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Catalytic hollow fibre based reactors for a enhance H_2 production by methanol steam reforming

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The use of asymmetric ceramic hollow fibres as a support of either catalysts, selective membranes or both catalyst and selective membrane at the same time, is the key step for an economical, large scale and effective H_2 production[i]. Nowadays, H_2 is not only widely used in industrial processes, but also it is growing the interest of using it as an energy vector in the scientific community[ii]. However, today, 96% of the total global H_2 production (45 million tons per year) comes from steam reforming of fossil fuels which is an endothermic and thermodynamic equilibrium limited process. Moreover, steam reforming of fossil fuels involves several stages such as production and purification, and produces a certain amount of CO_X, which has a greenhouse gas effect and it must be captured. The use of enhance reactors such as catalytic hollow fibre micro reactor (CHFmR) and catalytic hollow fibre membrane reactor (CHFMR) allow the intensification of the whole process.

In this context, methanol is a promising renewable source of H_2 since it can be easily decomposed in the presence of H_2O to produce H_2: $CH_3OH + H_2O \rightarrow CO_2 + 3H_2$ (ΔH^o = + 49.4 kJ/mol). In addition, the CO_2 produced during the methanol steam reforming (MSR) reaction is consumed by biomass growth which nearly closes the carbon loop. The chemical-physical properties of methanol, i.e. liquid at room temperature and atmospheric pressure, make it possible to be used as a “storage-molecule” of H_2 for on-board applications[iii].

Based upon all these, the main objective of this work is to develop both CHFmR and CHFMR and to compare their performance with that of a classic fixed-bed reactor (FBR) during the MSR reaction. With this propose, Al_2O_3 hollow fibres, synthesized by a phase-inversion technique followed by sintering at high temperature, have been employed as a support of $Cu/Zn/GaO_X$ based catalyst and Pd/Ag membrane in the development of the CHFmR and CHFMR, respectively. The $Cu/Zn/GaO_X$ based catalyst was successfully deposited inside the finger-like region of the both Al_2O_3 hollow fibre by co- precipitation and characterized by X-ray diffraction and SEM-EDS analysis. The Pd/Ag membrane was deposited by an electroless plating technique and was characterized by SEM, and He and H_2 permeability. A schematic representation of both enhance hollow fibre reactors it is shown in Figure 1. This preliminary study enables to identify the limiting stage of the whole process in each reactor, which allows the further optimization of both the CHFmR and CHFMR.

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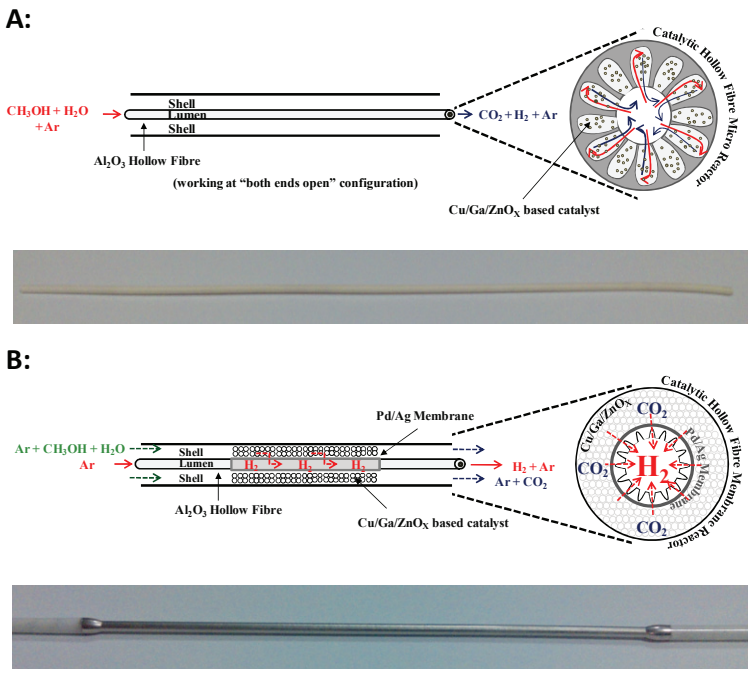

Figure 1 Schematic representation of: A) catalytic hollow fibre micro reactor (CHFmR) and B) catalytic hollow fibre membrane reactor (CHFMR) employed for an enhance H_2 production by MSR reaction.

A summary of the CH_3OH conversion and H_2 selectivity at different reaction temperatures using the CHFmR and a classic FBR is shown in Table 1. It has been observed that the dispersion of the catalysts inside the finger-like region of the Al_2O_3 hollow fibre not only enhances the CH_3OH conversion buy also improves the H_2 selectivity. For example, at 300 ºC the CH_3OH conversion in the CHFmR was 22.9 % which is 5.6 times larger than that obtained in a conventional FBR (4.1 %). Likewise, at 300 ºC the CO produced in the CHFmR was 1092 ppm which is 4 times smaller than that produced in a conventional FBR (4403 ppm). This behaviour suggests that the CHFmR intensifies the contact between the reactants and catalyst, whereas in the conventional FBR the conversion is limited by pore diffusion. In addition, the short contact time between the reactants and catalyst enables to achieve a maximum selectivity for a given catalyst.

On the other hand, the design of the CHFMR allows not only obtaining a high purity CO_X free H_2 production by MSR reaction but also working at significantly lower temperature than in a traditional FBR. At 300 ºC the methanol conversion in the CHFMR was 94 % which is 22 % higher than that obtained in the traditional fixed-bed reactor. Likewise, at 250°C and using a sweep gas of 100 ml/min in the CHFMR, the H_2 recovery index of the Pd/Ag membranes was 50%, which showed the feasibility of a large production of high purity H_2 (5.5 ml/mg.hr). Although, competitive adsorption of CH_3OH, H_2O and CO_2 on the Pd/Ag membrane surface decreases its H_2 permeability, their poisoning effect can be considered relatively weak at the MSR reaction operating conditions Finally, the Pd/Ag membrane was stable under the reaction conditions, showing high H_2 permeance (1.2×10^{-3} $molm^{-2}s^{-1}Pa^{-1/2}$ at 300 ºC) and permeability (7.6×10^{-9} $molm^{-1}s^{-1}Pa^{-1/2}$ at 300 ºC) and infinite selectivity to H_2.

Table 1 Performance during the MSR reaction of the CHFmR and conventional fixed bed reactor using as a catalyst the grounded from asymmetric Al_2O_3 hollow fibre impregnated with 10% $Cu/Zn/GaO_X$ based catalyst.

Temperature (ºC)	FBR		HFMR	
	CH_3OH Conv (%)	CO (ppm)	CH_3OH Conv (%)	CO (ppm)
150	0.0	n.d.	0.0	n.d.
190	0.1	28	0.1	n.d.
250	0.9	1218	2.6	33
300	4.1	4403	22.9	1092

n.d = no detected

Based upon these preliminary results, CHFmR and CHFMR open the door for new and promising applications in a near future, which was not possible before due to expensive production procedure and the complex set up process of the conventional membrane and micro-reactors.

Keywords: catalytic hollow fibre based reactors, H2 production, methanol steam reforming

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