

Medium-Temperature CO₂ Sorbents

Subjects: [Biology](#)

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Hydrogen is a promising energy vector, with a high calorific value (122 kJ g⁻¹), which is being considered as the cleanest energy option, with a zero-carbon footprint, since it burns cleanly, giving water as the only product. Therefore, if linked with renewable energy sources and CO₂ capture, it allows for decarbonizing a wide range of final sectors of use, providing clean power and heat to transport and stationary applications. Hydrogen is an important raw material of some industrial processes, such as hydrocracking, ammonia synthesis, methanol production, and the manufacture of hydrochloric acid; it is also a reducing agent in the steel industry.

H purity

CO capture

Ca-based sorbents

1. Sorption-Enhanced Water–Gas Shift Reaction

The water–gas shift reaction using syngas feedstock derived from coal gasification or steam methane reforming is a very common means of generating pure H₂. The syngas composition depends on several factors, such as the selected reforming or gasification process, the fuel composition, the S/C ratio, temperature and pressure conditions of the shift reaction. Usually, syngas that originated from natural gas has a higher H₂ and a lower CO₂ and CO content than coal-derived syngas (**Table 1**). Besides, it has very low levels of sulphur compounds because most of it is removed before the reformer to prevent catalyst poisoning, while coal-derived syngas typically contains more sulphur. As mentioned in the above sections, the WGS reaction can contribute to the syngas upgrade by converting CO into CO₂, which can be easily separated, and contributes to an additional production of H₂.

Table 1. Typical composition of syngas obtained by different processes and conditions.

mol % (Dry Basis)	SMR ^[1]	Coal Gasification ^[2]	Indian Coal Gasification ^[3]	Wood Pellets Gasification ^{[3][4]}	Rice Husk Gasification ^[3]
H ₂	71	13–18	9	7–34	25
CO ₂	6	7–9	0.6	6–16	14
CO	16	55–62	42	16–31	20
O ₂	--	--	--	1–3	--
N ₂	--	--	32	48–58	40
CH ₄	5	~7	17	1–4	0.9
C _x H _y	--	--	--	0.1–0.3	--

At low temperatures, the water–gas shift (WGS) reaction is thermodynamically favored, since its equilibrium constant decreases as temperatures increases ^[5], but not kinetically, as it is an exothermic reaction. Since the WGS reaction proceeds without change in the number of moles, pressure does not affect equilibrium, but up to the equilibrium moment total pressure can positively affect CO conversion since it increases the reaction rate ^{[6][7]}. To overcome thermodynamic and kinetic aspects, WGS reaction is carried out industrially in two steps: the first, high-temperature shift (HTS; 350–500 °C), using Fe-Cr catalysts, and the second, low-temperature shift (LTS; 200–250 °C), using Cu-Zn-Al₂O₃, that allows for achieving CO concentrations near 3% and 0.1%, respectively ^[8]. However, these two steps increase the complexity and the energy requirements of the process. Besides, if O₂ is present it acts as a poison for the HTS catalysts, due the oxidation of Fe₃O₄ into the inactive Fe₂O₃ ^[9]. In addition, the LTS catalysts require high-volume reactors and can lose activity easily, due to being susceptible to poisoning by S, and Cu sintering. If H₂S is present, a cobalt-molybdenum catalyst should be used ^[10]. On account of the limitations of commercialized shift catalysts, some improvements have been developed, such as replacing part of the metals with modified materials or doping with some alkalis ^[5]. Pal et al. ^[11] considered three more catalysts' categories, ceria and noble metal-based catalysts, carbon-based catalysts and nanostructured catalysts ^[12]. The WGS reaction requires a step for the CO₂ removal, usually the pressure swing adsorption technique is used.

