the present invention, there is furthermore provided a method for manufacturing a composite comprising a porous material and a separation membrane formed on a surface of the porous material, wherein, after the porous material is prepared, the porous material is subjected to a step of bringing a solution of the separation membrane or a solution of a precursor which becomes the separation membrane later into contact with a surface of the porous material at least once under applying pressure on an inside of pores of the porous material so as to keep the thickness of the composite layer at the predetermined level.

[0016]

In a method for manufacturing the separation membrane-porous material composite of the present invention, it is preferable that the contact in the aforementioned step is conducted by immersing the porous material in the solution of the separation membrane or the solution of a precursor which becomes the separation membrane later (immersion method).

[0017]

In a method for manufacturing the separation membrane-porous material composite of the present invention, it is also preferable that the pressure is applied by supplying pressurized gas into the pores of the porous material.

[0018]

In a method for manufacturing the separation membrane-porous material composite of the present invention, the pressure is preferably 1 to 1000 kPa, more preferably 10 to 500 kPa, and particularly preferably 50 to 100 kPa.

[0019]

A method for manufacturing the separation membrane-porous material composite of the present invention is suitably used in the case that the porous material has a monolithic shape.

[0020]

A method for manufacturing the separation membrane-porous material composite of the present invention is suitably used in the case that the separation membrane is a molecular sieve carbon film.

[0021]

According to the present invention, there is furthermore provided a method for forming the separation membrane on a surface of the porous material, wherein the method includes a step of bringing a solution of the separation membrane or a solution of a precursor which becomes the separation membrane later into contact with a surface of the porous material in a state that pressure of 1 to 1000 kPa is applied on the inside of the pores of the porous material by supplying pressurized gas into the pores.

[0022]

Since a composite layer formed at the interface between the porous material and the separation membrane has a thickness of 1 mm or less in a separation membrane-porous material composite of the present invention, the entire thickness of the separation membrane including the composite layer portion is thin in comparison with separation membrane-porous material composite bodies conventionally present as various kinds of filters. Since a composite layer has a small effective area of a separation membrane, it has particularly large pressure loss. Further, since a conventional filter has large pressure loss because the composite layer portion is thick. Therefore, a filter where a separation membrane-porous material composite of the present invention is employed has a small pressure loss in total and a high flux upon separation of a mixture.

[0023]

In a method for manufacturing a separation membrane-porous material composite of the present invention, the porous material is subjected to a step of bringing a solution of a precursor which becomes the separation membrane later into contact with a surface of the porous material at least once in a state that pressure is applied to the inside of pores of the porous material. When the solution of a precursor which becomes the separation membrane later is brought into contact with a surface of the porous material, the inside of the pores of the porous material is in a pressurized state. Therefore, the solution for a precursor (hereinafter sometimes referred to as precursor solution) hardly penetrates into the pores from the surface of the porous material, and almost all the precursor solution remains on the surface of the porous material and forms a separation membrane with formation of a quite thin composite layer at the interface therebetween. Therefore, according to a method for manufacturing a separation membrane-porous material composite of the present invention, a very thin composite layer having a uniform thickness can be formed at the interface between the porous material and the separation membrane. Also, the entire separation membrane including a composite layer portion compositely formed with the porous material can have a uniform thickness and can be made thin, of course, in comparison with a separation membrane manufactured without pressurizing the inside of the pores of the porous material.

[0024]

In addition, in a method for manufacturing a separation membrane-porous material composite of the present invention, since the entire separation membrane including the composite layer can be formed thin, just a small amount of the precursor solution used for forming the separation membrane is required.

[0025]

Further, in a method for manufacturing a separation membrane-porous material composite of the present invention, it is possible to employ an immersion method where a porous material is immersed in a precursor solution which becomes a separation membrane later as a preferable mode. Even by this method, the separation membrane is not formed thick on a surface of the porous material not to generate a factor of decrease in flux.

[0026]

Even by a method for forming a separation membrane on a surface of a porous material of the present invention, an effect similar to that by a method for manufacturing a separation membrane-porous material composite of the present invention by penetrating the precursor while applying pressure to the pores in the porous material can be obtained. That is, a method for forming a separation membrane on a surface of a porous material of the present invention is included as an embodiment for the method for manufacturing a separation membrane-porous material composite of the present invention.

[0027]

A method for forming a separation membrane on a surface of a porous material of the present invention and a method for manufacturing a separation membrane-porous material composite of the present invention exhibit an excellent effect in that a separation membrane-porous material composite of the present invention can be obtained.

