

## High permselectivities of microporous silica-modified $\gamma$ -alumina membranes

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In this letter the synthesis of composite membranes with pore sizes below 1 nm and with large permselectivities is described.

In the past few years ceramic membranes for use in gas separation applications and catalytic processes have been developed [1-4].  $\gamma$ -Alumina membranes, having an average pore diameter of 2.5 nm, a sharp pore size distribution and 50% porosity, can be formed by a sol-gel technique. Synthesis of supported as well as of non-supported layers is possible. The thickness varies between 50 and 200  $\mu\text{m}$  for the non-supported layers. The supported ones have a thickness between 1 and 5  $\mu\text{m}$ , the support being an  $\alpha$ -alumina multilayer system (Fig. 1).

The transport of pure gases through a thin, supported, crack-free layer of  $\gamma$ -alumina has been described [5]. In these systems, three gas transport mechanisms are important, when a pressure gradient is applied. These are Knudsen diffusion, occurring when the mean free path of the molecules is much larger than the mean pore radius of the medium, laminar flow, which occurs when the mean free path of the molecules is much smaller than the mean pore radius of the porous medium, and surface diffusion. This last mechanism occurs when the gas is adsorbed on the membrane surface and is mobile on this surface. The permeability  $F_0$  of a supported membrane, taking into account all three mechanisms, can be described by

$$F_0 = \frac{\varepsilon}{\tau} \left[ \frac{c_1 r}{M^{1/2}} + \frac{c_2 r^2 \bar{P}}{\eta} + \frac{c_3 D_s}{r} \left( \frac{dx_s}{dp} \right) \right] \quad (1)$$

where  $c_1$ ,  $c_2$  and  $c_3$  are constants,  $\varepsilon$  is the porosity,  $\tau$  the tortuosity,  $r$  the mean pore radius,  $M$  the molecular mass,  $\bar{P}$  the mean pressure in the system,  $\eta$  the viscosity of the gas,  $D_s$  the surface diffusion coefficient and  $x_s$  the percentage of occupied surface compared to a monolayer. The first term on the right-hand side represents Knudsen diffusion, the second laminar flow and the third surface diffusion.

From Equation 1 it is clear that gases can be separated by Knudsen diffusion due to differences in their molecular masses. This was shown to be valid for a supported  $\gamma$ -alumina membrane with a hydrogen-nitrogen mixture [6]. However, in cases where molecular masses are nearly equal and/or quite high ( $> 40 \text{ g mol}^{-1}$ ), another separation mechanism should be employed in order to achieve high separation factors.

Alternative separation mechanisms are e.g. surface diffusion (see Equation 1) and multilayer diffusion, which occurs when multilayer adsorption take place.

For these mechanisms to occur, it is in most cases necessary to introduce an interaction between the gas and the membrane surface by means of chemical modification. This was done for example by introducing silver in the  $\gamma$ -alumina separation layer, thereby creating an interaction with hydrogen and extra transport along the surface [7].

Surface diffusion and multilayer diffusion become more important when the pore size is decreased. This is demonstrated in Equation 1. It is therefore desirable to decrease the pore size of the  $\gamma$ -alumina separation layer, in order to increase the importance of surface diffusion as a separation mechanism. In many cases the surface (or multilayer) diffusion becomes the dominant mechanism when pore diameters are below 2 nm. Decreasing the pore size can be performed again by modification of the  $\gamma$ -alumina separation layer. This means that modification is not only performed to introduce a specific interaction between a gas and the membrane surface, but also to decrease the pore size. In this letter, modification of the  $\gamma$ -alumina separation layer with silica will be described. Silica was chosen, because it is known to be microporous [8] and thermally stable up to temperatures of 900°C, provided no water vapour at relatively high pressure is present [9].

First supported  $\gamma$ -alumina membranes were synthesized. A dry, porous support (pore diameter 0.4  $\mu\text{m}$ ) was brought into contact with a 0.6 M boehmite colloid suspension for 4 sec. The gel layer, formed due to the capillary action of the support, was then dried under controlled conditions and calcined at 600°C.

The membrane was characterized by helium gas permeability. Fig. 2a gives the permeability of the support (line 1), the support and top layer (line 2) and of the top layer (line 3). This last line is calculated from the first two lines by assuming the top layer and the support to be resistances in series [5]. The permeability of the top layer is then given by

$$F_{0,\text{top}} = \left( \frac{1}{F_{0,\text{sup}}} - \frac{1}{F_0} \right)^{-1} \quad (2)$$

where  $F_0$  is the permeability of the whole system,  $F_{0,\text{sup}}$  the permeability of the support and  $F_{0,\text{top}}$  the permeability of the top layer. As can be seen from Fig. 2a the dominant gas transport mechanism in the top layer is Knudsen diffusion. This could be expected, because surface diffusion is not present and the pores are so small (2.5 nm diameter) that laminar flow is negligible (see Equation 1).

