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HIGH TEMPERATURE GAS SEPARATION WITH ALUMINA MEMBRANES

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ABSTRACT

The most promising applications of ceramic membranes for gas separation is the use at high temperatures. The tubular three layer ceramic membrane system prepared by ECN for this purpose have been shown to be well suited up to temperatures of at least 500°C.
In the present paper the stability of the membranes at temperatures up to 600°C as well as the influence of the small increase in pore size for membranes exposed for long times to 500°C on the permeability for gas will be discussed.
The alumina membrane is characterized by both low and high temperature gas permeation and gas separation. At high temperatures the permselectivity is almost equal to the theoretical Knudsen diffusion separation factor.
The membrane performance at temperatures up to 500°C is given and the influence of temperature on the separation will be discussed. It is shown that the most important segregative transport mechanism is Knudsen diffusion and that the surface diffusion contribution of propane will decrease with increasing temperature.
Although the separation factor is low and modification of the membranes is necessary to increase selectivity, the Knudsen diffusion membranes can be used successfully in a number of high temperature applications.

INTRODUCTION

The ceramic membrane system has a tubular shape with an outer diameter of 14 mm and a length of 70 cm and consists of a porous alpha-alumina substrate coated with an alpha-alumina intermediate layer and a gamma alumina top layer on the outer side of the tube. This latter is the actual separation layer. Preparation and properties of this system are described extensively elsewhere [1,2] and will not be discussed here in detail.

The performance of low temperature gas separation with alumina membranes has been discussed elsewhere [1] and some implications of separation results at high temperature were given. In this paper results concerning high temperature (up to 500°C) gas permeation and separation are discussed and the influence of temperature on the stability of the gamma-alumina gas separation layer will be dealt with. One of the possible separation processes for the high temperature membranes is improvement of the conversion in dehydrogenation reactions. Therefore in this paper the permeation and separation of hydrogen and propane at elevated temperatures are studied.

THEORY OF GAS TRANSPORT

For gas transport through porous media several transport mechanisms are important [3,4]. Single component gas permeability without multilayer diffusion or capillary condensation can be described by:

$$P = \epsilon * \mu \left(c_1 * r/(M*T)^{½} + c_2 * r^2 * p / T + c_3 * D_s * \frac{dx}{dp} / r \right) \qquad (1)$$

in which ϵ is the porosity, μ is a shape factor, c_i are constants, r is the mean pore radius, M is molecular mass, T is the temperature, p is the mean pressure in the membrane, D_s is the surface diffusion coefficient and dx/dp is the change in surface coverage with pressure. Gas transport by Knudsen diffusion given by the first term right hand of side equation 1 is selective and the permeability ratio of gases is equal to the quotient of the square root of the molecular masses. Laminar flow (second term) is not selective. Surface diffusion is mainly governed by adsorption and mobility. For physical adsorption the contribution of this effect decreases with increasing temperature (third term).
Gas transport of multicomponent mixtures is often described in literature e.g. [4,5,6]. The method of Present and deBethune [5,6] is used here for calculating the theoretical separation factor for a binary mixture of gases. This model describes the separative (Knudsen) diffusion, the molecular diffusion and the viscous flow through the pores of the gas separation layer. The influence of laminar flow through the two layer substrate system, the influence of concentration polarization and occurrence of surface diffusion is not included in this model. No further description of this model will be given here.

EXPERIMENTAL RESULTS

The three layer tubular alumina membrane system consists of a substrate tube formed by extrusion out of a ceramic paste. After sintering and pretreatment of the tube, a thin (20 - 30 μm) alumina layer is film coated on the outer side of this tube. After heat treatment of this intermediate layer the actual gas separation layer is applied by slib coating with a boehmite sol. Subsequently firing at 600°C provides the ceramic gas separation membrane. For details about preparation and characterization see [1,2].
Characterization of the 70 cm long ceramic membranes by gas permeation and gas separation is done at both low and high temperatures (up to 500°C). Problems of end-sealing the membranes for use at elevated temperatures can be overcome by using a low-melting temperature glass as sealing material.

In table 1 the permeability for hydrogen and the permselectivities for hydrogen, helium and propane are given at several temperatures.

Table 1

temperature (°C)	permeability hydrogen p=1 bar Knudsen + laminar (10^{-6} mol/m^2.s.Pa)	permselectivity		
		H_2/He	H_2/C_3H_8	He/C_3H_8
25	43.0 + 17.5	1.49	2.96	1.99
250	30.0 + 10.4	1.48	3.71	2.51
475	23.8 + 6.8	1.45	4.03	2.77
theor. (*)		1.41	4.69	3.31

(*) assumed 100% Knudsen diffusion

The results of the gas separation measurements at both room temperature and 490°C for the gas mixture helium - propane are given in figure 1.
In this figure the measured separation factor is plotted against the pressure ratio (pressure feed side/pressure product side) for the three layer membrane system. The theoretical separation factor is calculated according to a model given in [6]. The following parameters for the model are used: - a pore radius of 3 nm for the pores in the top layer - a mean pressure of 1.3 bar (this pressure is about the same as the pressure during the experimental results) - a temperature of 490°C - a feed concentration of 40% helium.

