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(54) Title: PROCESS FOR PREPARING AN INORGANIC POROUS MEMBRANE.

(57) Abstract: The invention proposes a method for the making of an inorganic porous membrane applied onto a suitable carrier, such that for the shaping of a suitable covering onto this earner one starts with a by itself known starting sol, which is obtained by reacting in a suitable ratio of an organo-silicate and a methylated silane and cooling of the reaction mixture, whilst every covering step, executed with this reaction mixture, will be followed by a sintering step, for which according to the invention a strong dilution of this sol is used for at least the first covering step onto the carrier, and a modification of this sol, obtained by adding at least one material with low surface tension for improvement of the wetting by and the mobility of the sol particles, is used for the subsequent covering step(s). Each covering step is followed by a sinter treatment.

Title: Process for preparing an inorganic porous membrane.

The invention relates to the process for preparing an inorganic porous membrane, to be supported on a suitable carrier, according to the preamble of claim 1.

Such a process is known from EP 1 089 806 B1.

Although this known process results in membranes which are suitable for dehydration processes, the drawback of this known process is an unacceptably low yield, a bad reproducibility, and thus very high costs of usable membranes.

The invention aims to obviate these drawbacks.

This aim is obtained by a process as defined in claim 1.

Surprisingly the first application step in which one thus uses, according to the invention, a strongly diluted sol without surfactant results into a well adhering and very homogenously first layer on the support with well distributed nano-openings, while the subsequent layers, applied by using the thus modified diluted sol, to which the surface active agent has been added, builds-up a composite layer with the required final pores.

It is understood that, in the known process, one will never obtain in the first application step a satisfactory coating layer. When one tries to remedy this by applying a consecutive second step, it is found that this second, still wet, coating layer will only locally adhere to the surface of the first layer, because of local repellence of the wet sol by the already coated and sintered first layer, caused by large differences in surface tension, leading to a non-wetting behaviour, which results in small island formation onto the first coated and sintered layer. Cracks are formed during the sintering step at the edge of those formed islands, so that no satisfactory result is obtained. However when one uses in the first coating step a very diluted version of the stock sol as such and without a surface active agent and applies, after the usual sintering thereof, in a consecutive step or steps this highly diluted version with added thereto a surface active agent, such as e.g. Triton 100, one finds very surprisingly that each subsequent layer adheres perfectly to the proceeding applied and sintered layer. The final resulting membrane shows very good performance despite the use of surfactants. This is very surprisingly, because adding surface active agents into ceramic precursors is known to be used for promotion of pore formation.

Preferred embodiments of the process are described in the subclaims.

It has been demonstrated that, by executing the process as defined in the claims, it was possible to manufacture ceramic membranes for pervaporation with extremely good performance as to selectivity and with extremely high production yield.

The methodology according to the invention can be applied to any suitable ceramic porous carrier, onto tubular carriers, either on the outside or on the inside of such tubular

carriers, or onto any ceramic porous carrier in any shape, provided that the surface of the carrier around the pores thereof, there where the sol must adhere, so as to bridge the pores, is smooth and without defects

It is observed that the favourable influence of the addition of a surface active agent to the sol used in a process according to the prior art is described by S. Giessler et al in the Article < Hydrothermal Stability of modified Membranes for Gas Separation > , 6th World Congress of Chemical Engineering, Australia 23-27 September 2001. This Article reports on Laboratory Experiments only and is thus not representative for Industrial Application of this proposal. Moreover, this Article does not disclose the dilution of the sol in the strength as proposed by the present Invention and also does not disclose not to use the surfactant in the first coating step. This latter measure is, however, thought by the inventor to be critical in ensuring a commercially acceptable yield.

Test methodology

In order to judge the performance of the functionality of pervaporation membranes, each individual membrane tube is tested under identical conditions and the flux and selectivity is measured. Good functioning ceramic pervaporation membranes show a performance of about 2 to 3 kg/m^2/h throughput with selectivity of > 200, which equals to a water concentration of > 91% in the permeate, when measured under standard conditions as specified below. However in Quality Control a selectivity of 100 is used as threshold for approval.

Standard measurement conditions are: 95% Iso Propyl Alcohol, 5% water at 70°C, linear velocity to diminish concentration polarisation of 2 m/sec in tube 7 mm duct, giving a Reynolds number of at least 5000 and a vacuum was applied of about 10 mbar for applying sufficient driving force, where the permeate was condensed with liquid nitrogen in a glass cold trap.

Selectivity is defined as the ratio of water over organic in the permeate, divided by the ratio of water over organic in the feed.

Example

A stock sol with a concentration of 1 mol/litre silica material, according to the prior art, such as known from EP 1 089 806 B1 as mentioned above, was prepared as the starting material.

