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Novel catalytic membrane micro-reactors for CO_2 capture via pre-combustion decarbonization route

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Concerns over global climate change have resulted in technological developments for gradually reducing the production and/or the emissions of greenhouse gases particularly CO_2 by capture at the source. The decarbonization of fossil fuels is a technology for CO_2 mitigation in which carbon is removed before (pre-combustion) or after (pos-combustion) combustion. Pre-combustion decarbonization is an attractive route which can be applied, on a large scale. The process can be performed by combination of reforming reactions (i.e. steam reforming (SR)), water-gas shift (WGS) or gasification. Natural gas or coal/biomass can be used as raw-materials and an out-stream rich in hydrogen (H_2) is generated. The CO_2 produced is concentrated and captured by physical (e.g. cryogenic separation) or chemical processes. The reactions of interest in this research are steam methane reforming (SMR) (1) and water-gas shift (WGS) (2). The overall reaction is given by (3) below.

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H_{298} = +206.1\ \mathrm{kJ/mol} \quad (1)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_{298} = -41.15\ \mathrm{kJ/mol} \quad (2)$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \qquad \Delta H_{298} = +165.0\ \mathrm{kJ/mol} \quad (3)$$

Since SMR is endothermic and results in an increase in total molar flow, the reforming reactions are thermodynamically favoured at high temperatures and low pressures. On the other hand, the WGS reaction is exothermic with no change in the number of moles and is favoured at low temperatures. In conventional processes, the reactions are performed in separate fixed-bed catalytic reactors (FBRs) and the product separation is carried out in a second stage, normally, preceded or followed by a purification procedure. The required operating conditions, as well as the multistep character of the process, lead to high energy and operating costs.

This research aims to develop a catalytic hollow fiber membrane micro-reactor, which combines the SMR/WGS reactions and H_2 separation into a single compact unit. The membrane micro-reactor consists of a Pd-based hydrogen separation layer supported on an alumina hollow fiber substrate with a unique asymmetric structure: a sponge-like layer and a finger-like voids region (radial micro-channel). A catalyst is deposited in these micro-channels and as a result, they provide extremely high membrane surface area-to-volume ratios compared to conventional membrane systems, which is essential for application, and high catalyst loading in a single fiber [1] (Figure1).

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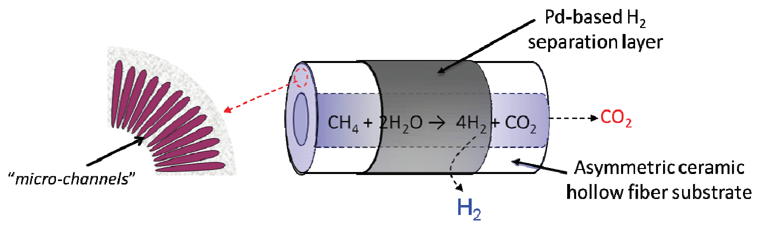

Figure 1 – Schematic representation of a catalytic hollow fiber membrane micro-reactor

The system is fed with methane and steam, while hydrogen, carbon monoxide and carbon dioxide are produced. The hydrogen is continuously removed from the reaction zone, which shifts the reaction towards the product side. As a result, the thermodynamic equilibrium limitations are overcome, a higher reactant conversion is achieved at lower temperatures and the energy-efficiency can be improved.

The asymmetric hollow fiber substrate, which is fabricated by combined phase inversion and sintering technique, has an ideal morphology to be used simultaneously as a substrate for the membrane deposition and as support for the catalyst. The outer sponge-like layer has a pore size between 100-150nm and a roughness which allows the deposition of a thin and defect-free palladium-based separation layer. H_2 permeation experiments have been performed confirming the preparation of a highly selective Pd-based membrane with a permeation flux of $14 L.m^{-2}.s^{-1}$ (450ºC and ΔP=3atm). The finger-like voids area consists of cylindrical channels with an entrances size of approximately 10µm. The operating temperature range for a catalytic hollow fiber membrane micro-reactor is from 300ºC to 600ºC.

Catalysts based on nickel and rhodium supported in SBA-15 with additional promoter are being developed using a sol-gel technique combined with impregnation. Preliminary measurements indicate that these catalysts have sufficient activity in the temperature range of interest. Current research is focused on control of the volume and pore size of the finger-like voids, and on the influence of the catalyst particles on the porosity and H_2 permeation flux.

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Keywords: CO_2 capture, Steam Methane Reforming, Water-gas Shift, Membrane Micro-reactor, Hydrogen Separation, Nickel-based catalyst, SBA-15.

Reference

[1] Kingsbury BFK, Li K. A morphological study of ceramic hollow fibre membranes, J. Membrane Science, 2009; 328 (1-2): 134-140.

Keywords: CO2 Capture, Steam Methane Reforming/Water-gas Shift, Membrane Micro-Reactor, Hydrogen Separation