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Development of Pd/PSS membranes improved by ceramic barrier layers for H_2 separators and membrane reactors

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1. Introduction

In the next years the demand of hydrogen will considerably increase calling for more efficient production and separation processes. Membrane reactors (MRs) combine in a single unit the reaction over the catalyst and the separation of one of the products. In the specific case of syngas or H_2 production by Steam reforming, water gas shift or dry reforming either from fossil or renewable sources of methane, the possibility of using MRs provides some advantages on both the process simplification and efficiency. Palladium based membranes were widely investigated in MRs. Thin palladium based membranes should possess high H_2 permeability and selectivity, thermal stability. In the recent years porous metallic supports have been studied to obtain thin, mechanically stable, defect-free and long lifetime Pd-based membranes. Pd membranes grown directly on the porous metal supports can work in applications where the operating temperature is below 400°C since at higher temperatures intermetallic diffusion will occur negatively affecting H_2 permeability and membrane stability. The introduction of a ceramic barrier layer between the metal support and the Pd layer can prevent the solid state diffusion and improve at the same time the surface characteristics of the porous metal supports for a better growth of the selective layer.

Our study focus on i) the deposition of alumina or zirconia barrier layers on porous stainless steel supports (PSS) through the dip-coating technique of either nanoparticulate sols or sub-micron powder dispersions and ii) on the growth of Pd layers by electroless plating technique in order to obtain stable H2 selective membranes for applications a temperatures higher than 400°C.

2. Methods

The PSS tubular supports were provided by both Mott (USA) and GKN Sinter Metals (Germany). The initial quality of the supports was evaluated through gas-liquid porometry. Commercial alumina and zirconia sols were used for the preparation of the ceramic barrier layer by the dip-coating technique. Sub-micron powder were used to prepared stable aqueous dispersions that were applied to the supports by the infiltration technique. Organic additives (e.g. polyvinyl alcohol or hydroxypropyl cellulose) were used both to control sol viscosity and improve the drying-stress resistance of the gel layers. Pd seeds were introduced in a second ceramic layer. The dense Pd layers were grown by the electroless plating technique. Membranes after each deposition step were carefully characterized through inert gas (He and N_2) permeation at room temperature. Optical microscopy and FE-SEM were used to check the quality of the surfaces and the thickness of the layers. Pure hydrogen and inert gas permeation test were used to calculate the ideal separation selectivity which was correlated with the amount of defect on the final composite palladium membrane. Finally the membrane performance was evaluated on different hydrogen rich mixtures.

3. Results and discussion

It was observed that on the surface of the PSS supports larger pores than the nominal grade porosity are often present and they can strongly affect the quality of the final Pd membrane especially when the thickness of the dense Pd layer has to be limited to less than 30 μm. Therefore a selection of the best PSS tubes through a gas-liquid porometer or a bubble test is essential. A first ceramic layer obtained by using submicron powder dispersion can improve the PSS support as well as the deposition of a ceramic layer from a commercial sol via the dip-coating technique. Figure 1 show the appearance of the surface of the PSS supports after modification with a ceramic layer obtained by the infiltration technique of ZrO_2 sub-micron powder dispersions.

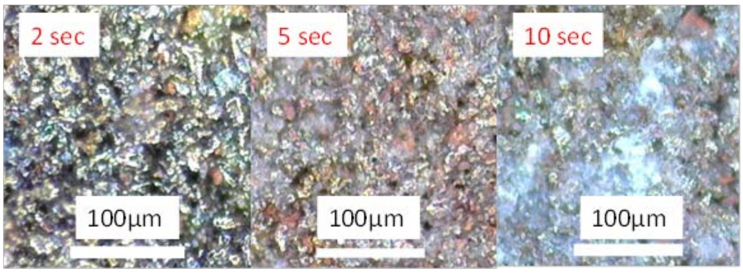

Figure 1. Optical microscopy of the PSS support surface after the sub-micron powder dispersion infiltration at different times.

The dense Pd layer obtained on the modified PSS supports has the typical "culliflower" morphology where the size of the grain was mainly related to the electroless operating conditions. Several electroless plating deposition were necessary to obtain a Pd membrane of sufficient quality for the high temperature tests. Good quality membranes were obtained with thicknesses between 15 and 20 μm. Figure 2 shows H_2/He permselectivity with the temperature for a Pd/Al_2O_3/PSS membrane. The membrane was tested at high temperatures for about 1500h and the exponent of the partial pressure was about 0.6.

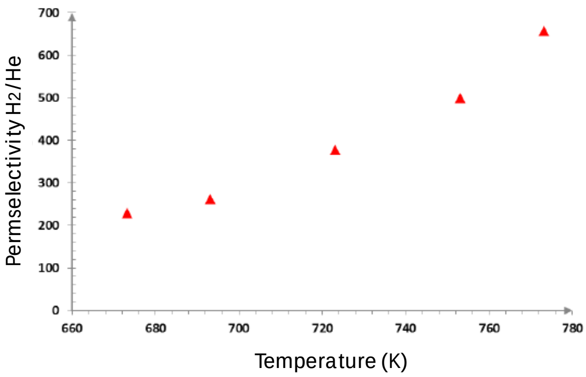

Figure 2. H_2/He permeselectivity of a Pd/Al_2O_3/PSS membrane

4. Conclusions

All the tests showed that the composite Pd/ceramic/PSS membranes exhibited a high hydrogen selectivity and good stability up to 500°C for about 1000 hours. The surface quality of the porous metal support is of paramount importance. Permeation tests at 500°C for 1500 h for the Pd/Al_2O_3/PSS membrane showed stable fluxes and permselectivity. In addition it was estimated the residual defectiveness by permeation measurements. Pd/ZrO_2/PSS membranes needed an higher calcinations temperature (> 600°C) and the surface functionalization of the PSS support with Zirconium isopropoxide improved the anchoring of the barrier layer. The deposition of a submicron powder dispersion allowed to realize a more uniform and defect-free zirconia layer via sol-gel and the final Pd thickness was about 15 microns. The obtained membrane showed promising results in terms of permselectivity for their application as H_2 separators or in MRs.