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(54) Title: A PROCESS FOR THE PREPARATION OF AN ASYMMETRIC MEMBRANE COMPRISING A MESO- OR MACRO-POROUS SUBSTRATE AND A MICRO/MESO-POROUS LAYER DEPOSITED THEREON AND AN ASYMMETRIC MEMBRANE

(57) Abstract: The present invention relates to a process for the preparation of an asymmetric inorganic membrane comprising a meso- or macro-porous substrate and a micro/meso-porous layer deposited thereon. The present invention also relates to asymmetric membranes having a pore diameter in the one digit nanometer range.



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A PROCESS FOR THE PREPARATION OF AN ASYMMETRIC MEMBRANE COMPRISING A MESO-OR MACRO-POROUS SUBSTRATE AND A MICRO/MESO-POROUS LAYER DEPOSITED THEREON AND AN ASYMMETRIC MEMBRANE

FIELD OF THE INVENTION

- 5 The present invention relates to a novel process for the preparation of an asymmetric membrane comprising a meso- or macro-porous substrate and a micro/meso-porous layer deposited thereon. The present invention also relates to novel asymmetric membranes having pore diameter in the one digit nanometer range.

BACKGROUND OF THE INVENTION

- 10 The industrial use of porous ceramic membranes for hot gas filtration and catalytic membrane reactors is on the rise. Ceramic membranes offer a higher thermal, chemical, and mechanical stability than polymeric membranes presently dominating in industrial practice. Presently, ceramic membranes with pore sizes in the nanometer range are obtained by slip-casting with a pore diameter of approximately 2 nm as the lower limit.
- 15 Many of the traditional processes for the preparation of porous ceramic membranes require several process steps, and yields membranes of varying quality. The typical problem is getting from micrometer substrate pores to membrane pores in a top-layer with mean diameter less than 10 nm. Traditional processes – typically involving colloidal suspensions of particles - require several deposition steps, in which the pore size for each step is smaller
- 20 than the pore size of the preceding step. This is necessary in order to avoid suction of the suspension deeply into the macro porous support by capillary forces.

Andersen et al. (J. Nanoparticle Res., Vol. 4, 405-416, 2002) have disclosed a process for the preparation of membranes by means of filtration of nanoparticles. The membranes obtained by the method had a mean pore diameter in the range of 30-70 nm.

- 25 A poster by Mosleh et al. ("Flame assisted synthesis of catalytic ceramic membranes", Poster at the Eighth International Conference on Inorganic Membranes, Cincinnati, Ohio, USA, 19 July 2004.) discloses a process for the preparation of membranes by means of filtration of nanoparticles. The membranes obtained by the method had fairly small pore diameters.

In order for the membranes to have commercial relevance, the mean pore diameter should preferably be 10 nm or lower, and the outermost layer should at the same time be as thin as possible and have a fine pore structure. Thus, there is a need for an improved method for the preparation of porous ceramic membranes.

5 BRIEF DESCRIPTION OF THE INVENTION

One object of the present invention is to provide a process for the preparation of an asymmetric membrane, said membrane comprising (i) a meso- or macro-porous substrate having a first porous surface and (ii) a micro/meso-porous layer deposited on and/or in the pore mouths of the first porous surface, said process comprising the step of leading a flow of
10 a carrier gas comprising an aerosol phase of metal oxide nanoparticle and/or metal nanoparticles through said first porous surface of said substrate whereby at least a fraction of said nanoparticles becomes deposited on and/or in the pore mouths of the first porous surface, wherein said nanoparticles have a mean diameter of at the most 20 nm, and wherein the size of the nanoparticles is gradually or incrementally decreased so as to obtain a
15 gradually or incrementally decreasing pore size in the outermost part of the micro/meso-porous layer.

Another object of the present invention is to provide an asymmetric membrane comprising (i) a meso- or macro-porous substrate having a first porous surface and (ii) a micro/meso-porous layer deposited on and/or in the pore mouths of the first porous surface, said meso-
20 or macro-porous substrate having a mean pore diameter in the range of 10 nm-10 μ m, and said micro/meso-porous layer having a thickness of in the range of 0.5-1000 nm and a mean pore size of at the most 10 nm, and wherein the meso/micro-porous layer has a gradually increasing pore size in the direction of meso- or macro-porous substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

25 **Figure 1.** Schematic of premixed flame reactor set-up.

Figure 2. Experimental apparatus for deposition and permeation study.

Figure 3. Dependence of permeance (F) on the mean gas pressure ($\bar{P}$) for H₂, He and N₂ in the support.

Figure 4. Dependence of $Y = F_i \sqrt{M_i}$ on the $X = \frac{\bar{P} \sqrt{M_i}}{\mu_i}$ for all gases H₂, He and N₂

together in the support.

Figure 5. Dependence of permeance (F) on the mean gas pressure ($\bar{P}$) across tube for nitrogen in the support and synthesized membrane after 10 and 20 minutes.

5 **Figure 6.** Dependence of F/δ on the mean gas pressure ($\bar{P}$) across top layer for N₂, He and H₂ in the synthesized membrane after 30 minutes.

Figure 7. Dependence of $Y = F_i \sqrt{M_i}$ or $Y = F_i \sqrt{M_i} / \delta$ on the $X = \frac{\bar{P} \sqrt{M_i}}{\mu_i}$ for all gases

H₂, He and N₂ together in the support and top layer after 20 minutes deposition.

10 **Figure 8.** Dependence of relative permeability on deposition time for nitrogen. Volumetric flow rate is measured at pressure difference $\Delta P = -0.5$ bar.

Figure 9. Dependence of the top layer thickness on deposition time. Pressure difference $\Delta P = -0.5$ bar and temperature 600 K.

Figure 10. Variation of $d_p \left(\frac{\varepsilon}{\tau} \right) (1 - \varepsilon)$ for the top layer versus deposition time.

15 **Figure 11.** Scanning electron micrograph of the cross-section of the support and the top layer alumina membrane after 40 minutes of deposition.

Figure 12. An "empirical" figure showing the normally observed correlation between precursor loading in a particle synthesis unit and the resulting morphology. Small concentrations result in very small, compact particles whereas an increase in concentration results in an increase in particle size and at even higher concentration aggregates of primary particles are formed (because there is insufficient residence time to sinter/coalesce the aggregate into a compact spherical particle).

25 **Figure 13.** Particle size distributions measure by a SMPS system at different saturator temperatures of the gas saturator unit. By reducing the saturator temperature, the feed rate of precursor molecules to the flame is reduced and the resulting particles decrease in size as seen on the figure. The measured data points are fitted with a logarithmic PearsonVII model.

Figure 14. Variation of Al-acetylacetonate saturator temperature during dynamic deposition experiment.

Figure 15. The three figures (left column) illustrate the build-up of a layer in the pore mouths of and on the surface of a substrate during a dynamic deposition experiment in which the particle size gradually decreases with time. The fairly coarse nanoparticles close the pore mouth of the substrate. Somewhat finer nanoparticles are deposited between the coarser nanoparticles in the pore mouth, and very fine nanoparticles are deposited on top and between the somewhat finer particles whereby an outer layer of nanoparticles are build on the surface of the substrate. In the final part of the deposition, the deposition rate (mass per time) is fairly low, but only a very thin layer of the finest nanoparticles is necessary. A continuous reduction of the particle size (diameter) can be obtained by continuously lowering the temperature in the saturator. The diagram (right hand side) illustrates the continuous reduction in particle diameter.

DETAILED DESCRIPTION OF THE INVENTION

15 The present invention, i.a., relates to the preparation of asymmetric membranes.

Thus, one aspect of the present invention relates to a process for the preparation of an asymmetric membrane, said membrane comprising (i) a meso- or macro-porous substrate having a first porous surface and (ii) a micro/meso-porous layer deposited on and/or in the pore mouths of the first porous surface, said process comprising the step of leading a flow of a carrier gas comprising an aerosol phase of metal oxide nanoparticles and/or metal nanoparticles through said first porous surface of said substrate whereby at least a fraction of said nanoparticles becomes deposited on and/or in the pore mouths of the first porous surface, wherein said nanoparticles have a mean diameter of at the most 20 nm, and wherein the size of the nanoparticles is gradually or incrementally decreased so as to obtain a gradually or incrementally decreasing pore size in the outermost part of the micro/meso-porous layer.

In an alternative aspect, the size of the nanoparticles is gradually or incrementally increased so as to obtain a gradually or incrementally increasing pore size in the outermost part of the micro/meso porous layer. Thus, the invention also relate to a process for the preparation of an asymmetric membrane, said membrane comprising (i) a meso- or macro-porous substrate having a first porous surface and (ii) a micro/meso-porous layer deposited on and/or in the pore mouths of the first porous surface, said process comprising the step of leading a flow of a carrier gas comprising an aerosol phase of metal oxide nanoparticles and/or metal

nanoparticles through said first porous surface of said substrate whereby at least a fraction of said nanoparticles becomes deposited on and/or in the pore mouths of the first porous surface, wherein said nanoparticles have a mean diameter of at the most 20 nm, and wherein the size of the nanoparticles is gradually or incrementally increased so as to obtain a
5 gradually or incrementally increasing pore size in the outermost part of the micro/meso-porous layer.

The expression "asymmetric" refers to the fact that the porous membrane has a inhomogeneous pore size distribution. In particular, the asymmetric membrane can be said to comprise two or several layers having different pore sizes – often represented by a
10 support layer (the meso- or macro-porous substrate) and one or more top-layers (the micro/meso-porous layer(s)).

By way of definition, a porous material having a pore diameter of more than 50 nm is defined as "macro-porous". A porous material having a pore diameter more than 2 nm, but 50 nm or less, is defined as meso-porous, and a porous material having a pore diameter of 2 nm or
15 less is defined as micro-porous.

Within the present context, the expression "micro/meso-porous" is intended to refer to a material having a pore diameter in the lower end of the meso-porous range or in the micro-porous range, typically a pore diameter of 10 nm or less, in particular less than 10 nm.

Substrate

20 In the process for the preparation of the asymmetric membrane, a meso- or macro-porous substrate is utilized. The substrate has at least a first porous surface, i.e. the porous surface on which the micro/meso-porous layer is to be build. Typically, the substrate has one or more other porous surfaces, e.g. at least a second porous surface, whereby a flow of a gas can pass through the first porous surface and exit via the second porous surface.

25 The meso- or macro-porous substrate may consist of one of a variety of materials such a alumina (e.g. α -alumina), silica, titania, magnesia, zirconia, chromia, ceria or other transition metal oxides and mixtures thereof. It may also consist of carbides (e.g. silicon carbide), nitrides (e.g. silicon nitride), carbon (e.g. graphite), porous structures made of sintered metal (e.g. partially sintered steel spheres).

In one embodiment, the meso- or macro-porous substrate essentially consists of a porous ceramic material (i.e. a metal oxide material), e.g. selected from the group consisting of alumina (e.g. α -Al₂O₃), magnesia, silica, and titania.

5 In another embodiment, the meso- or macro-porous substrate essentially consists of a porous material selected from the group consisting of carbides and nitrides, in particular silicon carbide and silicon nitride.

10 In another embodiment, the meso- or macro-porous substrate essentially consists of a meso- or macro-porous metal structure, such as a structure consisting of partially sintered metal particles (e.g. spheres), e.g. a porous steel tube in which the tube wall consists of partially sintered metal particles.

The pore diameter of the substrate is typically in the range of 10 nm-10 μ m, however more typically in the range of 100 nm to 8 μ m.

15 The physical form of the substrate may be a sheet or plate, a stack of plates, a single tube, a bundle of tubes, a monolite structure (e.g. as in a catalytic unit used for combustion engine exhaust systems), etc.

In one embodiment, the substrate is in the form of a porous tube wherein the micro/meso-porous layer is formed on the inner surface of the tube, see Figure 2. The micro/meso-porous layer may also be formed on the outer surface.

20 In another embodiment, the substrate is in the form of a monolite structure. In one variant hereof, the monolite structure has a plurality of parallel channels where the micro/meso-porous layer is formed on the inner surface of the channels.

The micro/meso-porous layer

25 The first porous surface of the substrate is characterised by a surface portion and a plurality of pore mouths. Thus, the surface immediately accessible for the build-up of the micro/meso-porous layer is the surface and the pore mounts. Consequently, the micro/meso-porous layer is formed on and/or in the pore mouths of the first porous surface.

Transport of particles from one point to another as an aerosol in a flowing gas is fundamental for the deposition of particles on surfaces. Small particles suspended in a gas are in continuous motion as a result of collisions with gas molecules, the so-called *Brownian*

motion. When the concentration of particles is not uniformly dispersed, diffusion by Brownian motion tends to produce a uniform concentration in the gas. Therefore, particles move away from areas of high concentration to regions of low concentration. When a particle collides with a wall/surface, the particle is "lost" from the gas phase and there is a reduction in the concentration of particles in the gas phase.

