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Investigation and simulation of the transport of gas containing mercury in microporous silica membranes

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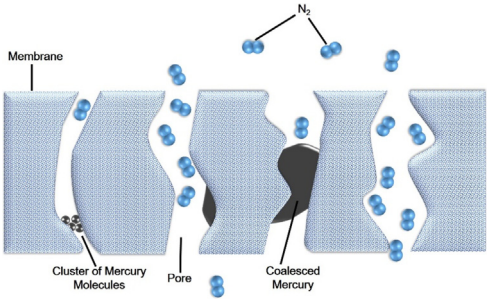
HIGHLIGHTS

- Condensable Hg vapour effect on N_2 permeation in microporous silica membrane.
- Significant Hg effect at 100 and 200 °C, though negligible at 300 °C.
- Hg effect correlated well with Hg adsorption on microporous silica xerogels.
- Oscillator model for gas transport including the Effective Medium Theory (EMT).
- The model's simulated results fitted well experimental results.

GRAPHICAL ABSTRACT



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ABSTRACT

This work investigates the effect of condensable Hg vapour on the transport of N_2 gas across cobalt oxide silica (CoOxSi) membranes. Experimental results suggest that Hg significantly affects N_2 permeation at 100 and 200 °C, though this effect is negligible at 300 °C. This effect was found to have a correlation with Hg adsorption on CoOxSi xerogels. In order to understand the Hg effect in the transport phenomena of N_2 permeation, the oscillator model was used to model gas transport through pores with different sizes. By including effective medium theory (EMT), the oscillator model fitted well the experimental results and gave good prediction of mass transfer in ultra-microporous materials with a tri-modal pore size distribution, such as silica membranes. It is postulated that Hg seeks lower level potentials in micro-pores, and therefore Hg molecules tend to block small pores (2.5–4 Å from 2.9 Å), or reduce the average pore size of larger pores (6.7–7.8 Å and 12–14 Å). Although N_2 permeation decreased with the presence of Hg, it did not decrease when the Hg load was increased by a factor of ten; this strongly suggests the adsorption of Hg molecules in the smaller pores (2.5–4.0 Å), or along the pore wall for the larger pore ranges (6.7–7.8 Å and 12–14 Å).

1. Introduction

Porous inorganic membranes have evolved since the early 1990s, when gas separation values were below 10, to values close

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Nomenclature

c	gas concentration (mol m^{-3})
D	diffusivity (m^2 s^{-1})
F	flowrate (mol s^{-1})
f_N	number density distribution (nm^{-1})
f_v	volume density distribution (nm^{-1})
g_N	number density distribution after some pore is blocked by Hg (nm^{-1})
K	equilibrium constant
K_m	mean equilibrium constant
k_B	Boltzmann constant (J K^{-1})
L	membrane thickness (nm)
l	pore length (nm)
M	molar mass (kg mol^{-1})
m	molecular weight (kg)
N	number of molecules in a pore
N_A	Avogadro's constant (6.022×1023 mol^{-1})
P	probability of a pore not being blocked by Hg
p	pressure (Pa)
p_r	radial momentum (kg m s^{-1})
p_z	axial momentum (kg m s^{-1})
p_θ	tangential momentum (kg m s^{-1})
q	concentration inside pore (mol m^{-3})
R_g	gas constant (J mol^{-1} K^{-1})
R_p	particle radius (m)
r	radial coordinate (m)
r_{c1}	radial coordinate where hopping commences (m)
r_{co}	radial coordinate where radial momentum is zero (m)
r_p	pore size (m)
S	perm-selectivity
T	temperature (K)
t	time (s)
W	weight (kg)

