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# Performance of a hybrid system sorbent–catalyst–membrane for $CO_2$ capture and $H_2$ production under pre-combustion operating conditions

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ABSTRACT

This paper presents experimental results obtained for different approaches used for the simultaneous capture of $CO_2$ and production of $H_2$ under precombustion conditions. A novel hybrid system adsorbent–catalyst–membrane has been designed at Ciemat which combines a sorption enhanced WGS process (which consists of a mixture of adsorbent and catalyst) with a hydrogen selective membrane. First, the individual performance of the membrane and the binary adsorbent–catalyst system is evaluated in terms of $H_2$ permeability, carbon monoxide conversion and $CO_2$ capture and best operating conditions are determined for both approaches. The crucial role of temperature and steam on the overall performance of the system is especially discussed. Finally, first experimental results obtained for the hybrid adsorbent–catalyst–membrane system are presented and the advantages and challenges of adding a $H_2$ selective membrane to the sorption-enhanced process are analysed.

## 1. Introduction

Some of the most promising alternatives to the use of liquid amines and PSA for the capture of $CO_2$ and $H_2$ production in pre-combustion processes are the use of solid sorbents for capturing $CO_2$ and the use of selective membranes for the separation of $H_2$.

Different approaches and process schemes, based on those up-and-coming technologies or on a combination of them, are being investigated by several authors to improve the capture of $CO_2$ and to increase the production of $H_2$ in gasification processes.

In the field of sorbents and catalysts development it is worth mentioning, among others, the efforts devoted to the preparation of new adsorbents with improved $CO_2$ capture capacity and tolerance to sulphur at intermediate temperatures for their application to WGS processes, the preparation of hybrid materials based on CaO for in situ capture of $CO_2$ at high temperatures or the development of bifunctional adsorbents capable to simultaneously catalyse the WGS reaction and capture $CO_2$ [1–3].

Regarding membranes technology for $H_2$ production and/or separation of $H_2/CO_2$ mixtures great advances are being gathered in the development of very thin Pd or Pd-alloy based membranes and in the design of new membrane supports based on ceramic or metallic hollow fibres, nanoporous hybrid silica membranes or novel non Pd metallic membranes such as vanadium membranes. A detailed review of the most recent developments in membranes and membrane reactors for $CO_2$ capture and $H_2$ production can be found in the literature [4,5].

Different hybrid system, based on the combination of several of the above mentioned technologies are also being studied in order to take advantages of the possible synergies between them. Two of these approaches are the WGS membrane reactor approach (WGSMR) or the sorption enhanced Water Gas Shift (SEWGS) process.

In a WGS membrane reactor a WGS catalyst is combined with a $H_2$ selective membrane. The continuous removal of $H_2$ from the reaction media by permeation through the membrane enhances the conversion of CO to $CO_2$ and $H_2$. This approach requires the use of a $H_2$ highly selective membrane and up to now dense Pd and Pd alloy based membranes can be considered the most advanced ones. This approach is being investigated by several research groups [6–8].

The combination of a $CO_2$ sorbent and a WGS catalyst in a WGS unit is known as the sorption enhanced WGS process (SEWGS) and it allows an increase in the conversion of CO due to the removal of one of the products ($CO_2$) by the sorbent. The WGS process is industrially performed using two adiabatic converters, one of them at high temperature using an iron–chromium based catalyst followed by a second WGS reactor usually run at significantly lower temperature. The SEWGS approach provides the opportunity to reduce the energy penalty associated to the cooling process between reactors due to the use of a single reactor that operates at

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high temperature. Suitable high temperature WGS catalysts to be used in a SEWGS process should be highly active at temperatures in the range of 300–500 °C, show resistance to sintering at temperatures above 450–500 °C and maintain a stable performance under cyclic operating mode.

For their application to SEWGS processes, suitable sorbents are required to have high $CO_2$ capture capacity and selectivity towards $CO_2$ at temperatures in the range of 300–500 °C, adequate sorption–desorption kinetics (easy regenerable), mechanical strength and low cost [9–11]. Only a few types of materials are reported in the literature to be able to meet the above mentioned objectives and among them hydrotalcites have demonstrated to be suitable to be used in processes such us the SEWGS process [12,13] or the sorption enhanced steam methane reforming [14,15]. Recently the possible effects of the presence of contaminants such as $H_2S$ are also being investigated [16].

However, both approaches (WGSMR and SEWGS) allow only for removal of one of the products of the WGS reaction ($H_2$ or $CO_2$, respectively) and usually the resulting reaction rate enhancement is not sufficient to achieve significant conversion at low temperatures.

The opportunity to take advantage of the synergies that can be created by the combined removal of $CO_2$ and $H_2$ has motivated the development of a novel hybrid system sorbent–catalyst–membrane that has been designed at CIEMAT. The whole system is known as the sorption enhanced water gas shift membrane reactor (SEWGSMR). To the best of our knowledge, very few references can be found in the literature on the performance of hybrid adsorbent–catalyst–membrane systems for WGS applications as for example the WGS-HARM hybrid system proposed by Harale et al. [17] so research in this direction is still needed.

