

## GAS SEPARATION MECHANISMS IN MICROPOROUS MODIFIED $\gamma$ - $\text{Al}_2\text{O}_3$ MEMBRANES

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### Summary

The transport of pure gases and of binary gas mixtures through a microporous composite membrane is discussed. The membrane consists of an alumina support with a mean pore diameter of 160 nm and an alumina top (separation) layer with pores of 2–4 nm. The theory of Knudsen diffusion, laminar flow and surface diffusion is used to describe the transport mechanisms. It appears for the composite membrane that Knudsen diffusion occurs in the toplayer and combined Knudsen diffusion/laminar flow in the support at pressure levels lower than 200 kPa. For the inert gas mixture  $\text{H}_2/\text{N}_2$  separation factors near 3 could be achieved which is 80% of the theoretical Knudsen separation factor. This value is shown to be the product of the separation factor of the support (1.9) and of the top layer (1.5). The value for the top layer is rather low due to the relatively small pressure drop across this layer. This situation can be improved by using composite membranes consisting of three or more layers resulting in a larger pressure drop across the separation layer.

$\text{CO}_2$  surface diffusion occurs on the internal surface of the investigated alumina membranes. At 250–300 K and a pressure of 100 kPa the contribution of surface diffusion flow measured by counterdiffusion is of the same order of magnitude as that resulting from gas diffusion. The adsorption energy amounts  $-25$  kJ/mol and the surface coverage is 20% of a monolayer at 293 K and 100 kPa. The calculated surface diffusion coefficient is estimated to be  $2-5 \times 10^{-9}$   $\text{m}^2/\text{sec}$ .

Modification of the internal pore surface with MgO increases the amount of adsorbed  $\text{CO}_2$  by 50–100%.

Modifications with finely dispersed silver are performed to achieve  $\text{O}_2$  surface diffusion.

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### Introduction

In the past few years a number of papers have been published concerning the preparation and characterization of microporous  $\gamma$ -alumina membranes [1–8,22,23]. Membranes with pore diameters of 2.5 nm or larger have been obtained with a narrow pore size distribution and a membrane porosity of 50% [1,2]. The formation of membranes on a support with pores of 120 nm diam-

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eter has been described [3]. More recently, the formation of membranes on multilayer supports with larger pores has been reported [8]. Liquid permeation and separation characteristics were measured [4–6] and, e.g., a cut-off value of a molecular weight of 2000 for polyethylene glycol was achieved. Recently, gas permeation characteristics of pure gases have been determined [8]. This paper will focus on the possibilities of microporous alumina-based membranes in gas separation.

If the pores of a porous medium are smaller than the mean free path of the gas molecules, gases can be separated due to a Knudsen diffusion mechanism, according to which light gases permeate faster than heavy gases. A well-known example is separation of uranium isotopes [9]. Separation factors for this example are very small; higher values are obtained if  $H_2$  or He are separated from other gases. These separation factors, which still are relatively small, are of interest, especially if a shift in the equilibrium of chemical reactions can be achieved by extracting  $H_2$  at high temperatures, e.g., in thermal decomposition of  $H_2S$  [10] or in dehydrogenation reactions. In this kind of reactions with gases like propane, butane or ethylbenzene the yield is very low, and the price of the product is mainly determined by the costs of the reactants. Therefore the reactor effluent is separated and the reactant is recycled. The energy consumption in this cryogenic process is tremendous. By using membrane reactors the gas is split into a hydrogen-rich and a hydrogen-poor gas mixture. Calculations show an increase in conversion per cycle by 30–50% for the dehydrogenation of hydrocarbons if a membrane reactor is added to a conventional reactor [26]. If a conventional reactor for the conversion of cyclohexane into benzene and hydrogen is replaced by a catalytic membrane reactor, the conversion increases from 20% to 80% and the reaction temperature decreases by 200°C [27].

Separation factors can be influenced by introducing an interaction between gas and pore wall, resulting in an additional transport along the surface. The occurrence of surface diffusion in porous materials is reported frequently [11–14]. In this paper surface diffusion of  $CO_2$  on  $\gamma$ -alumina is discussed. Separation layers can be chemically modified in order to change the surface diffusion properties of the membranes. In this way the pore size can be (locally) changed and/or the chemical character of the surface can be modified [24]. With smaller pore size it is expected that the gas–solid interaction and surface diffusion compared to gas diffusion increases. Recently it has been shown that interesting effects can also be obtained with multilayer adsorption, capillary condensation, and transport of the condensed component. For alcohol–water mixtures separation factors of over 100 have been achieved [22,23].

