Experimental investigation of the transport mechanism of several gases during the CVD post-treatment of nanoporous membranes

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HIGHLIGHTS

- Ceramic membranes were modified by applying a cyclic mode of CVD process.
- a-Alumina/silica tubes with a separation layer of 1 nm pore size were used as substrates.
- The substrates' pore structure evolution during the CVD processes was investigated.
- The permeance of He and N_2 gases with the progress of silica deposition was monitored.
- The permeation properties of the treated membranes were evaluated using several probe gases.

ARTICLE INFO

ABSTRACT

The current study stresses the importance of combining gas transport theories with experimental gas permeability results on the effort to elucidate nanopore structure evolution of nanofiltration membranes during their modification through the chemical vapour deposition technique. To this end, silica membranes of 1 nm nominal pore size were post-treated by applying a sequential cyclic CVD method at 573 K and the Tetraethyl-orthosilicate/Ozone reaction system. Alteration of the gas transport characteristics was investigated by conducting single gas permeance measurements of Helium and Nitrogen at selected temperatures following the completion of several CVD cycles. The experimental results were interpreted on the basis of gas transport theories combined with a model for the evolution of pore size distribution of the membrane's separation layer during silica deposition. By monitoring permeation properties of the treated membranes with the progress of deposition using Helium and Nitrogen as probe gases, optimized treatment conditions can be established in order to fabricate selective and highly permeable – with respect to Hydrogen gas – ceramic membranes. Furthermore, the dependence of the permeation properties on the pore size of the studied membranes before and after their CVD treatment was investigated by performing single-gas permeance measurements of several probe gases within a wide temperature range.

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1. Introduction

Over recent years, membrane technologies have been successfully applied in a number of industrial sectors, in many cases replacing traditional, energy-demanding and environmentally polluting separation techniques. Intensification of processes utilizing membranes has been applied for water desalination [1,2], oxygen/nitrogen separation [3–5], and natural gas purification [6,7].

Membrane filtration processes based on microfiltration (MF) and ultrafiltration (UF) units combined with reverse-osmosis (RO) systems have been implemented in municipal waste-water reclamation plants that produce water suitable not only for industrial use but also of potable quality [8,9]. Moreover, membrane-based separation has attracted significant attention for CO_2 capture applications (carbon capture and sequestration – CCS) because it has the potential to offer high energy savings, lower operating cost, and small unit foot-print. Separation of carbon dioxide from other gases is critically important for industrial applications such as hydrogen production [10–13], biogas purification [14], CO_2 scrubbing of power plant combustion exhausts [15–17] and capture of

List of symbols

C	concentration (mol m^{-3})	Q	permeance (mol m$^{-2\ -1}$ Pa^{-1})
D	diffusion coefficient (m^2 s^{-1})	q_{st}	isosteric heat of adsorption (J mol^{-1})
D_{MS}	Maxwell–Stefan or intrinsic diffusion coefficient (m^2 s^{-1})	R	ideal gas constant (=8.314 J mol^{-1} K^{-1})
d_k	kinetic diameter of gas molecules (m)	T	absolute temperature (K)
d_p	pore diameter (m)		
$\langle d_{p,eff} \rangle$	effective average pore diameter (m)	*Indices*	
E_a	apparent activation energy for diffusion (J mol^{-1})	C	configurational diffusion
E_m	activation energy for configurational diffusion (J mol^{-1})	f	feed side
ΔE_a	activation energy for Gas Translational diffusion (J mol^{-1})	g	gas phase in nanopores
		K	Knudsen diffusion
ΔE_d	activation energy for desorption of molecules from the pore walls into the intra-pore gaseous phase (J mol^{-1})	K_a	activated Knudsen diffusion
		o	pre-exponential constant
g_d	the probability that a molecule has sufficient energy to surmount an certain energy barrier and to make a jump with length λ and a velocity u, in the right direction (dimensionless).	S	surface diffusion
		s	adsorbed phase in nanopores
		sat	adsorbed phase in nanopores at the saturation coverage
		T	thermodynamic
ΔH_a	enthalpy of adsorption (J mol^{-1})	t	total
J	gas flux through membrane (mol m^{-2} s^{-1})		
K	Langmuir adsorption coefficient (Pa^{-1})	*Greek symbols*	
l	membrane thickness (m)	δ	ratio of pore diameter over kinetic diameter
n	adsorbed amount of gas (mol kg^{-1})	ε	porosity (dimensionless)
n_m	monolayer capacity of adsorbed gas (mol kg^{-1})	θ	surface coverage or occupancy (dimensionless, 0 < θ < 1)
M	molecular weight (mol g^{-1})	μ	correction factor
P	pressure (Pa)	ρ	density (kg m^{-3})
P_e	permeability coefficient or permeability (mol m m^{-2} s^{-1} Pa^{-1})	τ	tortuosity (dimensionless)

