Development of a Catalytic Hollow Fibre Membrane Micro-Reactor for High Purity H₂ Production

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ABSTRACT

This article describes development of a catalytic hollow fibre membrane micro-reactor (CHFMMR) for high purity H₂ production. Asymmetric Al₂O₃ hollow fibres produced by a phase-inversion and sintering technique were employed as a single substrate for both coating of the Pd membrane and impregnation of the 30%CuO/CeO₂ catalyst. The Pd membrane was first deposited onto the outer layer of Al₂O₃ hollow fibre using the electroless plating (ELP) technique, followed by impregnation of the 30%CuO/CeO₂ catalyst into the inner finger-like structure of the substrate using the sol-gel Pechini method. Performance of the proposed reactor was carried out using water gas shift (WGS) reaction as a sample reaction. A comparative study of conversion obtained in the WGS reaction as a function of the reaction temperature (from 200°C to 500°C) in a fixed-bed reactor, a catalytic hollow fibre micro-reactor (CHFMR) and the CHFMMR using different flow rates of a sweep gas (from 45 to 70ml/min) was performed, concluding that the conversion is the highest in the CHFMMR. It is important to highlight that, at 500°C and a sweep gas flow rate of

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75 ml/min, a conversion of 17% higher than the corresponding thermodynamic equilibrium conversion was achieved in the CHFMMR. In the operation of the CHFMMR, high purity H₂ has been obtained in the shell side, which was 78 % of the total H₂ produced in the WGS reaction.

Keywords: Catalytic hollow fibre membrane micro-reactor, Alumina hollow fibre, Hydrogen production, Pd membrane, Sol-gel method

1. Introduction

In recent years, interests in the development of micro-reactors for different catalytic reactions have increased due to the advantages that this technology offers in both homogenous and heterogeneous catalysis. The advantages of micro-reactor technology include: high surface area to volume ratio, high heat and/or mass transfer, low pressure drop, good phase contacting, instant mixing of reactants and high selectivity [1-5]. Moreover, micro-reactors can also be used for large scale production since they can easily be scaled up to industrial volumes by multiplying the number of micro-reactors, that additionally makes the system safer [6].

So far, a variety of micro-reactors has been proposed by a number of authors, where the effect of both design aspects and mode of operating conditions on the catalytic performance has been studied [7-9]. The development of commercially viable micro-reactor devices requires low-cost and standard fabrication techniques along with resistant materials that permit the synthesis of appropriate three-dimensional micro-channel structures under reaction conditions [10]. Moreover, since the geometric surface of the micro-channels is unable to provide sufficient specific surface area for impregnating catalysts, which are necessary for most of the catalytic

reactions, chemical treatments and porous coatings must be applied over the surface of the micro-channels walls [11].

On the other hand, although the use of micro-reactors has been reported as a powerful tool that is able to increase significantly the performance of catalytic reactions, the operation of micro-reactor is limited to the equilibrium conversion, similar to the conventional fixed-bed reactor. This limitation can be overcome by including a selective membrane into the micro-reactor design which removes one of the products from the reaction zone. Such concept, i.e. catalytic membrane micro-reactor, allows not only the reactor to work under optimum reaction conditions but also at significantly lower operating temperature and/or using less amounts of catalyst than conventional reactors, because of combining the reaction and separation steps in one unit.

Recently, we developed an Al_2O_3 hollow fibre with an asymmetric pore structure, i.e. a dense sponge-like outer region and an open porous finger-like inner region where a selective membrane and a catalyst can be deposited, respectively [12]. Moreover, the combination of high chemical, thermal and mechanical resistance of Al_2O_3 makes it an attractive option for a number of reactions under very different operating conditions. Since the Al_2O_3 hollow fibres have a tubular geometry with an outer diameter smaller than 2 mm, it is relatively easy to scale up by bundling the Al_2O_3 hollow fibres to a module, which makes the system safer. In comparison with conventional microreactor systems, the Al_2O_3 hollow fibre presents an advantage that insignificant heat loss through the tubing by conduction can be realised. In addition, the fact that Al_2O_3 hollow fibre lengths as long as 40-50 cm and as short as 1-2 cm can be employed, while maintaining their chemical and physical properties, allows their use not only for large-scale but also for small-scale applications such as on-

board H₂ production. Finally, Al₂O₃ hollow fibres are synthesised by a dry-wet spinning and phase-inversion technique followed by sintering at high temperature, which is a low-cost and fabrication technique.