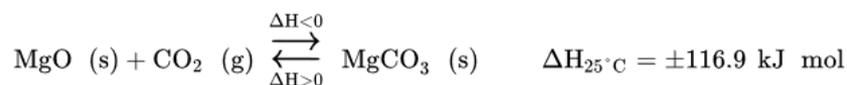
In recent years, the sorption-enhanced reaction (SER) has been studied, aiming to improve the performance of the WGS reaction and leading to sorption-enhanced water–gas shift (SEWGS) reactions. The SEWGS reaction consists of a WGS reaction with in situ CO₂ capture occurring simultaneously in a single reactor. The implementation of in situ CO₂ removal shifts the WGS reaction to its right side by capturing the CO₂ and, thus, increasing the H₂ yield. That is to say that in situ CO₂

capture overcomes the limitations related to the equilibrium, resulting in both higher CO conversion and enhanced H₂ production. The result is the production of a very-high-purity H₂ without the elevated costs associated to a separation process and a much more compact and simple process, associated with a higher energy system efficiency and lower capital costs.

The success of the SEWGS is highly dependent on the sorbent selected for the in situ CO₂ capture from the reaction medium. The adequate materials for this technology are medium-temperature solid sorbents. The hydrotalcite and modified hydrotalcite-based sorbents are largely studied [13][14][15][16], and exhibit low CO₂ sorption capacity, i.e., less than 0.1 g CO₂/g sorbent at medium temperatures, which in SEWGS will cause CO₂ saturation and reduction in H₂ production. Mg-based sorbents have also been applied in the enhanced CO₂ removal from WGS reaction, having a high theoretical carrying capacity, which makes it very attractive. Moreover, the integration of Mg-based sorbents allows one to remove the CO₂ at medium temperatures, that is, ranging from carbonation to calcination temperatures of 300 to 450 °C, respectively, without the need of low-temperature WGS reaction. The performance of SEWGS reaction in this range of temperatures can be greatly enhanced in the presence of suitable catalysts, i.e., with enhanced stability, applicability, and activity at medium temperatures [11]. The catalytic performance depends on the synthesis technique, the nature of the active site/phase, the type of support and the reaction environment [11][17][18][19]. At medium temperature, for single-stage WGS reaction, platinum-based catalysts and supports with oxygen storage capacity, such as CeO₂, are particularly favorable, because they show very high activity [6][20]. In practical applications, Mg-based sorbents are promising; however, more attention need to be paid to approach the theoretical carrying capacity. This type of sorbents show an abrupt decrease in the CO₂ carrying capacity under long-term cyclical operation, sintering, attrition, and potential competing sulphation reactions [21][22][23][24]. In fact, there is no record of pilot-scale projects in this area [24], but promising results have been obtained using Mg-based sorbents modified with alkali molten salts [22][23].

2. Enhancement of the H₂ Production with Mg-Based Sorbents

In recent years, there has been a significant growing interest among scientific researchers in using Mg-based sorbents for CO₂ capture [25]. There are various benefits associated to Mg-based compounds. Mg-based sorbent is nontoxic, noncorrosive and is largely available on nature, where it is abundant at a relatively low cost. It also offers a wide temperature range to work with, from room-to-medium temperatures. Its regeneration can occur below 500 °C, which is a moderately low temperature, when compared to the one used with high-temperature CO₂ basic metal oxide sorbents, such as Ca-based or alkali-based sorbents. Economic benefits unfold from using lower temperatures, since energy consumption is reduced, which in turn impacts positively in the system efficiency and the use of energy resources. In addition, Mg-based sorbents have a moderate basicity, which leads to a high theoretical CO₂ capture capacity of 1.09 g CO₂/g MgO. One mole of MgO can absorb one mole of CO₂, according to the reversible reaction described in following Equation [25].



