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PERMEATION OF ETHYLBENZENE AND HYDROGEN THROUGH UNTREATED AND CATALYTICALLY-TREATED ALUMINA MEMBRANES

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ABSTRACT

Experiments were conducted to measure the transport rates of ethylbenzene and hydrogen through an alumina inorganic membrane in a tubular geometry. The effective diffusivity was estimated from a membrane tube model and interpreted via a four-region picture of the membrane structure. Knudsen diffusion through the 40 Å narrow membrane pores appeared to control the overall separation. The membrane with catalytic treatment yielded effective diffusivities two orders of magnitude lower than the untreated membrane. Ethylbenzene and hydrogen diffuse independently of one another in both treated and untreated membranes.

INTRODUCTION AND BACKGROUND

The use of inorganic membranes as both separators and reactors in a single unit operation is of great interest, due to their advantages such as thermal and chemical stabilities, well defined pore size and stable tubular geometry. In particular, their use in simultaneous reaction/separation systems is capable of increasing yield due to their ability to shift equilibrium by preferential removal of products. The basis for preferential removal is the difference in transport rates of the species in the system. The present study examines the catalytic dehydrogenation of ethylbenzene to styrene and hydrogen. In order to design and evaluate membrane reactor performance, information on basic transport rates is needed.

There have been a number of analyses of the phenomena of diffusion and flow in porous media or membranes. Asaeda and Du (1) classified the separation mechanisms of gases by porous solid membranes into four types, as Knudsen diffusion, surface diffusion, capillary condensation with liquid flow and molecular sieving. They used a ceramic membrane to separate mixtures of water and alcohol in the gaseous phase by the last two mechanisms. Kameyama et al. (2) showed the possibility of using porous alumina membranes to selectively remove the hydrogen produced in the decomposition of hydrogen sulfide. Allawi and Gunn (3) reported an experimental study of simultaneous flow and binary diffusion through a plate comprised of four porous catalyst substrates for gases of molecular weights from 2 to 44.

Aris and Cussler (4) developed the theory of composite membranes, with one "active" layer whose permeability varies with solute concentration. The theory was developed based on a two layer polypropylene membrane plane. In 1988, Mohan and Govind (5) reviewed existing research in the application of combined reactive/separation processes using membranes. Sidhoum et al. (6) performed an experimental study on gas permeation through cellulose acetate hollow fibers. Haraya et al. (7) examined gas permeation and separation by an asymmetric polyimide hollow-fiber membrane and Shindo et al. (8) gave a theoretical analysis of multicomponent gas separation by means of a membrane with perfect mixing.

Most previous research has been performed on porous Vycor glass membranes or palladium alloy membranes, and the geometry of the membrane was planar. Research on cylindrical alumina membranes has been limited. Although the transport properties of the species in catalytic reaction processes with membranes are very important, there has been little reported in the literature on the diffusivities of species in gaseous reactive systems.

The objectives of this transport study are to investigate the transport properties of cylindrical alumina membranes at high temperatures for ethylbenzene/hydrogen/helium gas systems, and to investigate the effect of catalyst impregnation on the transport properties of the modified membranes.

MATHEMATICAL MODEL OF MEMBRANE TUBE DIFFUSION

A two-dimensional model of diffusion in a ceramic membrane tube was derived, based on the schematic shown in Fig. 1. Assume total flowrates (Q) unchanged by transport of diffusing species, and negligible axial diffusion in both membrane and flow regions. Also neglect radial gradients within the tube and shell regions.

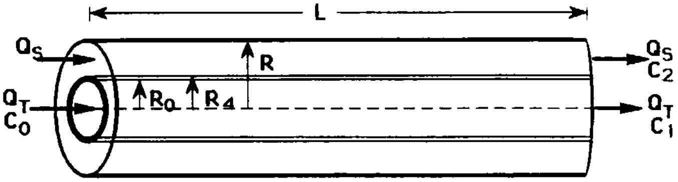

Figure 1. Schematic of the shell-and-tube reactor

For center tube:

$$\left(\frac{Q_T}{\pi R_0^2}\right)\frac{dC_T}{dZ} + \frac{2}{R_0}N_{Ar}\Big|_{R_0} = 0 \qquad (1)$$

$$C_T(0) = C_0$$

For shell side:

$$\left(\frac{Q_s}{\pi R_4{}^2}\right)\frac{dC_s}{dZ} - \frac{2}{R_4} N_{Ar}\bigg|_{R_4} = 0 \tag{2}$$

$$C_s(0) = 0$$

Ignoring the internal structure of the membrane, and representing all transport processes by an effective diffusivity D_{eff} based on total cross-sectional area of membrane, a material balance in the radial direction gives

$$r\,N_{Ar} = \frac{D_{eff}}{\ln(R_4/R_0)}(C_T - C_s) = \text{const.} \tag{3}$$

Substitution of (3) into the tube and shell equations (1) and (2) gives

$$\frac{dC_T}{dZ} + \frac{2\pi}{Q_T}\frac{D_{eff}}{\ln(R_4/R_0)}(C_T - C_s) = 0 \tag{4}$$

$$\frac{dC_s}{dZ} - \frac{2\pi}{Q_s}\frac{D_{eff}}{\ln(R_4/R_0)}(C_T - C_s) = 0 \tag{5}$$

