

A Study of the Catalyst/Absorbent Effect on the Hydrogen Production by Solid Absorption Enhanced Water Gas Shift (SAEWGS)

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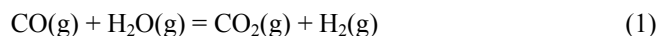
Abstract: The combination of the WGS and CO₂ solid absorption (SAEWGS) produce H₂ and CO₂ separation in one step. Experimental conditions: quartz-made fixed bed reactor at SV = 1500 h⁻¹, feed; 5 % CO, 15 % H₂O, balance He-N₂ and 600 °C, 1 atm. Absorbents tested were calcined dolomite (CaO*MgO) and sodium zirconate (Na₂ZrO₃) employing catalyst/absorbent mixtures in 1/1 and 1/2 weight ratios. A synthesized WGS catalyst (Fe-Cr) was used. Results using the mixture catalyst/absorbent = 1/2 with CaO*MgO generated 95 % of H₂ and 5 % CO₂ without CO. An increase in the catalyst/absorbent weight ratio from 1/1 to 1/2 also increased hydrogen from 89 to 95 %, respectively. This was attributed to slow CO₂ diffusion into the particle affecting absorption kinetics. Whereas, Na₂ZrO₃ produced only 70 % H₂, 29 % CO₂ and 1 % CO being a small CO₂ partial pressure responsible for the lower H₂ content. Using Na₂ZrO₃, the variation of the cat/abs ratio had no effect over the hydrogen content.

Keywords: Hydrogen production, CO₂ Capture, CaO*MgO, Na₂ZrO₃

1. INTRODUCTION

Among renewable energy sources, hydrogen plays a strategic role in generating electricity from fuel cells, mainly because only water vapor is produced during its electrochemical reaction with oxygen to produce electricity [1]. Currently, hydrogen is conventionally produced at large-scale using the steam methane reforming process (SMR) [2], followed by the partial oxidation of hydrocarbons (POX), biomass and coal gasification [3].

These processes generate Syngas (CO/H₂ = 1:2 ratio) as their main product [4]. For further Syngas conversion to CO₂ and H₂, the mixture is sent to another vessel where the water gas shift reaction (WGS) takes place, equation (1).



In order to increase the hydrogen concentration, CO₂ is normally

removed by an absorption system based on amines [5], by the use of H₂ selective membranes [6], or by molecular sieves (Pressure Swing Adsorption, PSA) [7]. However, in recent years new processes have been developed to simultaneously produce H₂ and capture CO₂. This reaction concept has awakened a great deal of interest in the scientific community because of the need to produce high purity hydrogen and the potential energy savings that this concept represents (≈ 23 %). The sorption enhanced water gas shift (SEWGS) [8,9] and sorption enhanced steam reforming (SER) [10,11,12] are among these new processes.

The SAEWGS process combines the WGS reaction, equation (1), with the CO₂ absorption by a metal oxide (MeO), equation (2), in a single step.



This MeO can be any metal oxide susceptible to be carbonated at appropriate reaction conditions. Additionally, it is possible to generate a high purity CO₂ stream through the regeneration of the metal oxide (reverse reaction 2) [13].

López et al., [10] W. J. Comas et al., [14] Fan et al., [15] Ste-

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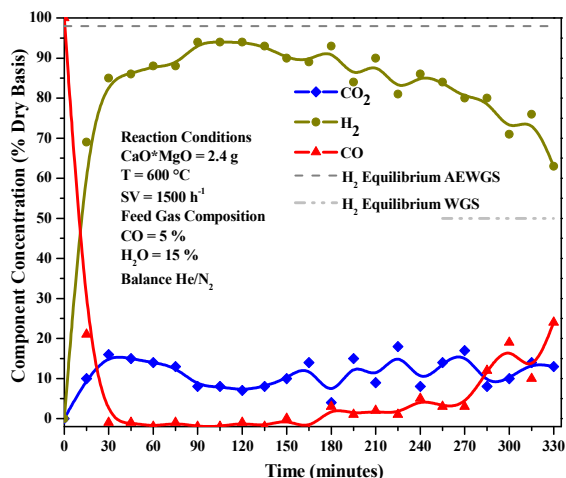