[0028]

Since a separation membrane-porous material composite of the present invention manufactured by employing a method for forming a separation membrane on a surface of a porous material of the present invention or a method for manufacturing a separation membrane-porous material composite of the present invention is manufactured with applying pressure into the pores of the porous material to control the penetration of a precursor solution into the pores from the surface of the porous material, the entire separation membrane including a composite layer portion is thin and has a uniform thickness. Therefore, the separation membrane-porous material composite of the present invention is excellent in selectivity in addition to a high flux as described above.

[0029]

If a composite having a porous material and a separation membrane formed on a surface of the porous material (separation membrane-porous material composite) is manufactured by a conventional method, for example, the immersion method where pressure is not applied into pores of the porous material instead of using a method for forming a separation membrane on a surface of a porous material of the present invention or a method for manufacturing a separation membrane-porous material composite of the present invention, the precursor solution which becomes a separation membrane later penetrates into pores from the surface of the porous material. As a result of having a difference caused by concave-convex surface of the porous material in the extent of the penetration, sometimes, a separation membrane having a uniform thickness cannot be formed. A filter using such a separation membrane-porous material composite has deteriorated separation performance at any cost. However, according to a separation membrane-porous material composite of the present invention manufactured by a method for forming a separation membrane on a surface of a porous material of the present invention or a method for manufacturing a separation membrane-porous material composite of the present invention, such a problem is not caused, and a filter having a satisfactory flax and satisfactory selectivity can be obtained.

[0030]

A separation membrane-porous material composite of the present invention manufactured by a method for forming a separation membrane on a surface of a porous material of the present invention or a method for manufacturing a separation membrane-porous material composite of the present invention can have a film having a uniform thickness without forming a sol layer as disclosed in Japanese Patent No. 3647985. Therefore, it can exhibits high selectivity even for a series having relatively small molecular weight and industrially high usability such as

CO_2/CH_4, N_2/O_2, and H_2O/EtOH. Since there is no influence of pressure loss due to a sol layer, a flux is also high. In addition, even in the case of forming a separation membrane on a sol layer, by employing a method for forming a separation membrane on a surface of a porous material of the present invention or a method for manufacturing a separation membrane-porous material composite of the present invention, components of the separation membrane is inhibited from penetrating into a sol layer, and thereby a high flux can be obtained.

Brief Description of the Drawings

[0031]

[Fig. 1] Figure 1 is a block diagram showing the entire machinery and tools of an apparatus used for forming a carbon film.

[Fig. 2] Figure 2 is a detailed view showing the inside of the container of the apparatus shown in Figure 1.

[Fig. 3] Figure 3 is a photograph showing a cross-section of the porous material in Example (Comparative Example 1).

[Fig. 4] Figure 4 is a photograph showing a cross-section of the porous material in Example (Example 1).

[Fig. 5] Figure 5 is a perspective view showing the whole of an embodiment of a separation membrane-porous material composite of the present invention.

[Fig. 6] Figure 6 is a schematic view showing an enlarged part of a cross-section of the inner wall of a cell of an embodiment of a separation membrane-porous material composite of the present invention.

Explanation on numeral references

[0032]

1: separation membrane-porous material composite, 2: partition wall, 15 & 16: end face, 17: peripheral face, 20: container, 22: sealant, 23: packing, 24: pressurized gas, 25: precursor solution, 26: tank, 27: regulation valve, 28: pump, 61: porous material, 62: substrate, 63: inter mediate layer, 64: dense layer, 65: composite, 66: carbon film.

Best Mode for Carrying out the Invention

[0033]

Hereinbelow, embodiments of the present invention will be described with referring to drawings. However, the present invention is by no means limited to these embodiments, and various changes, modifications, improvements, and replacements may be added thereto on the basis of those skilled in the art within a range of not deviating from the gist of the present invention. For example, the drawings show preferable embodiments of the present invention. However, no restriction is imposed on the present invention by embodiments shown by the drawings or information shown in the drawings. Upon carrying out or inspecting the present invention, a means similar or equivalent to that described in the present specification can be employed. However, a preferable and suitable means is as follows:

[0034]

First, a separation membrane-porous material composite of the present invention will be described. Figs. 5 and 6 are views showing an embodiment of a separation membrane-porous material composite of the present invention. Fig. 5 is a perspective view showing the whole, and Fig. 6 is a schematic view showing an enlarged part of a cross-section of an inner wall of a cell.

[0035]

The separation membrane-porous material composite 1 shown in Fig. 5 has a cylindrical outer shape as a whole and a monolithic shape (lotus root-like shape) having a plurality of cells 13 constituting fluid passages in the axial direction. Each of the cells 13 divided by the partition walls 12 which are porous bodies 61 has a circular cross-section perpendicular to the axial direction. On the inner wall surfaces of the cells 13 are formed carbon films 66 of molecular sieve carbon films. The inner wall surfaces mean the surfaces of the partition walls 12, which substantially form the open space of the cells 13.

