



CO_x free hydrogen production through water-gas shift reaction in different hybrid multifunctional reactors



M.A. Soria^a, Cláudio Rocha^a, S. Tosti^b, A. Mendes^a, Luis M. Madeira^{a,*}

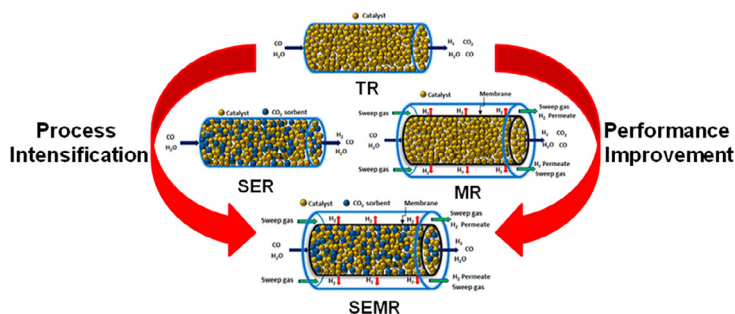
^a LEPABE – Chemical Engineering Department, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, s/n, 4200-465 Porto, Portugal

^b ENEA – FSN Department, C.R. ENEA Frascati, Via E. Fermi 45, Frascati (RM) I-00044, Italy

HIGHLIGHTS

- Experimental WGS study in different reactor configurations: TR, MR, SER and SEMR.
- H₂ and/or CO₂ separation from the reaction zone intensifies the process.
- The equilibrium is completely shifted allowing to obtain two ultra-pure H₂ streams in the SEMR.
- Using steam during regeneration enhances the hydrotalcite working sorption capacity.

GRAPHICAL ABSTRACT



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ABSTRACT

High-purity H₂ production from the water-gas shift (WGS) reaction was assessed. Since the WGS is limited by the equilibrium, different reactor types that allow to extract one or more products from the reaction medium, namely membrane reactor (MR; for H₂ separation), sorption-enhanced reactor (SER; for CO₂ capture) and sorption-enhanced membrane reactor (SEMR; for simultaneous CO₂ and H₂ removal), were used and compared with fixed-bed traditional reactor (TR). Experimental results were obtained with commercial materials, namely WGS Cu-based catalyst and K-doped hydrotalcite for CO₂ capture. Additionally, in the MR and SEMR, a self-supported Pd-Ag membrane for separating H₂ selectively from the reaction zone was used.

Experimental tests were performed at different temperatures and pressures, and the results obtained were compared with those predicted by theoretical simulations at the thermodynamic equilibrium. Moreover, in the case of SER, different methods for the hydrotalcite regeneration and the evaluation of its working sorption capacity under cycling conditions were also assessed. Not all sorbed CO₂ can be desorbed under dry conditions (pure nitrogen purging stream); however, if steam is used during the regeneration step, all sites can be effectively regenerated, allowing to have a stable working sorption capacity. Concerning the performance of the different hybrid reactors tested, i.e. MR, SER and SEMR, it was found that all are able of overcoming the TR limitations, with performances reaching conversion above the equilibrium for the feed composition. Nonetheless, only the SER and SEMR configurations allow to obtain high-purity H₂ in all reactor exiting streams under the operating conditions herein assessed.

* Corresponding author.

E-mail address: mmadeira@fe.up.pt (L.M. Madeira).

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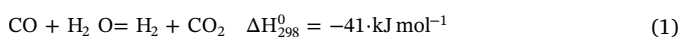
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1. Introduction

Hydrogen is recognized as an emerging new energy carrier due to its waste-free combustion, and high energy mass density [1]. It can be used not only as raw material in the chemical and petrochemical industrial sectors, but also in fuel cells and internal combustion engines without CO₂ emissions [2,3].

Hydrogen is produced from both renewable and non-renewable resources through diverse processes such as methane steam reforming, coal gasification, water electrolysis or biomass gasification [4]. Currently, methane steam reforming is the most widely route used to produce hydrogen at industrial scale [5]. The steam reforming stage, which produce syngas (a mixture of CO and H₂), is followed by two successive water-gas shift (WGS, Eq. (1)) reaction steps to maximize the conversion of CO [6]. Such reaction finds application in several industrial processes [7].



As the WGS is an equilibrium-limited reaction, apart from H₂ and CO₂ there are other chemical species (CO and H₂O) at the end of this reaction step, i.e. at the reactors' outlet.

Carbon monoxide is a poison both to several catalytic processes employed in fuels production and to anode catalysts currently used in polymer electrolyte membrane fuel cells (PEMFCs) [8,9], and so purification of the reformat gas prior to use is required. Thus, to obtain hydrogen with the required purity, a final pressure swing adsorption (PSA) unit is often required [10,11]. PSA reportedly produces high purity H₂, up to 99.9%, but the H₂ recovery is about 75–90% since part of the H₂ recovered is used to regenerate the adsorbent [11–13].

Alternatively, a sorption-enhanced reactor (SER) has been proposed as an effective approach to high-purity H₂ production with low concentration of CO, by shifting the thermodynamic equilibrium of the WGS reaction towards H₂ generation by *in-situ* removing CO₂ through adsorption. Nevertheless, the main disadvantage of the SER is that the CO₂ sorbent gets saturated at some point and then regeneration is needed. For obtaining cyclic operation, at least two parallel reactors are needed: while one is producing H₂, the other is being regenerated, i.e., CO₂ is being removed from the sorbent with an inert gas. This approach is similar to the one used in other cyclic adsorption processes like PSA [11,14].