## Theory

### Pure gases

In porous media combined Knudsen and Poiseuille flow takes place. For homogeneous media and pure non-sorbable gases the total permeability  $F_0$  (in mol/m<sup>2</sup>-sec-Pa) can be expressed as [13,15]

$$F_0 = F_{0k} + F'_{0p} \bar{P} \quad (1)$$

where  $F_{0k}$  is the permeability due to Knudsen diffusion and  $F'_{0p} \bar{P}$  the contribution due to laminar flow, which is linearly dependent on the mean pressure  $\bar{P}$  in the system.

$$F_{0k} = \frac{2 \epsilon \mu_k \bar{r} \bar{v}}{3 R T L} \quad (2)$$

$$F'_{0p} = \frac{\epsilon \mu_p \bar{r}^2}{8 \eta R T L} \quad (3)$$

where  $\epsilon$  is the porosity,  $\bar{r}$  the modal pore radius of the medium,  $\mu_k$  and  $\mu_p$  shape factors, which are both, in general, assumed to be equal to the reciprocal tortuosity of the medium,  $R$  the gas constant,  $T$  the temperature,  $\bar{P}$  the mean pressure,  $\eta$  the viscosity of the gas and  $\bar{v}$  the average molecular velocity

$$\bar{v} = \left( \frac{8 R T}{\pi M} \right)^{1/2} \quad (4)$$

where  $M$  is the molecular mass of the gas molecules.

The relative contribution of laminar flow to the total flow is determined by the ratio of the mean free path of the gas molecules to the modal pore size. In small pores, at low pressures and high temperatures, Knudsen diffusion is the predominant transport mechanism.

When the temperature and the pressure are such that adsorption of the gas molecules on the pore walls is important, the preceding laws for gaseous flow are no longer valid. Molecules adsorbed on solid surfaces may have considerable mobility and we must consider that additional gas transport exists as a surface flow in the direction of decreasing surface concentration.

The presence of surface flow is detected as a deviation of the total permeability from the gas phase permeability, given by Eqns. (1-3). The gas phase permeability for adsorbable gases can be calculated from permeability data for non-sorbable gases with the help of Eqns. (2) and (4). The mechanism of surface flow is rather complicated. This subject has been treated in many papers [e.g., 11-13]. For low surface concentrations the most general description is the two-dimensional form of Ficks' law: the surface permeability  $F_s$  (mol/m<sup>2</sup>-sec) equals

$$F_s = -\rho(1-\epsilon) \frac{D_s}{k_s^2} \frac{dq}{dl} \quad (5)$$

where  $\rho$  is the true density of the medium ( $\text{kg}/\text{m}^3$ ),  $D_s$  the surface diffusion coefficient ( $\text{m}^2/\text{sec}$ ),  $k_s^2$  the tortuosity of the surface,  $dq/dl$  the concentration gradient of the adsorbed species, and  $q$  the amount of species adsorbed ( $\text{mol}/\text{kg}$ ).

Assuming a linear pressure gradient and integrating the results of Eqn. (5) in an expression for the surface permeability, one obtains

$$F_{0s} = \frac{F_s}{\Delta P} = \frac{\rho(1-\epsilon) D_s}{k_s^2 L} \frac{dq}{dp} \quad (6)$$

where  $\Delta P$  is the pressure difference and  $L$  the thickness of the porous medium. The term  $dq/dP$  is given by the adsorption isotherm. The surface diffusion coefficient can be calculated from Eqn. (6) if the other parameters are known. Equation (6) can be rewritten considering that

$$\rho(1-\epsilon) q = \frac{S_v}{A_0 N_{av}} x_s \quad (7)$$

where  $S_v$  is the surface area ( $\text{m}^2/\text{m}^3$ ),  $A_0$  is the surface of an adsorbed molecule,  $N_{av}$  is Avogadro's number and  $x_s$  is the percentage of occupied surface compared to a monolayer.

$$S_v = \frac{2\epsilon}{\bar{r}} \quad (8)$$

so

$$F_{0s} = \frac{F_s}{\Delta P} = \frac{2\epsilon \mu_s D_s}{\bar{r} A_0 N_{av}} \frac{dx_s}{dP} \quad (\mu_s = 1/k_s^2) \quad (9)$$

Equations (1) and (9) can be added to obtain a more complete picture of flow through porous media. If the mean pore radius of the porous separation layer is taken as the variable, the total equation will be

$$F_0 = C_k \bar{r} + C_p \bar{P} \bar{r}^2 + C_s \bar{r}^{-1} \quad (10)$$

where  $C_k$  is  $F_{0k}/\bar{r}$ ,  $C_p$  is  $F'_{0p}/\bar{r}^2$  and  $C_s$  is  $F_{0s}\bar{r}$  and consequently they are independent of  $\bar{r}$ .