Particles are, thus, transported to the surface, where they adhere and deposit, by convective diffusion in flowing gas. This mechanism is of fundamental importance to the membrane formation by the aerosol route. When an aerosol flows from outside the macro- or meso-porous structure into a substrate pore, particles will begin to randomly hit and deposit on the wall of the pore by Brownian diffusion. Eventually, the pore mouths will be blocked by the deposited particles and a filter cake begins to form. The mathematical expression (transport of particle by convection and diffusion) describing the penetration of particles into cylindrical pores during the initial phase of deposition shows that the penetration depth increases when a) the pore size increases, b) the particle size increases and c) the temperature of the deposition decreases [Mosleh, 2004]. Both points b) and c) are a consequence of a reduction in the particle diffusion coefficient.

For a given substrate with known pore size and thickness, particle diameter, pressure drop and gas temperature, one can calculate (estimate) the penetration depth of particles assuming cylindrical pores. It is typically in the range of 50 nm–500 nm [Mosleh, 2004].

According to the process described herein, it is possible to obtain very small pore diameters in a very simple manner. Thus, it has been shown that the process renders it possible to obtain membranes where the mean pore diameter of the micro/meso-porous layer is at the most 10 nm, such as at the most 8 nm, or at the most 6 nm, e.g. at the most 2 nm, i.e. a truly micro-porous layer.

Thickness of the deposited micro/meso-porous layer mainly depends to the processing time as more and more nanoparticles will be deposited over time. Typically, however, the thickness of the deposited micro/meso-porous layer is in the range of 0.5-1000 nm, such as in the range of 1-100 nm.

As a consequence of the present invention, numerous process steps of conventional preparation methods for asymmetric membranes are eliminated. Suction of particle suspensions deeply into the meso- or macro-porous support is avoided since the particles are present as an aerosol. The Brownian motion of air-borne particles ensures that particles do not penetrate deeply into the macro-pores of the support material even though the nanoparticles typically are several orders of magnitude smaller than the pores. Consequently, only

one deposition step is necessary and the intermediate process steps of the liquid-based preparation methods, e.g. drying and calcination are eliminated.

Process step

5 The process comprises the step of leading a flow of a carrier gas comprising an aerosol phase of metal oxide nanoparticles and/or metal nanoparticles through said first porous surface of said substrate whereby at least a fraction of said nanoparticles becomes deposited on and/or in the pore mouths of the first porous surface. The size of the nanoparticles appears to be crucial, and the nanoparticles should have a mean diameter of at the most 20 nm.

10 The flow of the carrier gas comprises the nanoparticles. The carrier gas may be air, an inert gas (nitrogen, helium, argon, etc.), a combustion gas (e.g. a gas mixture comprising O₂, CO, H₂O, CO₂), etc. In one embodiment, the carrier gas is a combustion gas from the (flame) reactor in which the nanoparticles are prepared (see also below).

The carrier gas includes an aerosol phase of metal oxide nanoparticles and/or metal nanoparticles.

15 The nanoparticles may be produced by various method, e.g. by combusting a gas comprising one or more precursors for the nanoparticles, by combusting a liquid comprising one or more precursors for the nanoparticles, by thermal decomposition of precursors, by gas phase reaction of precursors, by sputtering metal clusters off a bulk metal source, or by evaporating metal atoms from a bulk metal source. Furthermore, CVD and MO-CVD may also be utilised.

20 In one embodiment, the aerosol phase of nanoparticles is prepared by (i) thoroughly mixing a gas stream of at least one evaporated precursor for said nanoparticles and a gas stream of a fuel and oxidant, thereby obtaining a fuel/precursor/oxidant gas mixture, and (ii) combusting said fuel/precursor/oxidant gas mixture. In a preferred variant hereof, the aerosol phase of nanoparticles is prepared in a premixed flame aerosol reactor. This
25 embodiment is further illustrated in the Examples section, and can be outlined as follows: In a premixed flame, fuel (hydrogen or methane) and air are introduced to a swirl mixer after passing through a preheater. The mixture of feed gases is fed to the burner through the swirl mixer to ensure high degree of mixing of fuel, oxidant and precursor. The combustion of fuel takes place just above the flame arrestor, which is a thick (0.5-1 cm) metal plate with small
30 cylindrical holes. The flame arrestor distributes the flow of the feed gases and prevents flashback of the flame front. The precursor is added to the flame as a vapour in a gas (e.g. nitrogen) stream from saturator unit that consists of a metal box with one or more metal

trays on which thin layers of the precursor powder are in contact with the nitrogen stream. The precursor has a certain sublimation pressure, which combined with the control of the heating element of the unit determines the concentration of the precursor in the carrier gas. For a liquid precursor, the saturator could be in the form of a bubble bottle kept at constant temperature. Within this embodiment, the concentration of the precursor plays an important role for the particle diameter of the resulting nanoparticles in that normal collision processes in particle formation will lead to mean particle diameters of more than 20 nm if the concentration is too high. Thus, it is preferred that the precursor concentration in said fuel/precursor/oxidant gas mixture is at the most 50 ppm, such as at the most 25 ppm, e.g. at the most 10 ppm.

The fuel and the oxidant for the above-mentioned combustion process should represent reactive mixture which – by combustion - can provide sufficient thermal energy in order to raise the temperature so as to decompose the precursor and allow the decomposed precursor form nanoparticles. Thus, the fuel may be selected from hydrogen and hydrocarbons (such as methane) and the oxidant may be selected from air, oxygen-enriched air, pure oxygen and diluted oxygen (e.g. oxygen diluted in argon).

The flame temperature has a strong influence on the particle/aggregate size and morphology. The flame temperature depends on the stoichiometric ratio of air with respect to the fuel.

Preparing very small and agglomerate/aggregate-free ceramic particles is the first and the most important step in obtaining membranes of desirable pore structure and porosity. Particles are formed in a collision/coalescence process and due to the high number concentration of particles following the nucleation, the collision rate is quite high and in order to obtain spherical particles as opposed to aggregates of collided primary particles, the coalescence (sintering) rate has to be high.

High temperature increases the sintering rate, which means the effective (mobile) diameter of aggregates decreases when the particle mass of an aggregate is sintered into a sphere. Therefore, at a given precursor loading, more compact particle structures can be obtained with a very high flame temperature. This is also verified by TEM pictures showing that the particles prepared under such conditions are small compact with no or little agglomeration. Consequently, the proper way of obtaining small spherical nanoparticles with little degree of aggregation is to feed a low concentration of metal precursor to a high-temperature flame. The influence of precursor concentration at otherwise constant operating conditions is shown in Figure 12.

In an alternative embodiment, it is believed that the aerosol phase of nanoparticles can be prepared by combustion of a solution of at least one precursor for said nanoparticles, said solution being sprayed as a droplet aerosol into a high-temperature combustion zone or furnace reactor. By such a combustion process, the nanoparticles are obtained by

5 evaporation of the droplet constituents and subsequent particle formation by decomposition of the metal precursors into metal or metal oxide nanoparticles in the particle diameter range of at the most 20 nm. Generally, the liquid constituents are atomized in a nozzle and the oxidant (e.g. air) and/or the fuel (e.g. methane) transports the droplets into a high-temperature zone, where the evaporation and decomposition of the precursor take place.

10 Useful precursors for nanoparticles are those which can be brought into a gas phase by sublimation or evaporation without decomposition. Illustrative examples of precursors for said nanoparticles are those selected from the group consisting of volatile metal compounds of acetyl acetonate complexes (e.g. aluminium acetyl acetonate ($\text{Al}(\text{acac})_3$), and platinum acetyl acetate ($\text{Pt}(\text{acac})_3$)), metal acetates, metal alkoxides (e.g. titanium isopropoxide, 15 aluminium tri-sec-butoxide), metal halides (e.g. TiCl_4), metal carbonyls (e.g. $\text{Fe}(\text{CO})_5$), in particular metal acetyl acetonates such as aluminium acetyl acetonate; and mixtures thereof.

The constitution of the nanoparticles will be defined by the precursors and the combustion conditions. Typically, the nanoparticles essentially consist of a material selected as single components or mixtures from the group consisting of alumina, magnesia, titania, silica, 20 zirconia, ceria, iron oxide, chromic oxide, tin oxide, copper oxide, and alumina-magnesia spinel.

In another alternative embodiment, the aerosol phase of nanoparticles is prepared by evaporation of metal atoms from a bulk metal source. This can be accomplished by means of laser ablation or by other method of heating (e.g. by electrical current) said metal source to a 25 temperature level where metal atoms can be evaporated (or sublimated) from the source.

In an alternative embodiment, the aerosol phase of nanoparticles is prepared by the heating in a hot plasma of a gas mixture or aerosol containing desired precursor metals either present as evaporated molecules or as small droplets of precursors dissolved in a solvent (e.g. metal nitrates in aqueous solution or metal alkoxides in organic solvent).

30 In another embodiment, the aerosol of nanoparticles is prepared by gas phase reaction of two or more molecules leading to the formation of a species, e.g. a metal oxide, in a state of supersaturation with subsequent nucleation of particles.

In still another embodiment, the aerosol of nanoparticles is prepared by thermal decomposition of precursor molecules, e.g. thermal decomposition of metal alkoxides in a tubular furnace reactor.

Although it is generally required that the nanoparticles have a mean diameter of at the most 20 nm, it is often advantageous if the mean diameter of the nanoparticles is at the most 15 nm, such as at the most 10 nm, e.g. at the most 5 nm.

A number of different methods are used to determine the particle size such as the SMPS system, TEM technique and BET measurement.

The mobility-equivalent particle size distribution is monitored by a scanning mobility particle sizer (SMPS) that consists of a differential mobility analyzer (DMA) and a condensation particle counter (CPC). In the DMA, the particles are charged and transported in an electric field of varying strength thus leading to a separation of particles of different mobility. The concentration of the various fractions of the distribution is monitored by the CPC. A computer controls the SMPS (DMA + CPC) system. It is necessary to cool and dilute the combustion gases before they can be led to the SMPS system. This can be done by a gas-ejector sampler.

The SMPS system has a limited size range for measurement of particle size distribution (Lower limit = 5 nm, Upper limit = 775 nm). When the smallest membranes are produced, the SMPS system cannot detect the particles (below 5 nm in size) and only transmission electron microscope (TEM) can be used to show the size/morphology of the particles. For this purpose the particles are deposited directly from the gas phase on TEM grids (copper grids with a 300 μm mesh covered by a carbon film). The grid is inserted in the hot gas for 5–10 seconds.

The surface area of collected particles (as a powder) is measured by BET-apparatus. The BET equivalent primary particle size can be calculated from measurement of the specific surface area.

Another important feature of the invention is that the size of the nanoparticles is gradually or incrementally decreased so as to obtain a gradually or incrementally decreasing the pore size in the outermost part of the micro/meso-porous layer.

With respect to the alternative aspect of the invention, the size of the nanoparticles is gradually or incrementally increased so as to obtain a gradually or incrementally increasing the pore size in the outermost part of the micro/meso-porous layer.

Where the nanoparticles are prepared by combustion of a gas comprising one or more precursors for the nanoparticles, a continuously or incremental reduction in nanoparticle size can be obtained by a gradually or incrementally reducing the precursor concentration in the precursor/fuel/oxidant mixture. As an example, the concentration of the precursor can be reduced from 50 ppm to 0.01 ppm over a time-scale of, e.g., 30 minutes of deposition. This leads to a corresponding reduction of the particle sizes measured by the SMPS system as can be seen in Figure 13. For the lowest concentration of precursor molecules depicted here (90°C), the main part of the particle distribution lies below the detection limit but the entire distribution can be estimated based on a fit to the normally obtained shape of a particle distribution prepared by flame processes. When the precursor concentration is gradually or incrementally increased, e.g. from 0.01 ppm to 50 ppm of a time-scale of, e.g., 30 minutes of deposition, this gives rise to a gradually or incrementally increasing pore size, cf. the above alternative aspect.

The flow of the carrier gas is lead through the meso- or macro-porous substrate by means of a pressure differential between a location at the first porous surface (the front of the substrate) and a location at a second porous surface of the substrate (the backside of the substrate). This is typically accomplished by applying a partial vacuum on the backside of the substrate or by applying elevated pressure of the aerosol phase compared. In most instances, the step of "leading a flow of a carrier gas through the first porous surface" can be seen as a "filtration process" where the porous substrate is used as a filter. This aspect is illustrated in Figure 14 in which the particle size of the nanoparticles is varied over time. For the process wherein the flame reactor is utilized, this may be obtained by lowering the temperature in the saturator.

In order to facilitate the formation of the micro/meso-porous layer on or in the micropores of the substrate, the substrate is preferably heated to above 300°C in order to obtain improved adhesion and thermal accommodation of the micro/meso-porous layer to the meso- or macro-porous substrate.

The process time is not particularly critical and may be selected in view of the intended layer thickness of micro/meso-porous layer, the concentration of the precursor, etc. The process is typically conducted for a period of 60 seconds to 1 hour, as will be illustrated with the examples.

Prior to each deposition experiment, the clean substrate together with the deposition chamber is preferably put in the oven and heated to the set-point temperature, e.g. typically a temperature in the range of 100°C-1200°C (e.g. 150°C-500°C).