Next a stable polymeric silica solution was

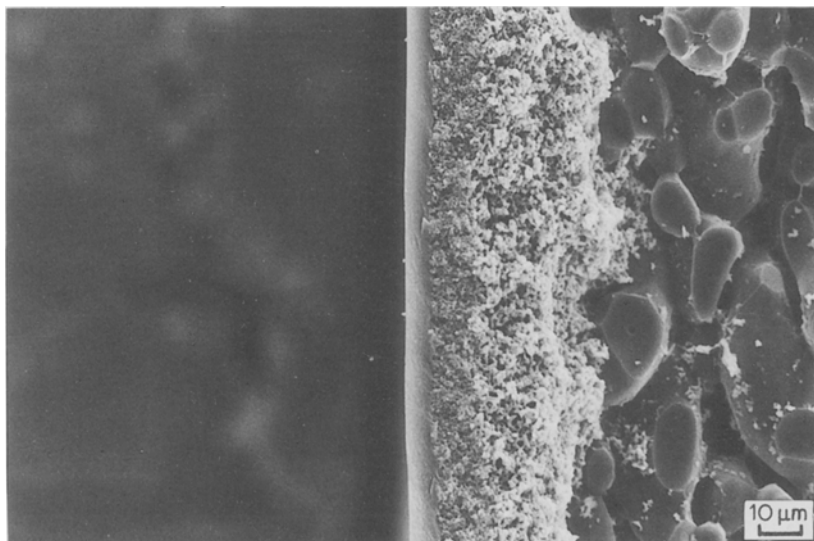


Figure 1 Alumina top layer applied by dipping on a Membralox (SCT) porous alumina multilayer support.

prepared. The solution was gelled, dried under controlled conditions and calcined at 400°C. Nitrogen adsorption-desorption was used to characterize this material. Fig. 3 gives the adsorption-desorption isotherm of the calcined silica gel. The adsorption and desorption branches coincide and no hysteresis is present. In the literature, this kind of isotherm is usually ascribed to microporous materials [10]. In this region, Kelvin's equation is not valid any more and there is no difference between adsorption and desorption. This means that the silica gel is microporous at 450°C, with a mean pore radius smaller than 1 nm. The porosity is about 25%.

The stable polymeric silica solution was then applied on the  $\gamma$ -alumina membrane. It is assumed that the applied silica has the same structure as the non-supported silica, in accordance with the structure of

non-supported and supported  $\gamma$ -alumina. This has to be proved, however. The structure of the silica-modified alumina membrane system was studied by gas permeability and XPS.

The silica-modified alumina membrane was characterized by gas permeability with several gases at room temperature. Because microporous systems are very sensitive to water, very pure gases were used, tubes were flushed before use and the membrane was first dried at 300°C. The results of these measurements are given in Fig. 2b. From this figure, three important conclusions emerge

First it is clear from the permeability of inert gases, e.g. nitrogen and helium, that the transport through the whole system (support plus  $\gamma$ -alumina separation layer) is Knudsen diffusion. Second it becomes clear, by comparison with Fig. 2a, that the permeability of