From Eqn. (10) it is clear that the contribution of surface diffusion can be increased and Knudsen diffusion and laminar flow can be increased by pore size reduction.

For a multilayer system the total permeability  $F_0$  can be expressed using a series model

$$F_0 = \left( \sum_i \frac{1}{F_{0,i}} \right)^{-1} \quad (11)$$

where  $F_{0,i}$  is the permeability of layer  $i$  given by Eqn. (1) and takes into account the surface permeability (Eqn. 6 or 9). In a two-layer system consisting of a top (separation) layer on a porous support, the permeability data can be corrected for the support (if  $F_{ok}$  and  $F'_{op}$  of the support are known) by using Eqn. (11).

### *Separation of binary gas mixtures*

Knudsen flow is inversely proportional to the square root of the molecular mass. So in this regime light gases permeate more rapidly than heavy ones. The ideal Knudsen separation factor for binary mixtures equals the square root of the ratio of molecular masses. The presence of surface diffusion influences the ideal separation factor  $\alpha^*$ .

The actual separation factor  $\alpha$  is defined as

$$\alpha = \frac{y}{1-y} \frac{1-x}{x} \quad (12)$$

where  $y$  is the mole fraction of the faster permeating component in the permeate, and  $x$  the mole fraction of this component in the feed.

In general, the actual separation factor is smaller than  $\alpha^*$ . This is due to backdiffusion, non-separative diffusion [25], concentration polarization on feed or permeate side and/or occurrence of Poiseuille flow in larger pores.

Equation (13) gives the effect of backdiffusion on the actual separation factor [16,17]:

$$\alpha = 1 + \frac{(1 - P_r) (\alpha^* - 1)}{1 + P_r(1 - y) (\alpha^* - 1)} \quad (13)$$

where  $P_r$  is the pressure ratio (defined as the permeate pressure divided by the feed pressure).

It is obvious from Eqn. (13) that the permeate pressure directly after the separation layer must be kept low. This conclusion will have important consequences for the way in which multilayer membranes have to be synthesized.

## **Experimental**

Separation layers were prepared using a sol-gel technique. A porous alumina support was dipped in a boehmite ( $\gamma$ -AlOOH) sol [3]. These supports are flat and circular with a 39 mm cross section, 2 mm thickness, 48% porosity, and a narrow pore size distribution around an average pore size of 160 nm. Thin gel layers were obtained by a fast slipcasting process due to the capillary action of the supports. Drying and calcining resulted in crack-free top layers without pinholes if the thickness was between 1 and 5–7  $\mu\text{m}$ . The properties of a type 1 support and of a separation layer, calcined at 450°C, are shown in Table 1.

TABLE 1

Structural data of the  $\gamma$ -alumina separation layer calcined at 450°C and of the support (type 1)

	Pore diameter (slit width) (nm)	Porosity ( $\epsilon$ )	Theoretical density ( $\rho$ ) (kg/m <sup>3</sup> )	BET-surface ( $S_{\text{BET}}$ ) (m <sup>2</sup> /g)	Tortuosity	Thickness ( $\mu\text{m}$ )
Separation layer	2.7	0.52	3700	285	6.5	4
Support	160	0.45	4000	-	2.5	2000

In order to change the surface properties some separation layers were chemically modified. This was performed by a hydrolysis followed by homogeneous precipitation of metal salts from aqueous solutions (ureum method [18]).

Counterdiffusion experiments in which fluxes through the porous layer were measured isothermal and isobaric were performed on relatively thick (0.206 mm) non-supported separation layers. The microstructure of these is the same as for thin supported layers.

The technique of evaluation of the fluxes in counterdiffusion is a variation of the well-known Wicke-Kallenbach method [19]. The complete experimental equipment consists of three major parts: the membrane cell, the flow system and the gas analyser. Flow rates were controlled by mass flow controllers (type Brooks 5850TR), the absolute pressure and pressure difference were measured by linear pressure sensors (type Validyne DP 15), and the gas composition of feed and permeate streams was determined by gas chromatography. The effluent streams were connected to a ten-way switching valve to permit analysis of both streams.