Subtract (5) from (4) to get

$$\frac{d}{dZ}(C_T - C_s) + \frac{2\pi D_{eff}}{\ln(R_4/R_0)}\left(\frac{1}{Q_T} + \frac{1}{Q_s}\right)(C_T - C_s) = 0 \quad \text{---}(6)$$

with initial condition

$$Z = 0,\ C_T - C_s = C_0 \tag{7}$$

The solution to equations (6) and (7) is

$$\ln\frac{C_0}{C_T - C_s} = D_{eff}\frac{2\pi}{\ln(R_4/R_0)}\left(\frac{1}{Q_T} + \frac{1}{Q_s}\right)Z \tag{8}$$

Use of this expression at Z = L, together with measured values of C_T, C_s, C_0, Q_T and Q_s, yields estimates of D_{eff}.

EXPERIMENTAL METHOD

A schematic diagram of the apparatus used for the gas transport study is given in Fig. 2. The diffusion and flow experiments were carried out in a modified diffusion cell using an exterior shell of 316 stainless steel tube containing a centered ceramic membrane tube. The untreated ceramic membrane tubes, 0.670 cm inside diameter, and 1.024 cm outside diameter, were supplied by Alcoa Separations Technology Division. They were made of alumina with a total wall thickness of 0.177 cm. The membrane medium consisted of a thin microporous membrane layer with mean pore size of 40Å and three layers of supporting substrates. The membrane components were fabricated from a transitional alumina, except for the large-pore substrate which was made of alpha-alumina. Two membrane tube lengths of 45.8 cm and 5.0 cm were used.

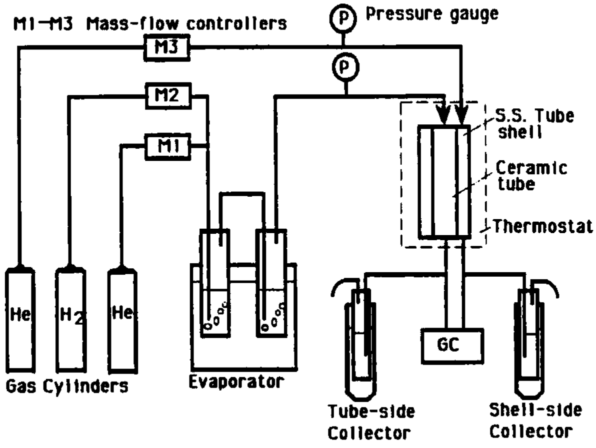

Figure 2. Experimental Apparatus

A certain concentration of saturated vapor of ethylbenzene, generated by flowing helium as a carrier gas through an evaporator, was fed inside the center membrane tube. High-purity hydrogen gas from a cylinder could also be mixed with a helium carrier gas and fed inside the centre membrane tube. Also, a helium purge gas was flowed co-current on the shell side to remove the species diffusing through the membrane. The diffusion cell was set in a constant-temperature oven during each experiment. All the experiments were carried out at atmospheric pressure. The inlet flow rates of the two high-purity gases He and H_2 were controlled and measured by electronic mass controllers on each side of the diffusion cell. The amount of ethylbenzene that diffused through the membrane tube was determined by collecting both tube and shell side effluent once steady state had been reached. The extent of hydrogen diffusion through the membrane tube could be determined by analysing the hydrogen concentration in the effluent by means of a gas chromatograph equipped with a constant volume gas sampling port.

The diffusion experiments were performed with both an untreated ceramic membrane tube and a catalytically-treated ceramic membrane tube. The experiments were carried out at temperatures of 100°C, 200°C and 300°C with helium-ethylbenzene, helium-hydrogen, and helium-ethylbenzene-hydrogen mixtures. The catalytically-treated membrane tubes were either treated by the incipient wetness technique alone with iron, potassium, aluminium and copper nitrate solutions or by incipient wetness followed by further deposition on the membrane surface with a commercial nominal iron oxide catalyst paste.

Experiments with a ceramic tube without the microporous thin membrane layer were also carried out for ethylbenzene, in order to test the transport resistance within the support alone. Unfortunately the experimental data showed that the rate of ethylbenzene transport was too high to be measured in this experimental configuration.