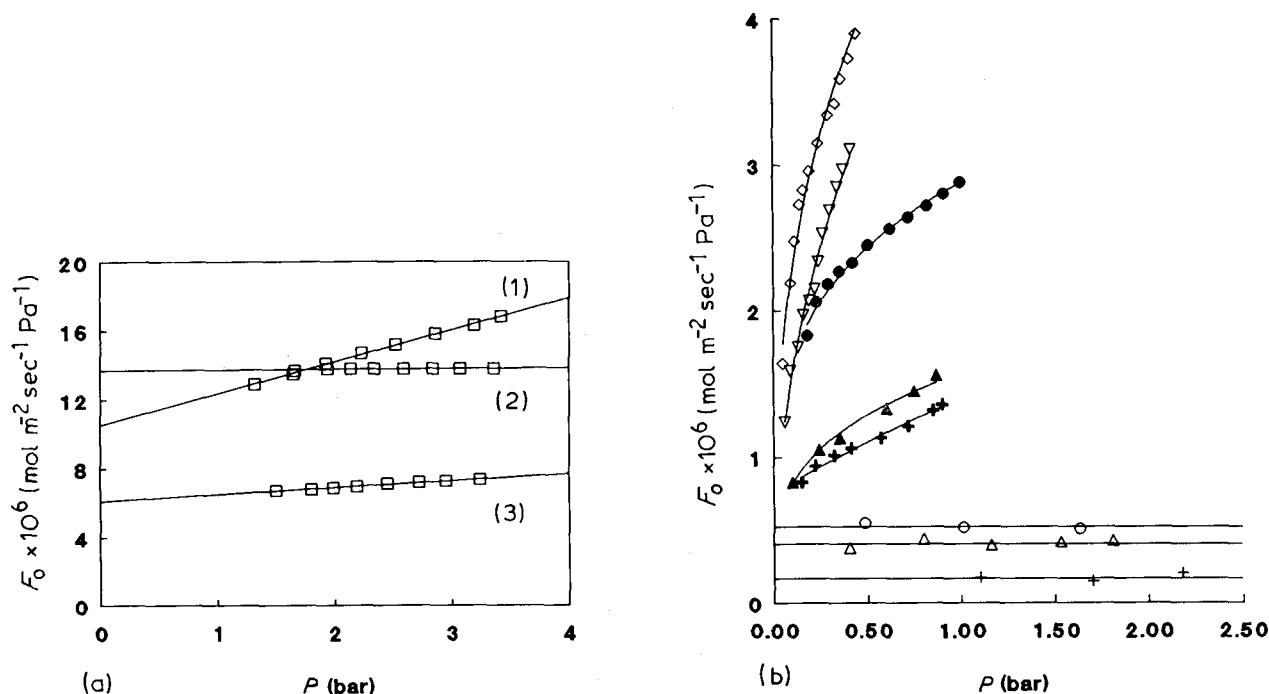


Figure 2 (a) Permeability as a function of mean pressure for helium of (1) support, (2) support + top layer and (3) top layer. (b) Permeability as a function of mean pressure for several gases of silica-modified  $\gamma$ -alumina supported separation layer: (+) nitrogen, ( $\Delta$ ) methane, (O) helium, (+) ethane, ( $\blacktriangle$ ) ethylene, ( $\bullet$ ) CO<sub>2</sub>, ( $\nabla$ ) propane, ( $\diamond$ ) propylene.

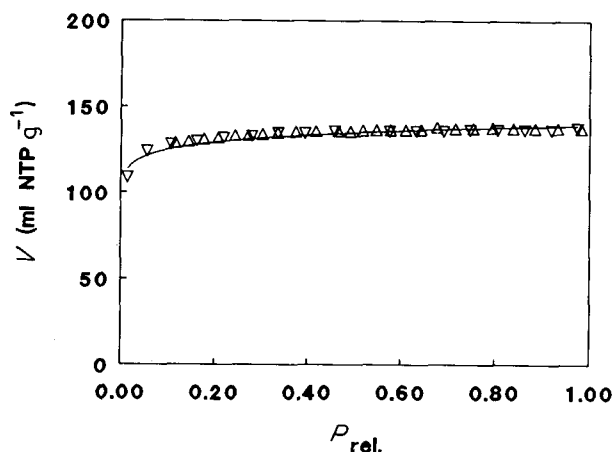


Figure 3 Nitrogen adsorption-desorption isotherm of silica at 77 K: ( $\nabla$ ) adsorption, ( $\Delta$ ) desorption.

the system has decreased by a factor of ten. These two phenomena can be explained by taking into account the thin silica layer. As discussed earlier, the pores in this silica layer are very small ( $< 1$  nm, see Fig. 3). This means that the resistance against gas transport of this layer is very large. Therefore, the permeability of the system is fully determined by the thin silica layer only. Hence the dominant transport mechanism is Knudsen diffusion, due to the very small pores of the silica layer. Thus, the permeability to inert gases for the system shows that silica is present on top of or inside the pores of the  $\gamma$ -alumina separation layer.

Thirdly, it appears that the transport of condensable gases is largely enhanced. The permeability to  $\text{CO}_2$ , propane and propylene all strongly increase with the mean pressure in the system. Permselectivity, which is the ratio of permeabilities, for  $\text{CO}_2$ - $\text{CH}_4$  can become as high as 10, and for nitrogen-hydrocarbon mixtures even 15. This means that effective separation of these mixtures with relative high permeabilities is possible.