Figure 1. Product gas composition results for the reactor at 600 °C with CaO*MgO for hydrogen production

vans et al. [16] and Wang et al., [17] reported the production of H₂ and CO₂ capture using CaO-based absorbent materials at high temperature. However, these absorbents presented considerable problems of sintering after their exposure to several reaction-regeneration cycles. Also, new synthetic CO₂ absorbents such as Li₄SiO₄ [18] and Na₂ZrO₃ [19] have been lately introduced. These solid absorbents have the main advantage of being thermally stable after large numbers of reaction-regeneration cycles, making them highly attractive to be used under the SAEWGS scheme. In recent studies a thermodynamic analysis of the WGS reaction indicated that could be carried out in a homogenous way. Furthermore, test performed in our laboratory examined the catalytic nature of the WGS reaction using an empty quartz-reactor; from that study, it was concluded that a catalyst was needed for the WGS to proceed at temperatures of interest (400-900°C) [20]. In another study MgO*CaO and Na₂ZrO₃ were used as CO₂ absorbents under the SAEWGS concept [21]. Quartz reactor tests containing only a CO₂ absorbent resulted that its surface acted as a catalyst for the WGS reaction and subsequently this also reacts with CO₂ forming a carbonate. However, as shown in the Figure 1, which is the reaction follow up using calcined dolomite at longer times than that reported by Escobedo et al. [21].

In this plot it can be observed around between 240-320 minutes, carbon monoxide gradually stops reacting and consequently hydrogen production decreases, as well as CO₂ content increases. This change in the product gas concentrations can be attributed to the almost complete carbonation of the calcined dolomite. When calcined dolomite is saturated (carbonated form), its CO₂ capture capacity is lost, and stops working as a WGS catalyst. This behavior can be highly inconvenient, especially when the stability of the process is at stake. In order to insure a high purity hydrogen production through the SAEWGS reaction in continuous way, the use of a WGS catalyst is proposed in combination with a CO₂ absorbent.

Most industrially used high temperature WGS catalysts are those based on iron and chromium oxides which have been reported to be

very selective for the water gas shift reaction at temperatures above 300 °C maintaining stability and resistance to sintering. The catalytically active phase is magnetite (Fe₃O₄) that usually comes from the partial oxidation of hematite (Fe₂O₃). However, pure magnetite catalysts suffer from sintering that reduces their activity. A stabilizer, Cr₂O₃, is commonly added and the combination of Fe₃O₄ and Cr₂O₃ gives commercially stabilized catalysts that can operate for several years before requiring replacement [22]. Literature indicates that Fe-Cr catalysts that are formulated within a molar ratio range between 8 and 10 are the ones present the highest catalytic activities towards WGS [23]. Considering this last, the Fe-Cr catalyst used in the present study is composed by a 9 molar ratio. The aim of the present work is to examine the effect of different catalyst/absorbent (cat/abs) weight ratios to produce high purity hydrogen (> 90 %) through the WGS and CO₂ absorption reactions using a fixed bed quartz reactor (600 °C, 1 atm.) and a mixture of a CO₂ solid absorbent (CaO*MgO or Na₂ZrO₃) and a Fe-Cr catalyst.

2. EXPERIMENTAL

2.1. Synthesis

Na₂ZrO₃ was prepared by the solid state synthesis following the procedure described elsewhere [24]. This was prepared from reagent grade precursors Na₂CO₃ (J. T. Baker) and ZrO₂ (Spectrum Chemical Mfg. Corp) in a 1:1 molar ratio. These reagents were mixed in an agate mortar and calcined in air at 900 °C for 4 h. Dolomite used in this study was acquired from Nuevo Leon (México) mines and calcined in air at 900 °C for 4 h.

A chemical precipitation technique was used to synthesize the high-temperature catalyst for the WGS reaction [25]. This involved the addition of aqueous solutions prepared from: Cr(NO₃)₃·9H₂O (JT Baker) and Fe(NO₃)₃·9H₂O (J. T. Baker) to a 30 % solution of ammonium hydroxide (precipitating agent) while maintaining a pH ≥ 9 at constant stirring and 25 °C. The amount of precursors was adjusted to obtain a catalyst with a Fe:Cr molar ratio of 9 and this was called “Fe-Cr” catalyst. Finally, the precipitate was filtered, washed, dried and calcined at 600 °C in air for 4 h.

2.2. Characterization

The crystalline structure was determined by X-ray diffraction (XRD) in a Phillips XPERTMPD with Cu K α , BET surface area of the samples was determined in an Autosorb 1 (Quantachrome Inc), while the morphology was examined in a JEOL JSM-5800LV scanning electron microscope (SEM,) using a detector of secondary electrons.