CO_2 from advanced power generation sources such as the integrated gasification combined cycle (IGCC) [18–20].

Apart from implementation in industrial gas separation processes, membrane technology has also focused extended research interest in fields such as photovoltaics, photocatalysis, batteries and biosensors. Photocatalytic membrane reactors prepared by immobilization of a photocatalyst onto porous membrane substrates have been developed with the aim to attain removal of organic pollutants from water [21,22]. Oriented titania nanotube membranes with a sensitizing material (e.g. CdS quantum dots) [23,24] and polymer electrolyte membranes containing redox mediators [25] have been incorporated in dye-sensitized solar cells, which showed promising photoharvesting and photoconversion efficiencies. On the other hand, recent studies have demonstrated that proton exchange membranes (PEMs), such as Nafion or hybrid polymeric/inorganic membranes, [26,27] can provide acceptable cell performance when employed in vanadium redox flow batteries (VRFBs) as the cell separator to transport ions between the catholyte and the anolyte while blocking the crossover of the electrolytes and preventing shorting of the electrodes [28]. VRFBs have received significant attention due to their potential as large-scale electric energy storage devices. Biocompatible polymeric membranes and coatings have been implemented in the field of biosensors such as the implantable glucose sensors, which have played a leading role on the blood glucose continuous monitoring. Several types of polymers have been employed for preparation of glucose biosensors, such as poly(vinyl alcohol) hydrogels [29], hydrophilic polyurethane with polyvinyl alcohol/vinyl butyral copolymer [30], poly(2-hydroxyethylmethacrylate) (polyHEMA) [31], polylactic-co-glycolicacid (PLGA) [32], etc.

In order for membranes to be rendered as economically viable and exhibit the necessary level of sustainability for utilisation in gas separation processes at the industrial scale they are required to exhibit high flux and high selectivity factors. Regarding microporous membranes (i.e. with pore widths, w, less than 2 nm [33])

the most efficient gas separation mechanism is molecular sieving. In this case, separation is attained via size exclusion, depending on the kinetic diameter of the gaseous components. However, the low permeability coefficients of gases permeating through the molecular sieving membranes (due to their narrow sub-micropores which are comparable to molecular dimensions) render their productivity insufficient for industrial gas separation or catalytic membrane reactor applications.

On the other hand, mesoporous membranes (2 nm < w < 50 nm [33]) exhibit enhanced permeability coefficients for all gases but they suffer from low selectivity, which for a given gas pair is limited down to the permeance ratio that is determined by adopting the Knudsen diffusion behavior for each component. Nevertheless, the selectivity can be significantly enhanced when one of the gas pair components is a condensable gas (vapour), by taking advantage of adsorption and capillary condensation phenomena that occur inside the mesopores [34–38]. At low relative pressures, a certain fraction of vapour is adsorbed on the pore walls, forming a layer of a statistical thickness t. As a result of the concentration (or chemical potential) gradient, this layer is not static but depending on the interaction forces, it either "slips" on the pore walls or moves by the hopping model (for stronger interacting species), adding an extra flux component on the vapour flow. This transport mechanism is known as surface diffusion. As the vapour's relative pressure increases, multilayer adsorption and especially capillary condensation in the finer pores (which induces additional capillary pressure gradients) plays a dominant role, thus resulting in higher permeation rates for the condensable component. Therefore, further enhancement on the separation efficiency (in favour of the condensable component) can be provided by capillary condensation. On the other hand, as the condensable component of a binary gaseous mixture condenses to a liquid phase within the pores, it hinders or totally blocks the transport of the non-condensable gas.

The porous structure of both mesoporous and microporous membranes (either symmetric or multilayered) can be modified