4ax Double Sided Thin Film Membranes

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Inorganic membranes are often synthesized as composites of thin films deposited on porous supports that provide mechanical stability. The selective films are typically made as thin as possible to allow for the fluxes of the permeating components through the membranes to be as high as possible. Sometimes the thin films are made up of multiple layers deposited on top of one another to cover up defects that would otherwise decrease selectivity. There is usually a trade-off between flux and selectivity, with thinner, higher flux membranes being less selective than thicker, lower flux membranes. This presentation will show how double sided membranes, with films deposited on both sides of a porous support, can have both higher fluxes and separation selectivities than single supported films of the same or even lesser total thickness. The selective thin film layers of composite membranes usually have much smaller pores than the porous materials on which they are supported. For example MFI zeolites with ~0.5 nm pores, in which diffusion of single molecules from site to site within the molecular-sized pores dominates the transport, are deposited on alumina or stainless steel supports with 20 – 500 nm pores, in which Knudsen or molecular diffusion or even viscous flow controls the transport depending on the permeation conditions. The transport through supported thin films is expected to be limited by the diffusion rate through the selective film, and the support resistance is often neglected in modeling or interpreting permeation behavior through composite membranes. Depending on the operating conditions, neglecting support effects can be reasonable and lead to proper analysis of results, or it can be a grave (yet unnecessary) mistake! Under certain operating conditions, support resistance can significantly influence the fluxes of permeants and the selectivity of a membrane. For example, butane permeation at 298 K through a 100 micron thick ZSM-5 membrane on a 3 mm thick, 0.5 micron porous support with a He sweep gas is less than half of what it would be through the same film without the support resistance. In this scenario, the permeating butane must diffuse through an essentially stagnant 3 mm thick boundary layer of He before reaching the flowing permeate stream. There is a partial pressure drop of butane associated with this transport through the support, i.e. the partial pressure of butane is higher at the zeolite/support interface than in the permeate stream. For sufficiently strong adsorption conditions (the adsorption equilibrium constant of butane on ZSM-5 at 298 K is approximately 14 bar-1), this slightly higher partial pressure at the zeolite/support interface can lead to substantially higher coverage of butane on the zeolite. The higher permeate coverage causes a smaller coverage gradient across the zeolite layer, which in turn results in a lower flux than would be achieved without the support resistance. The support resistance reduces the flux (as a percentage of the flux of an unsupported film) more for thinner zeolite layers, more strongly adsorbing components, lower temperatures, or for any change that increases the partial pressure drop across the support (thicker support, smaller support pores, etc.). Since the support resistance affects different molecules to varying degrees, for example by limiting more strongly adsorbing components more than less strongly adsorbing components, the separation selectivity can also be influenced by the support resistance. If the preferentially permeating component is the more/most strongly adsorbed molecule in a mixture, as is often the case, the selectivity as well as the flux will be lower due to the support resistance. Drat! Doubly foiled! By decreasing the effect of the support, both the flux and the selectivity can be increased. The physical properties of the support can be changed to some extent for this purpose, but as long as there is a support, these detrimental effects will still exist. We have shown by modeling the transport in supported zeolite films with Langmuir adsorption and Maxwell-Stefan diffusion that the support effects can be diminished by effectively moving the support resistance to higher coverage positions within the zeolite, i.e. closer to the feed side. If the support resistance occurs where the partial pressure is low (i.e. at the permeate side), the isotherm is steep and the coverage can be significantly affected. On the other hand, if the support resistance occurs where the coverage is closer to saturation (i.e. at the feed side), the isotherm is less steep and the small change in partial pressure caused by the support does not affect the coverage as much. In fact, for single component permeation, the flux is highest if the feed is on the support side and the permeate is in contact with the zeolite layer. This configuration cannot be used for mixture separation, however, because concentration polarization of the feed would occur in the support, severely limiting the selectivity. Therefore, a film, though it could be quite thin (1 micron or less) is needed on the feed side to prevent concentration polarization. Furthermore, the selectivity of a composite membrane approaches that of the support with decreasing zeolite thickness, and that of the zeolite with increasing zeolite thickness. Therefore, it can be desirable to have a thicker zeolite layer (or layers) than can be synthesized defect-free. By depositing a film also on the permeate side the effect of the support resistance on the coverage is lessened compared to a single zeolite film on the feed side, and the flux can be higher than that through a single deposited film. When the more strongly adsorbed component preferentially permeates, the flux of that component is increased by the double sided film configuration relatively more than that of the less strongly adsorbed component, and the selectivity is consequently also higher than that through a single film. Details of the modeling, analysis, application to relevant separations, and extension to membrane types other than zeolites will be presented, and hopefully lively discussions will ensue!