2.3. Reaction system and experimental conditions

Appropriate reaction conditions for SAEWGS system using calcined dolomite and sodium zirconate were selected from the thermodynamic analysis performed by Escobedo et al. [21], since at these conditions both absorbents combined with a WGS catalyst can produce an elevated CO conversion and a high hydrogen concentration.

A fixed-bed reaction system was built for the hydrogen production evaluation tests under the SAEWGS reaction concept, and details are found elsewhere [20]. In this system N₂, CO and He were fed to the reactor through the use of mass flow controllers (MFC's). Water was fed to the system using a 100DX-Teledyne Isco syringe pump and mixed with inert gas (N₂ and He) and then

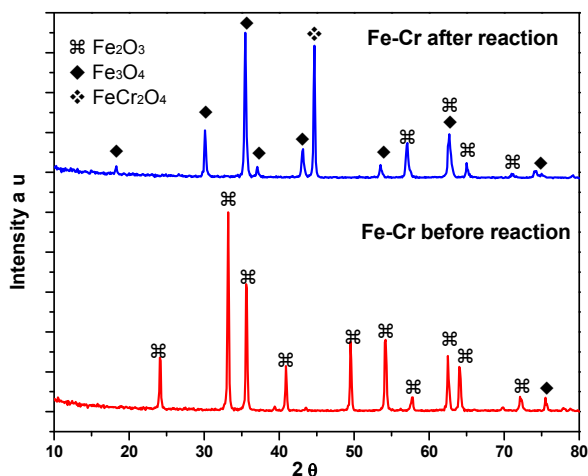


Figure 2. XRD of the Fe-Cr catalyst before and after the WGS reaction

evaporated by several heating tapes (preheating section) kept at 120 °C and then mixed with a CO stream. Mass flow controllers were used to insure a space velocity (SV) of 1500 h⁻¹. Feed concentrations of 5 % CO, 15 % H₂O, and balance N₂-He were used for the packed reactor tests. The fixed-bed reactor was made of quartz with dimensions of 20 cm. long and 2 cm. diameter, equipped with a thermo-well (for temperature monitoring) and containing 3 cm³ of the catalyst/absorbent mixture. Downstream, the reactor gas product was passed through a condenser to remove water and then analyzed using gas chromatography (GC) in a Perkin Elmer Instruments Clarus 500 equipped with TCD and FID detectors and a Porapak Q column.

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction

XRD diffraction patterns of Na₂ZrO₃ and calcined dolomite (CaO ·MgO) of the present study have been reported elsewhere [19]. The crystalline phases obtained after synthesis of the CO₂ absorbents corresponded to the Na₂ZrO₃ structure, while the calcined dolomite XRD pattern presented only CaO and MgO crystalline structures as a result of the decomposition of CaCO₃·MgCO₃ accompanied with the release of CO₂.

Figure 2 shows the diffraction patterns of the synthesized “Fe-Cr” catalyst, before and after reaction. The crystalline phase detected in the XRD pattern of the fresh catalyst was Fe₂O₃ (hematite), although isolated chromium phases were not observed, presumably due to its low concentration in the catalyst and/or because it is present in an amorphous form. This result is expected, since iron oxide can be obtained from the precipitation of its nitrate in the FeOOH form, when calcined at temperatures greater than 500 °C, producing predominantly the Fe₂O₃ oxide form (fresh catalyst). The signals exhibited by the spent catalyst corresponded to FeCr₂O₄ spinel structure (chromite) and Fe₃O₄ (magnetite), which acts as the catalyst active phase towards the WGS reaction. The Fe₃O₄ phase is the result of submitting hematite to an activation process, which consists in exposing it to a reducing atmosphere of 20 % H₂, followed by oxidation with steam, before the WGS take