The main objective of this work was the development of a catalytic hollow fibre membrane micro-reactor (CHFMMR) for pure H₂ production, using the asymmetric Al₂O₃ hollow fibre as a substrate for both Pd membrane and catalyst. With this purposes, water-gas shift (WGS) reaction has been chosen to test the performance of the CHFMMR, comparing its performance with a corresponding catalytic hollow fibre micro-reactor (CHFMR) and a fixed-bed reactor.

2. Experimental

2.1. Materials

Ce(NO₃)₃.6H₂O ($\geq$ 99.0%, Fluka Analytical) Cu(NO₃)₂.3H₂O (99.0%, Acros Organic), ethylene glycol (99+%, Acros Organic) and citric acid ($\geq$ 99.0%, Sigma-Aldrich) were used to prepare a homogeneous catalyst solution using the sol-gel Pechini method. Pd(NH₄)₂Cl₄ (ammonium tetrachloropalladate, 99.99%, Aldrich), SnCl₂.2H₂O, Na₂EDTA.2H₂O, HCl (37%), N₂H₄, AgNO₃, and NH₃.H₂O (28%) (Fisher Sci. Ltd) were used for preparing Pd membranes using the electroless plating (ELP) technique.

2.2. Preparation of Al₂O₃ hollow fibre substrates

Asymmetric Al₂O₃ hollow fibre substrates, which have a 1.9 mm O.D and a 1.0 mm I.D., have been fabricated by members of our research group through the processes of phase-inversion spinning and sintering technique. The work has been reported in detail elsewhere [12].

2.3. *Impregnation of 30%CuO/CeO₂ in Al₂O₃ hollow fibre for development of CHFMR*

30%CuO/CeO₂ has been chosen as a catalyst for the WGS reaction, prepared using the sol-gel Pechini method [13]. In a typical preparation, Ce(NO₃)₃·6H₂O (17.66 g) and Cu(NO₃)₂·3H₂O (9.11 g) were first dissolved in 50 ml deionised water, then followed by citric acid. The amount of copper used in this catalyst was similar to the work reported elsewhere by Li et al [14]. Citric acid was added to the solution with a mole ratio of citric acid to total metal ions of 2:1. After citric acid was fully dissolved, ethylene glycol was added into the solution with a ratio of citric acid to ethylene glycol of 1:1.2. The solution was further stirred for 24 hours to obtain homogeneous catalyst solution.

In a typical catalyst impregnation, the outer surface of Al₂O₃ hollow fibre was wrapped with the PTFE tape to prevent direct contact with the catalyst solution. The catalyst solution was injected using a glass pipette into the lumen of Al₂O₃ hollow fibres and this process was repeated several times. The Al₂O₃ hollow fibres were later immersed in the catalyst solution before being dried in an oven (Salvislab Thermocenter) at temperatures ranging from 60 – 90 °C for 24 hours and further dried at 115 °C for 2 hours to complete the polymerisation of a polymeric resin precursor. The calcinations process was later carried out at 400 °C for 1 hour. The catalyst loading in the Al₂O₃ hollow fibre was obtained by measuring the weight of Al₂O₃ hollow fibre substrates before and after calcinations steps. The mercury intrusion analysis was used to study the effect of impregnation process on the pore size of Al₂O₃ hollow fibre. Prior to analysis, samples were broken into sections of approximately 3 mm in length. Mercury intrusion data was collected at absolute pressure between 1.38×10^3 Pa and 2.28×10^8 Pa (0.2-33,000 psia) (Micromeritics

Autopore IV) with an equilibrium time of 10 s. The BET surface areas of the Al_2O_3 hollow fibre before and after the impregnation process were measured using N_2 adsorption isotherms (TriStar 3000). The permeation tests were carried out on bare Al_2O_3 hollow fibre and those impregnated with the 30%CuO/CeO₂ catalyst to study the permeability of the substrate before and after the impregnation process. The SEM-EDS analysis (INCA Energy by Oxford Instruments) was carried out to investigate the presence of the WGS catalyst on the inner surface of the Al_2O_3 hollow fibre.

