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Development of a catalytic hollow fibre membrane micro-reactor for high purity H_2 production

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ABSTRACT

This article describes development of a catalytic hollow fibre membrane micro-reactor (CHFMMR) for high purity H_2 production. Asymmetric Al_2O_3 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/CeO_2 catalyst. The Pd membrane was first deposited onto the outer layer of Al_2O_3 hollow fibre using the electroless plating (ELP) technique, followed by impregnation of the 30%CuO/CeO_2 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 70 ml/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 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 H_2 has been obtained in the shell side, which was 78% of the total H_2 produced in the WGS reaction.

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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 have 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

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a module, which makes the system safer. In comparison with conventional micro-reactor 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 H_2 production. Finally, Al_2O_3 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 H_2 production, using the asymmetric Al_2O_3 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

$Ce(NO_3)_3{\cdot}6H_2O$ (≥99.0%, Fluka Analytical) $Cu(NO_3)_2{\cdot}3H_2O$ (99.0%, Acros Organic), ethylene glycol (99+%, Acros Organic) and citric acid (≥99.0%, Sigma–Aldrich) were used to prepare a homogeneous catalyst solution using the sol–gel Pechini method. $Pd(NH_4)_2Cl_4$ (ammonium tetrachloropalladate, 99.99%, Aldrich), $SnCl_2{\cdot}2H_2O$, $Na_2EDTA{\cdot}2H_2O$, HCl (37%), N_2H_4, $AgNO_3$, and $NH_3{\cdot}H_2O$ (28%) (Fisher Sci. Ltd.) were used for preparing Pd membranes using the electroless plating (ELP) technique.

2.2. Preparation of Al_2O_3 hollow fibre substrates

Asymmetric Al_2O_3 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/CeO_2 in Al_2O_3 hollow fibre for development of CHFMR

30%CuO/CeO_2 has been chosen as a catalyst for the WGS reaction, prepared using the sol–gel Pechini method [13]. In a typical preparation, $Ce(NO_3)_3{\cdot}6H_2O$ (17.66 g) and $Cu(NO_3)_2{\cdot}3H_2O$ (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 h to obtain homogeneous catalyst solution.

In a typical catalyst impregnation, the outer surface of Al_2O_3 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 Al_2O_3 hollow fibres and this process was repeated several times. The Al_2O_3 hollow fibres were later immersed in the catalyst solution before being dried in an oven (Salvislab Thermocenter) at temperatures ranging from 60 to 90 °C for 24 h and further dried at 115 °C for 2 h to complete the polymerisation of a polymeric resin precursor. The calcinations process was later carried out at 400 °C for 1 h. The catalyst loading in the Al_2O_3 hollow fibre was obtained by measuring the weight of Al_2O_3 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 Al_2O_3 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/CeO_2 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 μm-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 h (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/CeO_2 into the finger-like structure of Al_2O_3 hollow fibre. The impregnation of 30%CuO/CeO_2 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 Al_2O_3 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 Al_2O_3 hollow fibre using the ELP technique. The Al_2O_3 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 Al_2O_3 hollow fibre substrates using a glass pipette and this process was repeated several times. The Al_2O_3 hollow fibres were then dried in an oven (Salvislab Thermocenter) at 60 °C for 24 h 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 Al_2O_3 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 h. 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.

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