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Composite catalytic-permselective membranes: Modeling analysis for H_2 purification assisted by water–gas-shift reaction

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HIGHLIGHTS

- Composite catalytic-permselective membrane (CCP) investigated for H_2 purification.
- CCP compared with gas permeation membrane and packed-bed membrane reactor designs.
- Simulations indicate superior H_2 recovery using Pd films via CCP design.
- CCP design with polymeric films aid CO_2–CO separation, reduce CO_2–H_2 separation.

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ABSTRACT

Composite catalytic-permselective (CCP) membrane designs, wherein a catalytic film is applied to the retentate surface of a permselective film, are capable of enhancing gas permeation rates and permselectivities by modifying the gas composition in contact with the permselective film surface via reaction–diffusion within the catalytic layer. Isothermal, two-dimensional models are employed to compare performance of a CCP membrane system against (i) an un-modified permselective film in a gas purification membrane (GPM) system, and (ii) an equivalent packed-bed membrane reactor (PBMR) system, for coupling water–gas-shift reaction with H_2 purification from a typical heavy hydrocarbon reformate mixture (9%CO, 28%H_2, 15%H_2O, 3%CO_2). Analysis is provided for the case of (i) an infinitely H_2-permselective Pd film, for exploring the potential for alleviating surface inhibition via CO using the CCP design, and (ii) a moderately CO_2-permselective polymeric film, for exploring the potential for enhancing CO/CO_2 separation via CCP design as compared to PBMR designs. For the former case, the CCP design is capable of enhancing overall permeation rates in GPM and PBMR configurations via alleviation of surface inhibition. In the latter case, simulations predict up to a 40% enhancement in reaction product-reactant (CO_2–CO) separation, at the cost of reduced product-product (CO_2–H_2) separation.

1. Introduction

Advances in H_2 purification technologies have been driven by an expanding global energy demand, dwindling fossil resources and increasing concerns regarding the environmental impact of electrical energy and fuels production. Hydrogen production remains a critical challenge in the petrochemical industry owing to its use both for catalytic upgrading of petroleum distillates to transportation and logistics fuels, and the catalytic removal of sulfur and nitrogen from increasingly 'sour' crudes populating the market [1–3]. The advent of biorefineries producing commodity chemicals and fuels from biomass is expected to further increase H_2 demands, as the high oxygen content of carbohydrate-derived biofuels require additional hydrotreating to achieve combustion properties comparable to their petroleum-derived counterparts [4–6]. Hydrogen has also been recognized for its potential as a universal fuel, derivable from both renewable (biomass, biogas) and non-renewable (petroleum, natural gas, coal) hydrocarbon resources [5,7,8]. H_2-driven fuel cells are capable of achieving significant improvements in fuel efficiencies as compared to existing internal combustion engines, without locally producing any emissions associated with hydrocarbon fuels combustion (volatile organic compounds, nitrogen oxides, sulfur oxides, particulates) [9–11]. The polymer electrolyte fuel cell (PEMFC) has been favored for transportation and portable applications due to its high power density and near-ambient operating temperatures (60–90 °C) [12,13].

Hydrogen is typically produced via oxidative reforming of hydrocarbons [1–3,7], which results in a reformate mixture containing significant amounts of steam, carbon dioxide and carbon monoxide. The latter is a significant poison both to several catalytic

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Nomenclature

$\hat{a}$	ratio of membrane surface area to fluid volume, m^{-1}
A_C	cross sectional area for flow, m^2
A_{mem}	membrane surface area, m^2
D_i^{eff}	effective diffusivity of species *i*, $m^2\ s^{-1}$
D_{ij}	binary diffusivity of solute *i* in solvent *j*, $m^2\ s^{-1}$
D_i^K	Knudsen diffusivity of species *i*, $m^2\ s^{-1}$
D_i^{mix}	molecular diffusivity of species *i*, $m^2\ s^{-1}$
F_i	molar flow rate of species *i*, mol s^{-1}
k_e	effective thermal conductivity of catalyst, W $m^{-1}\ K^{-1}$
k_f	forward rate constant for WGS, mol $m^{-3}\ s^{-1}\ Pa^{-2}$
k_{gs}	mass transfer coefficient at gas–solid interface, m s^{-1}
K_{eq}	equilibrium constant for water–gas-shift reaction, dimensionless
K_i	adsorption coefficient of species *i* on adsorption sites on membrane surface, dimensionless
M_i	molecular weight of species *i*, kg mol^{-1}
L	reactor/membrane system flow length, m
p_i	partial pressure of species *i*, Pa
P_i	membrane permeability of species *i*, mol $m^{-1}\ s^{-1}\ Pa^{-0.5}$ or mol $m^{-1}\ s^{-1}\ Pa^{-1}$
Pe	Peclet number, dimensionless
Q_i	flux of species i through the permselective layer, mol $m^{-2}\ s^{-1}$
r_i	rate of species *i* via WGS reaction, mol $m^{-3}\ s^{-1}$
R_g	universal gas constant, J $mol^{-1}\ K^{-1}$
r_p	catalyst pore diameter, m
$S_{i/j}$	apparent permselectivity of species *i* over species *j*, dimensionless