The obtained asymmetric membrane may be used as such, or it may be further surface-modified in order to be adapted to a particular use. Thus in one embodiment, the process comprises the subsequent step of chemically modifying the micro/meso-porous layer.

5 Examples of chemical modifications applicable are polymer coating, coating by chemical vapor deposition (CVD), coating by atomic layer deposition, and coating by liquid phase reactions.

The asymmetric ceramic membranes may be useful for many purposes, e.g. filtration in the presence of strong solvents, pervaporation, high-temperature gas separation, high-temperature particle filters, catalytic membrane reactors, etc.

10 In one embodiment, the ceramic membrane is prepared in a monolith-type structure, where the half of the monolith channels are inlet channels and the other half is outlet channels and the membrane is prepared on the walls of the porous monolith structure thus leading to a gas flow going into the monolith, through the wall and out through the exit channels. As a result, the monolith can serve as a particle filter or a gas separation device.

15 In another embodiment, the ceramic membrane is prepared in a single channel/multi-channels honeycomb monolith-type structure, where the membrane is prepared on the inner surface of the monolith channel/channels. The process will then cause particles to be retained on the inner surface of the membrane, whereas the permeate can penetrate the membrane and be transported to the outer surface of the honeycomb monolith. The membrane may also
20 be prepared on the outer surface of the honeycomb monolith structure, in which case the channel/channels in the honeycomb becomes the permeate side. The honeycomb monolith membranes can be used in a unit holding a multiplicity of honeycomb monolith membranes, thus increasing the filtration area per unit.

In another embodiment, the micro/meso-porous layer has catalytic properties. The catalytic
25 properties can be obtained by proper selection of the metal oxide nanoparticles and/or metal, and thereby initially by proper selection of the precursor or metal bulk. Examples of interesting catalytic membranes which can be achieved by the process of the invention are membranes doped with platinum for dehydrogenation reactions with direct separation of the produced hydrogen through the membrane. If used as particle filter for diesel soot, the
30 membrane top-layer may be covered by dispersed noble or transition metals in order to provide sites for catalytic decomposition of the deposited soot. In such embodiments, the active metal and support nanoparticles may be provided to the membrane preparation process as $\text{Al}(\text{acac})_3$ and $\text{Pt}(\text{acac})_2$ yielding small nanoparticles of $\text{Pt}/\text{Al}_2\text{O}_3$.

It is possible to deposit catalyst simultaneously with the deposition of particles or alternating with the deposition of particles. The catalyst may be deposited into the pores of the substrate or on top of the substrate. The catalyst can be noble metals, transition metals, pure metal oxides, or mixed metal oxides. The production of catalyst can be done by, but is not limited to, flame synthesis.

The produced membranes can also be used as membrane contactors, which is a device that achieves gas/liquid or liquid/liquid mass transfer without dispersion of one phase within another. This is accomplished by passing the fluids on opposite sides of a microporous membrane. By careful control of the pressure difference between the fluids, one of the fluids is immobilized in the pores of the membrane so that the fluid/fluid interface is located at the mouth of each pore.

This approach offers a number of important advantages over conventional dispersed phase contactors, including absence of emulsions, no flooding at high flow rates, no unloading at low flow rates, no density difference between fluids required, and surprisingly high interfacial area. Furthermore, membrane contactors offer operational flexibility, high mass transfer rates, compactness and easy scale up. The membrane contactor technology has been demonstrated in a range of liquid/liquid and gas/liquid applications in fermentation, pharmaceuticals, wastewater treatment, chiral separations, semiconductor manufacturing, carbonation of beverages, metal ion extraction, protein extraction, VOC removal from waste gas, and osmotic distillation (Gabelman and Hwang, 1999).

An asymmetric membrane

Another aspect of the present invention relates to an asymmetric membrane as such, preferably an asymmetric membrane prepared as described herein.

In particular, the present invention relates to an asymmetric membrane comprising (i) a meso- or macro-porous substrate having a first porous surface and (ii) a micro/meso-porous layer deposited on and/or in the pore mouths of the first porous surface, said meso- or macro-porous substrate having a mean pore diameter in the range of 10 nm-10 μ m, and said micro/meso-porous layer having a thickness of in the range of 0.5-1000 nm, such as 1-100 nm, and a mean pore size of at the most 10 nm, and wherein the meso/micro-porous layer has a gradually increasing pore size in the direction of meso- or macro-porous substrate.

The asymmetric membrane in particular has the features defined further above.

In one embodiment, the micro/meso-porous layer has catalytic properties, e.g. as described further above.

In a further embodiment, the micro/meso-porous layer is chemically modified, e.g. as described further above.

- 5 The invention is furthermore illustrated by means of the following non-limiting examples.

EXAMPLES

Flame aerosol synthesis of ceramic nano-particles

The general principle behind flame synthesis of materials is the decomposition and/or oxidation of evaporated metal-precursors in a flame thereby forming stable metal-oxide
10 monomers followed by nucleation, aggregation and - to some extent - coalescence of aggregated nano-particles [Gurav 1993, Pratsinis 1998]. This enables us to produce different types of materials ranging from pure (e.g. Al_2O_3 , ZnO , TiO_2) and mixed ceramic oxides (ZnAl_2O_4) to multi-component catalysts like $\text{Cu/ZnO/Al}_2\text{O}_3$, Pt/TiO_2 , Au/TiO_2 .

The flame-produced materials are in most cases attractive since they are formed directly in
15 one step and without any need for additional thermal treatment, which is normally applied during wet-chemistry routes in order to obtain the desired crystal phases. As a result, we have a flexible synthesis method where we can tune the product properties by changing composition and flame-operating conditions. We have the following main process variables:
Flame peak-temperature, residence time at elevated temperature by using quench cooling
20 [Hansen et al. 2001] and precursor loading and composition.

Most of porous ceramic membranes are multi-layer membranes consisting of several layers with a gradual decrease in pore size from the permeate side to the feed side of the membrane in order to avoid penetration of colloidal suspension deep onto support. One of the advantages of making ceramic membranes by deposition of flame generated particles
25 directly from the gas phase is that substrate tube with micron sized pores can be used directly without preparing any intermediate layers.

This is contrary to wet preparation techniques that need several deposition steps from colloidal suspensions with intermediate calcinations.

As will be shown, membranes without defects or cracks can be produced at high temperature by this flame-assisted method, which basically proceeds by continuous filtration of nano-particles the product gas of the flame reactor. The pressure drop across the membrane will be very uniform and crack-free because any non-uniformity in the layer structure will be leveled out by a local, temporary increase in deposition rate until e.g. the crack is sealed.

Experimental

The complete experimental equipment consists of three major parts: the flame reactor to produce aerosol particles, the deposition chamber to collect the produced particles on the substrate tube and the permeate cell to measure permeability.

10 Flame reactor

The premixed flame reactor is illustrated in Figure 1. Methane and air are introduced to a swirl mixer after passing through a pre-heater. The precursor is added to the flame as a vapour of aluminium acetyl acetonate ($\text{Al}(\text{acac})_3$) by sublimation of the precursor in a saturator unit, which consists of five trays on which thin layers of the solid precursor are in contact with a carrier gas of nitrogen. The saturator is heated by a heating element connected to a temperature controller. To prevent re-condensation of the precursor, the tubes connecting the saturator to the burner are kept heated above the temperature of the saturator. All feed gases and the precursor gas are fed to the burner through the swirl mixer to ensure high degree of mixing prior to combustion in the flat flame above the flame arrestor, which prevents flash-back.

Flame temperature measurements are carried out with a type S thermocouple without present of the precursor. The flow rate of CH_4 and air are fixed at 0.83 and 7.93 L/min, respectively (stoichiometric ratio). The total precursor carrier gas flow is held constant at 0.38 L/min. All flow rates are measured at 20°C by calibrated rotameters. The concentration (or partial pressure) of $\text{Al}(\text{acac})_3$ in the nitrogen carrier gas – and thus the feeding rate of precursor to the flame – is controlled by changing the temperature of the saturator unit. A saturator temperature of 138.8°C, which is well below the melting point of aluminium acetyl acetonate (196°C) is used as shown in table 1. This gives a precursor concentration of 8 ppm in the gas phase after the swirl-mixer.

30 Table 1. *Experimental conditions of CH_4 flame using $\text{Al}(\text{acac})_3$ as precursor.*

T_{adb}	T_{max}	T_{sat}	T_{cell}	CH ₄ flow	Air flow	N ₂ flow
[K]	[K]	[K]	[K]	[L/min]	[L/min]	[L/min]
2222	1200	412	600	0.83	7.93	0.383

T_{adb} =Adiabatic flame temperature, T_{max} =Maximum observed flame temperature, T_{sat} = Temperature of the saturator unit, T_{cell} =Temperature of the deposition cell.

Deposition chamber

The deposition experiments are carried out in a deposition cell similar to the one used by Andersen et al. (2002). A schematic diagram of the experimental apparatus used for the deposition study is given in Figure 2.

The chamber is made from stainless steel tube, with inside diameter of 10 mm and outer diameter of 20 mm, containing a cantered ceramic substrate tube. The alumina substrate tube is kept in place in the tube holder by two O-rings that provide a seal between the high and low pressure sides. The substrate tube does not touch the wall of the cell. The cell is held together with two clamps.

A *K-type* thermocouple measures the temperature inside the cell.

Permeate cell

Deposition chamber is used also as a permeate cell. Leakage tests up to trans-membrane pressure difference of 6 bars are carried out to make sure that the sealings are non-permeable.

All permeation measurements are carried out at room temperature, 293 K and at an outlet pressure of 1 bar. The gas flow rate is measured at the atmospheric pressure (P_0) with a flow calibrator.

Top layer formation

Nano-particles from the flame-produced aerosol adhere on the substrate surface by convective and diffusional transport in the flowing gas, which is withdrawn through the porous substrate tube. An understanding of this step is of fundamental importance to the

structure of the top layer of the asymmetric membrane. Particle deposition will initially take place inside the substrate pores, then rapidly shifts to pore blocking and finally a thin top layer is created. After the initial pore mouth plugging, a filter cake is formed by deposition of particles on the substrate surface.

- 5 In the following, the formation of the top layer will be described by a mathematical model connecting the process variables and measured transport properties of the membrane to an understanding of the membrane structure.

10 The gas enters the tube with a given particle number concentration, C_0 . The local particle deposition flux, J (particles/m²/s) at the substrate wall is given by the amount of gas being filtered, i.e:

$$J = \frac{QC_0}{2\pi RL} \quad (1)$$

where Q is volumetric flow rate of flame product gas through the porous tube wall, R and L are tube radius and length, respectively.

The deposition is carried out by filtration at a constant pressure drop. Therefore, Q decreases with time at a rate, which is controlled the structure of the top-layer.

- 15 The number of deposited particles, W , can be described by:

$$W = \frac{2\pi RL\delta_m(1-\varepsilon_m)}{v_p} \quad (2)$$

where δ_m is the membrane top layer thickness, ε_m is top layer porosity and v_p is the solid volume of a single particle.

In addition, W can be also expressed using the accumulated amount of particles from the filtered gas:

$$W = \int J(2\pi RL) dt = Q_0 C_0 \int \frac{Q}{Q_0} dt \quad (3)$$

Here Q_0 is the volumetric flow rate of gas withdrawn through the substrate tube for clean substrate ($t = 0$).

Combination of equations (2) and (3) gives the following expression for the membrane top layer thickness:

$$\delta_m (1 - \varepsilon_m) = \frac{v_p C_0 Q_0}{2\pi RL} \int \frac{Q}{Q_0} dt \quad (4)$$

- 5 The constant in front of the integral is the initial rate of the growth of the top layer thickness. The integral in equation (4) can be evaluated by permeability measurement under constant pressure filtration after a number of discrete deposition times.

- The product $v_p C_0$, which is the total particle volume per volume of gas, is independent of particle size distribution, i.e. $v_p C_0$ will not vary if the particles change from many small
 10 spherical particles to larger (and therefore fewer) aggregates of partially coalesced primary particles. We can compute $v_p C_0$ based on the total amount of precursor fed to the flame:

$$v_p C_0 = \frac{P^{sat}}{mRT^{sar}} \frac{M}{\rho} \frac{Q_c}{Q_T} \quad (5)$$

- Where M and ρ are the molecular mass and the density of metal oxide powder ($M_m O_n$),
 respectively. P^{sat} is the vapour pressure of metal precursor in the saturator, which is kept at
 temperature T^{sat} . Furthermore, Q_c and Q_T are the volumetric flow rate of carrier gas and
 15 total gas to the flame, respectively.

Transport of gases through porous media

- The mass transport of a single gas in porous media can be described by the *dusty gas model* (DGM) [Mason 1983, Tuchlenski 1998]. Based on DGM, the net flux of the gas through a porous media is composed of contributions from Knudsen diffusion and viscous flow according
 20 to following equation:

$$F = D_K + \frac{B_0}{\mu} \bar{P} \quad (6)$$

F is called the permeance and has the same unit as a diffusion coefficient and is defined as follows:

$$F = \frac{Q P_0 \delta}{A \Delta P} \quad (7)$$

ΔP is the pressure difference between two sides of the membrane tube, $\bar{P}$ is the arithmetic mean gas pressure, δ is the membrane thickness and $\bar{A}$ the logarithmic mean area of the membrane.

