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Surface Selective Approach to Separation of Propylene from Propane

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ABSTRACT

Membranes with high separation factors and permeation values are important for the success of high temperature membrane reactors. Microporous membranes with molecular sieving ability are potential candidates. In situations were the molecular size of the gases to be separated are very near, however, such size exclusion is not possible. The present paper describes a new technique to modify such microporous membranes by making use of special materials with adsorption selectivity to the gases in question. More importantly, the paper points out that the same adsorption selectivity does not always guarantee gas separation. The total adsorbed volume and the number of available sites are also influential in determining the real separation factors. By using the said technique, a membrane system is developed and tested for use in separating propylene from propane with commendable separation and permeation values.

INTRODUCTION

The separation of hydrocarbons by membrane methods is receiving increased attention because of the possibilities to avoid complex and space-occupying distillation columns. A gas permeation rate of 40 $m^3/m^2\cdot bar\cdot day$ is considered as the optimum value needed to enable membrane processes to be used for large scale industrial applications. The separation of saturated and unsaturated hydrocarbons like propane from propylene is supposed to be one of the most difficult tasks. The rather close molecular sizes of these gases makes it impossible to separate them by molecular sieving effects by, for instance, zeolite membranes (1).

Separation can generally be achieved if the concentration gradient across the micropore can be kept different for the individual gases, even when their diffusivities are the same. Because of the difference in chemical potentials, separation is realized. This requires membranes which have adsorption selectivity for these molecules. However, it is shown in this article that adsorption selectivity alone does not guarantee separation.

If the pore size of a membrane is comparable to the molecular size of a gas, the surface of the membrane and the pore are very important in determining the separation (2, 3). Because of dynamic limitations, direct molecular entry into the pore from the gas phase becomes difficult, making the surface mobility and concentration on the surface of increasing importance. The Barrer interface properties become rate determining (3) when the diameter of the pore approaches the size of the molecule.

Sol–gel synthesized silica membranes are well known for their microporous nature. These are shown to have very high molecular sieving properties when tested with combinations of large and small molecules (4) owing to their rather narrow pore size and distribution. However, these small pore-sized membranes show only a limited adsorption capacity for hydrocarbons. Sol–gel-made alumina membranes, on the other hand, are mesoporous and show reasonably high adsorption capacities. Unfortunately, the same mesoporous nature of these membranes keeps permeation in the Knudsen regime, limiting the separation factor between propane and propylene close to the ideal Knudsen factor of 1.02.

In other words, the absence of microporous membranes with reasonably high adsorption capacities to large hydrocarbon molecules presently limits the separation of nearly equal-sized molecules outside the possibilities of porous membranes. Better synthesis techniques are yet to be found to make microporous membranes out of alumina-like materials which show a high adsorption capacity to hydrocarbons.

The present paper treats the application of a simple but novel method of increasing adsorption capacity on the microporous layer and hence increasing the concentration gradient across the membrane. The simultaneous changeover from steady-state sorption controlled separation to an equilibrium concentration limited one increases the separation factor between propane and propylene to practicable values.

The potential application of the present concept is significant for gas separation by surface catalysis for membrane reactors.

EXPERIMENTAL

A silica sol was prepared by the hydrolysis of tetraethyl ortho-silicate (TEOS) in the presence of HNO_3 catalyst. The molar ratio of TEOS : water:ethanol:HNO_3 used was 1:6.4:3.8:0.085, and the synthesis was carried out at 65°C with 3 hours of refluxing. Alpha-alumina supports with a gamma-alumina intermediate layer were then dip coated with these sols. These membranes were dried and then calcined at 400°C. The details of this membrane synthesis and drying and the calcining conditions are reported elsewhere (4).

An alumina sol was made by standard techniques reported elsewhere (4). This standard sol was concentrated by evaporation and then redispersed in ethanol to a concentration of 0.125 mol/L. This gamma-alumina dip solution was used for making the alumina top-layer for the silica microporous membrane. Drying and calcining procedures were kept the same as those for the silica microporous layer.

Sorption studies were performed on unsupported membranes (gels) with Carlo Erba Sorptomatic 1900 equipment attached to a micro vacuum pump. Nitrogen adsorption studies at the liquid nitrogen temperature were used to characterize the material. Propylene and propane adsorption on silica and alumina calcined gels were carried out in the same setup. The total adsorbed volume, Henry slopes (K), and isosteric heat of adsorption (q_{st}) were calculated from adsorption isotherms of propylene (Pl) and propane (Pa) at different temperatures using standard expressions (5, 6).

Supported membranes of silica (Si) and silica with an alumina top-layer (Al–Si) were tested for helium (He) and Pl single gas permeations in a pressure-controlled setup equipped with analog flow readouts and programmed heating. An extensive description of the equipment and experimental procedures is given in Ref. 1. The apparent activation energy for permeation was calculated from an Arrhenius plot (5).

