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Experimental and modeling study of gas transport through composite ceramic membranes

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HIGHLIGHTS

- We demonstrate the concentration polarization and support effects in gas transport.
- Knudsen diffusion dominates the gas transport through near meso-scale support.
- Geometric factors determined by gas permeation agree with physical characterization.
- The outcome of CFD simulation points out the concentration polarization effect.
- The transport resistances involved in series in the gas transport were evaluated.

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ABSTRACT

Concerning the gas transport through ceramic membranes, insufficient attention is paid to concentration polarization (mass transfer) in the measuring cell or module used and to support effects. Therefore, the aim of this study is to demonstrate these effects based on a combined experimental and modeling study of two types of membranes. The gas permeation through a graded ceramic microporous membrane consisting of α-Al_2O_3/γ-Al_2O_3/silica was well simulated with the “Binary-Friction-Model” (α-Al_2O_3/γ-Al_2O_3 substrate) and the Maxwell–Stefan model (silica top-layer), respectively. For both the α-Al_2O_3 support and γ-Al_2O_3 interlayer, the geometric factors, such as the pore radius (r), and the ratio of porosity versus tortuosity (ε/τ) obtained from single gas permeation agree well with physical characterizations. Knudsen diffusion is the dominant transport mechanism through both the α-Al_2O_3 support and γ-Al_2O_3 interlayer and the support effect cannot be neglected due to significant contributions of transport resistance.

For the asymmetric BSCF membrane the comparison of experimental data and gas transport simulation using the “Binary-Friction-Model” and the “Wagner equation” coupled to a 2D fluent simulation to account for the local variations of oxygen concentration and gas velocities profiles show a deviation by a factor of ca. 2. The oxygen concentration profile and the gas velocity profile derived from 2D fluent clearly pointed out the concentration polarization effect, which resulted in a permeation reduction up to ca. 20.3%. The porous support exerts a great influence on the gas transport through the asymmetric BSCF membrane. With increasing sweep flow rates, the effect of concentration polarization is less pronounced, while the gas transport through dense and support layer become more important.

1. Introduction

Ceramic membranes have received significant attentions from both academia and industry, as they show great potential in several important applications. For example, ceramic microporous membranes are promising for, e.g., H_2 separation, the recovery of CO_2 from natural gas and the reduction of green-house gas emission from flue gas, while dense oxygen ion-conducting membranes enable O_2 separation from air at high temperatures. Ceramic membranes can also be incorporated into chemical reactors, in order to shift the reaction equilibrium towards the product side. Promising ceramic membrane candidates include zeolites, silica and carbon membranes (microporous), and perovskite and related membranes (dense), which are often supported on a porous substrate, such as α-alumina, zeolites or stainless steel.

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Many research groups have experimentally investigated ceramic membranes for relevant separation processes, e.g., H_2/CO_2, CO_2/CH_4, CO_2/N_2 and O_2/N_2 separation, aiming at a combination of high permeability and selectivity as well as improved (hydrothermal) stability.

Yet in many of the published papers aiming at an assessment of the transport properties of these membranes, insufficient attention is paid to concentration polarization (mass transfer) in the measuring cell or module used and to support effects. In the present literature, the support effect of the microporous membranes is often ignored or simply described with a single transport mechanism, such as bulk diffusion or viscous flow (Lito et al., 2010; van de Graaf et al., 1999; Jareman et al., 2004; Wirawan et al., 2011; Higgins et al., 2009). For example, Lito et al. (2010) examined the gas permeation of various gases through a microporous titanosilicate AM-3 membrane synthesized on alumina tubular support with a pore size of 3 μm and a thickness of ca. 1.5 mm. A simplified approach was proposed to account for the support effect by multiplying the gas permeation through the microporous layer with a geometric factor of the support, i.e., porosity, since the total area is only partially available for permeation. van de Graaf et al. (1999) studied the separation of ethane/methane and propane/methane mixtures with a silicalite-1 membrane on a stainless-steel support (composed of metal wool – thickness: 200 μm; porosity ca. 0.7, and sintered stainless-steel spheres – thickness: 3 mm; porosity: 0.2), for which a single transport mechanism of bulk diffusion was assumed. Currently, there are few reports on the modeling of gas transport through porous substrates with a pore size near mesoscale (Jareman et al., 2004; Wirawan et al., 2011). which can serve as intermediate layers to improve the combination of permeance and selectivity properties (Gu and Oyama, 2007). Wirawan et al. (2011) investigated the single and binary H_2/CO_2 permeation through a silicalite-1 membrane supported on α-alumina which consisted of two macroporous layers with a varying pore size of 100 nm and 3 μm (L1 and L2), respectively. The gas transport through L1 was simulated with Knudsen diffusion and viscous flow while the effect of L2 was neglected in the simulation. Bulk diffusion was considered negligible in the modeling. The transport parameters for the two layers were determined through a non-linear least square method from gas permeation data. Higgins et al. (2009) examined the permeation of several light gases through mesoporous silica membranes supported on a macroporous alumina layer. The two layers have a varying average pore size of 4.7 nm and 100 nm, and were described by a single transport mechanism of Knudsen diffusion and viscous flow, respectively.