Pore size distributions of the support material were determined with a mercury porosimeter (Carlo Erba, 200 series), and those of the toplayer with a Carlo Erba Sorptomatic (1800 series). Adsorption isotherms were determined using a Cahn 2000 electrobalance.

## Results and discussion

### *Knudsen diffusion*

Permeability measurements with two-layer membranes have been performed with He, H<sub>2</sub>, N<sub>2</sub> and CO<sub>2</sub> as test gases. First the permeability of the supports was measured as a function of the mean pressure, and the constants  $F_{0k}$  and  $F'_{0p}$  were determined. Then a separation layer was prepared on top of the support and the permeability was measured again. The permeability decreased only by 20–40%. This means that only about 30% of the total pressure difference is across the toplayer. A typical example is given in Fig. 1 for N<sub>2</sub> at room temperature. The thickness of the toplayer was 4.0  $\mu\text{m}$ .

The permeabilities can be corrected for the support, using Eqn. (11) (curve

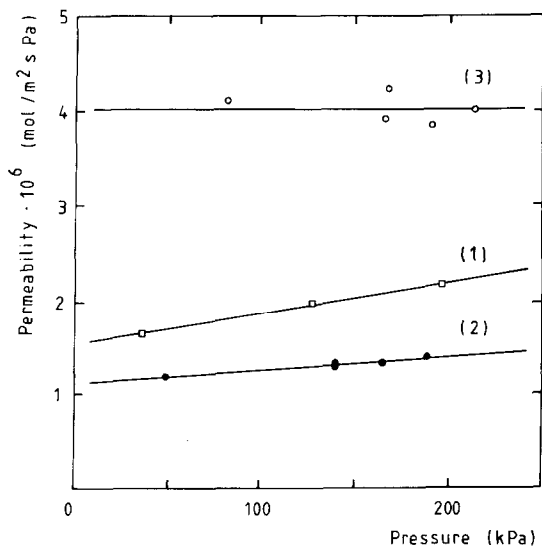


Fig. 1. The nitrogen permeability as a function of pressure of the support (curve 1), the support plus the alumina separation layer (curve 2) and the from curve 1 and curve 2 calculated permeability for the separation (top) layer (curve 3). The thickness of the support is 2 mm, the thickness of the separation (top) layer is 4  $\mu\text{m}$ .

3 in Fig. 1). For all gases the permeabilities through the top layer are independent of the mean pressure within experimental error. This implies that no laminar flow occurs as could be expected in these small pores (3 nm). For the different gases the observed ratios of the permeabilities are in accordance with the square root law of the molecular masses. It can be concluded that for the test gases Knudsen diffusion is the dominant transport mechanism in the top-layer. The only exception is  $\text{CO}_2$ , due to interaction between gas molecules and the pore wall. This will be discussed in the next section.

The observed permeabilities show reasonably good agreement with the permeabilities calculated using Eqn. (2). E.g., Fig. 1 shows an  $\text{N}_2$ -permeability of  $4.0 \times 10^{-6}$  mol/m<sup>2</sup>-sec-Pa for the toplayer only. Results from earlier work indicate an unusual high tortuosity for this material (6.5 [4]), therefore  $\mu_k$  is assumed to be 0.15. Substitution of the properties of the toplayer (Table 1) gives a permeability of  $5.0 \times 10^{-6}$  mol/m<sup>2</sup>-sec-Pa according to Eqn. 2.

Separation measurements with  $\text{H}_2$ - $\text{N}_2$  mixtures have been performed on two-layer membranes. The mole fraction  $\text{H}_2$  in the feed was 0.5. The observed ratios of permeabilities (= separation factor) are given as a function of the pressure ratio in Fig. 2. It can be seen that the measured effective Knudsen factor has a value of about 80% of the ideal Knudsen separation factor ( $\alpha = 2.9$ ,  $\alpha^* = 3.7$ ), if the feed pressure is about 10 times larger than the permeate pressure ( $P_f = 0.09$ ).