The mechanism of this enlarged transport is not quite clear yet. Since the gas-phase diffusion has decreased strongly, another transport mechanism must have become important. It is therefore likely that propane, propylene and  $\text{CO}_2$  are also transported along the surface, as indicated by the observed pressure dependence of the permeability. Due to the very small pores of the silica, this surface diffusion can become the dominant transport mechanism (Equation 1). Further research focuses on the study of the interaction between the aforementioned gases and silica. Next to this, permeability experiments are carried out at elevated temperatures ( $> 150^\circ\text{C}$ ) to study the effect of temperature on the transport behaviour. Thirdly, separation experiments on binary mixtures of  $\text{CO}_2$  with  $\text{CH}_4$  and hydrocarbons with nitrogen are carried out. It is expected that separation factors for these mixtures will be even higher than the permselectivities, due to a pore blocking effect of the adsorbed species.

X-ray photon spectroscopy (XPS) was used to characterize the surface of the silica-modified  $\gamma$ -alumina top layer. XPS is a surface technique to analyse the chemical composition and the binding state of the different elements. The sample is irradiated with

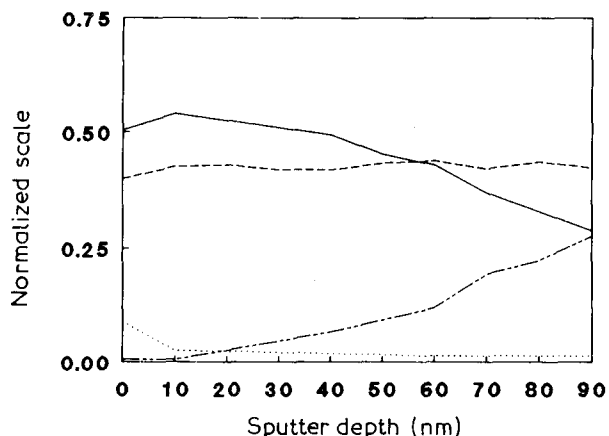


Figure 4 XPS analysis of silicon and aluminium as a function of sputter depth: (—) Si (2p), (---) O (1s), (····) C (1s), (-·-·-) Al (2p).

X-rays, and due to the energy of these X-rays electrons are emitted from inner orbitals. Since every element has a unique set of orbitals, the binding energy of the electrons is characteristic for the element and its binding state. The sampling depth of this technique is about 4 nm, so XPS is a very useful surface analytical technique. Without calibration of the signals with standards of known composition it can be used only in a qualitative sense.

XPS was used to determine whether silica was present on top of the  $\gamma$ -alumina separation layer or in the pores of this layer. In the first case one would expect to find only pure silica in the surface, in the second one would expect an aluminium:silicon ratio near 2:1. This ratio was calculated because  $\gamma\text{-Al}_2\text{O}_3$  is 50% porous and assuming that the pores are completely filled with  $\text{SiO}_2$ . With incomplete filling this ratio is larger. After analysis of the surface, about 10 nm was sputtered off the material by argon ion bombardment and a new analysis was done. This procedure was repeated several times.

Fig. 4 gives the silicon, aluminium, carbon and oxygen contents as a function of the sputter depth. In the beginning, only silica is present. This means that a very thin layer of silica is deposited on top of the  $\gamma$ -alumina separation layer. After about 30 nm, aluminium begins to show. The aluminium content slowly increases with sputter depth, while the silicon content slowly decreases. The reason for this is not quite clear. One would expect a more or less discontinuous jump to the predicted 2:1 aluminium:silicon ratio, if silica was present on top of the  $\gamma$ -alumina and also inside the pores of the  $\gamma$ -alumina. However, since the sputtering and analysis of porous materials with this technique is relatively unknown, it is possible that the technique gives rise to artefacts, like surface roughening and preferential sputtering. It is also possible that the layer thickness of the silica varies along the surface. Further research will be conducted towards reliable quantification of this method. From the experiment described it can only be concluded that a thin silica layer of about 30 nm is present on top of the supported  $\gamma$ -alumina separation layer.

It can be concluded that a microporous silica-modified  $\gamma$ -alumina membrane can be made through a

sol-gel process. A very thin layer of microporous silica (about 30 nm) is present on top of the  $\gamma$ -alumina membrane. This layer exhibits very good permselectivities towards  $\text{CO}_2$ - $\text{CH}_4$  and hydrocarbon-inert gas mixtures, with relatively high permeabilities. It is expected that selective separation with high fluxes can be realized with this membrane.

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