Greek letters

ε	Lennard Jones well depth (J)
ε_p	membrane porosity
η	areal density of sites on the pore surface (m^{-2})
θ	angular coordinate
λ	mass transfer conductance (mol s^{-1} Pa^{-1})
μ	chemical potential (J mol^{-1})
ρ_{sample}	sample density (kg m^{-3})
σ	Lennard Jones collision diameter (nm)
τ	hopping time (s)
τ_t	tortuosity
ϕ	potential (J)

or even higher than 1000. This major achievement has been possible by the control of the pore sizes of the membranes, allowing for the smaller gas molecule to permeate, whilst blocking the passage of the larger gas molecule. This is known as a molecular sieving mechanism as a result of molecular exclusion. Early major improvements in separation performance were reported by Verweij's group by late 1990s (de Vos and Verweij, 1998), where silica thin-films were prepared on the top of high quality interlayer substrates in clean rooms. This approach greatly reduced defects, and silica membranes reached H_2/CO_2 selectivities of around 100. The separation performance of membranes varies from case to case, based on the porous structure, adsorption properties and thickness of selective layers. In addition, mass transfer across a membrane is dependent on many factors such as membrane structure, gas property, temperature, pressure, and gas concentration which all affect gas fluxes (or production) and gas separation (or quality/purity). Therefore, different operating conditions require precise models to predict and explain the membrane performance.

In the case of silica derived membranes complying with molecular sieving transport, gas molecules in the gas phase must adsorb on the surface or at the pore entrance of the membrane. Due to a difference in concentration from the high pressure side (i.e., feed domain) to the low pressure side (i.e., permeate domain), this results in a concentration gradient which allows the gas molecules to jump between adsorption sites within the pores of the membrane (Burggraaf, 1999; Barrer, 1990; Zhdanov, 1985). This mechanism is known as surface diffusion. When pore size is reduced to dimensions below the Lennard Jones (L-J) diameter of the gas molecules (also known as the kinetic diameter), molecular attraction by physical adsorption is no longer feasible. In this case, there is a repulsive force between the pore entrance and the molecule which stops the molecule from entering. In other words, the potential for a molecule entering the pore is too high. Hence, the gas molecule requires much more energy to be able to diffuse through these pores smaller than the molecular L-J diameter (Xiao and Wei, 1992a; Xiao and Wei, 1992b). In this process, the gas kinetic energy is converted to potential energy when a gas molecule approaches a pore. In order to increase the gas potential and likewise permeation, energy must be supplied in terms of thermal energy which increases the kinetic energy. Since the gas needs extra energy to activate the transport, this process shows temperature dependency and is called activated transport which is generally a characteristic of molecular sieving silica membranes. This unique transport is usually observed in ultra-microporous membranes with pore sizes below 5 Å, as it is the case for silica derived membrane for separating H_2 or He from other larger gases (Darmawan et al., 2015; Gopalakrishnan et al., 2007; Yoshioka et al., 2001).

Surface diffusion and activated transport are the most common mechanisms in ultra-microporous membrane separation. Krishna and van Baten (2011) studied the effect of high binary gas selectivity caused by strong adsorption from one component and used Molecular Dynamics (MD) to simulate transport properties, as adsorption also affects gas selectivities. For activated transport, the gas permeation in ultra-microporous membranes generally decreases as a function of the gas kinetic diameter, so the membrane separates gases based on molecular size (Lange de et al., 1995; Igi et al., 2008; Liu et al., 2015; Boffa et al., 2008). The separation of industrial gas is more challenging due to complex mixtures of gases, water vapour and condensable vapours. Recently, Deonarine et al. (2017) reported that He permeance decreased by ~17% in a cobalt oxide silica membrane when exposed to a model tar compound (0.24 mol% toluene). This demonstrates the effect of condensable vapours in micro-pore structures. Yoshioka et al. (2003) used a molecular dynamics simulation to report the effect of condensable gas filling in microporous silica membranes. These limited studies clearly show that the effect of condensable gases can be significant in the separation of industrial gases.

A potential application of silica membranes is the separation of H_2 from syngas mixtures such as in coal gasification processes (Huth et al., 2012; Smart et al., 2010). A common feature of coal derived syngas mixture is the presence of mercury at small concentrations (Pavlish, 2003; Frandsen et al., 1994). There is a large body of research and engineering works published in the area of mercury capture in coal power stations to meet regulatory emis-