[0036]

In a separation membrane-porous material composite 1, for example, when a mixture of water and ethanol as a target of separation is introduced into the cells 13 from an end face 15 on the inlet side, water constituting the mixture is selectively separated by the carbon films 66 formed on the inner wall surface of the cells 13, passes through the partition walls 12, and discharged from the outermost peripheral face 17 of the separation membrane-porous material composite 1 before the mixture reaches the end face 16 on the outlet side. That is, the mixture can be divided into water as a substance and ethanol as the other substance. Thus, the separation membrane-porous material composite 1 can be used as a filter having high separation performance for water and ethanol, for example.

[0037]

As shown in Fig. 6, the separation membrane-porous material composite 1 is a composite having a porous material 61 (partition wall 12) and a carbon film 66 as a separation membrane formed on a surface of the porous material 61 (partition wall 12). The porous material 61 is constituted by a substrate 62 having an average particle diameter of 10 to 100 μm and an average pore diameter of 1 to 30 μm, an intermediate layer having an average pore diameter of 0.1 to 3 μm, and a dense layer 64 having an average pore diameter of 0.01 to 0.5μm from the inner side. A carbon film 66 is formed on the surface of the dense layer 64. A composite 65 is formed at the interface of the dense layer 64 (porous material 61) and a carbon film 66 and has a thickness of 0.00001 to 1 mm.

[0038]

Next, a method for manufacturing a separation membrane-porous material composite will be described with an example of a case of manufacturing the aforementioned separation membrane-porous material composite 1. Through the description, a method for forming a separation membrane on a surface of a porous material of the present invention will be described. First, the porous material 61 is obtained by a know method. For example, a substrate 62 having a monolithic shape is formed by subjecting a porous material to extrusion forming, followed by firing. Then, an inter mediate layer 63 and a dense layer 64 are formed on a surface of the substrate 62 using a porous material by a filtration film-forming method, followed by firing to obtain a porous material 61. The surface of the substrate 62 where the intermediate layer 63 and the dense layer 64 are formed is an inner wall surface of a cell 13.

[0039]

As the porous material for the substrate 62, alumina can be employed in that a pore diameter is hardly changed due to corrosion or temperature change and that sufficient strength can be obtained. In place of alumina, cordierite, mullite, silicon carbide, or the like, may be employed.

[0040]

As the porous material for the intermediate layer 63 and the dense layer 64, the same material as that for the substrate 62 can be used. Particles, e.g., alumina particles forming the intermediate layer 63 has a smaller average particle diameter than that of the particles, e.g., alumina particles forming the substrate 62; and particles, e.g., alumina particles forming the dense layer 64 has a smaller average particle diameter than that of the particles, e.g., alumina particles forming the intermediate layer 63. When the intermediate layer 63 and the dense layer 64 are formed by a filtration film-forming method, each of the porous materials is used as slurry obtained by mixing framework particles of alumina particles or the like having a desired average particle diameter of 0.3 to 10 μm, a sintering aid of a glass frit powder, and binder with a solvent such as water at a predetermined ratio. It is desirable that the slurry has a binder content of 2 to 10% by mass with respect to contents of inorganic substances constituting slurry.

[0041]

Next, a carbon film 66 (separation membrane) is formed on a surface of the porous material 61 obtained above. The surface of the porous material 61 where the carbon film 66 is formed is an inner wall surface of a cell 13 where the intermediate layer 63 and the dense layer 64 are previously formed and a surface of a partition wall 12. The carbon film 66 can be formed by bringing a precursor solution of a carbon film 66 into contact with a surface of the porous material 61 to form a film, which is carbonized at about 400 to 1000°C, preferably about 700°C in a nitrogen atmosphere. The carbonization may be performed in a reduced atmosphere of argon, helium, or the like, in a vacuum state instead of a nitrogen atmosphere. When the carbonization is performed at a temperature below 400°C, the selectivity and the permeability rate as a molecular sieve film may decrease because of insufficient carbonization. On the other hand, when the carbonization is performed at a temperature above 1000°C, the permeability rate may decrease because of shrinkage of pore diameters. The carbon film 66 may be formed at once or in repeated operations.