These earlier studies did not reach a consensus concerning the mechanism of gas transport through porous supports, especially for the small pore supports. Moreover, the simplified assumption of a single transport mechanism often observed in the modeling could not represent the real situation, as the dominant transport mechanisms vary with experimental conditions (temperature, pressure etc.), and thus a comprehensive "Binary-Friction-Model" taking into account three transport mechanisms, i.e., Knudsen diffusion, viscous flow and bulk diffusion is desired. Additionally, the transport parameters derived from the modeling have scarcely been validated with physical characterizations. In this study, we simulate the gas transport through near-mesoscale double-layer support with the "Binary-Friction-Model", using the relevant geometric factors determined from single gas permeation data. A layer-by-layer method is presented and results are compared with physical characterizations. The contribution of different transport mechanisms (e.g., Knudsen diffusion and viscous flow) across two support layers is evaluated in detail.

At present, there are few studies on the modeling of gas transport through O_2 transport membranes. Engels et al. (2010) integrated a membrane model with Aspen Plus, enabling the calculation of heat and mass transfer in an oxygen membrane module, which, nevertheless, neglects the concentration polarization and inlet effects. Hong et al. (2012) developed a numerical model for oxygen transport and fuel conversion processes in an ITM reactor, considering the local O_2 partial pressures at the membrane surface by using a finite-gap stagnation flow configuration, whereas it represents a simplified flow pattern. CFD has recently been recognized as a useful tool for the development of membrane processes as it can provide much valuable information on the gas hydrodynamics (Ghidossi et al., 2006). For example, Gozálvez-Zafrilla et al. (2011) employed computational fluid dynamics using COMSOL Multiphysics® to describe the effect of set-up geometry (e.g., gas inlet distance, gas inlet radius) and flow rate on the overall gas transport. The membrane investigated was self-supported. In this study, 2D fluent is coupled with the "Binary-Friction-Model" and "Wagner equation" to reveal the local variations of oxygen concentration and gas velocities profiles near the membrane surface as a result of O_2 permeation. Moreover, the concentration polarization effect, bulk diffusion and support effect that are involved as a series of resistances in gas transport are evaluated under the investigated conditions. Given the thickness of the membrane, the surface exchange limitations are considered as negligible.

2. Experimentals

2.1. Ceramic microporous membranes

In this study, the ceramic composite microporous membrane manufactured at Forschungszentrum Jülich consisting of three layers, i.e., α-Al_2O_3/γ-Al_2O_3/silica, was manufactured and examined layer-by-layer. First, three α-Al_2O_3 supports, i.e., samples 1, 2 and 3, with an outer diameter of 3.9 cm (disk-shaped), and a thickness of 2.5 mm, were manufactured by an in-house slip casting process. Single gas permeation tests of H_2 and CO_2 were carried out for samples 1 and 2 at 323 K and feed pressures of 1.5–2.5 bar (a) with the permeate side kept at atmospheric pressure. No sweep gas was used in the permeation test (the permeation setup at Forschungszentrum Jülich is depicted in Fig. 1). The powders of sample 3 were used to carry out Hg intrusion measurement (Pascal 140 and Pascal 440, Fisons plc) in order to determine porosity and pore size distribution.

Second, two γ-Al_2O_3 interlayers (mesoporous) with a thickness of 2.5 μm, were manufactured by a colloidal sol–gel coating procedure and deposited onto α-Al_2O_3 supports, i.e., samples 4 and 5. Single gas permeation of H_2 and CO_2 through the two composite substrates was carried out at 323 K, 373 K and 473 K and a feed pressure of 1.5–2.5 bar. No sweep gas was used in the permeation test and the permeate side was kept at atmospheric pressure. The powders of interlayer samples were used to carry out permporometry measurement in order to determine pore size distribution. In the end, a microporous silica layer with a thickness of 100 nm was prepared by a sol–gel process onto the composite

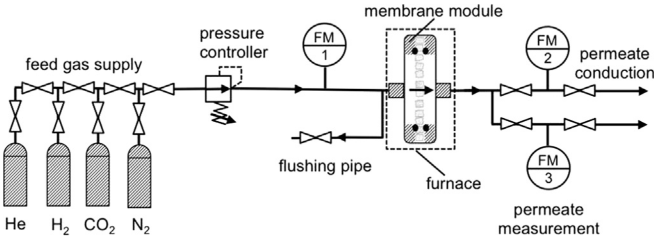

Fig. 1. Schematic diagram of the permeation setup, FM-Flowmeter.