2.4. Fabrication of Pd membrane

Pd membranes were plated onto the outer surface of Al_2O_3 hollow fibres using the ELP technique. Prior to the activation process, Al_2O_3 hollow fibres were cleaned using deionised water and activated subsequently by the conventional Pd-Sn activation procedure. The activation process was repeated six times, after which the surface colour of Al_2O_3 hollow fibre changed from white to dark brown. The Al_2O_3 hollow fibres activated with Pd seeds were then plated with Pd layer using the ELP technique and this process was repeated three times to obtain 6 micron-thick Pd membranes plated on the outer layer of Al_2O_3 hollow fibre. These Pd membranes were dried in an oven at 120 °C for 2 hours (Memmert). The thickness of Pd membrane was measured using the gravimetric method and it was confirmed using the SEM analysis. The permeation tests using pure H_2 and Ar were carried out to study the permeability of Pd membrane and to investigate the presence of pinhole structure on the surface of Pd membrane.

2.5. *Development of the CHFMMR and the catalytic activity tests*

In the development of the CHFMMR, a single step impregnation has been used to impregnate 30%CuO/CeO₂ into the finger-like structure of Al₂O₃ hollow fibre. The impregnation of 30%CuO/CeO₂ has been carried out after the fabrication of the Pd membrane in order to avoid the dissolution of copper into the plating solution due to the presence of ammonia and EDTA in the plating solution [15].

The outer surface of the Al₂O₃ hollow fibre was coated with a thin and gas-tight layer of white glaze except the central part of *ca* 10 cm, which was left for the plating of the Pd membrane. The Pd membrane was then plated on the outer surface of Al₂O₃ hollow fibre using the ELP technique. The Al₂O₃ hollow fibre with Pd membrane on its outer surface was wrapped with the PTFE tape to prevent a direct contact between the catalyst solution and the Pd membranes. A homogeneous catalyst solution was later injected into the lumen of Al₂O₃ hollow fibre substrates using a glass pipette and this process was repeated several times. The Al₂O₃ hollow fibres were then dried in an oven (Salvislab Thermocenter) at 60 °C for 24 hours and further dried at 115 °C to complete the polymerisation of a polymeric resin precursor. The catalyst solution would turn into xerogel, which adsorbed onto the inner surface of Al₂O₃ hollow fibre substrates. The oxidation of xerogel formed during the drying process was carried out in a tubular furnace (Vecstar Furnaces, VCTF/SP). The temperature was increased from room temperature to 400 °C at a rate of 5 °C and held for 1 hour. A flowing air was introduced into the lumen-side for completing the oxidation process. Argon was introduced on the outer surface of the Pd membrane throughout this process to prevent an oxidation of the Pd membrane which may cause a pin-hole formation. The morphologies of Al₂O₃ hollow fibre and the CHFMMR were studied using the scanning electron microscope (SEM) (JEOL JSM-5610LV).

The catalytic activity tests of the CHFMR were carried out using Al_2O_3 hollow fibres (without the Pd membrane on its outer surface) in two distinct configurations, open-both-end configuration and the dead-end configuration, as shown in Fig. 1. The Al_2O_3 hollow fibres, shown in Fig. 1a, enabled the reactants to flow through the lumen of Al_2O_3 hollow fibres whereas the dead-end configuration, shown in Fig. 1b, forced the reactant to permeate through finger-like structure and sponge-like structure. The open-both-end configuration and the dead-end configuration gave an almost similar CO conversions, showed that the open-both-end configuration used to examine the catalytic activity enabled the reactants to reach the 30%CuO/CeO₂ catalyst on the inner surface of Al_2O_3 hollow fibres.