[0042]

Figs. 1 and 2 are views showing an apparatus used for forming the carbon film 66 by an immersion method. Fig. 1 is a block diagram showing the entire machinery and tools, and Figure 2 is a detailed view showing the inside of the container shown in Figure 1. The apparatus 10 shown in Fig. 1 makes the same conditions as those for immersing the porous material 61 into a precursor solution 25. The apparatus 10 is constituted by a container 20 having the porous material 61 therein, a tank 26 storing the precursor solution 25, a pump 28 for supplying the precursor solution 25 from the tank 26 to the container 20, and a regulation valve 27 for adjusting pressure of pressurized gas 24 to be sent from a pressurized gas supply unit, which is not illustrated, to the container 20. As shown in Fig. 2, in the container 20 is housed the porous material 61 having the end faces 15 and 16, both sealed with a sealant 22 of glass material in the state that the end faces 15 and 16 are isolated from the peripheral face

17 by packings 23.

[0043]

Using the apparatus 10 shown in Figs. 1 and 2, pressurized gas is charged into the pores of the porous material 61 by manipulating the regulation valve 27 in the state that the porous material 61 is housed in the container 20 as described above. The pressurized gas is charged under a pressure of 1 to 1000 kPa. This makes the pressure in the porous material 61 also about 1 to 1000 kPa even though a pressure loss is generated in the porous material 61. Then, the pump 28 is operated to supply the precursor solution 25 to the inside of the cells 13, for example, from the end face 16 side to the end face 15 side of the porous material 61 housed in the container 20. Then, the pump 28 is stopped to be opened or the pump 28 is adversely operated to remove the surplus precursor solution 25 from the cells 13. Thus, a thin film made of the precursor solution 25 which becomes a carbon film 66 later can be formed on the inner wall surface of the cells 13 (surface of the porous material 61). Since the inside of the pores of the porous material 61 is pressurized by the pressurized gas at this time, the precursor solution is inhibited from penetrating into the inside (the inside of the pores) of the porous material 61 (dense layer 64), and the composite layer 65 is not formed thick. The carbon film 66 containing the composite layer 65 portion is a flat thin film having a uniform thickness, and thereby a high separation factor can be obtained with inhibiting a flux from being reduced.

[0044]

In order to form a carbon film 66 as a separation membrane, there may be employed, as a means to bring the precursor solution

25 into contact with a surface of the porous material 61, a means such as spin coating or spray coating instead of the immersion method. In the case that the porous material has a monolithic shape as the present embodiment, a carbon film can easily be formed by the immersion method. Here, the term "precursor" means a material capable of being converted into a separation membrane by, for example, firing the resultant after coating or immersion. Thus, in case of the carbon film, the precursor includes a thermosetting resin such as phenol resin, melamine resin, urea resin, furan resin, polyimide resin, and epoxy resin; a thermoplastic resin such as polyethylene; a cellulose resin, or a precursor substance of these resins.

[0045]

Thus, a precursor solution 25 for the carbon film 66 may be prepared by dissolving any one of the above mentioned materials in an organic solvent such as methanol, acetone, tetrahydrofuran, NMP, and toluene; water, or the like. When a film of the precursor solution 25 is formed, according to the kind of the resin contained in the solution, an appropriate thermal treatment may be employed. As the pressurized gas 24, argon, helium, or nitrogen may be employed. Indeed, as an exemplified example for a solution of separation membrane, silica sol can be given. The precursor other than those for the carbon film may include raw materials for forming zeolite film by using hydrothermal synthesis after applying seed of zeolite onto the porous material.

[0046]

In the present specification, the average pore diameter (μm) is measured by mercury penetration method. The average pore diameter is a value of a 50% particle diameter measured with an

X-ray transmission type particle size distribution measuring apparatus (Sedigraph 5000-02 type produced by Shimazu Corporation in Example described below).

Example

[0047]

Hereinbelow, the present invention will be described in more detail on the basis of Examples. However, the present invention is by no means limited to these Examples.

[0048]

(Example 1)

There was manufactured a substrate having a monolithic shape having an average particle diameter of 10 to 100 μm and an average pore diameter of 1 to 30 μm though forming by extrusion and firing. Next, on the inner wall surface of the cells of the substrate, alumina particles having an average particle diameter of 0.3 to 10 μm were deposited by a filtration film-forming method, followed by firing to form an intermediate layer having a thickness of 10 to 1000 μm and an average pore size of 0.1 to 3 μm. On the intermediate layer, alumina particles having an average particle diameter of 0.3 to 1 μm were further deposited by a filtration film-forming method, followed by firing to form a dense layer having a thickness of 1 to 100 μm and an average pore diameter of 0.01 to 0.5 μm. Thus, a porous material was obtained.

[0049]

Next, using the apparatus 10 shown in Figs. 1 and 2, helium gas having a pressure of 1 kPa was charged into the pores of the porous material, and, with pressurizing the inside of the pores, a precursor solution of a carbon film was formed on the inner wall surfaces of the cells of the porous material by an immersion method and carbonized at 700°C in a nitrogen atmosphere to further form a carbon film on the dense layer. Thus, a separation membrane-porous material composite was obtained.