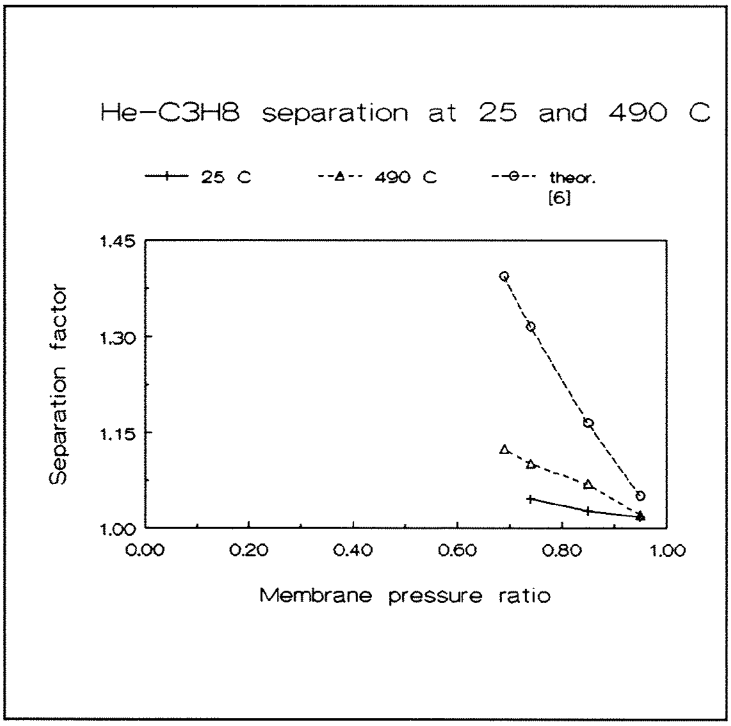

Figure 1 Separation factor vs. pressure ratio

From literature [7,8] it is well known that the top layer of the ceramic membranes used here will slightly change due to long use at temperatures above 500°C.
According to our measurements the gamma alumina top layer calcined for 5 hours at 600°C has pores of about 2.4 nm in radius. Exposed for 2000 h at 500°C the pore size increases to about 3.3 nm and is stable at this temperature. Due to this small pore size increase in the top layer the total permeability increases about 10% but the selectivity decreases only a few percent.

DISCUSSION

In table 1 it can be seen that the permeability for hydrogen decreases with increasing temperature. From equation 1, assuming that no hydrogen surface diffusion exists on gamma-alumina, it can be calculated that this decrease in permeability is almost according to the theory: the Knudsen diffusion decreases with an increase in $T^{½}$ and the laminar flow decreases with an increase in T.

If Knudsen diffusion is the only transport mechanism in the gas separation layer (pore size of about 4 nm) of the ceramic membrane system only moderate gas separation factors can be obtained. The permselectivity for hydrogen and helium is almost equal to the theoretical separation factor and is almost independent of temperature. In the case of propane and hydrogen or propane and helium the permselectivity increases with an increase in temperature because the permeability for propane decreases with temperature. Gas adsorption measurements of propane on gamma-alumina show a the surface coverage (assuming monolayer adsorption) of propane at 25, 50 and 250°C and 1 bar of about 0.79, 0.34 and 0.06 respectively. The adsorption is physisorption, so this adsorption will be mobile. From these adsorption measurements can be concluded that the increase in permselectivity is due to the smaller surface diffusion of propane at higher temperatures.

At 475°C the measured separation factor approaches the theoretical Knudsen diffusion separation factor, but due to laminar flow in the substrate system (about 20% of the gas transport resistance is across the substrate system) and a few small defects in the top layer it is not possible to reach the theoretical separation factor.
The results of gas separation experiment using binary gas mixtures can be seen in figure 1. These indicate an increase in selectivity with an increase in temperature. As explained this increase in selectivity is a result of the decrease of the propane surface diffusion.
The separation factor is smaller than expected from the permselectivities and also smaller than the separation factor calculated from the model [5,6]. This is a consequence of back diffusion and concentration polarization during the binary separation experiments. During permeation measurements with pure gases these process conditions do not appear. The difference between the measured separation factor and the separation factor calculated with the model described in [6] can be explained by concentration polarization, laminar flow in the substrate system, some defects in the top layer and possibly a small surface diffusion contribution. These effects are not included in the model used.

Although long exposure to high temperatures (up to 500°C) exhibits a small increase in the pore size of the top layer, almost no decrease is found in separation efficiency. The reason for this is that the ratio between the pore size and the mean free path of the molecules hardly changes. Still about 80% of the gas transport resistance occurs in the top layer.
According to [9] the conversion of propane to propylene in catalytic (alumina particles impregnated with chromium dioxide) dehydrogenation at 575°C is only 40.1% (selectivity = 90%). According to [9] the use of a ceramic membrane having a modal pore radius of 5 nm and a thickness of 4-10 μm on a porous support would give a conversion of 58.7%. From [9] it is not clear if these results are obtained experimentally or by calculation. Experimental determination of the use of porous membranes to increase the conversion in dehydrogenation reactions [10] indicate about the same improvement in conversion. So as a result of the use of the above described

membranes in dehydrogenation reactions it is possible to utilize more economical reaction conditions with only minor membrane selectivities.

CONCLUSIONS

Permselectivities for the pure gases hydrogen, helium and propane and gas separation factors measured with the binary gas mixtures helium and propane increase with an increase in temperature due to a decrease in surface diffusion of propane on gamma-alumina. Differences between experimentally obtained separations and theoretical models can be explained by process conditions.

Long term use of the alumina gas separation membranes at temperatures up to 500°C hardly changes the separation efficiency of the membranes.

Although the separation factor is not high, high temperature Knudsen diffusion membranes can be used successfully in certain applications e.g. equilibrium shift in dehydrogenation reactions: increase product yield and/or decrease energy requirements.

ONGOING INVESTIGATIONS

Testing the described ceramic membranes in for example dehydrogenation reactions will be discussed elsewhere. We are working on increasing the selectivity of the membranes by means of pore size decrease, increasing the stability of the membranes and scaling up the membranes to a module which can be used at high temperature gas separation.

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