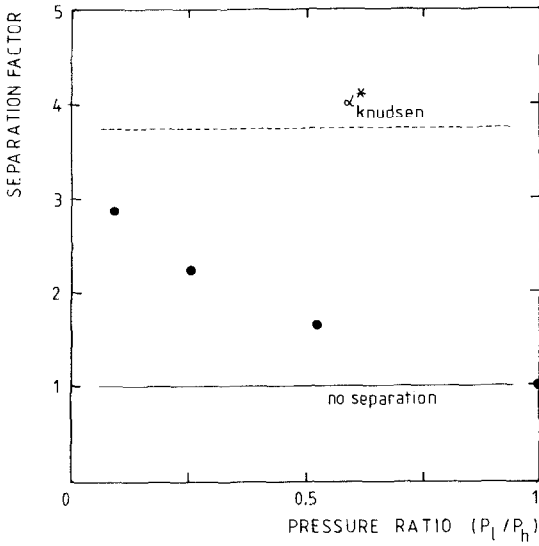


Fig. 2. The separation factor for a hydrogen–nitrogen mixture ( $H_2/N_2=1$ ) as a function of the pressure ratio  $P_1/P_h$  at an average pressure near 100 kPa.

TABLE 2

An example of pressure distributions and separation factors  $\alpha$  of the two-layer alumina membrane system

	Experimental	Calculated
$P_h$ (kPa)	78	
$P_i$ (kPa)		55
$P_1$ (kPa)	7	
$P_r$ (membrane system)	0.09	
$P_r$ (toplayer)	0.70	0.70
$P_r$ (support)		0.13
$\alpha$ (membrane system)	2.9	$2.9 \pm 0.2$
$\alpha_t$ (toplayer)		1.5
$\alpha_s$ (support)		1.9
$\alpha^*$ (Knudsen)		3.74

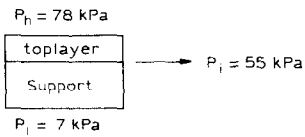


Fig. 3. An example of pressure distribution of a two-layer alumina membrane system.



In Table 2 and Fig. 3 an example of pressure distributions and separation factors of a two-layer membrane system is shown for the case that the pressure on the feed side is 78 kPa ( $P_h$ ) and the pressure on the permeate side is 7 kPa ( $P_l$ ). The  $H_2$  concentration increases from 50% in the feed to 74.5% in the permeate, which gives a separation factor of 2.9 (Table 2). In the following it will be shown that this separation factor can also be calculated.

In the toplayer Knudsen diffusion prevails. The difference between the ideal Knudsen separation factor ( $\alpha^* = 3.7$ ) and the actual separation factor of the toplayer  $\alpha_t$  (Table 2) is caused by backdiffusion (Eqn. 13). The pressure drop across the toplayer is calculated on basis of the known structure and is verified experimentally. It is found to be 30% of the total pressure drop. Consequently, the pressure ratio  $P_r$  (Eqn. 13) across the toplayer is 0.7, resulting in a separation factor between 1.3 and 1.8 (Eqn. 13). For the experimental situation of Table 2, an  $y$  value (mole fraction of hydrogen in permeate) of 0.745 is measured. With this value and a pressure ratio of 0.7 across the separation layer a separation factor for this layer ( $\alpha_t$ , Table 2) of 1.5 is calculated from Eqn. (13).

Obviously this cannot account for the measured value of 2.9. In the support, transport occurs partially by laminar flow and partially by Knudsen diffusion, resulting in a contribution to separation. The pressure ratio across the support is close to zero (Table 2), but the laminary flow causes the separation factors to be lower than the ideal Knudsen factor. Literature data, however, show that at these pressure levels (1 bar or less) and in pores of this size (diameter 160 nm), the separation efficiency can still be significant [16,20]. The pressure at the toplayer/support interface is 55 kPa ( $0.7 \times 78$  kPa, Table 2). Therefore the mean pressure in the support is 31 kPa. The mean pore radius is 80 nm. With these data a separation efficiency, defined as  $(\alpha_s - 1)/(\alpha^* - 1)$ , of 0.35 can be calculated from literature data [16,20] using equations in accordance with those of Present and deBethune [25]. With  $\alpha^* = 3.74$ , this means that  $\alpha_s = 1.9$ .

The combined effect of toplayer and support follows from Eqn. (12) by splitting the  $\alpha$  value for the complete system into  $\alpha_t$  (toplayer) and  $\alpha_s$  (support), considering the permeate of the separation layer as the feed for the support. This operation gives

$$\alpha = \alpha_t \cdot \alpha_s \quad (14)$$

which yields  $\alpha = 1.5 \times 1.9 = 2.9 \pm 0.2$ . This result is in good agreement with the experimental value shown in Table 2 and Fig. 2 (for  $P_r = 0.09$ ). It can be concluded that a less effective Knudsen separation factor of a large-pore system can be increased considerably by a thin layer with ideal Knudsen diffusion properties (in this case 50% increase).