In practice, most of Mg-based sorbents do not exhibit the expected theoretical capture capacity. In fact, these materials are characterized with low CO₂ capture capacity due to having slow kinetic reactivity [21][25]. As an example, commercial MgO powder presents a CO₂ capture capacity of only 20 mg CO₂/g MgO at 200 °C [26]. There are two main factors that are believed to explain both the poor capture capacity and the slow kinetics. Regarding the first one, this is related to the fact that MgO has a low surface area and, hence, does not expose its basic sites sufficiently well for CO₂ sorption. Taking the same example of the commercially available MgO as above, its surface area is between 8 and 35 m²/g [21]. Moreover, MgO has a volume expansion of 2.49 times [21] caused by the formation of MgCO₃. This product layer ends up covering with dense layers the adjacent basic active sites of the MgO sorbent, inhibiting the CO₂ sorption to proceed. This evidence supports the fact that the poor sorption capacity is a surface phenomenon [25]. The other reason lies in MgO's intrinsically high lattice enthalpy. Low porosity is also often related to low kinetics, since MgO's strait pores obstruct the CO₂ diffusion through them and, thus, delay the adsorption equilibrium [25]. In addition, MgO has a poor thermal and mechanical stability.

The circulation of the Mg-based sorbent between both the carbonation and the regeneration reactors is illustrated in **Figure 1**.

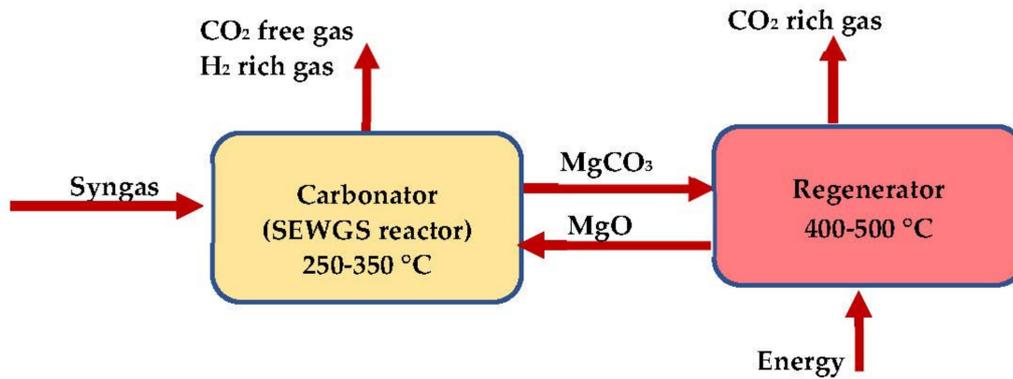


Figure 1. Carbonation–regeneration cycle of Mg-based sorbent.

In order to understand the thermodynamic limitations that lead to constraints of the operational conditions associated to the equilibrium described in Equation (22), the CO₂ partial pressure, P_{CO_2} , in function of the dissociation or equilibrium temperature, T_{eq} , is plotted in Figure 2; this is calculated using in following Equation^[27].

$$T_{\text{eq}} = 13636 / (\ln [\text{bar}] / P_{\text{CO}_2}) + 20.01) - 273.15$$