[0050]

The separation membrane-porous material composite obtained above was evaluated by a water-ethanol pervaporation method. As the test conditions, a ratio of H_2O:EtOH was 10:90% by mass, and the supplied liquid had a temperature of 75°C. Table 1 shows the amount of consumption of the precursor solution used for forming the carbon film and pervaporation performance (a separation factor and flux). In addition, Fig. 4 shows a photograph of a cross-section of the porous material in the stage of forming the precursor solution of a carbon film on the inner wall surfaces of the cells of the porous material. In Example 1, two separation membrane-porous material composite bodies were manufactured under the same conditions, and Fig. 4 shows a photograph of a cross section of one of them.

[0051]

(Example 2)

A separation membrane-porous material composite was manufactured in the same manner as in Example 1 except that the inside of the pores was pressurized by helium gas having a pressure of 50 kPa and charged into the pores of the porous material. The separation membrane-porous material composite was evaluated by a water-ethanol pervaporation method under the same conditions as in Example 1. Table 1 shows the amount of consumption of the precursor solution used for forming the carbon film and pervaporation performance (a separation factor and flux).

[0052]

(Example 3)

A separation membrane-porous material composite was manufactured in the same manner as in Example 1 except that the inside of the pores was pressurized by helium gas having a pressure of 100 kPa and charged into the pores of the porous material. The separation membrane-porous material composite was evaluated by a water-ethanol pervaporation method under the same conditions as in Example 1. Table 1 shows the amount of consumption of the precursor solution used for forming the carbon film and pervaporation performance (a separation factor and flux).

[0053]

(Example 4)

A separation membrane-porous material composite was manufactured in the same manner as in Example 1 except that the inside of the pores was pressurized by helium gas having a pressure of 1000 kPa charged into the pores of the porous material. The separation membrane-porous material composite was evaluated by a water-ethanol pervaporation method under the same conditions as in Example 1. Table 1 shows the amount of consumption of the precursor solution used for forming the carbon film and pervaporation performance (a separation factor and flux).

[0054]

(Comparative Example 1)

Two separation membrane-porous material composite bodies were manufactured in the same manner as in Example 1 except that the inside of the pores was not pressurized a separation membrane was formed by penetrating the precursor solution. The separation membrane-porous material composite bodies were evaluated by a water-ethanol pervaporation method under the same conditions as in Example 1. Table 1 shows the amount of consumption of the precursor solution used for forming the carbon film and pervaporation performance (a separation factor and flux). In addition, Fig. 3 shows a photograph of a cross-section of the porous material in the stage of forming the precursor solution of a carbon film on the inner wall surfaces of the cells of the porous material. In Comparative Example 1, two separation membrane-porous material composite bodies were manufactured under the same conditions, and Fig. 3 shows a photograph of a cross section of one of them. As can be taken from Fig. 3, the presence of a blackish colored relatively thicker layer around the pores may be observable while the presence of the blackish colored thick layer around the pores is hardly observable in case of the cross section of the Fig. 4 mentioned above. This difference can bring a big improvement in the filtration performance.

[0055]

(Comparative Example 2)

A separation membrane-porous material composite was manufactured in the same manner as in Example 1 except that the inside of the pores was pressurized by helium gas having a pressure of 1500 kPa and charged into the pores of the porous material a separation membrane was formed by penetrating the precursor solution. The separation membrane-porous material composite was evaluated by a water-ethanol pervaporation method under the same conditions as in Example 1. Table 1 shows the amount of consumption of the precursor solution used for forming the carbon film and pervaporation performance (a separation factor and flux).

[0056]

[Table 1]

	Applied Pressure (kPa)	Separation factor α H_2O/EtOH	Flux (kg/m^2h)	Amount of consumption of precursor solution(g)
Example 1	1	200	0.9	2.0
Example 2	50	2000	0.9	1.5
Example 3	100	1200	1.0	1.2
Example 4	1000	800	1.1	1.0
Comp. Ex. 1	0	120	0.8	2.4
Comp. Ex. 2	1500	40	1.0	0.9

[0057]

(Example 5)

Next, using the apparatus 10 shown in Figs. 1 and 2, helium gas having a pressure of 1 kPa was charged into the pores of the porous material, and, with pressurizing the inside of the pores, a precursor solution of a carbon film was formed on the inner wall surfaces of the cells of the porous material by an immersion method and carbonized at 700°C in a nitrogen atmosphere to further form a carbon film on the dense layer. Thus, a separation membrane-porous material composite was obtained.

