



Enhancing the low temperature water–gas shift reaction through a hybrid sorption-enhanced membrane reactor for high-purity hydrogen production



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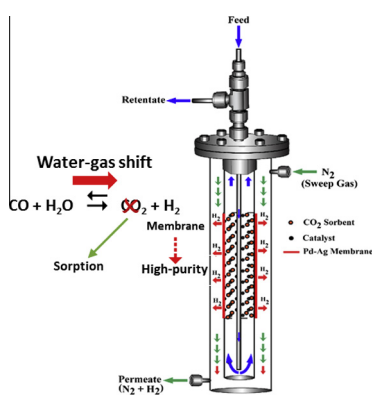
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HIGHLIGHTS

- Multifunctional sorption-enhanced membrane reactor.
- The coexistence of both the membrane (H₂ separation) and the CO₂ sorbent act simultaneously.
- The WGS equilibrium is completely shifted allowing to obtain two ultra-pure H₂ streams.
- Process integration by combining CO₂ and H₂ removal in a single unit is beneficial for H₂ production.

GRAPHICAL ABSTRACT



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ABSTRACT

The low temperature water–gas-shift reaction (LT-WGS) has been assessed by means of a hybrid sorption-enhanced membrane reactor (HSEMR) that combines both CO₂ and H₂ removal from the reaction zone. The performance of this reactor has been compared with that obtained by (i) a traditional and (ii) a sorption-enhanced (only CO₂ is removed) reactor operating in the same operational conditions. Cu/ZnO–Al₂O₃ and K₂CO₃-promoted hydrotalcite materials have been used as a catalyst and CO₂ sorbent, respectively. A self-supported Pd–Ag membrane tube has been used in order to selectively separate the H₂. The CO₂ sorption capacity, in the presence and absence of water vapour, of the potassium-promoted hydrotalcite has been determined by means of breakthrough experiments. The presence of water vapour enhanced the sorption capacity of the hydrotalcite in the experimental conditions used. Concerning the performance of the HSEMR, results clearly show that when both CO₂ and H₂ are removed from the reaction zone, the hydrogen production through the reversible LT-WGS reaction is enhanced compared to either a traditional or a sorption-enhanced reactor, allowing overcoming equilibrium limitations and obtain a pure H₂ stream.

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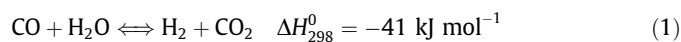
1. Introduction

Hydrogen is an important raw material widely used in the chemical industry (i.e. oil refining and production of bulk chemicals such as methanol and ammonia) and as clean energy vector

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for fuel cells and internal combustion engines [1,2]. Global demand of hydrogen is even growing. Currently, most of the hydrogen produced in the world involves methods such as methane steam reforming (MSR), coal gasification, water electrolysis, biomass gasification and thermochemical process, being MSR the most widely used among them [3,4]. In MSR, the outlet stream contains a large amount of CO as by-product along with hydrogen (H_2/CO ratio >3); the CO content varies between 8% and 10% depending of the feedstock composition and conditions used [5]. In order to purify the hydrogen in the MSR reactor effluent and/or tune the CO/H_2 ratio, the syngas stream can be treated in a water–gas shift (WGS, Eq. (1)) reactor.



This chemical equilibrium-limited reaction is a mildly exothermic and hence is thermodynamically favoured at low temperatures, although kinetically favoured at high temperatures. For this reason, to obtain high CO conversion, the WGS reaction is industrially carried out in two successive steps at different temperatures, namely: (i) a high-temperature water gas-shift (HT-WGS) reactor operating between 350 °C and 550 °C and (ii) a low-temperature water–gas shift (LT-WGS) reactor at 200–300 °C. The first shift reactor works with iron-chrome oxide catalysts and has an output stream containing 1.5–4.0% CO, while the second reactor operates with copper–zinc oxide catalysts where the CO outlet composition is reduced to about 0.5–1.0% [5,6].

The gas produced from the WGS reaction contains other components (mainly CO, CO_2 , H_2O and CH_4) apart from H_2 . Remaining steam can be relatively easily removed by water condensation, while CO_x and CH_4 are often removed through processes such as pressure swing adsorption (PSA) to produce high purity hydrogen [7]. This PSA process generally operates at near ambient temperature (20–40 °C) using CO_2 microporous physisorbents such as activated carbons and zeolites [8]. With this cyclic PSA, hydrogen with 99.99% purity is obtained but the H_2 recovery is about 75–90% only since part of the H_2 recovered is used to regenerate the adsorbent [9]. This means that a considerable amount of H_2 produced in this process is lost.