The structural parameter B_0 is related to the porous medium and is independent of the gas type.

$$B_0 = \frac{d_p^2}{32} \frac{\varepsilon}{\tau} \quad (8)$$

D_K is the effective Knudsen diffusion coefficient and related to the pore diameter (d_p), porosity (ε), tortuosity (τ), temperature (T) and molecular weight (M) of the gas by:

$$D_K = \frac{d_p}{3} \sqrt{\frac{8RT}{\pi M}} \frac{\varepsilon}{\tau} \quad (9)$$

- 10 Q is the gas flow rate measured at the pressure P_0 (normally atmospheric pressure). Because the permeance (F) is independent of the membrane, equation (6) can be used for any type of membrane.

From the experimental gas permeation data, a plot of the permeance, F , versus the mean

- 15 gas pressure ($\bar{P}$) will give a straight line, where D_K and $\frac{B_0}{\mu}$ can be determined from the intercept and slope of the straight line.

This is actually the most simple and accurate way to estimate the coefficients D_K and $\frac{B_0}{\mu}$. These values can be used for the determination of the structural parameters such as mean pore size (d_p) and the geometric factor (ε/τ) by using the combination of equations (8) and (9).

$$d_p = \frac{32\mu}{3} \sqrt{\frac{8RT}{\pi M} \frac{B_0/\mu}{D_K}} \quad (10)$$

$$\frac{\varepsilon}{\tau} = \frac{9\pi M}{256RT\mu} \frac{D_K^2}{B_0/\mu}$$

- 5 Using the assumption of cylindrical pore geometry, the relation between the porosity and tortuosity is [Uchytel 1994, Uchytel 1996]:

$$\tau = \frac{1}{\varepsilon} \quad (11)$$

From equations (10) and (11) one can calculate porosity and tortuosity factors.

- 10 If several gases are used for the permeation measurements, more reliable values of the parameters can be obtained from the linear treatment of all gas permeation data [Uchytel 1996].

By using equation (6), one can obtain:

$$\frac{Q P_0 \delta}{A \Delta P} \sqrt{M_i} = \frac{d_p}{3} \sqrt{\frac{8RT}{\pi}} \frac{\varepsilon}{\tau} + \frac{d_p^2}{32} \frac{\varepsilon}{\tau} \frac{\bar{P}}{\mu_i} \sqrt{M_i} \quad (12)$$

where index i refers to the applied gas. This equation can be reduced to following equation.

$$\left(F \sqrt{M_i} \right) = I + S \left(\frac{\bar{P} \sqrt{M_i}}{\mu_i} \right) \quad (13)$$

where I (interception) and S (slope) contains constants and parameters from equation (12). Equation (13) is not only independent of the membrane geometry (shape and dimensions) but also of the gas type. It depends only on membrane microstructure such as pore size (distribution), porosity and tortuosity.

- 5 A mean pore diameter (d_p) and a geometric factor (ε/τ) can be obtained from the linear regression method by following relations.

$$d_p = \frac{32}{3} \sqrt{\frac{8RT}{\pi}} \frac{S}{I} \quad (14)$$

$$\frac{\varepsilon}{\tau} = \frac{9\pi}{256RT} \frac{I^2}{S}$$

Mass transfer through two layer membrane

- The analysis described above is more complex for gas transport through a two-layer composite membrane that contains the original substrate tube and a top layer, i.e. two different pore structures in series.

After deposition, the one-layer support tube becomes a two-layer composite membrane consisting of a support the deposited top-layer.

Considering steady-state conditions, the gas flow rate through each layer can be calculated from following relationships.

- 15 For the membrane top-layer, the gas flow rate is.

$$Q P_0 = \frac{\bar{A}_m}{\delta_m} \left(D_K^m + \frac{B_0^m}{\mu} \cdot \frac{P_1 + P_{\text{int}}}{2} \right) (P_1 - P_{\text{int}}) \quad (15)$$

For support layer the gas flow rate is.

$$Q P_0 = \frac{\bar{A}_s}{\delta_s} \left(D_K^s + \frac{B_0^s}{\mu} \cdot \frac{P_{\text{int}} + P_2}{2} \right) (P_{\text{int}} - P_2) \quad (16)$$

Where **s** and **m** refer to the support and membrane top layers, respectively.

P_{int} is the interlayer pressure that can be calculated from the positive root of the following quadratic equation, obtained by solving equation (16) for P_{int} .

$$\left(\frac{P_{\text{int}}}{P_0}\right)^2 + 2K_s\left(\frac{P_{\text{int}}}{P_0}\right) - \left(\left(\frac{P_2}{P_0}\right)^2 + 2K_s\left(\frac{P_2}{P_0}\right) + 2K_s\left(\frac{Q\delta_s}{A_s D_K^s}\right)\right) = 0 \quad (17)$$

The solution for P_{int} is.

$$\frac{P_{\text{int}}}{P_0} = -K_s + \sqrt{\left(\frac{P_2}{P_0} + K_s\right)^2 + 2K_s\frac{Q\delta_s}{A_s D_K^s}} \quad (18)$$

- 5 From the experimental gas permeation data, one can calculate the interlayer pressure if the structure parameters of the clean substrate tube is known.

The dimensionless number K_s refers to support layer and has been introduced by in Andersen et al. (2002):

$$K_s = \frac{\mu D_K^s}{P_0 B_0^s} \quad (19)$$

- 10 The dimensionless number K_s is related to the shift in mechanism of mass transport through the support (similar to the Knudsen number, Knudsen flow dominates when $K_s \gg 1$ and viscous flow when $K_s < 1$).

It can be shown that:

$$K_s = \frac{64}{3\pi} Kn \approx 6.8 Kn \quad (20)$$

Where the dimensionless number Kn is the Knudsen number for the support pores. The permeance over the top layer can be calculated with the knowledge about interlayer pressure P_{int} .

$$F_m = D_K^m + \frac{B_0^m}{\mu} \bar{P}_m \quad (21)$$

where

$$F_m = \frac{Q P_0 \delta_m}{A_m \Delta P_m} \quad (22)$$

5 is called membrane permeance and

$$\Delta P_m = P_1 - P_{int} \quad (23)$$

is the pressure difference across the membrane top layer and

$$\bar{P}_m = (P_1 + P_{int})/2 \quad (24)$$

is the arithmetic mean gas pressure over the top layer. Here, δ_m is the membrane top layer thickness and $\bar{A}_m$ the logarithmic mean area of the top layer.

10 The membrane thickness δ_m can be estimated from measurements on **Scanning Electron Microscopy (SEM)** images of membrane cross section cuts.

If the Knudsen diffusion is the dominant mass transfer mechanism across top layer

($B_0^m \approx 0$), the following is obtained:

$$\frac{F_m}{\delta_m} = \frac{(d_p)_m}{3\delta_m} \sqrt{\frac{8RT}{\pi M}} \frac{\epsilon_m}{\tau_m} \quad (25)$$

It can be seen that equation (25) does not give any uncoupled information about membrane thickness, pore size and porosity and it is not possible to estimate both $\left(\frac{\varepsilon}{\tau}\right)_m$ and $d_p(m)$.

However, if the SEM-estimation of δ_m is combined with equation (4), then the pore diameter of the top-layer can be estimated once the permeance in equation 25 for a given gas has been measured.

Perm-selectivity

One of the most important factors affecting the ability of porous ceramic membrane to carry out separation is perm-selectivity of the membrane.

The experimental perm-selectivity of the membrane can be measured by ideal separation factor, as defined in equation (26), from the measured permeabilities of pure species "i" and "j".

$$\alpha_{ij}^* = \frac{\text{Permeability of gas "j"}}{\text{Permeability of gas "i"}} = \frac{F_j}{F_i} \quad (26)$$

The separation factor as determined from gas mixtures is generally not the same as defined by equation (26). They are similar only when all interactions between gases and the pore wall can be neglected (negligible surface diffusion).

Results and discussion

Characterization of the generated particles

The surface area of produced particles collected on a glass fibre filter is measured by nitrogen adsorption at 77K using the BET-method. The BET-equivalent primary particle size can be calculated by following formula, assuming that primary particles – either present as individual particles or in aggregates – are spherical:

$$d_{BET} = \frac{6}{\rho_p \cdot SSA} \quad (27)$$

where ρ_p and SSA are the particle bulk density and specific surface area (m^2/g), respectively. A value of 4 g/cm^3 is used for ρ_p .

Using the experimental conditions listed in table 1, the alumina particles have a specific surface area of $380 \text{ m}^2/\text{g}$ and the corresponding primary particle size of 4 nm .

- 5 The particle size distribution (concentration vs. particle mobility diameter) is monitored by a **Scanning Mobility Particle Sizer** (SMPS from TSI). A computer controls the SMPS system and collects information about the measured distributions. It is necessary to cool and dilute the combustion gases before they can be led to the SMPS system.

Under the mentioned flame operating condition all particles were below 15 nm in diameter.

- 10 Consequently, we know that we are operating under flame conditions where the particles are considerably smaller than that of the study of Andersen et al. (2002), where average particle sizes were ranging from 33 nm to 88 nm . As will be shown below, using smaller particles (or aggregates) will result in a membrane structure with smaller pores than the $30\text{-}70 \text{ nm}$, which were reported earlier.

15 **Characterization of the porous structure of the support**

The substrate tubes have an inside and outside diameter of 6.5 mm and 9.5 mm , respectively. For all experiments, the substrate tubes are cut into small pieces (of length between $35\text{-}40 \text{ mm}$) with an effective membrane tube length of 20.5 mm , i.e. the length of the deposition cell shown in Figure 2. The porous tube is made of $\alpha\text{-Al}_2\text{O}_3$.

- 20 For characterization of the porous structure of the support, two methods are used, namely bubble point test and permeation method. For the permeation tests, hydrogen, helium and nitrogen are used.

The proposed model for the gas permeation in ceramic membranes has been used for the evaluation of the structure parameters of the support sample tube. Figure 3 shows the linear

- 25 dependency of permeability of H_2 , He and N_2 on the arithmetic mean gas pressure $\bar{P}$ in the support tube. In Figure 4, the data for all gases are represented as in equation (13), i.e.

$F_i \sqrt{M_i}$ as a function of $\frac{\bar{P} \sqrt{M_i}}{\mu_i}$. Data points for all three gases now fall nicely on the same line.

Using equation (13) and (14) with the slope and interception from Figure 4, the values of the structural parameters d_p and ε/τ of the substrate tube are obtained. The data – using the three gases separately and as combined linear regression – are summarized in table 2. The results show good agreement between the values of the mean pore diameter and geometric factor determined by the nitrogen, hydrogen, helium and all gas together. Based on all data points, the pore diameter of the porous support tube is 4.6 μm .

Table 2. *Structure parameters of support tube evaluated from gas permeation data.*

Gas	M [g/mol]	d_p [μm]	ε/τ	ε^1 %	τ^1
N ₂	28.014	4.01	0.132	36.3	2.75
He	4.0030	4.43	0.109	33.0	3.03
H ₂	2.016	4.87	0.0917	30.3	3.30
All gas data		4.62	0.101	31.8	3.14

¹Under assumption of $\varepsilon = 1/\tau$

A value of 0.07 m²/g has been obtained for specific surface area of the support tube measured by BET-apparatus. From the permeability measurements, table 2, a porosity of 31.8 % is calculated. Combined with the specific surface area, a BET-equivalent pore size [Lowell, 1979] can be calculated as $(d_p)_{\text{BET}} = 4 \varepsilon / (\rho \times \text{SSA}) = 4 \times 0.318 / (4 \times 0.07) = 4.57 \mu\text{m}$.

The BET pore diameter calculated based on specific surface area of the support tube is in good agreement with the data listed in table 2.

In addition, the bubble point method provides a simple means of characterising the maximum pore size in the substrate tube. The bubble point test shows a pressure difference of 305.4 mbar. It corresponds to maximum pore diameter 9.5 μm .

Characterization of the asymmetric membrane

The membranes are characterized by gas permeability measurement and scanning electron microscopy (SEM). The scanning electron microscopy technique is used to examine the porous structure of the deposited top-layer and its thickness. Cross-section cuts of the synthesized membrane samples are prepared and coated with gold as a standard pre-treatment technique.

Analysis of the experimental measurements using the model for gas permeation through an asymmetric membrane consisting of a support layer and one separation layer is in the following used to determine the values of a mean pore diameter and geometric factor of the deposited top layer.

10 Permeability measurements

Because of the presence of the support layer, it is difficult to measure the pore size distribution of the top-layer. Therefore, a subtraction method is used to determine the average pore size of membrane layer. This is done by first measuring the permeation data for the support only and then for the entire asymmetric membrane, i.e. support and top-layer.

15 The permeability data for the membrane top-layer are calculated by subtracting the permeation data for the composite system from that of the support only using a resistance-in-series approach.