[0058]

(Discussion)

As shown in the results of Examples 1 to 4 in Table 1, good separation performance was imparted to the separation membrane-porous material composite bodies manufactured by pressurizing the inside of the pores with charging pressurized gas having a pressure of 1 to 1000 kPa into the pores of the porous material upon forming a film by using the precursor solution. It is clear in comparison with separation performance of the separation membrane-porous material composite bodies manufactured by a conventional method without pressurization (Comparative Example 1). In addition, from the results of Examples 1 to 4, it can be understood that specifications of an obtained separation membrane-porous material composite where priority is given to a separation factor α or a flux can be adjusted by regulating the pressure. On the other hand, as shown by the results of Comparative Example 2, it is understood that good separation performance cannot be obtained when pressure in the pores is made too high. This is presumed that a portion having no carbon film is formed because of the low separation factor α and the low amount of consumption of the precursor solution.

Industrial Applicability

[0059]

A separation membrane-porous material composite according to the present invention can widely be used for, for example, a filter for selectively separating a specific substance (e.g., gas) from a mixture of a plurality of substances (e.g., gas).

CLAIMS

1. A method for manufacturing a composite comprising a porous material and a separation membrane formed on a surface of the porous material,

wherein, after preparing a porous material,

the prepared porous material is subjected to a step of bringing a solution of a separation membrane or a precursor solution which becomes a separation membrane later into contact at least once with a surface of the porous material when pressure is applied at least once to the inside of pores of the porous material from a face of the porous material opposite to said surface to which the solution is applied.

2. A method for manufacturing a composite according to Claim 1, wherein the contact in said step is conducted by immersing the porous material in the solution of the separation membrane or the precursor solution which becomes the separation membrane later.

3. A method for manufacturing a composite according to Claim 1 or Claim 2, wherein pressure is applied by supplying pressurized gas into the pores of the porous material.

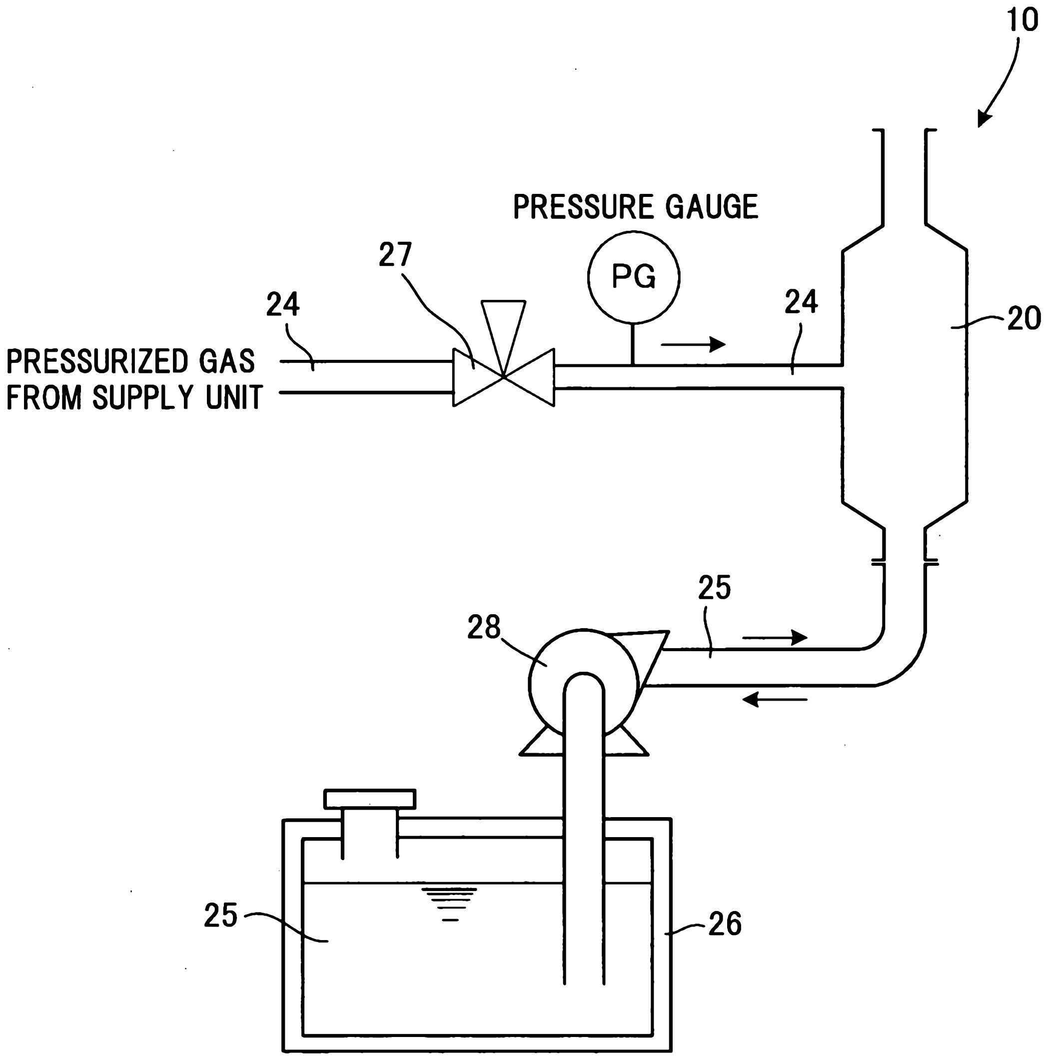
4. A method for manufacturing a composite according to any one of Claims 1 to 3, wherein the pressure is 1 to 1000 kPa in terms of gauge pressure.

