



## Studies on water–gas-shift enhanced by adsorption and membrane permeation



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### ABSTRACT

A new sorption enhanced membrane reactor (SEMR), consisting of a packed adsorbent-catalyst bed (10% CuO/CeO<sub>2</sub> catalyst and a hydrotalcite-derived Mg–Al mixed oxide) around a tubular Pd/Ag hollow fibre membrane, has been proposed to obtain high purity H<sub>2</sub> and simultaneous capture of CO<sub>2</sub> during the water gas shift reaction. For comparison purposes, catalytic activity tests were carried out at atmospheric pressure and operating temperatures between 100 °C and 550 °C in three different catalytic reactors: (1) a fixed-bed reactor (FBR), (2) a sorption enhanced reactor (SER) and (3) a new SEMR. In all cases, the feed mixture Ar/CO/H<sub>2</sub>O ratio was 11/1/0.75 with a space velocity of 22 L/g h. The performance of the FBR was used as a reference to compare with the results obtained from the SER and SEMR. The H<sub>2</sub> yield at 350 °C using the SER was 80%, which is 33% higher than that obtained in the traditional FBR and 18% higher than the corresponding thermodynamic equilibrium. However, due to the high CO/H<sub>2</sub>O ratio ( $R > 1$ ), undesirable side-reactions such as C deposition become important at temperatures higher than 400 °C. A similar behaviour was observed using the SEMR, however in this case, a high purity CO<sub>x</sub> free H<sub>2</sub> production was obtained. This preliminary study shows relevant data obtained using a SER and the new SEMR, which allows for the better understanding and design of multifunctional catalytic reactors.

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### 1. Introduction

The transition from current brown hydrogen economy to a green economy is set to occur in upcoming decades [1,2]. However, in the meantime, efforts must be focused on making this transition as environmentally friendly as possible [3,4]. Today, 96% of the global H<sub>2</sub> production is based on steam reforming of fossil fuels followed by the water gas shift (WGS) reaction, which produces about 250 million tons per year of CO<sub>2</sub> [5,6]. At this point, membrane and sorbent technologies are the growing interest in scientific community due to their potential for controlling and managing CO<sub>2</sub> emissions. The development of H<sub>2</sub>-selective inorganic membranes, such as Pd-based membranes, allows not only the production of high purity H<sub>2</sub> from fossil fuels but also capture the CO<sub>2</sub> in a subsequent step [7]. Likewise, the synthesis of new materials such as lithium ceramics, hydrotalcites and calcium-based materials allow in-situ capture of CO<sub>2</sub> at a wide range of temperatures [8].

Pd-based membranes are extensively studied, either for H<sub>2</sub> separation/purification or reaction processes, due to its advantages

over the traditional technologies. Compared to traditional fixed-bed reactors (FBR), catalytic membrane reactors (CMR), combining an active catalyst and an H<sub>2</sub> permselective membrane in a single unit, have demonstrated their enhanced performance in different processes and under a wide range of reaction conditions [9,10]. In this respect, the attractive physical and chemical properties of ceramic hollow fibres along with their low-cost manufacturing process suggest them as the key step for suitable intensification of today heterogeneous catalytic gas phase process [11–14]. It has been demonstrated that the higher surface area/volume ratio of the ceramic hollow fibres in comparison with the convective ceramic or stainless steel tubular supports results in a more efficient use of the membrane deposited on its outer surface. Moreover, a hollow fibre membrane reactor (HFMR), which consists of a packed catalyst bed around a Pd-based coated ceramic hollow fibre membrane permits the reduction of the amount of Pd wasted in a CMR and to decrease significantly the final volume size of the reactor. Among the existing Pd-based membranes, the physical and chemical properties of the Pd/Ag alloy membranes make them suitable candidates for these applications. First, Pd/Ag alloy membranes show higher H<sub>2</sub> permeability than Pd membranes in a temperature range of 150–450 °C due to their higher H<sub>2</sub> solubility [15,16]. Secondly, the melting point of the Pd/Ag alloys is higher than that of pure Pd,

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which increases their sintering resistance and enables them to work at higher temperatures than Pd membranes [17]. Finally, the fact that Pd/Ag alloy membranes do not show an  $\alpha$ - $\beta$  phase transition makes them resistant to embrittlement at temperatures below 300 °C [18,19].