Multicomponent separation experiments were done with a Wicke–Kallenbach (1) setup attached to a gas chromatograph for permeate, feed, and retentate analysis. Equimolar mixtures of Pl and Pa were used with an argon sweep at 1 bar and 15 mL/min flow. Separation factors were calculated by taking the ratio of permeate to feed concentration of the individual components.

RESULTS

Calcined silica membrane materials (gels) showed type 1 (microporous) nitrogen adsorption isotherms with a total adsorbed volume corresponding to 20% porosity. Horvath–Kawazoe analysis performed on the isotherm revealed a mean pore size of 5.5 Å. The helium permeation measurements shown in Fig. 1 (Si) support this, showing microporous diffusion with an activation energy of 9.3 ± 0.4 kJ/mol.

However, calcined alumina gels showed only type 4 isotherms (mesoporous) with a total porosity of 50%. BET analysis revealed a pore size

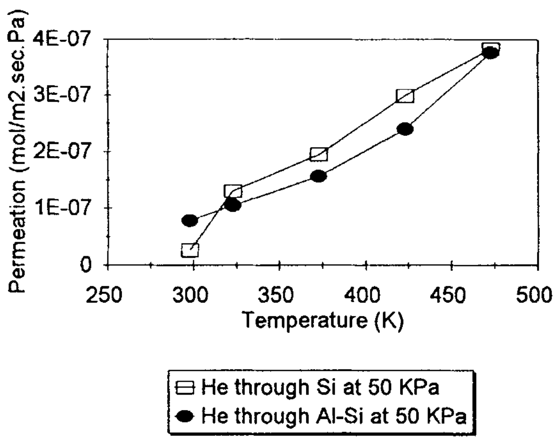

FIG. 1 Helium permeation through microporous Si and Al–Si membranes.

of 36 Å. Supported membranes made from this sol showed a Knudsen-type permeation behavior for helium as in the case of a standard gamma-alumina intermediate layer (4). As expected, the coating of this alumina sol over the microporous silica layer didn't change the gas transport characteristics of the silica layer (Fig. 1). The apparent activation energy for helium diffusion was calculated as 10.2 ± 0.7 kJ/mol for this silica with an alumina top-layer membrane system (Al–Si).

However, in the case of adsorbing gases wherein the total permeation also makes a sorption contribution (3), the results were seemingly different for the two membranes. The propylene permeation results shown in Fig. 2 reveal this. Al–Si membranes seem to have around 4 times the permeation for propylene. By comparing Pl and He permeations, it seems that at low temperatures Al–Si membranes pass more propylene than helium. Si membranes, on the other hand, show lower propylene permeation throughout.

Figure 2 also shows the amount of adsorption of Pl at 50 kPa over silica and alumina unsupported membrane materials at room temperature. Apparently alumina adsorbs more gas molecules per unit weight of the sample. However, the increase in Pl permeation through Al–Si membranes is more pronounced than this sorption increase.

Table 1 shows the calculated q_{st} of Pl and Pa over silica and alumina at different surface coverages. q_{st} of Pl over silica clearly drops as the coverage increases. Other effects are almost negligible.

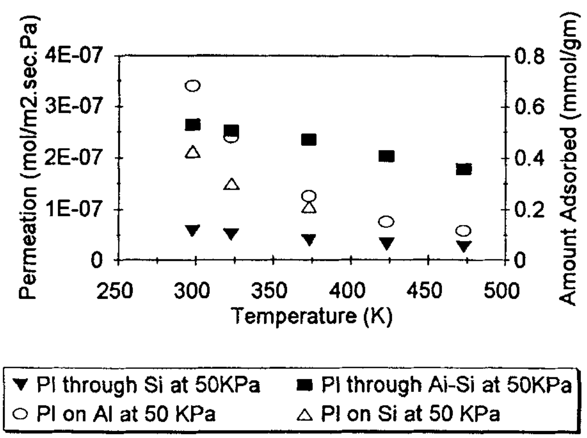

FIG. 2 Adsorption on the membrane top-layer material and permeation through the propylene membrane.

The results of multicomponent separation measurements through the membranes and calculated Henry (*K*) ratios (Pl to Pa) from sorption isotherms on membrane materials are shown in Fig. 3. Room temperature separation results are not reported because of large scattering owing to pore blockage. Separation factors of the multicomponent mixtures through the silica membrane are very low, mostly in the range of 1. However, membranes with an alumina top-layer showed reasonably good separation factors (1.5 to 2) throughout the temperature range investigated. The initial Henry slope ratios (Henry slope of Pl to that of Pa) of Al shown in Fig. 3 represent the multicomponent separation (Pl/Pa) results for Al–Si

TABLE 1
Isosteric Heat of Adsorption of Propylene and Propane over Alumina and Silica at Different Levels of Sorption