Figure 5 shows the permeability measurements for nitrogen in the original support and synthesized membrane after 10 and 20 minutes deposition time. The permeability drops significantly in the first 10 minutes and compared to the data from $t=0$, the influence of pressure difference is reduced at $t=10\text{min}$ (and $t=20\text{min}$). The change from 10 to 20 minutes is merely a small down-shift of the line from a deposition time of 10 minutes. This already now indicates Knudsen diffusion as the dominant transport mechanism in the growing top-layer since the two lines at 10 and 20 minutes are almost parallel with only a reduction in total permeability.

The permeability measurements for hydrogen and helium also have been done after every deposition time. These measurements can be seen in Figure 6 after 30 minutes deposition. The permeability hardly changes with increasing pressure difference, meaning that the transport of gases through the top layer is controlled by the Knudsen diffusion mechanism.

30 The experimental separation factors, as defined in equation (26), are calculated from the measured permeability of pure hydrogen, helium and nitrogen. The comparison between the theoretically predicted (Knudsen) and experimentally derived separation factors are given in table 3. For hydrogen and helium, the separation factors evaluated from the measured permeation and from Knudsen diffusion compare very well. The separation factors along with

the pressure-independent permeability verify that Knudsen diffusion dominates the transport of gases in the deposited top layer.

Table 3. Separation factor calculated from permeability measurements together with Knudsen separation factor.

Deposition time [min]	10	20	30	40	Knudsen
H ₂ /N ₂	2.91	3.03	3.08	2.90	3.74
He/N ₂	2.03	2.07	2.10	2.05	2.65
H ₂ /He	1.43	1.46	1.46	1.41	1.41

5

Using the horizontal lines for t=30 minutes (Figure 6) – and similarly for t=10, 20 and 40

minutes - it is possible to get a values of $\frac{d_p}{\delta} \left(\frac{\varepsilon}{\tau} \right)$ for the membrane top-layer using the interception with the vertical axis using equation 25 as derived or the two-layer membrane.

The results are summarized in table 4. For each deposition time, the results based on each gas separately are almost identical as they should be according to theory. The average values for each deposition time – as summarized in the last row of table 4 – will be used in the following analysis.

10

Table 4. Structure parameter $\frac{d_p}{\delta} \left(\frac{\varepsilon}{\tau} \right) \times 10^3$ of top layer evaluated from gas permeation data at difference deposition time.

Deposition time [min]	10	20	30	40
Gas type				
N ₂	5.66	5.31	4.13	4.87
H ₂	5.49	4.77	5.31	3.27
He	5.04	4.89	4.50	4.41
All gas together	5.13	4.85	4.65	4.38

Figure 6 shows data points representing only one membrane layer, i.e. the top-layer. Therefore, as in Figure 4, we can also show the subtraction data from Figure 6 in a combined form by plotting the top-layer data according to equation (13). In Figure 7, the clean
 5 substrate tube and the top-layer membrane after 20 minutes deposition are shown. Both data-sets fall convincingly on separate straight lines, which justify the subtraction procedure in the present analysis.

The next step in estimating the pore diameter of the top-layer is to evaluate the integral of equation (4), i.e. the total amount of deposited membrane material. To do so, the volumetric
 10 flow rate, Q , of gas through the membrane is measured at different deposition times at atmospheric pressure (1 bar) at a pressure difference of 0.5 bar and a temperature of 600 K, i.e. the deposition condition.

Figure 8 shows the relative volumetric flow rate (Q/Q_0) for N_2 as a function of deposition time. The volumetric flow rate decreases significantly during the first ten minutes of
 15 deposition but then levels off in a much slower, linear decrease thereafter. This corresponds to the trend shown in Figure 5: there is a dramatic change in the permeance from $t=0$ to $t=10$ minutes but the change from 10 to 20 minutes is much less significant. The data in Figure 8 can be split into two parts: a rapid initial drop, and a subsequent slow (linear) decay. Consequently, the mechanism of membrane formation during the first period seems
 20 different from that of the later period. The layer formed during the first ten minutes consists of smaller pores because the particles, especially the smaller ones, can enter the pores and the deposition occurs internally in the substrate tube followed by pore-mouth blocking inside the pores thus making an inhomogeneous intermediate layer.

Using the Q/Q_0 data from Figure 8, we can use equation (4) to calculate the growth quantity
 25 $\delta(1-\varepsilon)$ after each deposition time step, c.f. table 5. Under the present flame and deposition conditions, the constant in front of the integral in equation (4) is 20.8 nm/min. From Figure 8, it can be seen that the volumetric flow rate remains almost constant except for the first ten minutes so one can expect that the quantity $\delta(1-\varepsilon)$ must vary almost linearly with the deposition time. Figure 9 shows a linear growth rate of the top-layer thickness, $\delta(1-\varepsilon)$,
 30 once the initial pore-mouth blocking for $t < 10$ minutes is completed.

Table 5. Structure parameters of the top layer evaluated from all gas permeation data at different deposition times.

Deposition time [min]	10	20	30	40
$\delta(1-\varepsilon)$ [nm]	190	362	533	701
$\frac{d_p}{\delta}\left(\frac{\varepsilon}{\tau}\right)\times 10^3$	5.13	4.85	4.65	4.38
$d_p\left(\frac{\varepsilon}{\tau}\right)(1-\varepsilon)$ [nm]	0.977	1.76	2.48	3.07

We have already carried out the calculation of the structural parameter presented in table 4,

5 $\frac{d_p}{\delta}\left(\frac{\varepsilon}{\tau}\right)$. Eliminating the layer thickness, δ , from the two first rows of table 5 give an indirect

parameter for the pore size of the deposited top-layer, i.e. $d_p\left(\frac{\varepsilon}{\tau}\right)(1-\varepsilon)$, which has the unit of meters (nm). The pore size calculated based on these data will be an average for the entire top-layer, which consists of an inhomogeneous intermediate initial layer (produced in the first 10 minutes) and a more homogeneous top layer, i.e. a well-defined filter cake.

10 In Figure 10, one can see that the indirect pore size parameter, $d_p\left(\frac{\varepsilon}{\tau}\right)(1-\varepsilon)$, increases with deposition time towards an asymptotic value. If the deposition would have been carried out in much longer time, the average pore size of the top-layer would be fully dominated by the more well-defined filter cake of deposited nano-particles (similar to Andersen et al. 2002). But in order to get a thin membrane, there is no use in continuing the deposition after the

15 Knudsen-regime rapidly has been obtained.

Finally, the SEM images after 40 minutes deposition, Figure 11, clearly shows the asymmetric structure of the thin membrane. The top-layer does not extend deeply into the support structure but the rough surface of the pore-mouths is made more even during the preparation of the top-layer. Using the insert with high resolution, the top layer thickness can

be estimated to 7–10 μm . The porosity can then be calculated from equation (4) as having a range of 90–93 %.

If we assume that $\tau = 1/\varepsilon$, which is a good approximation at high porosities, a value of 1.1 for the tortuosity can be obtained.

- 5 A thin membrane in the uppermost part of the porous support is in principle already formed during the first ten minutes before the more well-defined top-layer is formed. Therefore, since the pore size parameter of Figure 10 increases with time, one can expect that the pore size of the inhomogeneous intermediate layer must necessarily be less than that obtained as an average value of the entire layer. Based on data from table 5 combined with the
- 10 measured 7-10 μm membrane thickness, one can calculate an average pore diameter of the entire top-layer of 6 nm. However, again the pore diameter in the initial part of the top-layer formation must be smaller than that. In these calculations, it is assumed that the porosity of the inhomogeneous intermediate layer is 2/3 (an average between the substrate porosity $\approx 1/3$ and the top layer porosity ≈ 1). Correspondingly, it is also assumed that the tortuosity is
- 15 $3/2$ ($\tau = 1/\varepsilon$).

Membrane formation using the dynamic operation approach

- In this experiment the possibilities of making deposition of particles with gradually decreasing size is demonstrated by a dynamic operation of the precursor saturator. The saturator temperature remains constant (approximately at 140°C) during the first two minutes and
- 20 decreases gradually there after down to approximately 90°C. Figure 14 shows the variation of saturator temperature during the deposition experiment. The slow drop in saturator temperature corresponds to a continuously decreasing particle size as illustrated and shown on figures 12 and 13.

Table 6. Separation factors calculated from permeability measurements shown together with the ideal Knudsen separation factor.

25

Permeability [m/s]		Separation factor		Knudsen separation factor
N ₂	5.55	H ₂ /N ₂	3.59	3.74
He	14.5	H ₂ /He	1.38	1.41
H ₂	19.9	He /N ₂	2.61	2.65

The separation factors, c.f. table 6, of the top-layer calculated from the permeability measurements are very close to the Knudsen factors. The factors of table 6 are even higher than those presented in table 3. These enhanced separation factors are consistent with an even further decrease in pore size – well below 5 nm. The dynamic experiment thus shows that we are able to gradually close the top membrane layer with smaller and smaller particles thereby in a very short deposition time obtaining a very thin layer with a high separation factor. The corresponding reduction in pore size over one deposition step is 3 orders of magnitude.

Figure 15 illustrates the progress during the dynamic experiment. The pore mouth is represented by too large irregular structures of the support and filtration process proceeds with smaller and smaller particles giving the uppermost layer with the finest pore structure and largest separation factors.

Conclusions

Asymmetric alumina membranes consisting of a macro-porous support with a thin micro/meso-porous top-layer have been prepared by deposition of flame-produced nanoparticles on a macro porous alumina support in a one-step process. The pore diameter in the prepared top-layer cannot be measured directly but based on results of a derived two-layer model, the pore size of the top-layer can be estimated to maximum value of 6 nm. The key factor in obtaining such a small pore size using this method is to produce very small particles, less than 10 nm, in the flame synthesis unit.

The prepared membrane has an ideal separation factor, which in the range of normal experimental accuracy is identical to the Knudsen separation factor.

The permeability of H₂, He and N₂ for the top layer hardly changes with the trans-membrane pressure difference also showing that the transport of gases through the top layer is controlled by the Knudsen diffusion mechanism.

The preparation of the micro/meso-porous top-layer, proceeds using the coarse alumina membranes support as a filter for constant-pressure nano-particle filtration where the filter "cake" is the micro/meso-porous membrane. The volumetric flow rate during the membrane preparation decreases significantly over the first few minutes of deposition where particles deposit in the slightly into the pore mouths of the support and closes the pore openings. Hereafter, the volumetric flow rate decreases much slower – on a relative scale. In fact, the graph of the volumetric flow rate as a function of time can be split into two parts. First a rapid initial drop, and a subsequent slow decrease. The mechanism of membrane formation

during the first period is different from that of the later period. During the first period, the particles can enter the pores, and the deposition occurs internally in upper layer of the substrate tube followed by pore mouth blocking thus making an inhomogeneous intermediate layer. A more well-defined filter cake is formed on top of this initially formed layer.

- 5 Interestingly, in order to get a high flux in a Knudsen-separation membrane, the layer must be as thin as possible. This is exactly what we can obtain and explore using the flame-deposition method.

The deposited layers have porosities higher than 90 %. SEM images show that the particles have been deposited uniformly with homogeneous properties. In the one-step process of
10 deposition, the pore size decreases three orders of magnitude, i.e. from 4-5 μm to below 6 nm. This shows that membranes can be produced without using any intermediate layers. This is a dramatic improvement of wet preparation techniques needing several deposition steps (with intermediate calcinations) in order to avoid severe intrusion of particles in the pores the support.

- 15 Membranes without any defects or cracks can be produced by this method. The cracks will be blocked by further deposition in local areas with lower pressure drop.

To obtain membranes with even smaller pores (molecular size separation), the use of even lower precursor concentrations is necessary due to the corresponding reduction in the particle size from the flame unit.

- 20 Using a gradually decreasing particle size in a dynamic deposition experiment results in a very thin top-layer with a high separation factor. A thin layer is advantage for optimizing the flux at a given separation factor.