In order to study the usefulness of the finger-like structure for the WGS reaction, Al_2O_3 hollow fibres impregnated with 30%CuO/CeO₂ catalyst were ground into powder (to eliminate the finger-like region) for using them as a fixed-bed reactor for the sake of comparison. The Al_2O_3 powder, with particle size approximately 100 μm , was packed into 6 mm ID ceramic tube. The packed-bed length was approximately 20 mm and the mass transfer limitation across the bed was negligible.

The catalytic activity tests in a fixed-bed reactor, the CHFMR (without the Pd membrane) and the CHFMMR were carried out under atmospheric pressure over a temperature range of 300 °C to 500 °C. The feed mixture contains CO (5%) and water vapour which was supplied to the reactor by flowing argon through a glass bubbler containing deionized water at 60 °C. The mole ratio of water vapour to CO was kept at 0.5 throughout the catalytic activity test. The WGS reactions were carried out at a space velocity of 80,000 $\text{cm}^3\text{g}^{-1}\text{hr}^{-1}$. In a typical catalytic activity test, the weight of the WGS catalyst was 18 mg and the total flow rate was 24 $\text{cm}^3\text{min}^{-1}$. The concentration of the products were measured using a TCD gas chromatography

(Varian-3900) while the actual flow rate was measured using a bubble flow meter. The GC injections for gas analysis for every reactor used in this study were repeated three times to obtain more reliable results. The CO conversion is defined as follows:

$$\text{CO conversion (\%)} = \frac{1 - F_{CO}^{out}}{F_{CO}^{in}} \times 100\% \quad (1)$$

In the operation of CHFMMR, H₂ produced in the WGS reaction would be separated using the Pd membrane on the outer surface of the CHFMMR. The removal of H₂ from the reaction zones was carried out using a co-current flow of a sweep gas to create a concentration gradient across the Pd membrane. The H₂ recovery index which represents the ability of Pd membranes to perform H₂ permeation is defined as follows:

$$\text{H}_2 \text{ recovery index (\%)} = \frac{F_{H_2}^{Permeate}}{F_{H_2}^{Permeate} + F_{H_2}^{Retentate}} \times 100\% \quad (2)$$

3.0 Results and Discussion

3.1 Al₂O₃ hollow fibre substrates

The morphologies of the Al₂O₃ hollow fibres, used as a substrate for both the Pd membrane and the 30%CuO/CeO₂ catalyst in the development of the CHFMMR, were studied using the SEM. Fig. 2a-b shows the SEM images of the cross sections of an Al₂O₃ hollow fibre at different magnifications. As can be seen, Al₂O₃ hollow fibre prepared by a phase-inversion technique followed by sintering process at a high temperature has an asymmetric pore structure, which consisted of finger-like voids approximately 80 % of the fibre cross-section with the remaining 20 % consisting of a sponge-like region [12]. At a higher SEM magnification, the difference in the pore size distributions between the finger-like structure and the sponge-like region can be examined. The narrow pore size distribution of sponge-like structures enabled the

deposition of a thin Pd membrane on the outer surface of the Al_2O_3 hollow fibre whereas the open pore structure of the finger-like region enabled the impregnation of the 30%CuO/CeO₂ catalyst in the inner surface of the Al_2O_3 hollow fibre.