5. A method for manufacturing a composite according to any one of Claims 1 to 4, wherein the porous material has a monolithic shape.

6. A method for manufacturing a composite according to any one of Claims 1 to 5, wherein the separation membrane is a molecular sieve carbon film.

7. A method for forming a separation membrane on a surface of a porous material, wherein the method includes a step of bringing a solution of a separation membrane or a precursor solution which becomes a separation membrane later into contact at least once with a surface of the porous material when applying pressure of 1 to 1000 kPa, in terms of gauge pressure, at least once to the inside of pores of the porous material by supplying pressurized gas into the pores from a face of the porous material opposite to said surface to which the solution is applied.

FIG. 1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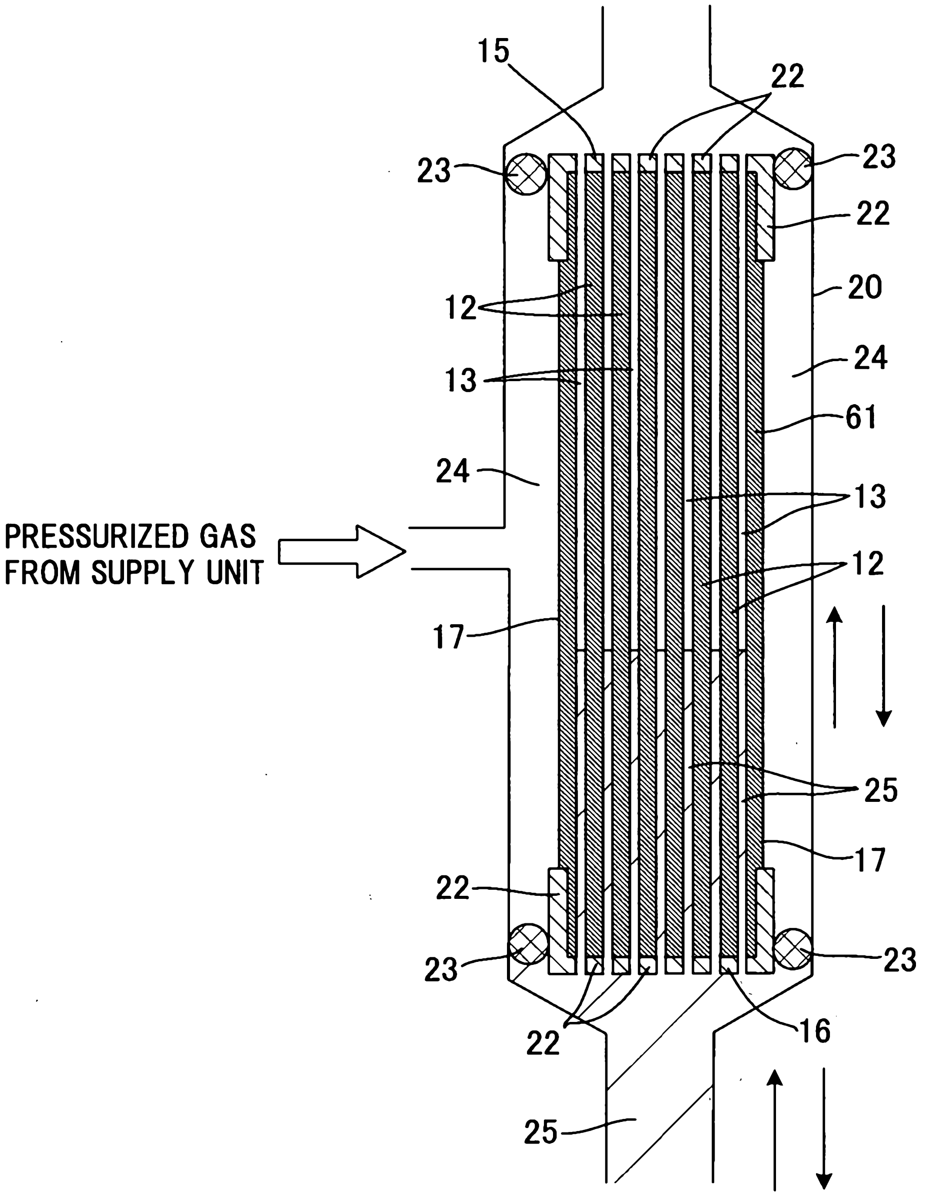
PRESSURE GAUGE
PG
27
24
24
20
PRESSURIZED GAS
FROM SUPPLY UNIT
25
28
25
26

