Effect of membrane treatment on CO competitive adsorption on ~3µm Pd/23wt.%Ag membranes

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Introduction

Palladium based membranes enable hydrogen separation from mixtures. To find widespread application, such membranes need to be thin, yet durable, under relevant conditions in terms of species present in the mixtures and pressure differences required to maintain a driving force for the permeation. Adsorption processes will have increased impact on the permeation as the thickness is reduced to a level where bulk hydrogen diffusion is no longer rate controlling. Upon integration with a (catalytic) reaction, hydrogen production and purification may be achieved in a single unit. The removal of hydrogen through a membrane may under certain conditions shift the reaction equilibrium towards higher conversion.

SINTEF has developed a unique fabrication technique for Pd alloy membranes [1], with thicknesses down to 1 µm and permeances in the range $5\text{-}20\cdot10^{-3}$ $mol\cdot m^{-2}\cdot s^{-1}\cdot Pa^{-0.5}$. Significantly increased permeation was obtained after heat treatment in air [2], as also demonstrated by others [3]. The object of our study was to determine whether such membranes when applied to microchannel structures can withstand high differential pressures without further support, and to investigate and possibly manipulate the effect of CO (and CO_2) competitive adsorption in this relatively well-defined flow system in which different gas phase, surface and bulk transport phenomena should be possible to separate.

Materials and Methods

The microchannel configuration consisted of a stainless steel feed housing with either 6 ($1\cdot1\cdot13$ mm^3) or 17 ($0.2\cdot0.2\cdot13$ mm^3) parallel channels, a stainless steel plate with apertures corresponding to the channel geometry and a permeate side open housing. The Pd/Ag thin films were deposited on silicon substrates by dc magnetron sputtering (CVC 601) from a Pd/Ag23 wt% target [1], and then lifted off the substrate and sealed between the channel housing and the stainless steel plate providing for 0.78 or 0.44 cm^2 active membrane area. Permeances were determined in pure hydrogen to ensure well-defined conditions. The effects of CO and CO_2 were studied separately under conditions were hydrogen concentration gradients along the channels were minimized, before and after treatment of the membrane in air at 300 C over 5 days. Sweep gas was never used except to check for leaks between experiments. The data are discussed in relation to a classic Fick-Langmuir transport equation [4] as well as a model incorporating the elementary adsorption steps.

Results and Discussion

1.4 µm Pd/Ag23wt% membranes could withstand differential pressures up to 470 kPa without further support and without reaching the burst pressure when sealed to the system of six 1 mm wide channels. Hydrogen separation from 1:1 H_2:N_2 mixtures without the use of a sweep gas was demonstrated and the various gas phase and membrane transport effects which may influence data interpretation could be controlled [5].

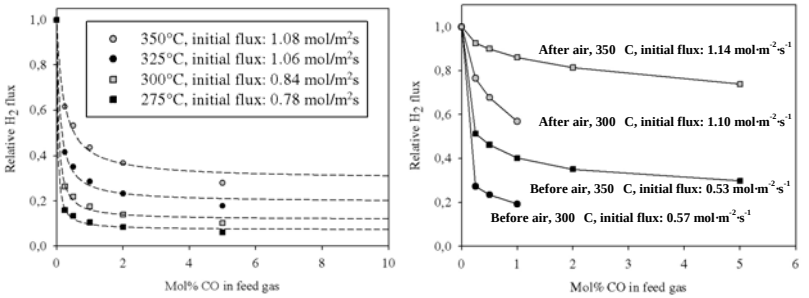

Figure 1. a) Effect of mol% CO in feed on permeation through a 3 µm Pd/23wt%Ag membrane for different temperatures with the initial hydrogen flux at 0 mol% CO given in the legend. The fitted function (---) is also shown. b) Effect of air treatment on the CO sensitivity of a 3 µm Pd/23wt%Ag membrane. The flux is normalized with the flux before CO exposure under equivalent H_2 partial pressure and temperature. Total pressure: 300 kPa. Feed flow: 360 Nml/min H_2 and 40 Nml/min (N_2 + CO). No sweep gas.

Figure 1a illustrates the dramatic effect of CO on membrane permeation, even at concentrations as low as 0.5%, and how this can be fitted with a combined Fick-Langmuir model based on the approach of Barbieri et. al [4]. Figure 1b shows that the impact of CO adsorption is significantly reduced by heat treatment in air. This can be explained as relative changes in bond strength of adsorbed species in a model incorporating the elementary steps.

CO_2 also has a negative effect on permeation. Although much smaller, it slowly reduces the permeation without reaching a stable level over extended time on stream (200 h). It is also slowly reversed upon CO_2 removal from the stream, and hence not easily explained by CO formation through reverse WGS only.

The results show that hydrogen separation from reactant/product mixtures containing CO and CO_2 represents a major challenge, but that opportunities exist for prediction and manipulation of the adsorption processes to the benefit of permeation.

References

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