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Mass Transport in the Hierarchical Porous Structure of Zeolite-Based Composite Membranes

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1. Introduction

A *conditio sine qua non* for membrane development is the elimination of non-separable flows and the minimization of flows of low separability. Generally the most simple model of transport in zeolite-based composite membranes is assumed to involve a parallel flow of species through a zeolitic phase on one side and through non-zeolitic pores on the other.

The above model is tested in the present work using composite membranes prepared in our laboratory. Also a technique was developed to quantify the contribution of Knudsen diffusion to species flow through silicalite-1-based membranes. The technique is based on the dynamic responses of a semi-open diffusion cell. A binary mixture of CH_4 and N_2 was applied at the cell inlet to a stepwise change of gas composition. IAS theory [1] showed a minimum deviation of the behaviour of the individual species in this mixture from that of the single components. This allowed to decouple constitutive Maxwell-Stefan equations. This fact, together with a quasistationary regime which is established due to a negligible accumulation of sorbing species in the membrane, made it possible to essentially simplify the mathematical description of the dynamic experiment.

2. Results

In the present study, as a testing mixture we used $CH_4 + N_2$ with a molar ratio 1: 4. The properties of the sorbing species led to decoupled mass balance equations of methane and N_2 in the closed chamber of a Wicke-Kallenbach (*W-K)* cell. After integration of these equations for the initial conditions characterizing the dynamic run one obtains the following expressions for system responses to a stepwise change of the flowing gas composition at the cell inlet (the change was from pure N_2 to the above mixture):

$m/m_0 \equiv M = 1 - \exp\{-\omega_{CH4}\, t\}$ (1) $X = \exp\{-\omega_{N2}\, t\} - \exp\{-\omega_{CH4}\, t\}$ (2)

where m and m_0 is the actual and maximum mass of methane, respectively, accumulated in the chamber of the *W-K* cell. The variable X is defined as $X = \Delta p_\Sigma(t)/\Delta p_{CH\,4}(0)$ *i.e.* as the time dependence of the total pressure excess in the cell chamber normalized by the magnitude of the initial partial pressure change $\Delta p_{CH\,4}(0)$ of CH_4 at the cell inlet which is realized at constant p_Σ at the cell inlet. ω_{CH4}, ω_{N2} are reciprocal values of the relaxation times of the transient responses of the species content in the cell chamber to a stepwise change of their partial pressures at the cell inlet. These quantities are expressed in terms of a mean transport pore model [2] for the system of non-zeolitic pores and in terms of Maxwell-Stefan approach for zeolitic phase [3] one has

$$\omega_i = f\, f_{WK}\, x_{Kn} \left(M_i\right)^{-1/2} + f_{WK}\, f_z\, H_i\, Đ_i \tag{3}$$

with $f_{WK} \equiv A/V \equiv$ membrane cross-section area/ chamber volume [m^{-1}], $f \equiv 97T^{1/2}$, $f_z \equiv \varepsilon_i / L_z$ [m^{-1}], $L_z \equiv$ effective thickness of the zeolitic layer, $\varepsilon_i \equiv$ fraction of the membrane cross-section area occupied by the zeolite phase, $M_i \equiv$ molar mass of species i, $H_i \equiv$ dimensionless Henry constant of species i, $Đ_i \equiv$ Maxwell-Stefan diffusion coefficient of species i in the zeolitic phase, $x_{Kn} \equiv$ dimensionless texture characteristic of non-zeolitic pores defined as:

$$x_{Kn}=(\varepsilon_a.r_m/\tau_p).L_z^{-1} \tag{4}$$

ε_a, r_m and τ_p are the porosity of defect pores, their mean radius and the tortuosity, respectively.

When the above testing mixture is used, the response $X(t)$ exhibits a maximum X_{max} at time t_{max}. For X_{max} we deduced the relation $X_{max} = y^{1/(1-y)} - y^{y/(1-y)}$ where $y = \omega_{CH4}/\omega_{N2}$. The high sensitivity of X_{max} to membrane quality together with the high X_{max} reproducibility (the relative difference of X_{max} for repeated experiments is on average less than 2.5 %) should prompt effort to construct a membrane quality scale based on the present approach. For composite membranes silicalite-1-α-alumina and selected testing mixture the lower bound to X_{max} is strict: $X_{max} = 0.102$. We estimated the upper bound experimentally to $X_{max} \approx 0.3$.

Construction of the quality scale is based on the following conventions: (i) the first term in Equation (3) which is related to non-zeolitic pores vanishes when $X_{max} = 0.3$, (ii) the following experimental data are used as scale basis: $H_{CH\,4} = 34.66$ [4], $H_{N2} = 8.25$ [5], $Đ_{CH4} = 2.2 \times 10^{-10}$ m^2/s [6].

Aspects examined in relation to the defect formation in composite membranes were texture of interlayer, ageing of the synthesis batch and temperature program and atmosphere of template removal.

3. Conclusions

The approach of composite membrane characterization via dynamic responses of semi-open *W-K* cell consists in an evaluation of transport related parameters $(\varepsilon_a.r_m/\tau_p)$, L_z and χ_i. The latter quantity represents the fraction of the total flow of species *i* due to Knudsen diffusion.

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