t^{Pd}	palladium permselective film thickness, m
t^{Poly}	polymer permselective film thickness, m
t_c	catalyst layer thickness, m
T	temperature, K
V_{cat}	catalyst volume, m^3
x	axis of diffusion
X_i	fractional conversion of species *i*, dimensionless
x_j	mole fraction of species *i*, dimensionless
z	axis of gas flow
$\%R_i$	percent of recovery of species *i*, dimensionless
Greek Symbols	
$\alpha_{i/j}$	intrinsic permselectivity of species *i* to species *j*, dimensionless
β	Prater number, dimensionless
ΔH°_{Rxn}	heat of reaction of WGS, J mol^{-1}
Φ	normalized Thiele modulus, dimensionless
ε	porosity of catalytic bed, dimensionless
ξ	ratio of initial rate of desired permeate through the permselective film to WGS reaction, dimensionless
ρ_c	catalyst density, g m^{-3}
τ	tortuosity factor, dimensionless
θ_i	surface coverage factor, dimensionless
v_i	atomic diffusional volume of species I, dimensionless
σ	residence time, s
ζ	ratio of desired permeate through the permselective film to that across the catalytic film, dimensionless

processes employed in fuels production and to anode catalysts currently employed in PEMFCs [1,9], necessitating purification of the reformate gas prior to use. Gas purification via permselective membranes has garnered significant attention over the past two decades owing to the advantages of low energy consumption, continuous operation and high capacities as compared to solvent absorption, cryogenic distillation or pressure-swing adsorption [14–16].

Palladium and its alloys (e.g., Pd–Ag, Pd–Cu) present infinite theoretical permselectivities towards H_2 over all other gases, owing to a H_2-specific permeation mechanism comprised of dissociative H_2 adsorption followed by dissolution and bulk diffusion of atomic H through the dense metal film [17–19]. However, Pd membranes are limited by high materials costs (~23 USD/g), corrosion by hydrocarbon [20,21] or sulfur [22,23] contaminants, and significant reduction in permeance in the presence of carbon monoxide owing to competitive surface chemisorption [24–26]. To-date, strategies to alleviate these challenges have focused upon the discovery of new alloy compositions capable of increased H_2 permeabilities and chemical resistance [27,28], or the development of new materials capable of achieving competitive H_2 purities. Polymeric materials present a low-cost alternative to Pd at the expense of lower gas permselectivities [29–31]. Research to-date has focused upon enhancing permeabilities and permselectivities via modification of the polymer film chemistry [29,31].

Recovery of purified H_2 from reformate mixtures may be enhanced by coupling gas purification with water–gas-shift reaction (WGSR). The exothermic reaction of CO and H_2O (Eq. (1)) yields CO_2 and H_2; by continuously removing one of the reaction products via a permselective membrane, equilibrium limitations on CO conversion may be removed in accordance with LeChatelier's Principle [32–34].

$$CO + H_2O \Longleftrightarrow H_2 + CO_2 \quad \Delta H^{\circ}_{298} = -41.1\ \text{kJ/mol} \tag{1}$$

The coupling of WGSR with gas purification is typically achieved by packing the retentate volume of the gas purification membrane with water–gas-shift catalyst. The resulting packed-bed membrane reactor (PBMR) configuration has been reported for coupling water–gas-shift with H_2-permselective Pd membranes [33,35] and CO_2-permselective polymeric membranes [32,36] to produce high-purity H_2 from reformate mixtures. While the PBMR design enables gas purification to enhance catalytic reaction rates, the permselective film remains directly exposed to contaminants.

To address this limitation, an alternative approach to coupling catalytic reaction with gas purification has been developed wherein a sufficiently thick catalyst layer is washcoated over the retentate surface of the permselective film, such that undesired contaminants are catalytically destroyed before reaching the permselective surface. Likewise, catalytic production of desired permeating species in close proximity to the permselective surface further enhances gas permeation rates. This composite catalytic-permselective (CCP) membrane design was first demonstrated for preventing corrosion of ultra-thin (200 nm) Pd films by methanol reactant in a miniaturized membrane reformer [37]. One-dimensional modeling under inlet/feed conditions (assuming inlet compositions for feed and sweep volumes) [38] for a CCP membrane coupling reversible WGSR with a permselective Pd film for H_2 recovery from diesel reformate predicted up to an 80% reduction in CO partial pressure at the catalyst-Pd interface relative to the bulk fluid CO partial pressure. Equivalent increases in H_2 partial pressure at the Pd surface corresponded to a predicted enhancement of H_2 permeation rates of ~5% under inlet conditions, neglecting any inhibitory effects of CO upon Pd permeability. Analysis of an equivalent CCP membrane coupling water–gas-shift