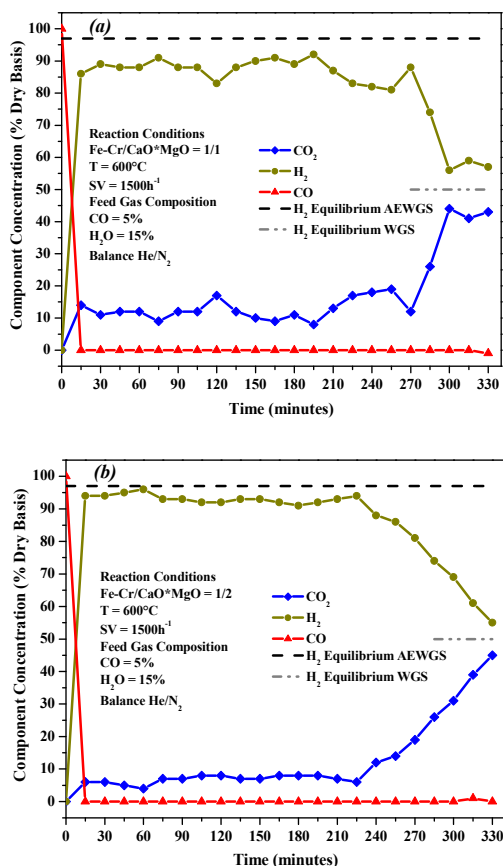


Figure 3. Product gas composition results for the reactor at 600 °C with a mixture of Fe-Cr/CaO·MgO for hydrogen production (a) (cat/abs) = 1/1, (b) (cat/abs) = 1/2

place. The formation of the FeCr₂O₄ spinel structure is favored by the presence of Cr₂O₃ (thermal stability promoter) and a reduced iron phase under activation process conditions [26].

3.2. Evaluation of the catalyst/absorbent mixture for H₂ production through SAEWGS

The effect of the catalyst/absorbent weight ratio on the product gas H₂ content was studied in the fixed-bed reaction system. 1/1 and 1/2 catalyst/absorbent (cat/abs) weight ratios were used to evaluate the hydrogen production and results of the dry-inert free (He and N₂) gas composition as a function of time were obtained for each sample.

3.2.1. Fe-Cr/CaO·MgO mixture

Results of the Fe/CaO·MgO mixture using a cat/abs = 1/1 weight ratio are shown in Figure 3 (a). In this Figure the product gas composition is plotted as a function of reaction time. The experimental H₂ concentration can be compared to the equilibrium concentration (obtained in the thermodynamic analysis) represented by a black dotted line (97 % H₂). During the first 270 minutes of reaction it can be observed that dolomite properly absorbed the CO₂ produced within the reaction system achieving a maximum H₂ concentration of 89 % accompanied with 11 % CO₂. After 270

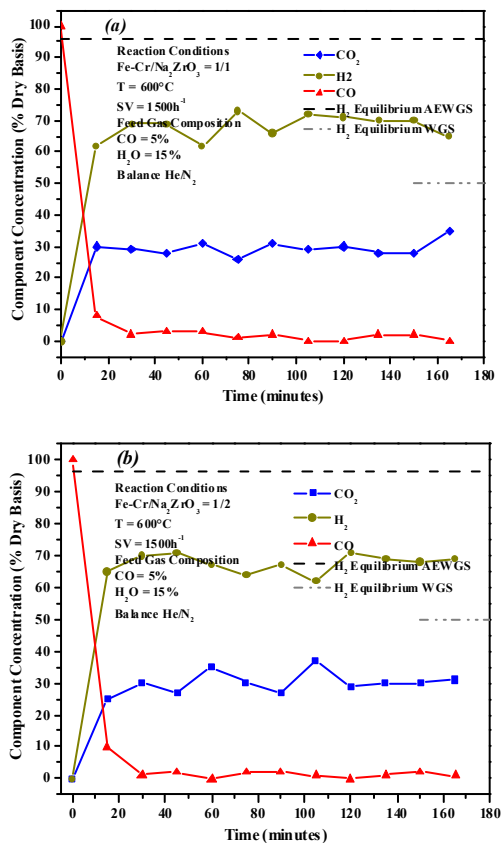


Figure 4. Product gas composition results for the reactor at 600 °C Fe-Cr/Na₂ZrO₃ for hydrogen production
(a) cat/abs = 1/1, (b) cat/abs = 1/2

minutes of reaction, dolomite is almost fully carbonated and the concentration of CO_2 increased, while that for H_2 decreased to reach the equilibrium value for the WGS reaction (without absorbent) at 600 °C, which is represented by a centered dotted line (50 % H_2 and 50 % CO_2). A zero CO concentration was observed during all the run, indicating a complete CO conversion and an active catalyst even at times where the carbonation reaction was over (after 270 min).