The novel hybrid system developed at Ciemat consists of a high $CO_2$ capture capacity sorbent, a high temperature commercial WGS catalyst and a dense Pd membrane highly selective to $H_2$. The selection of the different elements (sorbent, catalyst and membrane) that shaped the proposed hybrid system was done based on the following criteria: compatibility of best operating conditions, degree of development of the technology and availability and they were selected based on our previous works [18–21]. Using those criteria a K-doped hydrotalcite with high $CO_2$ capture capacity under WGS operating conditions, a commercial Fe–Cr high temperature WGS catalyst and a dense Pd-based membrane highly selective to $H_2$.were selected as the most suitable to build the hybrid system. A bench-scale Pd membrane reactor, available at Ciemat, was used as the base case for the design of the new hybrid system.

In this paper the influence of main operating parameters (pressure, temperature, volume ratio adsorbent/catalyst and steam) on the performance of the proposed hybrid system is evaluated and cyclic behaviour was tested using four sorption–desorption cycles. Main advantages and limitations of the proposed novel system versus the other two approaches (SEWGS and WGSMR) are also discussed.

## 2. Experimental

### 2.1. Test rigs

Two different experimental test rigs have been used in the work presented in this paper. The experiments carried out to test the sorbent, the catalyst and the binary system adsorbent/catalyst were performed in a Microactivity Pro lab-scale Unit. It is an automatic and computerised laboratory rig that consists of a stainless steel tubular reactor of OD 12.8 mm, ID 10 mm and 380 mm long housed in a one single zone SS304 oven. The maximum operating gas flow rate is 4.5 nL/min. The unit can work at up to 700 °C and 30 bar. Desired gas mixture is produced synthetically using mass flow controllers (Hi-Tech) and deionised water is metered by a piston pump (Gibson 307) and vaporised before entering the reactor. A more detailed description of this reaction system can be found elsewhere [19].

The $H_2$ separation experiments and the hybrid system adsorbent–catalyst–membrane tests have been performed at bench-scale in a Pd-based membrane reactor facility in which a gas flow-rate of up to 2 $Nm^3/h$ can be treated at a maximum temperature of 1200 °C and up to 20 bar. A schematic of this experimental setup is shown in Fig. 1.

The facility consists of a tube and shell membrane reactor that holds a tubular Pd-based membrane supplied by CRI Catalyst Co., USA. It has local control and on-line remote control, based on R485 digital communications.

The process is automatically monitored and the main operating parameters are continuously recorded. Pure gas components ($H_2$, CO, $CO_2$, and $N_2$) are supplied from gas cylinders to the mixture preparation section. Steam is produced by feeding water to an electrically heated coiled tube vaporiser by means of a displacement pump (Dosapro). Dry gas and steam are mixed before entering the reactor. Permeate and retentate gas flow rates are measured with mass flow metres. An additional sweep gas line is prepared to use $N_2$ or steam as sweeping gas if necessary. A more detailed description of the facility can be found elsewhere [21].

For both series of studies, inlet gas, exit gas, permeate and retentate gas compositions are measured by gas chromatography using a CP4900 Varian gas chromatograph equipped with two columns, a Porapack and a molecular sieve column and with two thermal conductivity detectors.

### 2.2. Sorbent

A potassium carbonate doped hydrotalcite based material was used in these experiments. This sorbent was selected in our previous work [18] among different types of materials as the most appropriate, in terms of $CO_2$ capture capacity and regenerability, to be used under conditions of WGS processes (temperatures in the range of 300–500 °C and presence of steam). It was supplied by SASOL (Germany) in pellets of 5 mm × 5 mm. The sorbent was prepared by calcination of the supplied material at 600 °C for 4 h.

### 2.3. Catalyst

The catalyst used in this work is a commercial Fe–Cr high temperature water gas shift catalyst that proved to be highly active at temperatures above 350 °C [20]. This catalyst is currently being used in the 14 MWth pre-combustion $CO_2$ capture plant in Puertollano IGCC plant [22] and according to the information provided by the manufacturer, Johnson Matthey, chemical composition of the catalyst is $Fe_2O_3$ 88 wt%, $Cr_2O_3$ 9 wt%, and CuO 2.6 wt%. [23]. For using it in the proposed hybrid systems, the performance of the catalyst in the temperature range of 250–400 °C was studied in detail in this work. The catalyst was supplied in pellets of 6 mm × 3 mm and the amount used in each test was 5 g.

### 2.4. Membrane description

As mentioned previously, the membrane used in this work is a pre-commercial prototype supplied by CRI Catalyst Co., USA. The membrane consists of a 0.012 $m^2$ active surface area composite Pd-based membrane prepared on a porous stainless steel tubular support (O.D. = 2.54 cm; $L$ = 15 cm) welded to a 316 SS tube which is closed in one end. According to the supplier the membrane provides a permeance in the range of 20–40 $Nm^3/m^2\,h\,bar^{0.5}$. The whole