One alternative to the PSA process to separate H_2 is by removing it from the reaction zone by means of one H_2 perm-selective membrane. In this way, not only is possible to obtain ultra-pure H_2 , suitable for fuel cells [5], but also the equilibrium limitation can be circumvented by shifting the WGS reaction to the products side in a single unit. Hydrogen perm-selective membranes have been developed using mainly palladium and its alloys [10–12]. These Pd-based membranes show a very high H_2 selectivity and allow reaching CO conversions close to 100% in membrane reactors (MR) for the LT-WGS reaction [11,13].

On the other hand, the capture and simultaneous separation of CO_2 from the reaction zone has also been proposed [9,14]. This process, so called sorption enhanced water gas shift, allows to overcome the equilibrium limitation maximizing the H_2 production from the syngas as well. Different oxide materials as CO_2 sorbent, such as calcium oxide, lithium zirconates and lithium silicates, have been extensively studied [15,16]. Nevertheless, these sorbents have a poor CO_2 capacity at low temperatures and for their regeneration temperatures above 700 °C are required. Furthermore, these materials exhibit a progressive loss of their CO_2 sorption capacity under consecutive cycles of adsorption–desorption. However, hydrotalcite-like (HTs) materials could be an attractive option for CO_2 sorption because of their high sorption capacity at lower temperatures (200–400 °C), which are compatible with WGS reaction [17–19]. Moreover, HTs present a lower requirement of energy input for their regeneration, as well as acceptable working capacity after multiple cycles and suitable kinetics of carbon dioxide sorption and desorption [18–20].

A new field of research herein addressed deals with the study of innovative multifunctional reactors by combining the MR concept with the sorption-enhanced one. This has a large number of advantages: (i) the process may be performed in a single unit, which simplifies the overall hydrogen production, (ii) compared to a MR, it allows decreasing the required Pd membrane area, often limitative due to its price, (iii) the reaction may be conducted with a lower H_2O/CO ratio, thereby reducing steam usage and operational costs, (iv) fuel-cell grade (i.e. high-purity) hydrogen can be directly produced, and (v) the process captures CO_2 , so that is environmentally friendly and allows eliminating the need for a dedicated CO_2 capture unit.

The aim of this work is to study this new concept in a multifunctional hybrid sorption-enhanced membrane reactor. For this purpose, a self-supported Pd–Ag membrane and a commercial hydrotalcite mixed with a LT-WGS Cu-based catalyst have been used. In practice, and because the sorbent regeneration is necessary when the CO_2 starts breaking through the column, and to ensure a continuous production, the use of two parallel reactors is envisaged; while one of them is producing H_2 , the other one is the regeneration stage. Thus, each of these reactors requires repetition of reaction–regeneration cycles along time.

2. Experimental

For the experiments, a commercial K_2CO_3 promoted hydrotalcite supplied by Sasol was used. This material, containing 17 wt.% of K_2CO_3 and Mg/Al mass ratio of 0.5, was labelled as MG30-K.

2.1. Thermogravimetric and differential scanning calorimetry (TG–DSC) analysis

TG–DSC analysis of fresh MG30-K sample was performed in a thermobalance NETZSCH SSA 449F3 Jupiter. Approximately 20 mg of sample was placed in a platinum basket and heated in N_2 flow (50 ml_N/min) from room temperature up to 900 °C at a heating rate of 10 °C/min. All data analyses were performed using NETZSCH Proteus Thermal Analysis software.

2.2. Breakthrough measurements

Carbon dioxide breakthrough runs were carried out in a stainless steel tube (120 mm long and with 10 mm o.d.), which was placed into an electric oven (Memmert, Type UNE200), controlled by a programmable temperature controller. 2.8 g of hydrotalcite framed in both ends by mean of two discs of stainless steel mesh (10–15 μm) were used. In order to minimize pressure drop along the bed, the particle size of the hydrotalcite used in the experiments was between 355 and 550 μm . Before the experiments, the MG30-K sample was heated under 100 ml_N/min of N_2 at 300 °C during 2 h (to remove loosely interlayer water, as described below).

Experiments were carried out in the presence as well as in absence of water vapour. Thus, different feeds were used: (i) for dry conditions 10 or 15 vol.% of CO_2 and balance N_2 and (ii) for wet conditions 15 vol.% of CO_2 , 5, 15 or 25 vol.% of H_2O and balance N_2 . Both CO_2 and N_2 were fed to the process with mass flow controllers (model F201 from Bronkhorst High-Tec) whereas the water vapour was produced in a Controlled Evaporation and Mixing (CEM) system (Bronkhorst High-Tec). In both cases, the total flow rate (dry basis) was kept at 100 ml_N/min . The experiments were carried out at 1, 2 and 3 bar of total pressure.

Evolution of the outlet CO_2 dry composition was monitored by an online infrared based CO_2 analyser (model 4210 from Servomex); the H_2O present in the outlet stream was condensed

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