A smaller pressure ratio across the separation layer (obtained by modification techniques and/or larger pore sizes of the substrate) will result in larger  $\alpha$  values or in the same  $\alpha$  values at larger total pressure ratios [24].

### Surface diffusion

As mentioned earlier deviations from the square root law of molecular masses occur if the gas molecules interact with the pore wall. CO<sub>2</sub> adsorption takes place on the alumina top layers. Adsorption isotherms are given in Fig. 4; at 1 bar and 20°C the amount of CO<sub>2</sub> adsorbed is 0.5 mol/kg membrane material. It can be calculated that for this situation the surface concentration amounts 20% of a monolayer coverage ( $S_{\text{BET}} = 285 \text{ m}^2/\text{g}$ ,  $\rho = 3700 \text{ kg/m}^3$ ,  $\epsilon = 0.52$ ).

From the adsorption data at different temperatures the isosteric heat of adsorption can be determined by using the Clausius–Clapeyron equation

$$E_{\text{st}} = -R \left( \frac{\delta \ln P}{\delta (1/T)} \right)_q \quad (15)$$

A value of  $-25 \text{ kJ/mol}$  is calculated (Fig. 4), which is a characteristic value for physisorption or weak chemisorption. It is generally accepted that there is a correlation between the activation energy for surface flow and the heat of adsorption [11–13]. The ratio normally varies between 0.3 and 0.5. From these results it can be expected that part of the adsorbed molecules is mobile on the surface.

In Fig. 5, pure gas permeabilities at room temperature of N<sub>2</sub> and CO<sub>2</sub> through the top layer in a two-layer membrane (corrected for the supports) are compared. Because CO<sub>2</sub> is heavier than N<sub>2</sub>, CO<sub>2</sub> is expected to permeate slower than N<sub>2</sub> if only Knudsen diffusion would occur (Knudsen factor 0.8, dashed line in Fig. 5). The observed permeability for CO<sub>2</sub>, however, is of the same order of magnitude, and even somewhat larger than for N<sub>2</sub>. The difference between calculated and measured CO<sub>2</sub> permeability amounts to  $0.9 \text{ mol/m}^2\text{-sec-Pa}$  for a  $4 \mu\text{m}$  thick layer. This is about 30% of the total permeability, and it is attributed to surface diffusion.

The surface diffusion coefficients can be estimated using Eqn. (6) and the

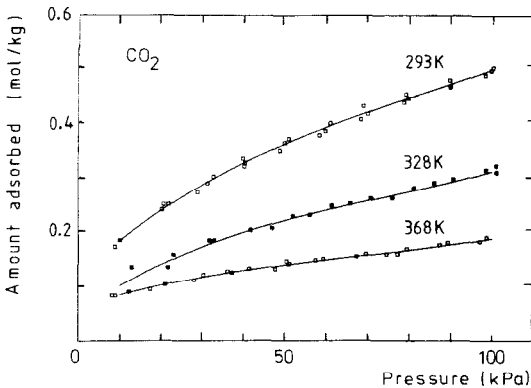


Fig. 4. The CO<sub>2</sub> adsorption ( $q$  in mol/kg) on unmodified  $\gamma$ -alumina membranes as a function of pressure and temperature (in this case  $q = 2.43 x_s \text{ mol/kg}$ ).

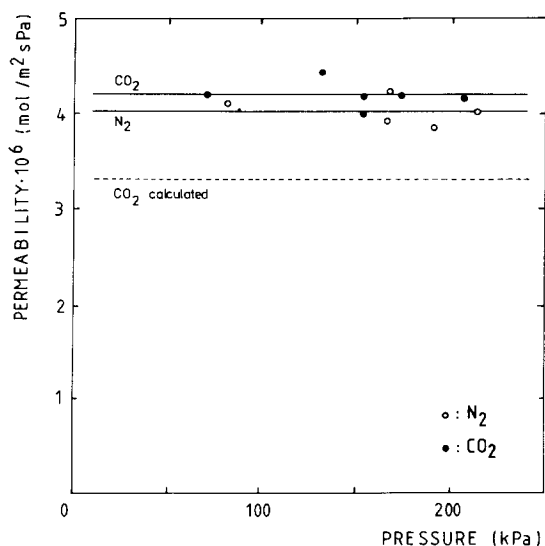


Fig. 5. The permeabilities of CO<sub>2</sub> and N<sub>2</sub> (see Fig. 1) as a function of pressure for the separation layer calculated from permeation data of the composite membrane system. The dashed line is the expected value for CO<sub>2</sub> permeability if only Knudsen diffusion occurs ( $T=293$  K).