RESULTS AND DISCUSSION

In Table 1 are shown some observed effective diffusivities of ethylbenzene in the untreated membrane tube obtained at various temperatures for the ethylbenzene-helium or ethylbenzene-hydrogen-helium gaseous systems. All the diffusivities are in the range of 0.02 - 0.08 [cm^2/s], and increase as the temperature increases.

Table 1. D_{eff} for ethylbenzene, 5 cm. uncoated tube

T [°C]	D_{eff} [cm^2/s]
100.0	2.46×10^{-2}
200.0	4.25×10^{-2}
300.0	6.75×10^{-2}
100.0*	2.79×10^{-2}
200.0*	4.86×10^{-2}
300.0*	7.46×10^{-2}

* Mixtures of H_2 and ethylbenzene

The results indicate that the diffusivities obtained in the experiments performed with a mixture of H_2, helium and ethylbenzene are very close to those from the experiments performed with only ethylbenzene and helium. In other words, the introduction of the small hydrogen molecules does not strongly influence the diffusion of the larger ethylbenzene molecules through the membrane. The diffusional activation energy of ethylbenzene is approximately 7-8 KJ/mol as shown in the upper curve of Fig. 3.

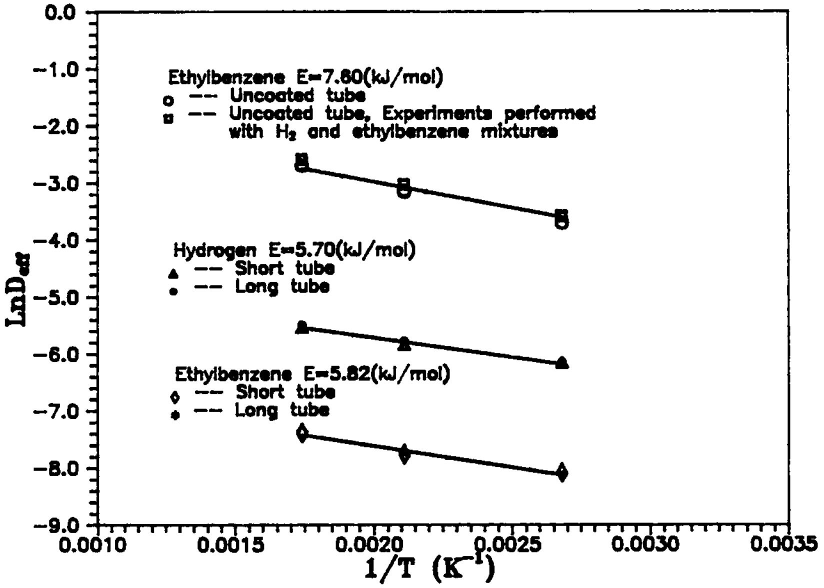

Figure 3. Diffusional Activation Energy of ET and H_2 in Ceramic Membrane Tube

The untreated membrane structure consists of four layers. Assuming no convective flow in any of the layers, the overall diffusion resistance is given by a simple addition of resistances:

$$\frac{1}{D_{eff}} = \sum_{i=1}^{4} \frac{\ln(R_i/R_{i-1})}{\ln(R_4/R_0)} \frac{1}{D_i} \tag{9}$$

For each layer region i,

$$D_i = D_{sp,i}\ (\theta_i/\tau_i) \tag{10}$$

where the straight pore diffusivity D_{sp} is a combination of molecular diffusivity D_{AB} and Knudsen diffusivity D_K:

$$1/D_{sp,i} = 1/D_{AB,i} + 1/D_{K,i} \tag{11}$$

So there are potentially four porosities and four tortuosities. Assume that in the untreated tube all θ_i are equal (to θ) and all τ_i are equal (to τ): the mean tortuousity is then found from

$$\tau = \frac{\theta}{D_{eff}} \left[\sum_{i=1}^{4} \frac{\ln(R_i/R_{i-1})}{\ln(R_4/R_0)} \left(\frac{1}{D_{AB,i}} + \frac{1}{D_{K,i}} \right) \right]^{-1} \tag{12}$$

Calculations show that inside the thin membrane layer (40Å pore size), the straight pore diffusivity is predominantly Knudsen diffusion D_K; in the outer support layer (125,000Å pore size), molecular diffusion D_{AB} is the main diffusion mechanism. As a consequence, equation (9) predicts that the largest contribution to the diffusional resistance comes from the thick large-pore support. Experiments then give τ of about 3-6. As it was not possible to measure the resistance of the support alone in a separate experiment, as noted above, it cannot be the dominant resistance. It is possible that pressure-driven bulk flow is the main transport mechanism in the support region, due to the large pore size and the possibility that a small pressure gradient existed in the experimental set-up. Neglecting the resistance in the large pores would give a tortuousity in the range 12-20 which is somewhat high but not unreasonable.

