



## Full Length Article

## Study of sour water gas shift using hydrotalcite based sorbents



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## ABSTRACT

One of the most promising alternatives to the use of liquid amines and pressure swing adsorption (PSA) for H<sub>2</sub> production and CO<sub>2</sub> capture in pre-combustion processes is the so called sorption-enhanced water gas shift reaction concept (SEWGS). This study presents the performance in SEWGS of two sorbents, a K-promoted hydrotalcite with Mg/Al ratio = 2, which based on our previous work was selected as the most promising CO<sub>2</sub> capture sorbent tested under sweet water gas shift (WGS) operating conditions, and a bi-functional material prepared by impregnation of the K-promoted hydrotalcite with Co and Mo in order to enhance the catalytic properties of the material.

Short term sour CO<sub>2</sub> capture tests and WGS tests at similar operating conditions (T = 300–350 °C; P = 15 bar) were carried out in order to study the effect of the presence of H<sub>2</sub>S in the feed gas stream in the CO<sub>2</sub> capture capacity and catalytic activity of both sorbent materials as well as to compare their performance in developed tests. Finally, the feasibility of using the bifunctional material for sour SEWGS processes was also studied.

Impregnation with Co-Mo did not adversely affect the adsorption capacity of the K-promoted hydrotalcite and enhanced catalytic activity, allowing total CO conversion even after adsorption capacity had been reached.

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## 1. Introduction

Biomass gasification processes produce a synthesis gas that can be used as a source of hydrogen by means of the water-gas-shift reaction. The water gas shift (WGS) process is industrially performed using two adiabatic converters, one of them at high temperature followed by a second WGS reactor usually run at significantly lower temperature to overcome equilibrium limitations.

The application of sorption-enhanced water gas shift reaction (SEWGS) to syngas streams for simultaneous H<sub>2</sub> production with CO<sub>2</sub> capture combines two processes in one single unit, which provides the opportunity to reduce the energy penalty associated to the cooling between reactors required in the conventional process. Firstly, the conversion of the CO present in the syngas into CO<sub>2</sub> and H<sub>2</sub> by means of a high temperature WGS catalyst is carried out and secondly, the capture of the produced CO<sub>2</sub> by a high capacity CO<sub>2</sub> sorbent. By combining both processes and according to the Le Chatelier principle, the continuous removal of CO<sub>2</sub> from the reaction medium by the sorbent enhances the conversion of CO to CO<sub>2</sub> and H<sub>2</sub>, allowing an increase in process efficiency.

Integrating in situ removal of CO<sub>2</sub> with the water gas shift reaction of biomass-derived syngas has been demonstrated to largely simplify the process and cut down the production cost, enhancing the H<sub>2</sub> yield and reducing the CO level in the produced gas at levels below 0.2 mol% [1]. As biomass is usually claimed to be a carbon neutral fuel, CO<sub>2</sub> capture from biomass syngas would produce a net decrease in emissions.

For the application of SEWGS technology to gasification processes, it needs to be taken into consideration that, depending on the feedstock, significant amounts of H<sub>2</sub>S might be present in the syngas, with values that can be ranging from a few hundred ppm to a few vol%. In the case of biomass the amount of expected H<sub>2</sub>S in the producer gas ranges between 400 and 600 ppm [2]. Syngas containing more than 4 ppm of hydrogen sulphide (H<sub>2</sub>S) is commonly referred to as "sour" [3]. Therefore, the availability of materials able to operate (i.e. to maintain the catalytic and/or adsorptive functions) under sour conditions is necessary in order to guarantee the advantages of SEWGS processes in presence of hydrogen sulphide.

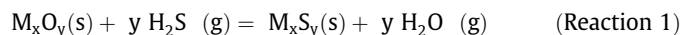
Regarding the catalytic function, some of the earliest heterogeneous catalysts used industrially in the high temperature step of the WGS reaction are Fe-based. However, the activity of Fe-based catalysts is affected by the presence of sulphur compounds [4]. Although some authors claim that small concentrations of H<sub>2</sub>S

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(<50 ppm) have only a minor effect on the activity of this type of catalysts, higher concentration (>250 ppm) have been reported to be extremely deleterious, causing a loss of approximately half of the original catalyst activity [5].

Conversely, for sour applications, the catalysts usually require the presence of sulphur in the gas stream to become catalytically active and to remain in its active phase. The metal oxide in the sour shift catalyst reacts with sulphur and forms metal sulphides (see Reaction (1)), which constitute the active state of the catalyst [6].



One of the families of catalysts widely used for sour WGS applications is Mo-based. The addition of iron group metals to Mo catalysts has been reported to improve Mo catalyst activity by having a synergistic effect on water gas shift reaction [7–9]. In this line, CoMo catalysts supported on Al<sub>2</sub>O<sub>3</sub> and Mg-Al oxides have been reported as sulphur-tolerant catalyst for WGS reaction, where the presence of Mg-Al oxides increased the shift activity of CoMo catalysts at high temperature as well as their stability [8,10–12]. In literature it is also possible to find some references to the successful use of CoMo based catalysts under H<sub>2</sub>S contents from 1 ppm to 2000 ppm for their application to SEWGS processes [13].