results of Fig. 4. The surface tortuosity is assumed to be equal to the tortuosity through the gas phase, which is 6.5. With increasing coverage the surface diffusion coefficient  $D_s$  varies from 2 to  $5 \times 10^{-9}$  m<sup>2</sup>/sec. These coefficients are comparable with diffusion rates in liquids, but are relatively low in comparison with literature data for surface flow [11]. Using the correlation equation of Sladek and Gilliland [12] derived from a large group of substrate materials, a value for  $D_s$  of  $10\text{--}20 \times 10^{-9}$  m<sup>2</sup>/sec is estimated. A similar value is found for diffusion of C<sub>2</sub>H<sub>4</sub> on activated alumina [13] also with an isosteric heat of adsorption of nearly  $-25$  kJ/mol. It is not clear why this difference occurs.

Counterdiffusion measurements have been performed at 100 kPa with N<sub>2</sub> and CO<sub>2</sub> on thick non-supported alumina top layers (thickness  $206 \pm 2$  μm). Results are presented in Fig. 6. The dashed line is the theoretical Knudsen separation factor. At 293 K the ratio of the permeabilities is the same as for the permeation experiments at the same temperature (Fig. 5). At higher temperatures the separation factor decreases to the Knudsen factor. This is probably due to a decreasing surface concentration, resulting in a less important surface transport contribution. At lower temperatures the CO<sub>2</sub> flow becomes significantly larger than the N<sub>2</sub> flow, which implies that surface diffusion is becoming more important. At  $-35^\circ\text{C}$  the separation factor is around 2. This means that the CO<sub>2</sub> flow along the surface is larger than through the gas phase. Probably the same result can be obtained at higher temperatures provided that

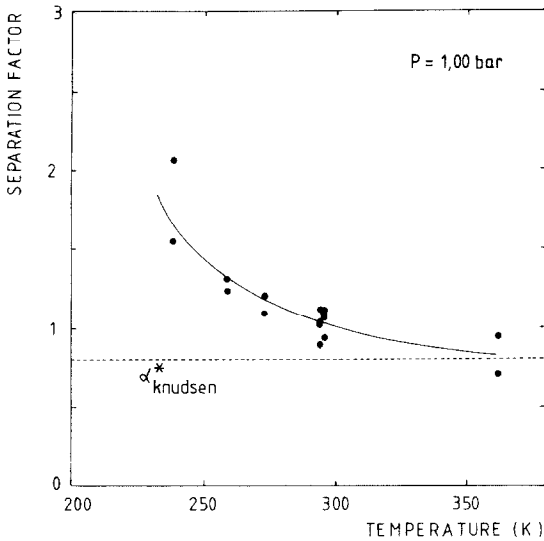


Fig. 6. The separation factor for  $\text{CO}_2\text{-N}_2$  estimated from counterdiffusion experiments as a function of temperature at an average pressure of 100 kPa.

the pressure is increased to a level where the surface coverage is the same as at  $-35^\circ\text{C}$ .

These measurements are performed in the current program. Indications are obtained that probably multilayer adsorption and/or capillary condensation takes place, resulting in higher separation factors.

The interaction between pore wall and  $\text{CO}_2$  can be improved by changing the type and amount of acid and/or basic sites on the inner surface of the alumina top layers. This can be done by chemical modification of the pore walls with other materials.

Modification can also give rise to pore size reduction, resulting in an increasing importance of surface diffusion as a transport mechanism. This can be easily seen from Eqn. (10).

By modification of the pores with MgO,  $\text{CO}_2$  adsorption is enhanced. At 293 K the amount of adsorbed  $\text{CO}_2$  increased by 50% compared to non-modified layers under the same experimental conditions. No decrease of the average pore size could be detected, however, with  $\text{N}_2$  adsorption/desorption measurements. This does not exclude the presence of local pore size reduction (local constrictions), which is under investigation now. The presence of MgO also improves both the chemical and thermal stability of the separation layer (spinel formation).

Preliminary counterdiffusion measurements on MgO-modified non-supported layers at 293 K show a light decrease in separation factor, in comparison to measurements on non-modified material. This may be due to a decrease in

surface diffusion coefficient by an increased activation energy for migration. In further research attention will be paid to this point.