3.2 *Impregnation of 30%CuO/CeO₂ into the Al_2O_3 hollow fibre*

The impregnations of 30%CuO/CeO₂ catalyst into the finger-like structure of the Al_2O_3 hollow fibre were carried out using the sol-gel Pechini method [13]. Conventionally, the drying processes of various catalyst solutions using the sol-gel Pechini method are carried out at temperatures ranging from 90 °C to 150 °C to facilitate the polymerization process between ethylene glycol and citric acid [13]. The impregnations of 30%CuO/CeO₂ into Al_2O_3 hollow fibre had been carried out using the conventional approach but the amount of the catalyst obtained was very low because the sol-gel formed in this process swelled and spread, leaving the inner surface of Al_2O_3 hollow fibre substrates, consequently caused a reduction in the amount of CuO/CeO₂. Therefore, a reduction in the drying temperature was essential to ensure a maximum amount of CuO/CeO₂ could be impregnated onto the inner surface of the Al_2O_3 hollow fibre.

In this study, two-step drying processes were carried out to turn homogeneous catalyst solution to xerogel and to increase the amount of catalyst in the inner surface of Al_2O_3 hollow fibre. The pre-drying process was first carried out at temperatures ranging from 60 °C – 90 °C to allow the removal of excess solvent (water) and to avoid excessive swelling of sol-gel which could reduce the amount of 30%CuO/CeO₂ in Al_2O_3 hollow fibre. Fig. 3 the amount of 30%CuO/CeO₂ impregnated into the inner surface of Al_2O_3 hollow fibre, which show a slight increase when the pre-drying temperature was decreased from 90 °C to 60 °C. The pre-drying process was

recognized as a crucial step that could influence the amount of catalyst during the sol-gel impregnation. The maximum amount of 30%CuO/CeO₂ could be impregnated was around 6% when the pre-drying process was carried out at 60 °C and this condition has been chosen for the impregnation of the catalyst into Al₂O₃ hollow fibre in the development of the CHFMR and the CHFMMR.

Fig. 4 shows the mercury intrusion data for Al₂O₃ hollow fibres before and after the impregnation process. Two different pore size distributions corresponding to the sponge-like structure ($d_p = 0.1 \mu\text{m}$) and the entrance of the finger-like voids ($d_p = 10 \mu\text{m}$) can be clearly seen. After impregnated with 30%CuO/CeO₂, the pore size distribution in the sponge-like region and finger-like structure decreased from 0.15 to 0.08 μm and from 9.17 to 8.97 μm , respectively. The impregnation of the 30%CuO/CeO₂ catalyst into Al₂O₃ hollow fibres reduced the size of micro-pores and macro-pores in both regions but a significant decrease can be seen in the size of micro-pores in the sponge-like region. The reduction in the pore size distribution in both regions can be associated with the ability of a homogeneous catalyst solution to diffuse through a transverse network of narrow channels and to form a highly porous xerogel after being subjected to a drying process. The calcination process, which carried out afterward, oxidised the xerogel into catalyst particles which partially filled the pores of Al₂O₃ hollow fibre substrate.

The specific surface area of the Al₂O₃ hollow fiber increased from 2.2 to 7.1 m²/g after a catalyst impregnation process. The presence of 30%CuO/CeO₂ in the inner surface of Al₂O₃ hollow fibre impregnated using the sol-gel Pechini method resulted in an increase in the specific surface area of the Al₂O₃ hollow fiber. It has been known that the mixed oxides produced using the sol-gel Pechini method has higher specific surface areas compared to other conventional approaches [16].

Permeation tests were carried out using pure N_2 on the Al_2O_3 hollow fibre before and after impregnated with 30%CuO/CeO₂ to study the effect of the catalyst impregnation process on the permeability of the Al_2O_3 hollow fibres and the results are shown in Fig. 5. The permeation data for a bare substrate suggested that Al_2O_3 hollow fibres consisted of the finger-like structure and the sponge-like region was permeable to N_2 . The permeability of Al_2O_3 hollow fibres reduced when 30%CuO/CeO₂ was impregnated into its inner surface and a 27% decrease in the N_2 permeability was observed at the highest pressure difference. This occurred due to the presence of 30%CuO/CeO₂ that reduced the micro-channel volume particularly in the sponge-like region.