List of symbols

	$\bar{A}$	Logarithmic mean area of the membrane [m^2]
25	B_0	Structure parameter related to the porous medium [m^2]
	C_0	Particle concentration inside the membrane tube [$\#/\text{m}^3$]
	D_K	Knudsen diffusion coefficient [m^2/s]
	d_p	Mean pore diameter of the membrane or the support tube [m]
	F	Permeance of the gases through the porous media [m^2/s]
30	F_s	Permeance of the gases through the porous support [m^2/s]
	F_m	Permeance of the gases through the top layer [m^2/s]
	I	Intercept of the permeance line [m^2/s]

	J	Local particle deposition flux at the substrate tube [$\#/(m^2s)$]
	M	Molecular weight [kg/mol]
	P	Gas pressure [Pa]
	P_0	Atmospheric pressure [Pa]
5	P_{int}	Interlayer pressure between top layer and support [Pa]
	p^{sat}	Saturator pressure of metal precursor at saturator temperature [Pa]
	$\bar{P}$	Mean gas pressure across tube [Pa]
	Q	Volumetric flow rate of the permeable gas through the membrane [m^3/s]
	Q_0	Volumetric flow rate of the permeable gas through the clean support [m^3/s]
10	Q_C	Volumetric flow rate of the carrier gas [m^3/s]
	Q_T	Total volumetric flow rate [m^3/s]
	R	Gas constant = 8.31451 J/(mol $\times$ K)]
	S	Slope of the permeance line [$m^2/(Pa \times s)$]
	SSA	Specific surface area [m^2/g]
15	T	Temperature [K]
	t	Time [s]
	T_{max}	Maximum measured flame temperature [K]
	T^{sat}	Saturator temperature [K]
	δ	Membrane thickness [m]
20	ε	Porosity [-]
	τ	Tortuosity [-]
	μ	Gas viscosity [$Pa \times s$]
	α_{ij}	Separation factor of species " i " respect to " j "
	α_{Kn}	Knudsen separation factor
25	ρ_p	Particle density [kg/m^3]
	ΔP	Pressure difference [Pa]
	ε / τ	Geometric factor related to the porous media [-]
	Kn	Knudsen number
	K_s	Dimensionless number related to the Knudsen number in support layer

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CLAIMS

1. A process for the preparation of an asymmetric membrane, said membrane comprising (i) a meso- or macro-porous substrate having a first porous surface and (ii) a micro/meso-porous layer deposited on and/or in the pore mouths of the first porous surface, said process
5 comprising the step of leading a flow of a carrier gas comprising an aerosol phase of metal oxide nanoparticle and/or metal nanoparticles through said first porous surface of said substrate whereby at least a fraction of said nanoparticles becomes deposited on and/or in the pore mouths of the first porous surface, wherein said nanoparticles have a mean
10 diameter of at the most 20 nm, and wherein the size of the nanoparticles is gradually or incrementally decreased so as to obtain a gradually or incrementally decreasing pore size in the outermost part of the micro/meso-porous layer.
2. The process according to claim 1, wherein the gradual or incremental reduction in nanoparticle size is obtained by a gradually or incrementally reducing the precursor concentration in the precursor/fuel/oxidant mixture.
- 15 3. The process according to any one of the preceding claims, wherein the mean pore diameter of said micro/meso-porous layer of said asymmetric membrane is at the most 10 nm.
4. The process according to any one of the preceding claims, wherein the thickness of the deposited micro/meso-porous layer is in the range of 0.5-1000 nm, such as in the range of
20 1-100 nm.
5. The process according to any one of the preceding claims, wherein the aerosol phase of nanoparticles is prepared by (i) thoroughly mixing a gas stream of at least one evaporated precursor for said nanoparticles and a gas stream of a fuel and oxidant, thereby obtaining a fuel/precursor/oxidant gas mixture, and (ii) combusting said fuel/precursor/oxidant gas
25 mixture.
6. The process according to claim 5, wherein said aerosol phase of nanoparticles is prepared in a premixed flame aerosol reactor.
7. The process according any one of claims 5 and 6, wherein the precursor concentration in said fuel/precursor/oxidant gas mixture is at the most 50 ppm.

8. The process according to any one of the claims 5-7, wherein the fuel is selected from hydrogen and hydrocarbons and the oxidant is selected from air, oxygen-enriched air, pure oxygen and diluted oxygen.

5 9. The process according to any one of the claims 1-4, wherein said aerosol phase of nanoparticles is prepared by combustion of a solution of at least one precursor for said nanoparticles, said solution being sprayed as a droplet aerosol into a high-temperature combustion zone or furnace reactor.

10 10. The process according to any one of the claims 5-9, wherein the precursor(s) for said nanoparticles is/are selected from the group consisting of volatile metal compounds of acetyl acetate complexes, metal acetates, metal alkoxides, metal halides, and metal carbonyls; and mixtures thereof.

15 11. The process according to any one of the preceding claims, wherein the nanoparticles essentially consist of a material selected from the group consisting of alumina, magnesia, titania, silica, zirconia, ceria, iron oxide, chromic oxide, tin oxide, copper oxide, and alumina-magnesia spinel.

12. The process according to any one of the claims 1-4, wherein said aerosol phase of nanoparticles are prepared by evaporation of metal atoms from a bulk metal source.

13. The process according to any one of the preceding claims, wherein the mean particle diameter of the nanoparticles is at the most 15 nm.

20 14. The process according to any one of the preceding claims, wherein the meso- or macro-porous substrate essentially consists of a porous ceramic material selected from the group consisting of alumina, magnesia, silica, and titania.

25 15. The process according to any one of the claims 1-13, wherein the meso- or macro-porous substrate essentially consists of a porous material selected from the group consisting of carbides and nitrides, in particular silicon carbide and silicon nitride.

16. The process according to any one of the claims 1-13, wherein the meso- or macro-porous substrate essentially consists of a meso- or macro-porous metal structure, such as a structure consisting of partially sintered metal particles.

17. The process according to any one of the preceding claims, wherein the process comprises the subsequent step of chemically modifying the micro/meso-porous layer.

18. The process according to any one of the preceding claims, wherein the micro/meso-porous layer has catalytic properties.

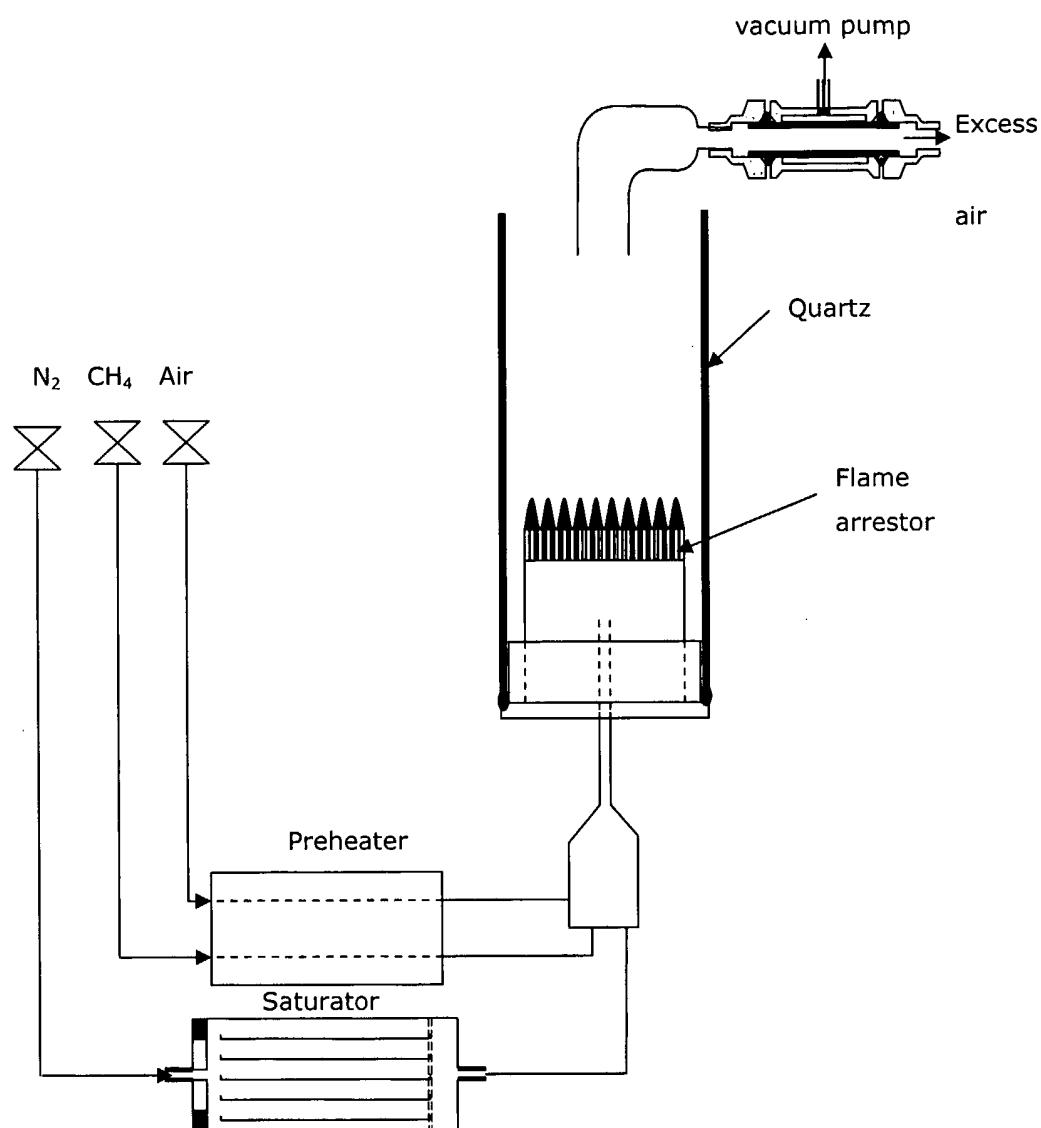
5 19. The process according to any one of the preceding claims, wherein the substrate is heated to above 300°C.

10 20. An asymmetric membrane comprising (i) a meso- or macro-porous substrate having a first porous surface and (ii) a micro/meso-porous layer deposited on and/or in the pore mouths of the first porous surface, said meso- or macro-porous substrate having a mean pore diameter in the range of 10 nm-10 µm, and said micro/meso-porous layer having a thickness of in the range of 0.5-1000 nm, and a mean pore size of at the most 10 nm, and wherein the meso/micro-porous layer has a gradually increasing pore size in the direction of meso- or macro-porous substrate.

15 21. The asymmetric membrane according to claim 20, wherein the micro/meso-porous layer has catalytic properties.

22. The asymmetric membrane according to any one of the claims 20-21, wherein the micro/meso-porous layer is chemically modified.

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**Figure 1**

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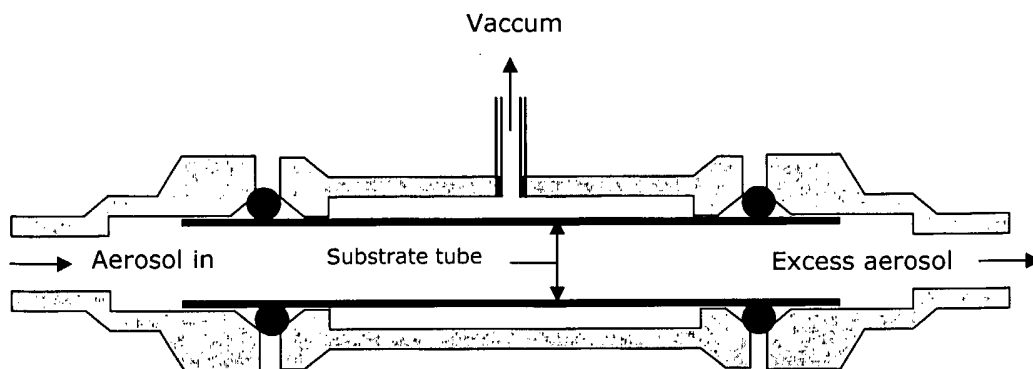


Figure 2.

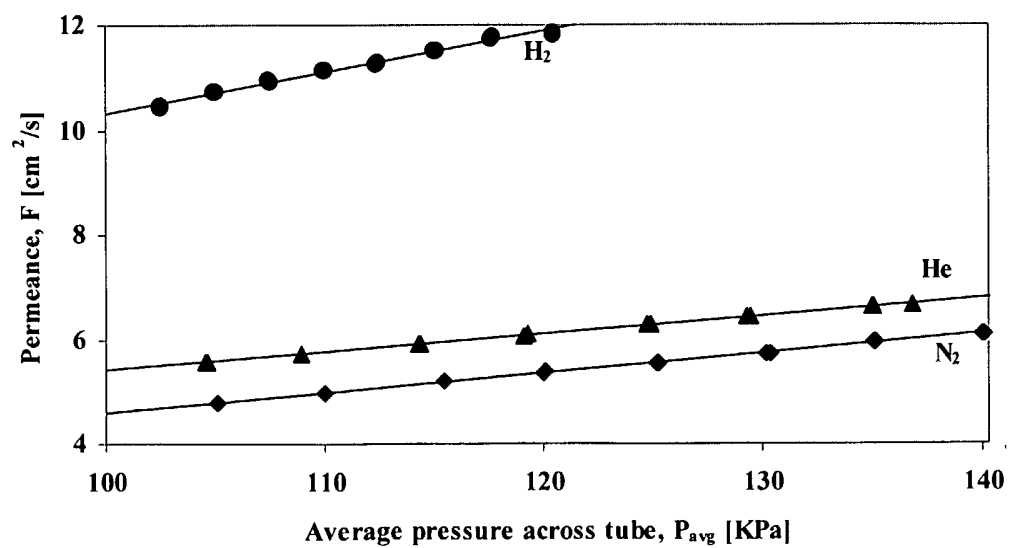


Figure 3

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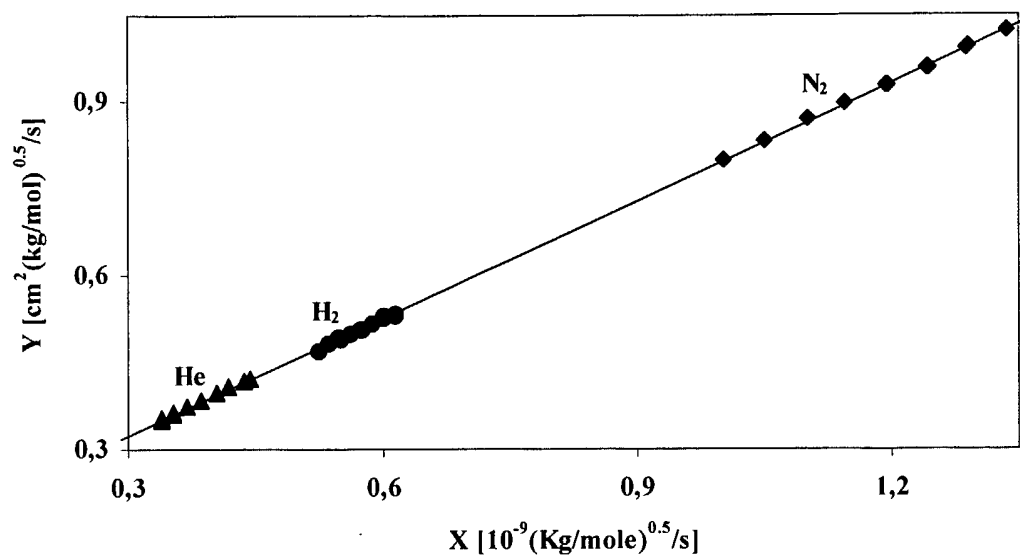