On silver, several types of adsorbed oxygen species are present. Probably one of them is mobile at temperatures between 200 and 300°C [21]. Modifications of separation layers with silver have been performed in order to achieve oxygen surface diffusion. Results concerning this subject will be presented in a following paper.

## Conclusions

Membranes have been prepared consisting of a support with large pores and a thin, ultrafine porous  $\gamma$ -alumina top layer. These membranes are suitable for separations with a Knudsen diffusion mechanism and can be applied at temperatures up to 800°C. The separation factors approach the theoretical Knudsen values and a further improvement is expected when multilayer supports are applied.

Transport of non-adsorbing gases through these two layer composites can be successfully described by taking into account Knudsen and Poiseuille flow in the supports, and using a series resistance model. The dominant transport mechanism in the top layer is Knudsen diffusion.

Surface diffusion of  $\text{CO}_2$  in the  $\gamma$ -alumina toplayers is found. The surface flow rate depends on surface concentration and surface diffusion coefficient and thus on temperature and pressure. It is of the same order of magnitude as the flow rate through the gas phase. At room temperature the surface diffusion coefficient increases from 2 to  $5 \times 10^{-9}$  m<sup>2</sup>/sec with increasing coverage (till 25% of a monolayer). The adsorption energy of  $\text{CO}_2$  is found to be  $-25$  kJ/mol at temperatures between 20 and 100°C. Surface diffusion rates and adsorption energy can be changed by modification of the  $\gamma$ -alumina, e.g. by  $\text{MgO}$ .

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## List of symbols

$A_0$	surface area of an adsorbed molecule	(m <sup>2</sup> )
$C_k$	$F_{0k}/\bar{r}$	(mol/m <sup>3</sup> -sec-Pa)
$C_p$	$F'_{0p}/\bar{r}^2$	(mol/m <sup>4</sup> -sec-Pa)
$C_s$	$F_{0s} \cdot \bar{r}$	(mol/m-sec-Pa)
$D_s$	surface diffusion coefficient	(m <sup>2</sup> /sec)

$d$	pore size (slit width)	(m)
$E_{st}$	isosteric heat of adsorption	(kJ/mol)
$F_0$	total permeability of gas	(mol/m <sup>2</sup> -sec-Pa)
$F_{0k}$	permeability due to Knudsen diffusion	(mol/m <sup>2</sup> -sec-Pa)
$F_{0p}$	permeability divided by pressure due to laminar flow	(mol/m <sup>2</sup> -sec-Pa)
$F_{0s}$	permeability due to surface diffusion	(mol/m <sup>2</sup> -sec-Pa)
$F_s$	surface permeability	(mol/m <sup>2</sup> -sec)
$(k_g)^2$	tortuosity factor for gas permeation	(-)
$(k_s)^2$	tortuosity factor for surface diffusion	(-)
$L$	thickness of the membrane system	(m)
$M$	molecular mass of gas molecules	(kg/mol)
$N_{AV}$	Avogadro's number	(-)
$\bar{P}$	mean pressure	(kPa)
$\Delta P$	pressure difference across the membrane system	(kPa)
$P_r$	pressure ratio (permeate pressure $P_1$ divided by feed pressure $P_h$ )	(-)
$q$	gas amount adsorbed	(mol/kg)
$R$	gas constant per mole	(8.317 J/mol-K)
$\bar{r}$	modal pore radius of the solid medium	(m)
$S_{BET}$	BET surface of the membrane	(m <sup>2</sup> /kg)
$S_v$	surface area of solid system per unit of volume	(m <sup>2</sup> /m <sup>3</sup> )
$T$	absolute temperature	(K)
$\bar{v}$	average molecular velocity	(m/sec)
$x_s$	fraction of surface covered by adsorbed molecules	(-)
$x$	mole fraction of faster permeating component in feed	(-)
$y$	mole fraction of faster permeating component in permeate	(-)

### Greek symbols

$\alpha$	actual separation factor	(-)
$\alpha^*$	ideal (Knudsen) separation factor	(-)
$\alpha_t$	separation factor of the toplayer	(-)
$\alpha_s$	separation factor of support	(-)
$\epsilon$	porosity of the membrane system	(-)
$\eta$	viscosity of the gas (mixture)	(N/m <sup>2</sup> -sec)
$\rho$	true density of the solid medium	(kg/m <sup>3</sup> )
$\mu_k$	shape factor for Knudsen diffusion	(-)
$\mu_p$	shape factor for laminar flow	(-)

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