Another procedure for shifting the equilibrium consists of blending the catalyst with a CO<sub>2</sub> adsorbent, so-called sorption-enhanced fixed bed reactors (SER). In this case the equilibrium shift is accomplished by the selective removal of one of the reaction products (CO<sub>2</sub>). Several examples of successful SERs have already been reported in the literature for other reactions [20–23]. For this purpose, an ideal CO<sub>2</sub> sorbent should exhibit high capture capacity, durability, fast capture/release kinetics and good mechanical strength. In this respect, hydrotalcites show fast kinetics and high CO<sub>2</sub> capture capacity in the temperature range of 200–500 °C in addition to maintaining a high stability during cyclic carbonation [24,25].

It is important to mention the advantages of using either CMR and SER over traditional FBR. First, they present the possibility of working at significantly lower temperatures and/or using lower amounts of catalyst. Secondly, they combine the processes of generating and separating H<sub>2</sub> or capture CO<sub>2</sub> in a single step, which is possible due to either the high H<sub>2</sub> selectivity of the Pd-base membrane or the high CO<sub>2</sub> selectivity of the sorbent. Finally, they overcome thermodynamic limitations by selectively removing one of the products from the reaction medium, which shifts the equilibrium to the products side according to Le Chatelier's principle.

The integration of both membrane and sorbent technologies is a critical step for process intensification of the WGS reaction:  $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ . Since the early 1960s [26], the WGS reaction has been performed in industry as a three-stage process. In the first stage, the CO reacts with H<sub>2</sub>O to produce CO<sub>2</sub> and H<sub>2</sub> in a high temperature (HT) reactor. In the second stage, the remaining CO (0.1% vol) is oxidized in a low temperature (LT) reactor. Finally, H<sub>2</sub> and CO<sub>2</sub> are separated in a separation unit, which usually consists of a selective adsorbent bed. Even though a lot of work has been done to optimize each of these stages, a three-stage process is less economically feasible than a single-stage process. In this regard, integrating the whole process into a single-stage process by using a sorbent enhance membrane reactor (SEMR) could significantly decrease the cost of H<sub>2</sub> production compared with the current three-stage process.

The concept of the SEMR, which integrates both a packed adsorbent-catalyst bed and a selective membrane in a single reactor, was originally proposed by B. Park and T.T. Tsotsis in 2001 [27–29]. In their study [27], they reported the performance in esterification reactions of a so-called hybrid adsorbent-membrane reactor (HAMR) system, which combined a water-permeable polymeric membrane and a hydrophilic adsorbent in one unit. The HAMR shows several advantages over either CMR or SER. First, the HAMR system allows for higher conversion and yields than that obtained in either CMR or SER along with a maximum selectivity. In addition, the operational flexibility of the HAMR system enables in situ regeneration of the selective adsorbent under reaction conditions. The potential applications of both HAMR [30,31] and circulating fluidized-bed HAMR [32–35] systems for hydrogen production by methane steam reform and water gas shift reactions have recently been studied. However, the number of publications in this area is still limited.

For these reasons, the goal of this work is to develop a novel SEMR, which integrates both a SER and CMR in a single unit. The original configuration of the SEMR allows continuous high purity H<sub>2</sub> production together with in situ CO<sub>2</sub> capture in the WGS reaction. The performance of the SEMR was compared with that of both FBR and SER. Three different parameters (i.e., catalytic activity, H<sub>2</sub> permeability of the Pd/Ag alloy membrane and CO<sub>2</sub> adsorption on

the hydrotalcite under the WGS reaction conditions) were studied in order to optimize the performance of the SEMR.