In the operation of CHFMMR, the pressure difference across Al_2O_3 hollow fibre was negligible because the separation of H_2 from reaction zone was carried out using a sweep gas. The permeability data in Fig. 5 suggests that permeability difference between bare Al_2O_3 hollow fibres and those impregnated with 30%CuO/CeO₂ was negligible when the pressure difference used in the permeation test was very low. Asymmetric Al_2O_3 hollow fibres impregnated with 30%CuO/CeO₂ still have higher permeability which sufficient for reaction products, produced during the WGS reaction, to reach Pd membrane on the outer surface of Al_2O_3 hollow fibres and it could still be used as a substrate for both the Pd membrane and the catalyst in the development of the CHFMMR.

An elemental analysis using the SEM-EDS surface mapping technique was carried out on the cross-section of Al_2O_3 hollow fibres to study the dispersion and distribution of the 30%CuO/CeO₂ catalyst. Fig. 6 shows the presence of Cu and Ce after the impregnation process. An asymmetric distribution of 30%CuO/CeO₂ catalyst in the finger-like region showed that more catalyst particles can be seen on the region

that close to the Al_2O_3 hollow fiber lumen side. This behaviour might be associated with an insufficient driving force to push excess catalyst sol-gel deeper into the finger-like structure and this caused an accumulation of the 30%CuO/CeO₂ catalyst in the narrow threshold of this structure. However, a uniform dispersion for both Cu and Ce on the cross-section of the substrate indicated that the sol-gel Pechini method successfully dispersed the 30%CuO/CeO₂ catalyst into the Al_2O_3 hollow fibres.

3.3 *Deposition of the Pd membrane onto Al_2O_3 hollow fibre substrates*

The outer surface of Al_2O_3 hollow fibre was seeded with Pd particles using a conventional activation process before the deposition of Pd membrane. This process has been recognised as a crucial step for growing a uniform and dense Pd membrane [17]. Fig. 7a and Fig. 7b shows the outer surface of the Al_2O_3 hollow fibre before the activation process and after 6 activation steps, respectively. After 6 activation steps, the outer surface of Al_2O_3 hollow fibre has been fully covered with Pd clusters with an average particle size of 50 nm as shown in Fig. 2b. The use of Al_2O_3 hollow fibre as the support for Pd membrane eliminated the necessity of using an intermediate layer, which is typically applied to close macropores and prevent the intermetallic diffusion at higher temperatures, due to a small and narrow pore size distribution of sponge-like region in the outer layer and stability of Al_2O_3 at higher temperatures [18,19]. The Pd membrane obtained using the ELP technique is shown in Fig. 7c. The thickness of the Pd membrane was 6 μm , which was close to 5.4 μm estimated by the gravimetric method. According to Ma et al., [20] the thickness of Pd layer has to be at least three times higher than the maximum pore diameter of a porous substrate to avoid leaks on the surface of Pd membrane. Although the actual thickness of the Pd membrane used in this study was higher than its theoretical value (the largest porous

size was around 0.3 μm), it was an advantage in avoiding the formation of defects due to the sintering of Pd particles at high temperatures during the WGS reaction [21]. Fig. 7d shows that the Pd membrane on the outer surface of Al_2O_3 hollow fibre plated using ELP technique has homogeneous and uniform surface and free from defects.

Permeation tests were carried out on the Pd membrane using pure H_2 and Ar gases in order to test the H_2 permeability and H_2/Ar selectivity before being used in the CHFMMR. Fig. 8a shows the H_2 permeation flux through the Pd membrane as a function of square root pressure difference estimated between shell and lumen side pressures. The graph shows that the permeation of H_2 increased as the temperature and/or the pressure in the lumen of Al_2O_3 hollow fibre was increased. The linear fit shows that the H_2 permeation through the Pd membrane followed the Sievert's law. From Fig. 8, the H_2 permeances of Pd membrane were 6.9, 8.3, 9.5 and 10.7 $\text{L}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{atm}^{-1/2}$ at 300, 350, 400 and 450 $^\circ\text{C}$, respectively. On the other hand, Ar did not permeate through the Pd membrane at any testing conditions applied during the permeation tests, showed an infinite selectivity of the Pd membrane towards H_2 . Based on these results, it can be concluded that the Pd membrane plated on the Al_2O_3 hollow fibre was absolutely dense and free from defects, which was in agreement with the result obtained in the SEM analysis as shown in Fig. 7d.