FIG. 2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22
23
23
22
20
12
24
13
61
24
13
PRESSURIZED GAS FROM SUPPLY UNIT
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17
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23
22
16
25

FIG. 3

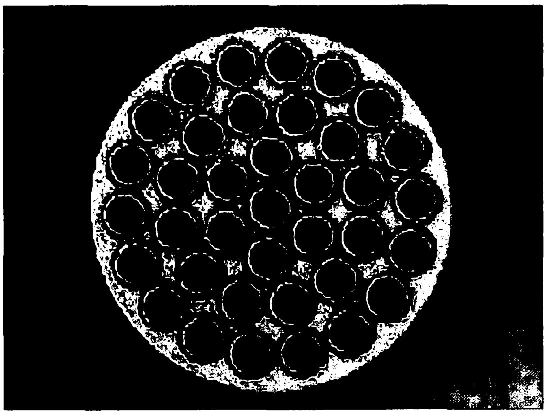

FIG. 4

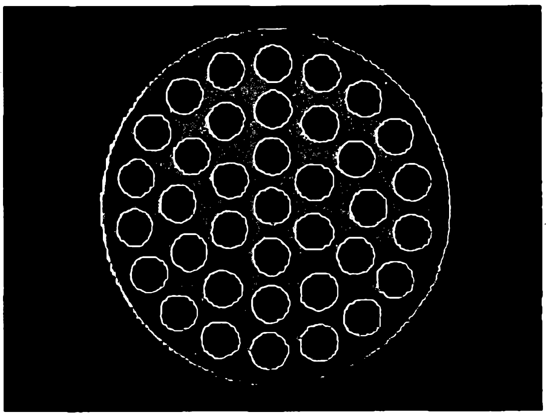

FIG. 5

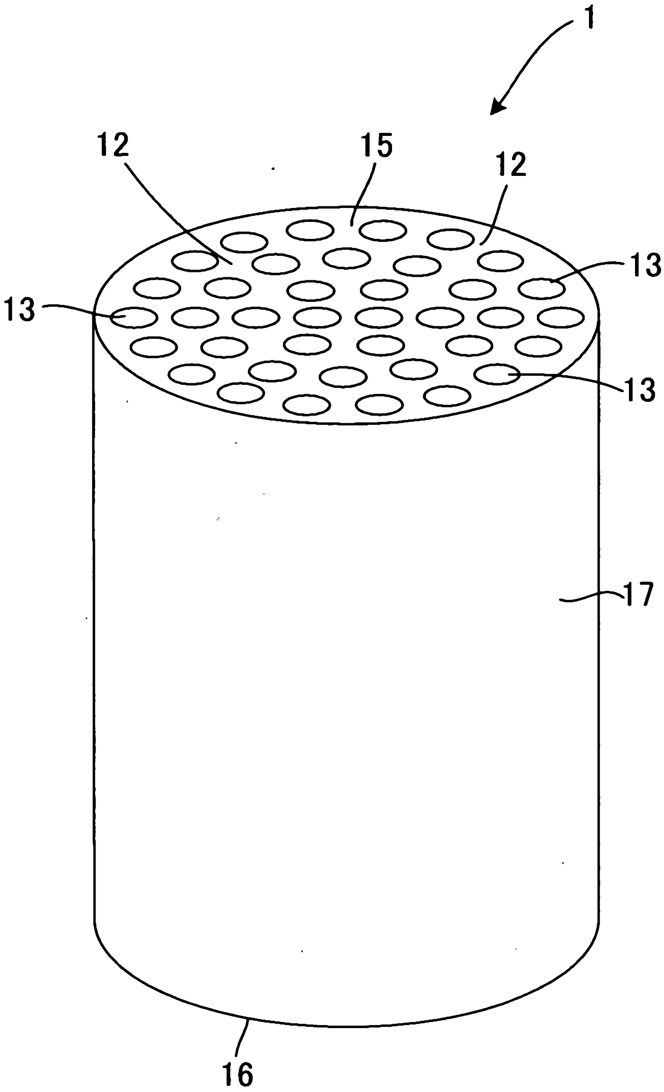

FIG. 6