## 2. Experimental

### 2.1. Synthesis of the 10%CuO/CeO<sub>2</sub> catalyst

The 10% CuO/CeO<sub>2</sub> catalyst was prepared using the sol-gel Pechini method. Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (99.0% Fluka Analytical) and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (99% Acros Organic) were dissolved in 50 mL deionized water. The amount of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O were calculated for a 10% CuO loading. After both metal nitrates were fully dissolved, citric acid (99.0% Sigma-Aldrich) was added to the solution with a molar ratio of 2:1 of citric acid to metal ions. The process was continued by adding ethylene glycol to the solution such that the molar ratio between citric acid and ethylene glycol was 1:1.2. The catalyst solutions were kept stirring for 3 h and later placed in an oven (Salvislab Thermocenter) for drying at 115 °C for 24 h to form a foamy dry gel. The dry gel was then calcined in a tubular furnace (Vecstar Furnaces, VCTF/SP) at 400 °C for an hour. Information about the characterization of the 10% CuO/CeO<sub>2</sub> catalyst can be found elsewhere [36].

### 2.2. Synthesis of hydrotalcite-derived Mg–Al mixed oxides

A hydrotalcite with a Mg/Al ratio of 3 was synthesized by coprecipitation at low supersaturation conditions and under sonication. 1 mol/L solutions of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Fluka, >99%) and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Panreac, 98%) were mixed in a 3:1 molar ratio. A volume of 150 mL of this solution was added drop-wise to 100 mL of 0.2 M K<sub>2</sub>CO<sub>3</sub> (Panreac, 99%) under vigorous stirring and ultrasound irradiation at room temperature. The pH was kept at 10 by adding appropriate quantities of 1.6 M NaOH (Prolabo, 98%) solution. The precipitate was then separated by high-speed centrifugation, washed in deionized water in order to remove the alkali metals and the nitrate ions to a pH of 7, and dried in an oven at 100 °C for 24 h. The resulting hydrotalcite was calcined at 450 °C under air flow for 7 h to obtain the mixed oxide. Further details on the preparation procedure are given in [31].

### 2.3. Fabrication of Al<sub>2</sub>O<sub>3</sub> hollow fibres

Asymmetric Al<sub>2</sub>O<sub>3</sub> hollow fibres were prepared using 1  $\mu\text{m}$ , 0.3  $\mu\text{m}$ , 0.05  $\mu\text{m}$  and 0.01  $\mu\text{m}$  Al<sub>2</sub>O<sub>3</sub> powders (from Alfa Aesar), polyethersulfone (Radial A300, Ameco Performance), N-methyl-2-pyrrolidone (HPLC grade) and Arlacel P135 (Polyethyleneglycol 30-dipolyhydroxystearate, Uniqema) using a phase-inversion technique, followed by sintering at high temperatures. A detailed procedure for the synthesis of these hollow fibres can be found elsewhere [37].

### 2.4. Fabrication of the Pd/Ag membrane

The synthesis of the Pd/Ag membranes requires ammonium tetrachloropalladate, (Pd(NH<sub>4</sub>)<sub>2</sub>Cl<sub>4</sub>, 99.99%, Aldrich), palladium chloride (PdCl<sub>2</sub>, 99.999%, Aldrich), tin chloride (SnCl<sub>2</sub>·2H<sub>2</sub>O, Fisher Sci. Ltd.), ethylenediaminetetraacetic acid (Na<sub>2</sub>EDTA·2H<sub>2</sub>O, Fisher Sci. Ltd.), hydrochloric acid (HCl, 37%, Fisher Sci. Ltd.), hydrazine (N<sub>2</sub>H<sub>4</sub>, Fisher Sci. Ltd.), silver nitrate (AgNO<sub>3</sub>, 99.99%, Fisher Sci. Ltd.) and ammonium hydroxide (NH<sub>3</sub>·H<sub>2</sub>O, 28%, Fisher Sci. Ltd.).

Prior to coating the Pd/Ag membrane, the outer surface of the Al<sub>2</sub>O<sub>3</sub> hollow fibre was coated with a thin and gas-tight layer of white glaze in order to block the pores in the coated area; only 10 cm in the central part of the Al<sub>2</sub>O<sub>3</sub> hollow fibre were left uncoated where the Pd/Ag membrane was deposited by electroless plating technique. Before the activation process, the Al<sub>2</sub>O<sub>3</sub> hollow fibres

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