Austin Chemical Engineering

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Editorial

Pd-Based Membranes for High Temperature Applications: Current Status

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Received: March 25, 2016; **Accepted:** March 28, 2016; **Published:** March 29, 2016

Editorial

On an industrial scale, hydrogen is currently mainly produced by reforming of natural gas, an endothermic reaction system carried out at high temperature (>850°C) followed by high and low temperature water-gas-shift reactors and final hydrogen purification step(s). This conventional system is only efficient at very large scales, where heat integration can be optimized and the excess heat can be exported in the form of steam/power. The main problems for the reaction system are the thermodynamic constrains that limit both the steam methane reforming (endothermic) and water gas shift reactions (exothermic). To achieve high conversions and high hydrogen yields with high efficiency, complex heat integration is required. Up to today, this process is still responsible of plenty greenhouse gas emissions since carbon dioxide capture actions are not implemented at industrial scale. Furthermore, the system cannot be easily scaled down and becomes rather inefficient at smaller scales. The efficiency of the process can be increased by exploiting process integration and process intensification. In this respect, integrating hydrogen production reactions and hydrogen recovery through membranes results in shifting of the equilibria and thus higher efficiencies can be obtained.

Membrane reactors for methane steam reforming have been widely studied using perm selective Pd-based membranes (Pd-MR) for H_2 separation [1-3]. In these novel reactors it has been demonstrated that reforming efficiencies can be improved, where much higher fuel conversions are obtained at much lower temperatures [4-6]. For small-scale hydrogen generation, especially for combined heat and power applications, high conversions can be achieved even at 600°C [7].

Membrane reactor technology has not achieved a consolidated maturity, which implies that the interest on this research field is continuously growing. Research over the last decade has brought the production of thin (< 5μm) dense Pd-based membranes with very high permeation and selectivities [8]. However, it has been observed they suffer from loss in hydrogen perm-selectivity during long-term operation at temperatures above 500°C [9,10]. It was reported that Ag sublimation in the case of Pd-Ag membranes, grain growth or problems associated to the membrane preparation procedure could generate pinholes on thin membranes [11,12]. On the other hand, the support material and its morphology could also strongly influence the performance of the membrane. A good adhesion of the Pd layer onto the support is required to assess high perm-selectivities. If the roughness of the support is not optimum, very thin membrane layers might not be able to completely cover all the pores of the support, thus decreasing the purity of the H_2 permeated. Two main support materials have been used for the preparation of thin Pd-membranes, ceramic and metallic supports, which show different advantages and disadvantages. From one side, ceramic supports show an increased H_2 transport through the support (higher permeances). However, the sealing of the membrane becomes complex and at high temperatures the different thermal expansion of the ceramic support and the Pd layer might cause defects on the surface. On the other side, when considering metallic supports the connection of the membranes to the reactors is much simpler. However, the transport of hydrogen through the metallic matrix is hindered and becomes the main resistance for hydrogen permeation. Furthermore, if the metallic membrane is operated at high temperatures (> 500°C), interaction between the components of the support (mostly Ni, Fe and Co) and the Pd layer takes place. This interaction implies the formation of Pd-alloys, thus reducing the active surface for permeation [13-15].

As discussed, ceramic supported membranes are preferred when high hydrogen fluxes are targeted, whereas metallic supported membranes are more suitable if simple coupling of the membranes in reactors is desired (especially in large multi-tubular reactors). Nowadays, many research groups are putting efforts on improving membrane preparation methods to enhance long-term thermal stability of these membranes, either by producing denser selective layers and/or defect-free microstructures [16,17]. Another main limitation of membrane reactors technology is thermal stability of the membranes, which is not fully guaranteed above 550°C. Nowadays, the main research direction on this issue is related to the substitution of Ag by another element with higher melting points (i.e. Pt, Ru) to produce improved Pd-alloy membranes [18,19].

Sealing issues with ceramic supported membranes for high temperature applications have been recently investigated in the literature. Different methods such as soldering or the use of inorganic adhesives have been studied, although they were not able to provide the required leak-free conditions. Another solution which is up to now the most promising approach is based on the use of graphite gaskets [20]. Recently a sealing procedure based on high temperature Swagelok nuts and graphite ferrules has shown a leak-tight sealing for a week operation in a fluidized bed membrane reactor for steam methane reforming [10,21]. Constant hydrogen fluxes through the

Citation: Gallucci F, Fernandez E, Medrano JA, Pacheco Tanaka DA and van Sint Annaland M. Pd-Based Membranes for High Temperature Applications: Current Status. Austin Chem Eng. 2016; 3(1): 1025.

membrane with sustained ideal selectivities were achieved during the experiment, although more experimental investigation is needed to fully prove the sealing method.

The main issue related to metallic supports is the formation of undesired alloys when operating at high temperatures which reduce the surface area and are responsible of pinholes formation. Recently this problem has been addressed by the deposition of ceramic barriers in between the support and the Pd layer [22]. These barriers consist in ceramic nanoparticles onto the metallic support. It has been demonstrated that the roughness of the metallic support and the thickness of the ceramic barrier are two parameters with a strong influence on the quality of the final membrane. Thermal stability has been assessed for more than a month and post analysis characterization has demonstrated that the ceramic barrier avoids the metallic interaction.

Membrane reactors is thus a very promising technology which is nowadays in its last stage before industrial implementation; many projects foresee membrane reactor piloting to assess thermal stability and lifetime of the membranes under realistic industrial conditions. Also possible interactions between the membrane and catalysts or gas impurities such as sulphur could limit the applicability of Pd-based membrane reactors and these are being assess at lab-scale and pilot scale as well.

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Austin Chem Eng - Volume 3 Issue 1 - 2016
ISSN : 2381-8905 | www.austinpublishinggroup.com

Citation: Gallucci F, Fernandez E, Medrano JA, Pacheco Tanaka DA and van Sint Annaland M. Pd-Based Membranes for High Temperature Applications: Current Status. Austin Chem Eng. 2016; 3(1): 1025.