Regarding the CO<sub>2</sub> capture function, suitable sorbents for their application to SEWGS processes are required to have high CO<sub>2</sub> capture capacity and selectivity towards CO<sub>2</sub> at temperatures in the range of 300–500 °C, adequate sorption-desorption kinetics (easy regenerable), mechanical strength and low cost [14]. Only a few types of materials are reported in literature to be able to meet the above mentioned pre-requisites and among them, hydrotalcites have demonstrated to be suitable to be used in processes such as the SEWGS process [14,15].

The suitability of K-doped hydrotalcites for different sorption-enhanced processes has been demonstrated under sweet syngas operating conditions for sorption-enhanced steam reforming processes [16–18] or SEWGS processes [19–22]. However, only a few works can be found in literature for processes carried out under sour operating conditions. One of the most recent works has reported a good performance of hydrotalcite based sorbents for their application to SEWGS processes with H<sub>2</sub>S content in the gas of up to 2000 ppm [23]. Even though those materials had shown complete CO conversion before CO<sub>2</sub> breakthrough (prior to CO<sub>2</sub> saturation of the sorbent) under SEWGS conditions, (which makes the presence of catalysts pointless), the aim of creating bi-functional materials is to optimize both functions, converting CO into CO<sub>2</sub> and H<sub>2</sub>, and simultaneously capturing CO<sub>2</sub> under sour conditions improving the performance showed by the sorbent (e.g. by increasing the purity of the hydrogen obtained or the cyclic steady-state volumetric CO<sub>2</sub> capacity and with that, cycle times). Almost pure H<sub>2</sub> is expected to be produced during the sorption step, and a CO<sub>2</sub> + H<sub>2</sub>S stream is meant to be obtained during the regeneration step.

In this work a bi-functional material suitable for sour SEWGS processes applicable to gasification technologies is presented. The new material consists of a K-promoted hydrotalcite impregnated with a CoMo catalyst. Different series of experimental tests have been performed to investigate the catalytic activity, CO<sub>2</sub> capture capacity and synergies between both functions in the material developed. First, the effect of the presence of H<sub>2</sub>S in the CO<sub>2</sub> capture capacity and catalytic activity of the sorbent alone (K-promoted hydrotalcite) towards the WGS reaction was studied in order to determine its suitability for the development of a bi-functional material. Then, the performance of the developed bifunctional material comprising the K-promoted hydrotalcite impregnated with CoMo catalytic active phase was studied and compared with the behaviour of the sorbent alone in CO<sub>2</sub> capture

and WGS tests under sour conditions in order to determine the feasibility of its use in SEWGS processes.

## 2. Experimental section

### 2.1. Test rig

An automatic and computerised laboratory rig was used for the reactions studied in this work. This system consists of a HASTELLOY tubular reactor of OD 9.2 mm and 300 mm long housed in a one single zone SS304 oven which is able to heat the reactor up to 700 °C. Maximum operating gas flow rate is 4.5 NL/min and maximum operating pressure is 20 bar. Desired gas mixture is produced synthetically using mass flow controllers (Hi-Tech). Deionised water is fed by a piston pump (Gibson 307) and vaporised before entering the reactor.

Fig. 1 shows a diagram of the testing rig. A more detailed description of the reaction system can be found elsewhere [24].

Feed and exit gas stream composition was measured by gas chromatography using a CP4900 Varian gas microchromatograph equipped with two columns, a Porapack HP-PLOT Q and a Molecular Sieve HP-PLOT MoleSieve and with two thermal conductivity detectors.

### 2.2. Materials

A potassium carbonate doped hydrotalcite based material was used in these experiments. This sorbent was selected in our previous work [25] among different types of materials as the most appropriate, due to its high CO<sub>2</sub> 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 in pellets of 5 × 5 mm. Mg/Al ratio in K-promoted hydrotalcite is 2 and it is impregnated with 20 wt% K<sub>2</sub>CO<sub>3</sub>.

Based on the thermogravimetric results obtained for K-promoted hydrotalcite in our previous work [25] this material was prepared by calcination at 600 °C in static air for 4 h to guarantee that all CO<sub>2</sub> was released from the structure and then kept in a dryer overnight.

A bi-functional material was prepared by simultaneous impregnation of the K-promoted hydrotalcite (pulverized in advance) according to the incipient wetness impregnation method with the CoMo catalytic active phase. First, Mo was impregnated using an aqueous solution of molybdenum nitrate. After this, cobalt was added using an aqueous solution of cobalt nitrate. Final metal content in samples is 2.59 wt% of Co and 5.02 wt% of Mo. After impregnation, the samples were calcined for 3 h at 400 °C. It was supplied by ITQ (CSIC) in powder form.

### 2.3. Characterisation of materials

Total sulphur was determined using a LECO CS-244 analyser (by LECO Instruments SL). The sample was combusted in oxygen, which converted the sulphur to SO<sub>2</sub>, and total sulphur was then determined by infrared absorption.

### 2.4. Experimental procedure

Two different types of studies were undertaken: CO<sub>2</sub> capture tests and WGS/SEWGS reaction tests. For those tests performed with the hydrotalcite alone 10 g of sorbent was used. For those experiments performed with the bifunctional material 5 g was used in each test (differences in the amount of materials employed are related to the bi-functional material provided). All materials tested in this work (sorbent and bi-functional material) were pre-

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