Figure 4

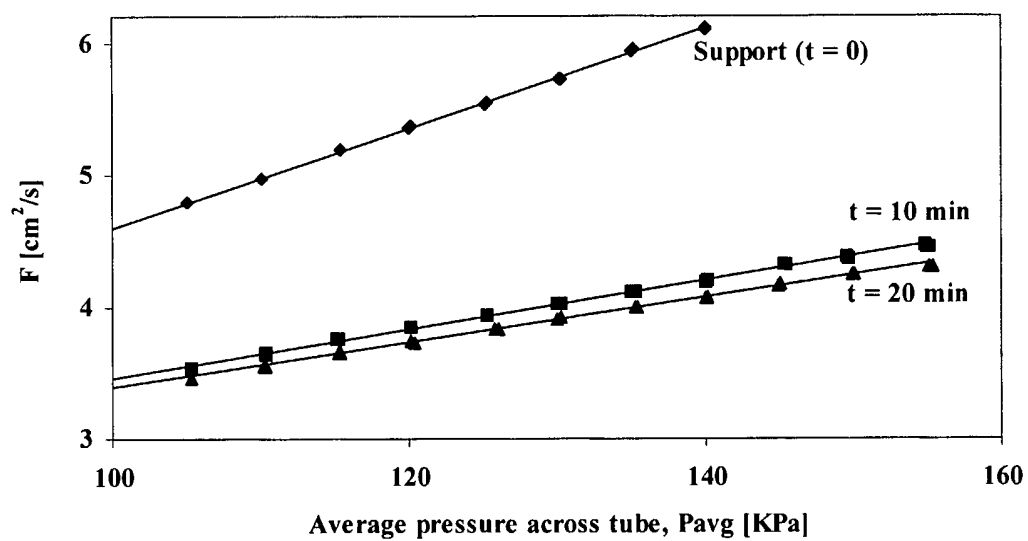


Figure 5

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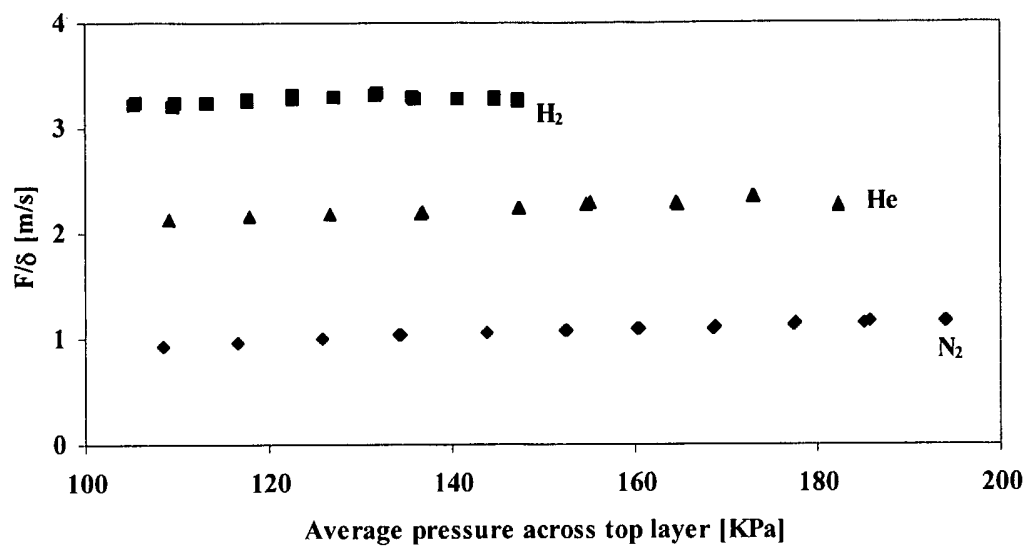


Figure 6

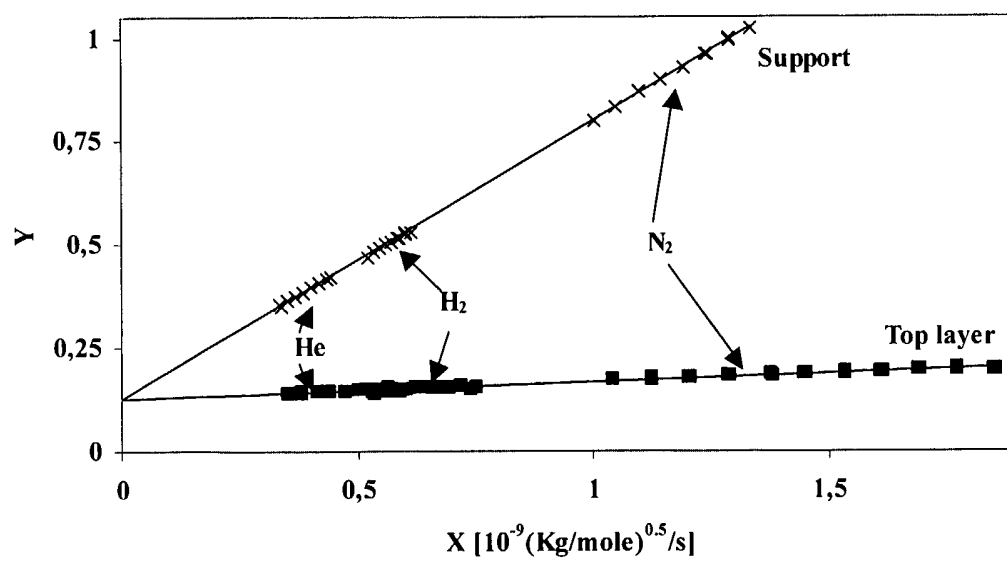


Figure 7

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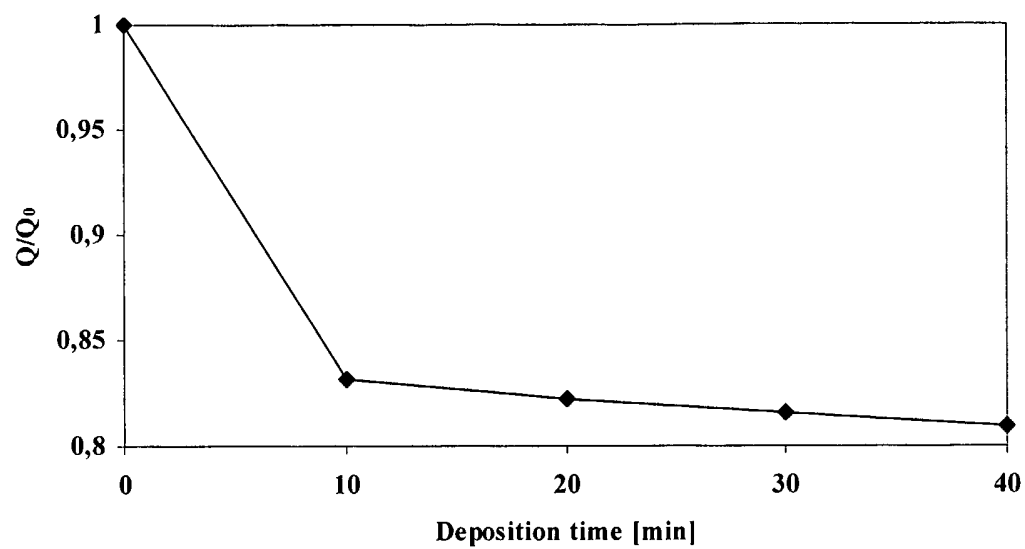


Figure 8

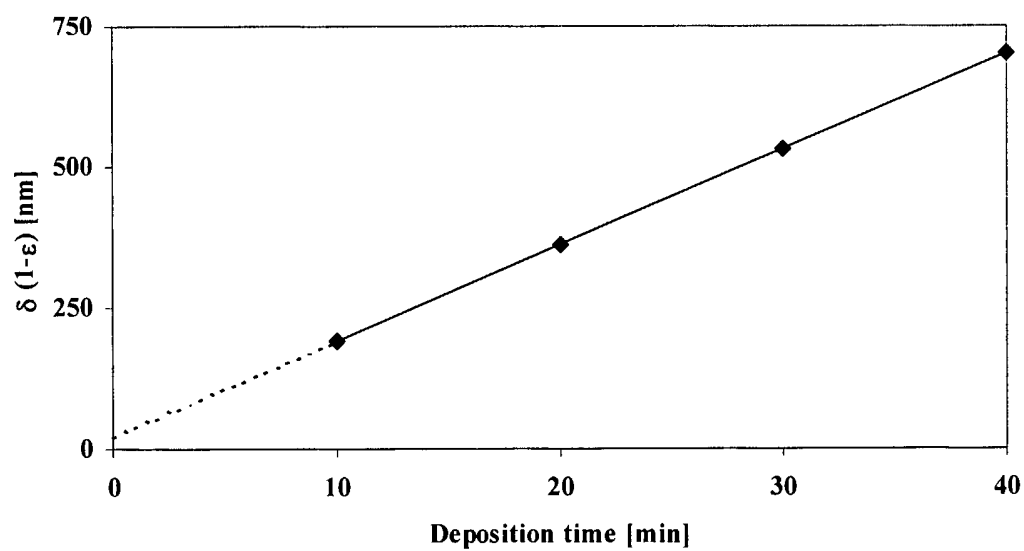


Figure 9

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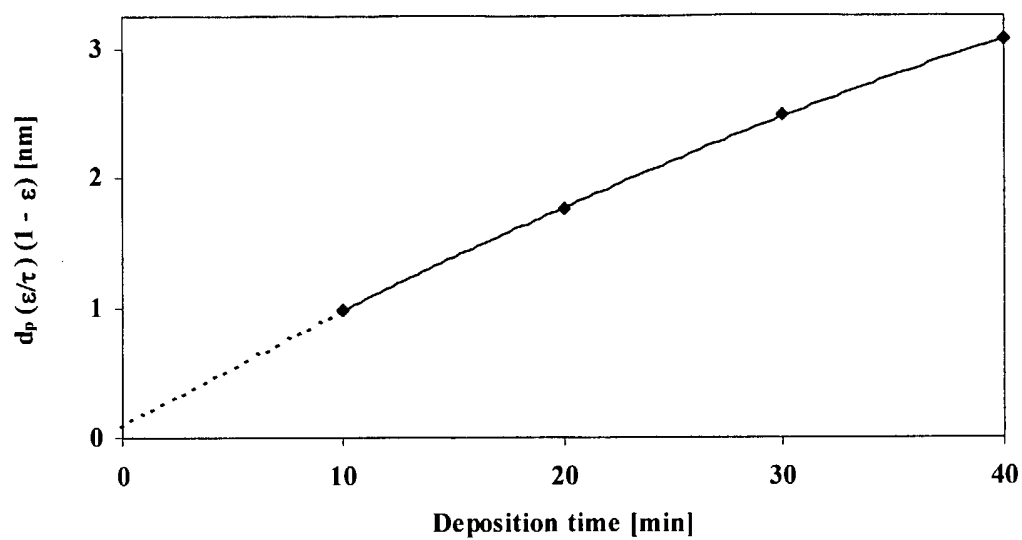