Different sorbents like hydrotalcites [15–17], CaO-based materials [18,19], MgO-based materials [20–22], lithium zirconates [23–25] and lithium silicates [26,27] have been reported in the literature as CO₂ sorbents for SERs technologies. It is expected, from a good CO₂-selective sorbent, to have a high CO₂ sorption capacity and selectivity at moderate temperatures, effective regeneration at moderate temperatures, good hydrothermal and mechanical stability and low cost. Since one of the goals in this work is to perform experiments at relatively low temperatures (300–350 °C), a hydrotalcite sorbent was used. It displays high CO₂ equilibrium capacity and fast sorption kinetics, good regeneration and has a great stability [15,28,29]. Moreover, the fact that the CO₂ capacity of hydrotalcites is strongly enhanced in the presence of steam makes them an even better sorbent for use in the WGS process, where water is a reactant [30].

Besides the CO₂ sorption-enhanced process, palladium based membrane reactors (MRs) have also shown to be promising for overcoming equilibrium limitations in reversible reactions like the WGS, yielding high-purity streams of H₂ with low concentration of CO [31,32]. This is reached by shifting the thermodynamic equilibrium of the reaction toward H₂ generation by *in-situ* removing H₂ through permeation. Pd-based membranes are currently the most promising for high-purity H₂ production in MRs, especially Pd alloys (e.g. Pd–Ag) that are less sensitive than pure Pd to embrittlement (caused by the presence of H₂ at temperatures below 300 °C and pressures below 2 MPa) and poisoning (caused by contact with CO, for example) [33–36]. Tosti *et al.*

[37] demonstrated that self-supported dense Pd–Ag (with 23–25 wt.% of Ag) tubular membranes with finger-type configuration are highly durable and reliable since they allowed to attain complete H₂ selectivity and no failures were observed after long time of thermal and hydrogenation cycles. These characteristics, together with high permeability, make such membranes very promising for high-pure H₂ production. Due to these reasons, in this work one of such membranes was used.

The WGS reaction has been identified as one of the processes wherein both H₂ yield and purity can be improved by using either a MR [38–40] or a SER [17,41,42]. To apply this technology with the simultaneous removal of both products, it is necessary to use a H₂-selective membrane and a CO₂-selective sorbent, in a hybrid sorption-enhanced membrane reactor (SEMR). This reactor has several advantages: (i) the reaction and purification of the generated stream can be performed in a single unit; (ii) it allows decreasing the necessary Pd–Ag membrane area, compared to a MR, which is important due to its price; and (iii) high-purity H₂ can be directly produced with simultaneous CO₂ capture [11].

This work aims at comparing the performance of different reactor types (for the low temperature WGS reaction) including a traditional fixed-bed reactor (TR) and hybrid reactors, namely MR, SER and SEMR. In a previous work [11] we have studied the WGS reaction in a SEMR, but in this case, a longer Pd–Ag membrane and higher temperatures of reaction were employed, allowing to reach improved hydrogen recoveries. Moreover, comparison between obtained experimental values and simulated thermodynamic limits are now addressed, along with the assessment of the hydrotalcite working sorption capacity during reaction tests.

2. Experimental

2.1. Reactor types and materials

Fig. 1 shows a conceptual scheme of the different reactors studied. The sorption-enhanced reactor (SER) is similar to the fixed-bed traditional reactor (TR) with the difference that in such reactor the catalyst is mixed with the CO₂ sorbent for removing the CO₂ as it is being formed, shifting the reaction toward the products. In the case of a membrane reactor (MR) or a SEMR, the perm-selective membrane divides the reactor into the reaction and the permeate zones; hydrogen selectively permeates the membrane from the reaction zone (retentate) to the permeate side due to hydrogen partial pressure gradient across the membrane. Such driving force can be increased using an inert sweep gas flow (e.g. He, N₂, steam, etc.) or by (vacuum) pumping in the permeate side.

The reaction experiments were carried out with a commercial Cu-based WGS catalyst manufactured by Johnson Matthey (Ref. HIFUEL230), which requires operating temperatures between 200 and 350 °C. In the case of the SER and SEMR, a K-promoted hydrotalcite (MG30-K) supplied by Sasol was used as well. More details about MG30-K can be found elsewhere [11].

2.2. Experimental set-up

The fixed-bed and sorption-enhanced reactors consist of a stainless steel tube with a length of 120 mm and 10 mm o.d., which was loaded with the Cu-based catalyst (355 < Ø < 550 μm) diluted with glass beads (Sigma Aldrich 212–300 μm) in the case of the TR, and mixed with the MG30-K hydrotalcite (355 < Ø < 550 μm) in the SER. Along the bed 2 thermocouples were placed at 40 and 80 mm from the inlet.

The MR and SEMR consist of two tubes with different diameters (cf. Figs. 1c and d); the tube with lower diameter is the self-supported Pd–Ag membrane (with 23–25 wt.% of Ag – length of 120 mm, 10 mm o.d. and 150 μm of wall thickness), which was welded at both ends to steel tubes to form the permeator tube. The steel tube of higher diameter is where the sweep gas goes in, as it flows in the annular section,

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