Table 2. D_{eff} for ethylbenzene and H_2, coated tube

Tube length, Catalyst Impregnation	T [°C]	D_{eff} [cm^2/s] Ethylbenzene ($\times 10^{-4}$)	D_{eff} [cm^2/s] Hydrogen ($\times 10^{-3}$)	$\frac{(D_{eff})_{HY}}{(D_{eff})_{EB}}$
45.8 cm, Incipient wetness	100.0	3.38	1.86	5.63
	200.0	4.49	2.60	5.80
	300.0	5.90	3.61	6.12
	100.0*	3.23	2.13	6.59
	200.0*	4.54	3.09	6.82
	300.0*	5.92	4.09	6.91
45.8 cm, Incipient wetness and deposition	100.0	2.97	2.29	7.72
	200.0	4.36	3.14	7.20
	300.0	5.71	4.04	7.07
	100.0*	3.20	2.43	7.58
	200.0*	4.49	3.48	7.74
	300.0*	6.02	4.50	7.48
5.0 cm, Incipient wetness	100.0	3.07	2.00	6.69
	200.0	4.43	2.79	6.31
	300.0	6.02	3.84	6.39
5.0 cm, Incipient wetness and deposition	100.0	3.09	2.10	6.80
	200.0	4.35	2.89	6.34
	300.0	6.04	3.92	6.50

* Mixtures of H_2 and ethylbenzene

The diffusivities shown in Table 2 were obtained from the experiments with catalytically-treated tubes, of two different lengths, at various temperatures for the ethylbenzene, hydrogen or ethylbenzene-hydrogen mixture systems. The effective diffusivities of ethylbenzene were 3.0 - 6.0 x 10^{-4} [cm^2/s] and of hydrogen about 2.0 - 4.5 x 10^{-3} [cm^2/s]. For both species the diffusivities increase with increasing temperature. Also, these two species do not influence each other even in the treated tubes. The two different methods of catalyst impregnation gave values of the species diffusivity through the membrane that were essentially the same. The treated tubes, however, gave two orders of magnitude lower diffusivities than the untreated tubes. The diffusional activation energy of ethylbenzene in these catalytically-treated tubes is slightly lower than that obtained from the untreated tubes as shown in Fig. 3. The diffusional activation energy of hydrogen is about 5-6 KJ/mol.

After the membrane tube was impregnated with catalyst, the catalyst species may well have accumulated inside each layer, thus blocking some pores or reducing their pore size. This may explain the observed increase in diffusional resistance following catalytic treatment.

The ratio of ethylbenzene effective diffusivity to hydrogen effective diffusivity is in the range 6-8 (see Table 2). This result agrees well with the theoretically-predicted ratio of Knudsen diffusivities of 7.3, indicating that the expected preferential removal of hydrogen will occur.

CONCLUSIONS

Diffusion experiments for ethylbenzene/helium, hydrogen/helium and ethylbenzene/hydrogen/helium gas systems were performed with a thin microporous ceramic membrane supported on coarse porous substrate tubes to obtain the following results:

1) The diffusion in the coated membranes appears to be of Knudsen type.
2) Impregnation of the catalyst by the incipient wetness method lowers the diffusivities of both hydrogen and ethylbenzene in helium. This may be a result of pore blockage.
3) The diffusivity of ethylbenzene in the membrane is not changed when a layer of the commercial catalyst is deposited on a membrane previously treated by incipient wetness.

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NOMENCLATURE

C_T = concentration of species in tube side, [mol/cc]
C_S = concentration of species in shell side, [mol/cc
C_0 = initial concentration in tube side, [mol/cc]
C_1 = concentration of species at the end of tube side, [mol/cc]

C_2 = concentration of species at the end of shell side, [mol/cc]
D_{eff} = effective diffusivity, [cm^2/s]
$D_{K,i}$ = Knudsen diffusion coeff. in layer i, [cm^2/s]
$D_{AB,i}$ = molecular diffusion coeff. in layer i, [cm^2/s]
$D_{sp,i}$ = overall straight-pore diffusion coeff. in layer i, [cm^2/s]
D_i = diffusion coeff. in layer i, [cm^2/s]
E = diffusional activation energy, [KJ/mol]
L = length of the tube, [cm]
N_{Ar} = molar flux in radial direction, [mol/scm^2]
P = pressure, [atm]
Q_T = volume flow rate in tube side, [cc/s]
Q_S = volume flow rate in shell side, [cc/s]
R_0 = inner radius of tube, [cm]
R_i = radius of layer i of tube, [cm]
R = radius of shell tube, [cm]
r = radial coordinate, [cm]
T = temperature, [°C]
Z = axial coordinate, [cm]
τ = tortuosity
θ = porosity

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