Figure 10

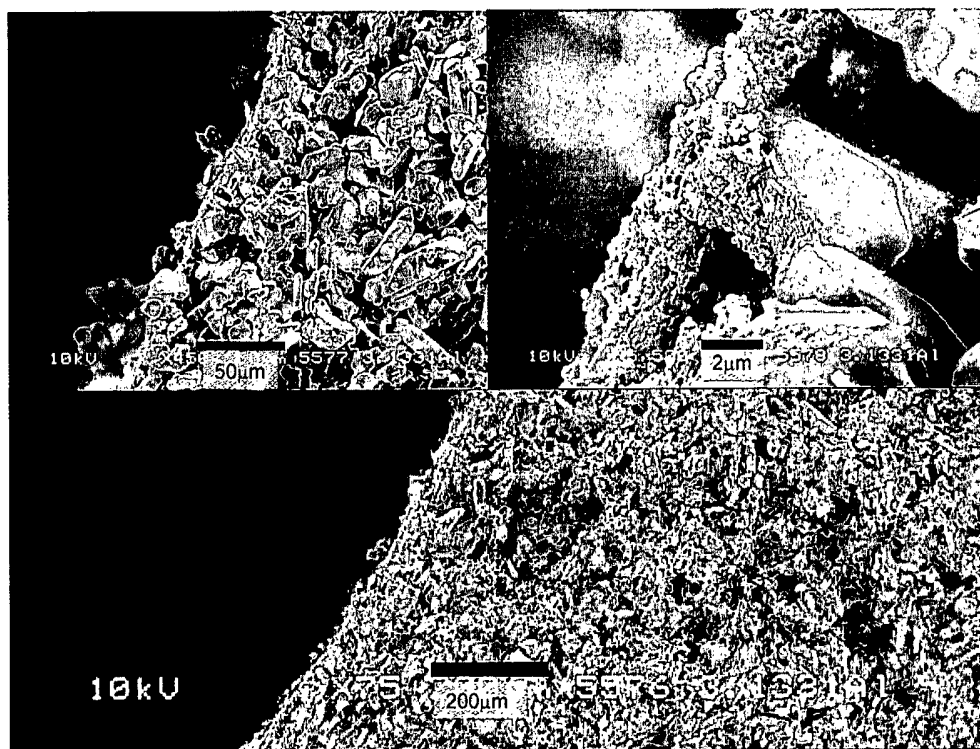


Figure 11

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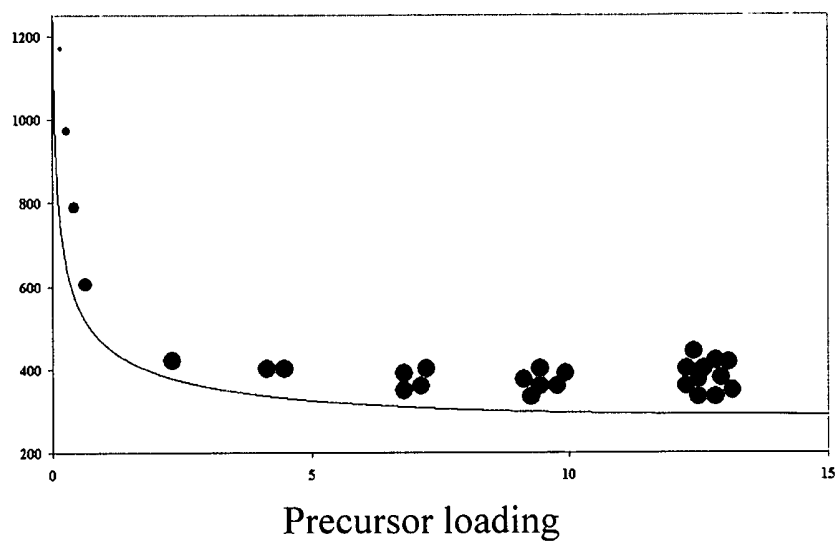
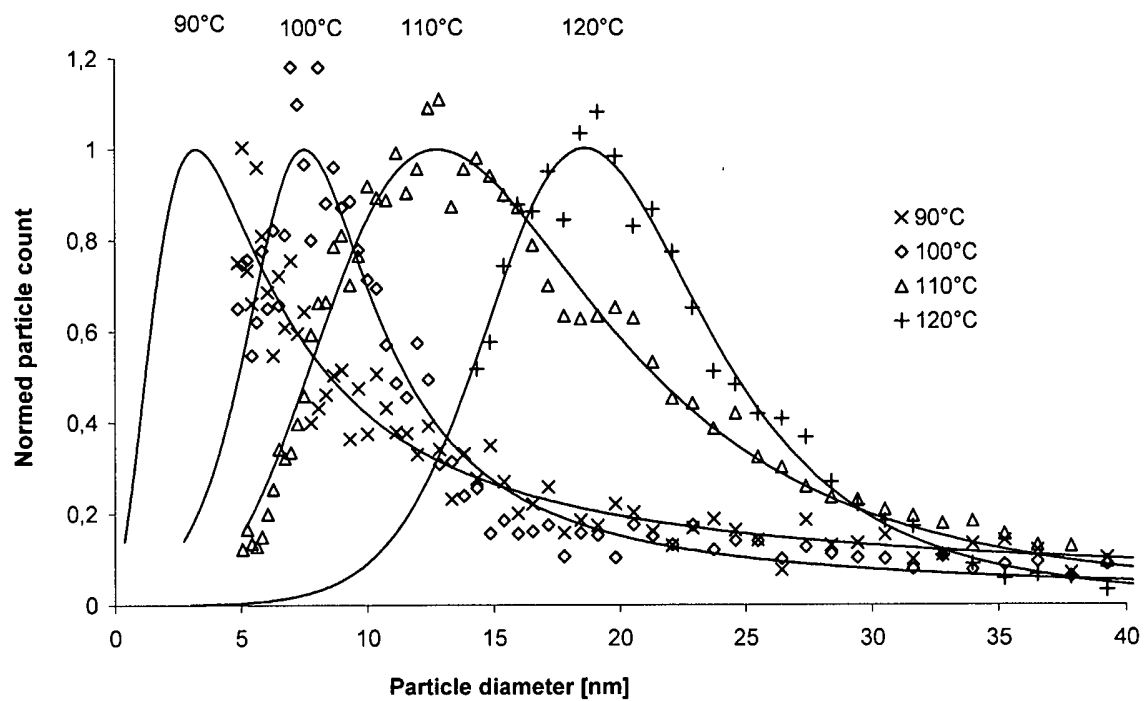
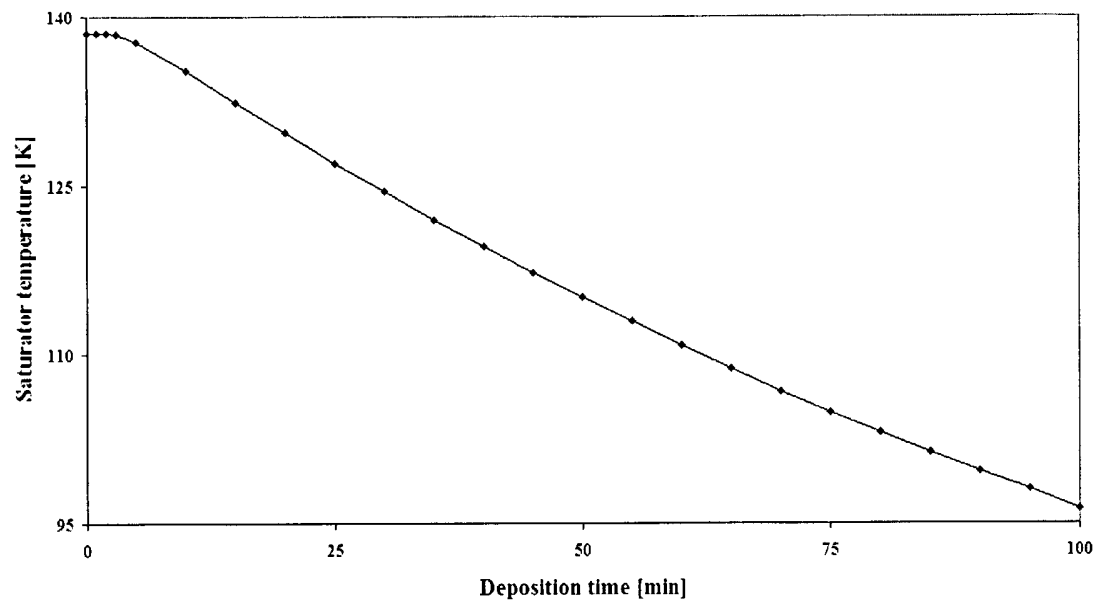
Specific surface area ($\sim 1/d_p$)

Figure 12

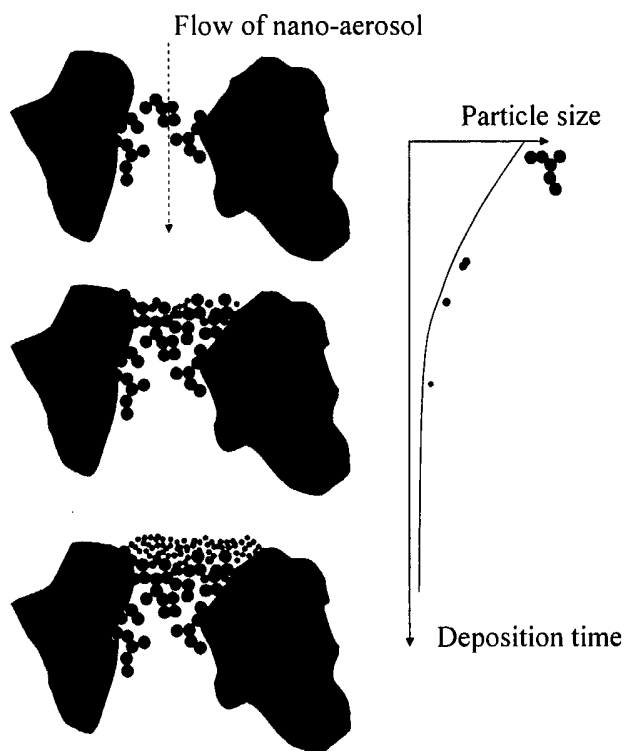
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**Figure 13**

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**Figure 14**

10/10

**Figure 15**

INTERNATIONAL SEARCH REPORT

DK2005/000620

A. CLASSIFICATION OF SUBJECT MATTER

B01D71/02 B01D67/00 C01B13/20 B01J35/06 B01J37/02

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 C23C C01B C01F B01J C04B

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, PAJ, COMPENDEX, INSPEC, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	MAJID MOSLEH., ET AL.: "Flame assisted synthesis of catalytic ceramic membranes" EIGHTH INTERNATIONAL CONFERENCE ON INORGANIC MEMBRANES, 'Online! 19 July 2004 (2004-07-19), XP002331257 CINCINNATI, OHIO, USA Retrieved from the Internet: URL:http://www.che.utoledo.edu/icim8/viewpaper.cfm?ID=731> 'retrieved on 2005-06-07! cited in the application the whole document	1-6,8, 10-14, 18-21
A	----- -/--	7,9, 15-17,22

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search

6 February 2006

Date of mailing of the international search report

17/02/2006

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Lançon, E

INTERNATIONAL SEARCH REPORT

DK2005/000620

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	SUNE K. ANDERSEN, ET AL.: "The formation of porous membranes by filtration of aerosol nanoparticles" JOURNAL OF NANOPARTICLE RESEARCH, vol. 4, 2002, pages 405-416, XP002331258 NETHERLANDS cited in the application the whole document	1-6,8, 10-14, 18-21
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A	TUE JOHANNESSEN, ET AL.: "Product engineering by high-temperature flame synthesis" 4TH EUROP. CONG. OF CHEM. ENG., 'Online! 21 September 2003 (2003-09-21), XP002331259 GRANADA, SPAIN Retrieved from the Internet: URL:http://lww.kt.dtu.dk/publications/getpub.php?view=1652> 'retrieved on 2005-06-07! abstract	1-8,10, 11, 13-16, 18,20,21
P,A	-& MOSLEH M. ET AL: "Product engineering by high-temperature flame synthesis" INTERNET ARTICLE, 'Online! XP002331260 Retrieved from the Internet: URL:http://216.239.59.104/search?q=cache:qWEWE_6D_4gJ:www.dechema.de/granada/TOPIC%2520-%2520013/P-13-032.pdf+johannessen+mosle+h+membrane+product+engineering+high+temperature+flame&hl=n1> 'retrieved on 2005-06-07! abstract	
A	----- DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; 22 April 2004 (2004-04-22), JOHANNESSEN, TUE ET AL: "Constructive aerosol technology - synthesis and use of nanostructured materials in aerosol form" XP002331262 retrieved from STN Database accession no. 140:290806 abstract & DANSK KEMI, vol. 84, no. 9, 2003, pages 28-31, ISSN: 0011-6335 ----- -/--	1,5-8, 10,11, 14-16, 18,20,21

INTERNATIONAL SEARCH REPORT

DK2005/000620

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JENSEN J R ET AL: "A study of Cu/ZnO/Al ₂ O ₃ methanol catalysts prepared by flame combustion synthesis" JOURNAL OF CATALYSIS, ACADEMIC PRESS, DULUTH, MN, US, vol. 218, no. 1, 15 August 2003 (2003-08-15), pages 67-77, XP004432695 ISSN: 0021-9517 the whole document in particular: abstract; page 68, column 1, line 1 - page 69, column 1, line 5 ; figure 1 ; table 2; page 77, column 2, line 1	1-8,10, 11,13, 18,20,21
A	US 2004/137209 A1 (ZELLER ROBERT ET AL) 15 July 2004 (2004-07-15) abstract; claims; figures 1-3 paragraph '0044! example 1	1,5,6,9, 11,12, 14-16,20
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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