	Isosteric heat of adsorption (q_{st}) in kJ/mol (± 1) at different sorption levels (mmol/g)				
Membrane–gas	0.1	0.2	0.3	0.4	0.5
Al–Pl	18.8	16.4			15.7
Al–Pa	15	15.5	16.6		
Si–Pl	19.7	17.2			11.9
Si–Pa	7	6.6		8.5	

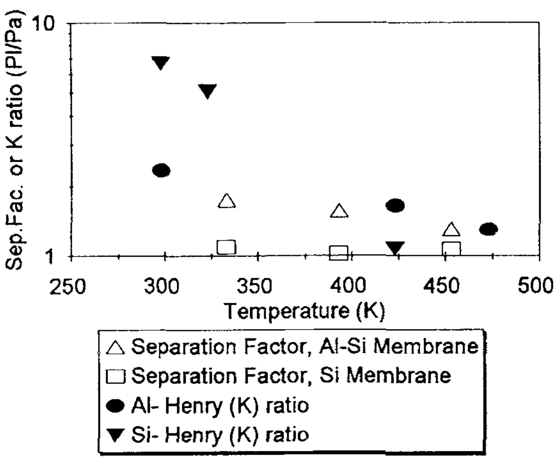

FIG. 3 Measured separation factors of Pl/Pa through the membranes and calculated Henry ratios from the adsorption isotherms.

membranes throughout the temperature range investigated. However, this is true for Si membranes only at high temperatures. The very high Henry ratios between Pl and Pa seen at low temperatures for silica are not realized during multicomponent separation (Pl/Pa) experiments.

DISCUSSION

The single gas helium permeation results presented in Fig. 1 show that both membranes are microporous in nature. The similarity of apparent activation energies clearly shows that no significant meso/macro defects were introduced by the dipping of alumina over microporous silica. Helium permeations of the two membranes are nearly all through the temperature range investigated. This is not unexpected because the resistance offered by the mesoporous alumina layer is very small compared to the microporous layer and hence the drop in gas-phase transport is rather small. Micropore blockage or silica layer thinning effects by the new top layer are either counterbalancing or insignificant.

The effect of sorption on permeation is apparent from the permeation diagrams (Fig. 2) of propylene through the membranes. Both membranes show a decrease in permeation with temperature for this adsorbing molecule. Apparent activation energies cannot be calculated because of the decrease in slope, which itself shows that the isosteric heat of adsorption becomes dominant in the overall permeation. High values of q_{st} will strongly decrease the concentration of the molecules in the micropore at high temperature, hence decrease the permeation (4, 7).

The q_{st}s of both materials were calculated for PI (Table 1). As is shown, the q_{st} of PI over alumina remains almost constant even at a coverage of 0.5 mmol/g. This shows the large adsorption capacity of the material. However, silica gave a totally different picture, showing a decrease in q_{st} with increasing coverage. However, Pa with nearly the same molecular size showed constant isosteric heats on silica and alumina independent of coverage (Table 1). The difference in q_{st} between Pl and Pa in silica is significant. On first examination this points to a possible higher separation of Pl from Pa through silica membranes.

Initial Henry slope ratios (*K* ratios) of the gases (Fig. 3) over the membrane materials also show the same trend (6). However, multicomponent separation results shown in the same figure gave a different picture. It is shown that the Al–Si membrane gave appreciable separation factors for Pl/Pa mixtures. The reported separation factors (for instance, 1.75 at 60°C and at a single gas permeation of around 40 $m^3/m^2 \cdot day \cdot bar$) are among the highest available for this gas combination, and hence show the importance of the new concept. These separation factors seem to be correlated to the initial Henry slope ratios. However, in the case of silica, the separation factors always remain close to 1. High temperature Henry ratios are almost identical to the multicomponent separation factors. However, at low temperatures a strong deviation is apparent.

The results mentioned above evidently indicate the peculiarity in Pl sorption over these silica membranes under steady-state conditions. Only a small number of active sites are available under this condition for the molecules to diffuse. Very low and stable q_{st} values of Pa over silica support this. The low propylene permeation and low separation between Pl and Pa can therefore be justified.

Apparently alumina has a larger number of homogeneous adsorption sites for both the gases and hence the separation factor is well represented by the Henry ratio. At reasonably high adsorption capacities the membrane surface can act as a reservoir of surface-adsorbed molecules. This means that diffusion through the micropore is slower than enrichment of the surface, keeping the separation adsorption equilibrium concentration-dependent (8). This shows the importance of having a large number of uniform adsorption sites along with sorption selectivity in order to realize separation.

CONCLUSION

1. Permeation of adsorbing molecules through microporous membranes is shown to be sorption controlled.

2. Alumina-coated silica microporous membranes show appreciable separation factors between Pl and Pa over a wide range of temperatures.
3. Having a large number of uniform adsorption sites is shown to be an important parameter along with sorption selectivity in order to realize gas separation.

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