Hydrogen production results for the $\text{cat/abs} = 1/2$ weight ratio using calcined dolomite are presented in Figure 3 (b). The maximum H_2 concentration was 95 % and only 5 % CO_2 for the first 210 minutes of reaction. These experimental data were very close to SAEWGS equilibrium concentrations (97 % H_2 and 0 % CO_2). CO concentration was zero throughout the entire reaction, confirming that the Fe-Cr catalyst present in the mixture (cat/abs) was still active after 330 minutes of reaction. Furthermore, after 210 minutes, the CO_2 and H_2 concentration reached values close to WGS equilibrium as a result of the dolomite carbonation. Therefore, it is evident that an increase in the cat/abs weight ratio from 1/1 to 1/2 also increased the hydrogen content from 89 to 95 %, respectively. This behavior can be due to the fact that a greater amount of absorbent is needed to retain CO_2 into the dolomite because CO_2 diffusion to the interior of the particle is known to be the rate determin-

ing step in this material absorption kinetics [8] and therefore, a greater amount of absorbent would be reflected in a larger amount of CO_2 absorbed as observed in Figure 3 (a) and (b).

3.3.2. Fe-Cr/Na₂ZrO₃ Mixture

Figure 4 (a) shows product gas composition results of the reactor at 600 °C for a $\text{cat/abs} = 1/1$ weight ratio using Na_2ZrO_3 as absorbent. The experimental maximum hydrogen concentration for the first 160 minutes of reaction was only of 71 %, 21 % less compared to the SAEWGS equilibrium H_2 concentration (96 %), while other gases were 29 % CO_2 and about 1 % of un-reacted CO . The hydrogen concentration observed in Figure 4 (a) is presumably due to a low CO_2 partial pressure present in the reaction system as reported in the literature [27], thus limiting the CO_2 absorption reaction kinetics. This effect prevents the material to properly remove CO_2 in order to achieve higher H_2 concentrations. Despite of the low CO_2 partial pressure, sodium zirconate reacted to form sodium carbonate, since the experimental H_2 concentration is greater than the equilibrium concentration for the WGS reaction (50 %). Results of the product gas concentration as a function of time are plotted in Figure 4 (b) for a cat/abs ratio of 1/2. In this Figure the H_2 , CO_2 and un-reacted CO concentrations are similar to those obtained using the $\text{cat/abs} = 1/1$ ratio.

Under the studied conditions (600 °C, 1 atm.), these results suggest that variation of the cat/abs weight ratio has little or almost negligible effect over the hydrogen concentration in the product gas. Also, it can be inferred that the most important factor for Na_2ZrO_3 carbonation is the CO_2 partial pressure, because small values of this eventually inhibit fast carbonation kinetics to produce a high purity H_2 stream in the product gas [27].

Comparing the behaviors between the combined use of a conventional WGS catalyst and a CO_2 absorbent, cat/abs , (Figures 3 and 4) and the use of a bifunctional material (absorbent-catalyst), such as dolomite or sodium zirconate (behavior reported in Escobedo et al. [20 and 21]) under the SAEWGS scheme, it can be assumed that the main advantages to use cat/abs are 100 % CO conversion throughout the entire test and the stability of a process for continuous hydrogen production. Additionally, this option has a further advantage that can be easily applied to current commercial WGS technologies.

4. CONCLUSIONS

The use of $\text{CaO}*\text{MgO}$ as CO_2 absorbent H_2 produced a maximum concentration of 95 % and 5 % CO_2 under a space velocity of $SV = 1500\text{ h}^{-1}$, $\text{CO}/\text{H}_2\text{O}$ ratio = 1/3, 600 °C, 1 atm. and $\text{cat/abs} = 1/2$ ratio. An increase in the cat/abs weight ratio from 1/1 to 1/2 also augmented the hydrogen content from 89 to 95 %, respectively. Whereas, Na_2ZrO_3 only produced a 71 % H_2 concentration accompanied with 29 % CO_2 and 1 % of un-reacted CO ($\text{cat/abs} = 1/2$). The variation of the cat/abs weight ratio using Na_2ZrO_3 as absorbent has little or almost negligible effect over the hydrogen concentration in the product gas. This behavior was attributed to a low CO_2 partial pressure within the reactor, thus limiting the sodium zirconate carbonation. The stability of a process for continuous hydrogen production through SAEWGS concept and 100 % CO conversion justify the combined use of a WGS catalyst and CO_2 absorbent.

5. ACKNOWLEDGMENTS

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