3.4 *The WGS reaction in a catalytic hollow fibre membrane micro-reactor (CHFMMR)*

A comparative study of the CO conversion obtained in the WGS reaction as a function of the reaction temperatures in a fixed-bed reactor, the CHFMR and the CHFMMR using different flow rates of a sweep gas are shown in Fig. 8. Experimental error of data points shown in Fig. 9 was below $\pm 4.9\%$. Under similar

reaction conditions, a 23 % increase in the CO conversion was obtained in the CHFMR compared to the fixed-bed reactor. The improvement in the catalyst activity was due to the presence of a thin layer of the 30%CuO/CeO₂ catalyst with a high surface area on the inner surface of Al₂O₃ hollow fibres. The use of Al₂O₃ hollow fibres as a substrate resulted in a more efficient utilization of the 30%CuO/CeO₂ catalyst compared to its conventional counterparts such as pellets or extrudates. In addition, the finger-like region can be considered as a set of hundreds of conical micro-channels that were perpendicularly distributed around the lumen of the Al₂O₃ hollow fiber. In these micro-channels, the reactants were efficiently mixed and this contributed to an increase in the CO conversion. The result also shows that the CO conversion of the CHFMR increased to its equilibrium value when the reaction temperature was increased to 500 °C.

The thin Pd membrane plated on the outer surface of the CHFMMR enabled the separation of H₂ produced during the reaction from the reaction zone, resulted in an increase in the CO conversion up to 20% from the corresponding values of the CHFMR. The increase in the CO conversion can be explained in accordance with the “Le Chatelier” principle, the removal of one or more reaction products will shift the conversion towards products formation. It is interesting to note that at 500 °C and a sweep gas flow rate of 75 ml/min, the CO conversion increased from 45% in the CHFMR to 60% in the CHFMMR, which was 15% higher than the thermodynamic equilibrium value. Fig. 10a also shows that the production rate of CO_x free H₂ from the CHFMMR was influenced by the reaction temperatures and the sweep flow rates, showed that the Sieverts’ law governed the H₂ transport through the Pd membrane.

In order to study the performance of the Pd membrane during the operation of the CHFMMR, the H₂ recovery index was calculated at different temperatures and

the flow rates of the sweep gas shown in Fig. 10b. This index is typically used to describe the efficiency of Pd membranes and can be defined as the H_2 fraction permeated through the Pd membrane with respect to the total amount of H_2 produced during the WGS reaction. As can be seen, H_2 recovery index for every sweep factors remained constant as the temperature was increased from 300 °C to 500 °C, indicated the reaction temperature has an insignificant effect on permeability of the Pd membrane. However, the H_2 recovery index increased as the flow rate of the sweep gas was increased. The higher the flow rate of the sweep gas, the higher the pressure difference across the Pd layer, thus increased the H_2 permeability through the Pd membrane.

In the operation of the CHFMMR, high purity H_2 has been obtained in the shell side, which was 78 % of the total H_2 produced in the WGS reaction. Higher recovery of H_2 was obtained in the shell-side of the CHFMMR although the pressure difference across the Pd membrane was only induced using the sweep gas. It is predicted that the H_2 recovery index might still be increased up to 100 %, which represent a complete removal of H_2 from reaction zone, if the sweep gas is replaced by the use of vacuum extraction in the shell side of the CHFMMR.

It is important to highlight that the Pd membrane shown good stability even though it was heated at higher temperatures and used for long periods of time during the WGS reaction. All the CHFMMR prepared and tested in this work in WGS reactor have shown a good reproducibility.