A) Coat solution concentration of the diluted Methyl-silica sol: coating the first layer with 0.05 mol/litre to be used for the first coating.
Added to this: Triton 100 in 5% weight fraction, based on the weight of the Methyl-silica compound to be used in the second and subsequent coatings.
Number of subsequent coatings with sintering after every coating: 2x
Number of batches and tubes: 3 batches, in total 8 ceramic membrane tubes
Yield of 100%, average selectivity of 1395
Worst batch: yield 100%, average selectivity 817
Best batch: yield 100%, average selectivity 1652

B) Coat solution concentration of the diluted Methyl-silica sol: coating the first layer with 0.05 mol/litre to be used for the first coating.
Added to this: Triton 100 in 5% weight fraction, based on the weight of the Methyl-silica compound, plus different amounts of hexane, from 5% up to 20%, to be used in the second and subsequent coatings.
Number of subsequent coatings with sintering after every coating: 2x
Number of batches and tubes: 4 batches, in total 6 ceramic membrane tubes
Yield of 100%, average selectivity of 2237
Worst batch: yield 100%, average selectivity 821
Best batch: yield 100%, average selectivity 3416

C) Coat solution concentration of the diluted Methyl-silica sol: coating the first layer with 0.01 mol/litre to be used for the first coating.
For the second coating a concentration of 0.025 mol/litre methyl-silica sol was used, in which 50% of the solvent ethanol was replaced by IPA. Added to this for the second coating: Triton 100 in 5% weight fraction, based on the weight of the Methyl-silica compound to be used in the second coating.
The third coating was identical as the second coating.
Number of subsequent coatings with sintering after every coating: 2x
Number of batches and tubes: 1 batch, 4 ceramic membrane tubes
Yield of 100%, average selectivity of 2078
Worst tube: selectivity 506
Best tube: selectivity 3863

D) Coat solution concentration of the diluted Methyl-silica sol: coating the first layer with 0.15 mol/litre to be used for the first coating.

For the second coating a concentration of 0.025 mol/litre methyl-silica sol was used, in which 50% of the solvent ethanol was replaced by IPA. Added to this for the second coating: 2% weight fraction Triton 100.

The third coating was identical as the second coating except 10% Triton 100 was used instead of 2% Triton 100.

Number of subsequent coatings with sintering after every coating: 2x

Number of batches and tubes: 8 batches, 76 ceramic membrane tubes

Yield of 100%, average selectivity of 436

Worst batch: yield 100%, average selectivity 267

Best batch: yield 100%, average selectivity 1120

CLAIMS

1) A process for preparing an inorganic porous membrane, to be supported on a suitable carrier, in which, for obtaining a coating on this carrier, one starts from a basic sol obtained by reacting a mixture of an organo-silicate and a methylated silane in suitable ratios, cooling this reaction mixture, followed by coating and subsequent coatings on a suitable carrier, in which each step of coating with this reaction mixture is followed by a sintering treatment, characterised in that a strongly diluted version of this basic sol is used, for the first coating step onto the carrier and a modification of this basic sol, prepared by adding thereto at least one surface active agent to improve the wettability and moving behaviour of the sol particles and the material of the thus modified sol, is used for the subsequent coating steps of the carrier.

2) A process according to claim 1, characterised in that one prepares the strongly diluted sol with a dilution of 5 to 200, resulting in a concentration of 0.005 – 0.20 mol/litre silica material, diluted with ethanol.

3) A process according to claim 1 and 2, characterised in that one prepares the modified coat sol for the second and subsequent coatings by using a mixture of the original solvent ethanol in the diluted coat-sol by adding a solvent with low surface tension from the range of alkane solvents with C-chain >3 and < 10 Carbon atoms, more specifically pentane, hexane or heptane, preferably hexane.

4) A process according to claim 1 to 3, characterised in that one uses the alkane in a concentration range of preferably between 0.5% to 50%, more specifically in between 1% and 20%.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D71/02 B01D67/00 B01D61/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	S. GIESLER ET AL.: "Performance of hydrophobic and hydrophilic silica membrane reactors for the water gas shift reaction" SEPARATION AND PURIFICATION TECHNOLOGY, vol. 32, 2003, pages 255-264, XP002567575 paragraph [02.1]; tables 1-2 the whole document	1-4

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DUKE M C ET AL: "Carbonised template molecular sieve silica membranes in fuel processing systems: permeation, hydrostability and regeneration" JOURNAL OF MEMBRANE SCIENCE, ELSEVIER SCIENTIFIC PUBL.COMPANY. AMSTERDAM, NL, vol. 241, no. 2, 1 October 2004 (2004-10-01), pages 325-333, XP004525738 ISSN: 0376-7388 paragraph [0002]; table 1 paragraph [0005] the whole document	1-4
X	Y. LANFANG ET AL.: "Preparation and properties of hydrophobic organic-inorganic silica hybrid films" PROC. SPIE, vol. 5774, 2004, pages 267-270, XP002567576 DOI: 10.1117/12.607289 paragraph [0001] - paragraph [02.1] the whole document	1-4
A	EP 1 089 806 A1 (STICHTING ENERGIEONDERZOEK [NL] STICHTING ENERGIEONDERZOEKCENT [NL]) 11 April 2001 (2001-04-11) cited in the application paragraph [0015] the whole document	1-4
A	DE LANGE R S A ET AL: "Formation and characterization of supported microporous ceramic membranes prepared by sol-gel modification techniques" JOURNAL OF MEMBRANE SCIENCE, ELSEVIER SCIENTIFIC PUBL.COMPANY. AMSTERDAM, NL, vol. 99, no. 1, 14 February 1995 (1995-02-14), pages 57-75, XP004041471 ISSN: 0376-7388 the whole document	1-4
A	DE VOS R M; VERWEIJ H: "Improved performance of silica membranes for gas separation" JOURNAL OF MEMBRANE SCIENCE, vol. 143, 1998, pages 37-51, XP002567577 the whole document	1-4

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/NL2009/000203

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1089806 A1	11-04-2001	NONE	