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PhD Title : Elementary Mechanisms in Gas Separation using Zeolite Membranes: Experiment and Molecular Modeling

Membrane science is at the heart of processes impacting our economy/ecology with applications in energy storage/conversion, environmental protection, gas separation, etc. [Nature 543, 690 (2017)] Technologies are available for large molecules but the separation of small molecules like CH_4 and CO_2 - relevant for the reduction of greenhouse gases and the gas industry - remains a challenge because they interact weakly/not specifically [Nature 532, 435 (2016)]. In this context, nanoporous silica membranes such as zeolite films are promising because they are permeable barriers through which gases are separated according to their size, diffusivity and concentration. However, despite a growing number of studies on these materials, the mechanisms of separation and transfer, especially at the interfaces between the gaseous and confined phases, remain poorly understood [Nat. Mast. 15, 401 (2016)]. Thus, because of the existence of surface resistances whose thermodynamic or geometrical origin is not elucidated (barrier of free energy, surface amorphization, etc.), the science of membranes faces a major challenge: Macroscopic separation cannot be reliably predicted from molecular coefficients (selectivity, self / collective diffusion).

This PhD thesis aims to elucidate the fundamental elements of separation/transport in zeolite membranes via a study coupling experiment and molecular modeling. Using neutron scattering (QENS / INS, reflectivity) and gradient-field NMR experiments combined with molecular simulations (Monte Carlo, molecular dynamics), we will study the behavior of gaseous mixtures (H2O / CH4 / CO2) on membranes of silicalite-1 which is grown on macroporous γ-alumina. The orientation / geometry of the zeolite film whose thickness is known to vary from ~ 0.5 to 5 microns is ideal for probing surface barriers because they allow a series decomposition of surface / volume contributions. Samples, already available from A. Julbe / M. Drobek / A. Ayral in Montpellier, are relevant for a neutron study because in pure silica ● Experiment. Using a neutron approach, we will study the adsorption and diffusion (INS, QENS, NSE) of the gases in the volume of the samples of various thicknesses. In-situ reflectivity will be developed to characterize the gas density profile at the surface as a function of partial pressure and relate it to surface energy barriers. This strategy will be complemented by NMR experiments and laboratory separation measures ● Modeling. The adsorption of gas mixtures will be studied by Monte Carlo Grand Canonical simulation but also by Umbrella Sampling to probe possible free energy barriers impacting interfacial transport [Nat. Comm. 7, 11890 (2016)]. The dynamic properties will be evaluated by molecular dynamics (self / collective diffusion, translational / rotational, inelastic spectrum) but also by non-equilibrium dynamics (permeability measurement which is intimately linked to the collective diffusion). From the experimental / numerical data, the models developed at LIPhy will make it possible to predict long-term transport (relevant for real separation processes) from molecular coefficients [Nat. Comm. 6, 6949 (2015), Phys. Rev. E 91, 032133 (2015)].

In conclusion, this subject at the interface between physics and chemistry is fundamental but has a strong application potential. Based on an approach combining experiment and theory, this topic should provide a deep molecular understanding of these systems and allow optimizing their design and use.