Conclusions

This study demonstrates that Al_2O_3 hollow fibre, which has an asymmetric porous structure, can be used as a single substrate for both the Pd membrane and the

30%CuO/CeO₂ catalyst in the development of a CHFMMR for CO_x free H₂ production. The finger-like region in the Al₂O₃ hollow fibre was made up by a set of hundreds of conical micro-channels which were perpendicularly distributed around the fibre lumen in which the reactants could be efficiently mixed.

A thin layer of 30%CuO/CeO₂ catalyst with a high surface area was successfully deposited into Al₂O₃ hollow fibres using the sol-gel Pechini method. The use of Al₂O₃ hollow fibres resulted in a more efficient utilization of the 30%CuO/CeO₂ catalyst compared to its conventional counterparts such as pellets or extrudates. This makes Al₂O₃ hollow fibres as a efficient support not only for the Pd membrane but also for the 30%CuO/CeO₂ catalyst. The maximum amount of 30%CuO/CeO₂ catalysts deposited into the finger-like region of the Al₂O₃ hollow fibre was approximately 6% when the drying process was carried out at 60 °C.

The catalytic activity results obtained for the WGS reaction in a fixed-bed reactor, the CHFMR and the CHFMMR showed that the conversion in a CHFMMR was the highest. At 500 °C and at a sweep flow rate of 75 ml/min, the conversion increased from 43% in a CHMFR to 60% in a CHFMMR, which was 17% higher than the corresponding thermodynamic equilibrium conversion. In addition, high purity H₂ has been produced in the shell side of the CHFMMR during the WGS reaction. This study shows that H₂ permeability through the Pd membrane increases with temperature and sweep gas flow rate. The Pd membrane plated on the Al₂O₃ hollow fibre, with a thickness of approximately 6µm and a defect-free surface, showed an good stability during the WGS reaction, even though it was used at higher temperatures for long periods of time.

Based upon these results, the CHFMMR offers important advantages over existing H₂ production systems and can be presented as a promising system to

produces CO_x free H₂ by WGS reaction. Furthermore, the fabrication techniques and process understanding generated from this study are generic and may be applied to a wide range of heterogeneously catalysed gas phase reactions which are related to H₂ production.

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Figure Captions

- Fig. 1 Schematic diagram of operational modes for the CHFMR
- Fig. 2 SEM pictures of an Al_2O_3 hollow fibre at different magnifications before Pd deposition and catalyst impregnation.
- Fig. 3 Catalyst loading deposited into the finger-like region of the Al_2O_3 hollow fibre as a function of the drying temperature.
- Fig. 4 Hg porosimetry of Al_2O_3 hollow fibre before (—) and after (---) catalyst impregnation.
- Fig. 5 Fluxes of N_2 through the Al_2O_3 hollow fibre as a function of the transmembrane pressure before (■) and after (□) catalysts impregnation.
- Fig. 6 Cu and Ce distribution SEM-EDS images of the Al_2O_3 hollow fibers after catalyst impregnation.
- Fig. 7 SEM pictures of the top surface of the Al_2O_3 hollow fibre before (a) and after (b) activation process (c) cross-section of the Al_2O_3 hollow fibre after Pd deposition and d) top surface of Pd membrane.
- Fig. 8 a) Fluxes of H_2 through the Pd membrane as a function of the difference in the square roots of the transmembrane pressure at different temperatures: (■) 300°C, (●) 350°C, (▲) 400°C and (◆) 450°C.
- Fig. 9 Conversion as a function of the temperature in WGS reaction: (···) thermodynamic equilibrium, (□) fixed-bed reactor, (○) the CHFMR and the CHFMMR using different flow rates of sweep gas: (■) 50 ml/min, (▲) 65 ml/min and (●) 70 ml/min.
- Fig. 10 a) H_2 permeation through the Pd membrane during WGS reaction as a function of the temperature at different sweep gas flow rates: (■) 50 ml/min, (▲) 65 ml/min and (●) 70 ml/min. b) H_2 recovery index as a

function of the reaction temperature at different sweep gas flow rates: (■)
50 ml/min, (▲) 65 ml/min and (●) 70 ml/min.

Figures

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