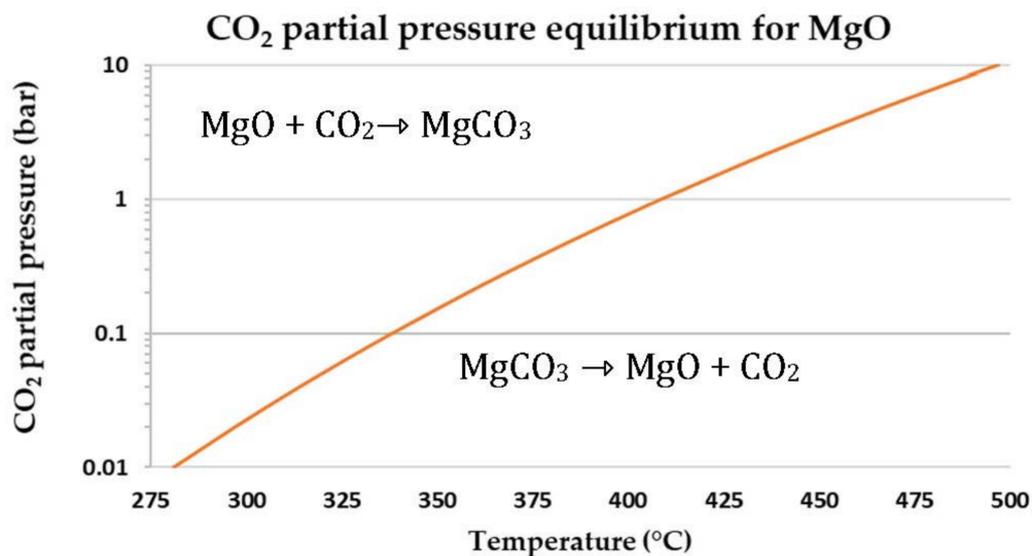


Figure 2. MgCO₃ equilibrium curve relating the temperature to the CO₂ partial pressure.

The thermodynamic equilibrium of MgCO₃ decomposes itself in MgO and CO₂, at 1 bar and above 300 °C; the CO₂ pressure represents a limitation in what concerns increasing the working temperature^[28]. Only if working at higher pressures would higher operating temperatures be possible to consider, but both kinetic and uptake could still be a concern and a limitation for practical applications^{[26][28]}. The possibility of working at relatively low temperatures makes MgO compounds attractive to explore, especially for SEWGS reaction, but it is mandatory to overcome uncompetitive capacities and low sorption kinetics rates first. In this sense, researchers started to study different paths to enhance their performance, based on the sorbents' dependence on intrinsic and extrinsic factors.

Most promising approaches aiming to improve the CO₂ capture performance of Mg-based sorbents by upgrading their internal properties consist of the following: synthesizing mesoporous MgO, producing MgO from effective magnesium precursors, dispersing MgO on inert supports and doping MgO with alkali molten salts (AMS). The doping with alkali metal salts is the most widely recognized promising approach^[25].

Most recent experimental works is to improve the CO₂ uptake capacity of these materials up to 0.7–0.8 g CO₂/g sorbent^[29]. The alkali carbonates and the alkali nitrates/nitrites are the most commonly used^[21]. In general, three categories of alkali doping are considered: alkali carbonate doping, alkali nitrate/nitrite doping and binary or ternary alkali doping.

Regarding alkali carbonate doping, the CO₂ mechanism sorption is believed to happen in two steps. The first step consists in the quick generation of basic sites on the MgO surface, due to the established interactions between the sorbent and the alkali metal carbonate molecules. The nature of the AMS highly impacts the kinetics and the sorption capacity of the doped MgO sorbent at this stage because the basicity level of the produced active sites is influenced by the size of the ion salt. The second step is the slow formation of the double carbonate phase between the Mg and the AMS [24]. Concerning the alkali nitrate/nitrite, it was shown by Zhang et al. [30] that a MgO sorbent doped with NaNO₃ exhibiting good CO₂ sorption kinetics and a MgO conversion of 75% against of only 2% for an undoped MgO, both at 330 °C and ambient pressure. It was stated that molten NaNO₃ provides an alternative reaction pathway to traditional gas–solid reactions, by acting as a phase transfer catalyst between bulk MgO and CO₂ molecules which, in turn, facilitates the sorption reaction. It was described as the promoting effect of the molten nitrate. In addition, molten alkali metal nitrates are shown to prevent the formation of a rigid, CO₂-impermeable, and monodentate carbonate layer on the surface of MgO as it occurs with bare MgO, but to promote the rapid generation of carbonate ions to allow a high rate of CO₂ uptake. The binary doping with alkali nitrate/nitrite is also an interesting matter of study. Zhao et al. [31] compared the CO₂ sorption capacities of the single NaNO₃ and of the binary NaNO₃/NaNO₂ doped MgO sorbents. The latter showed higher CO₂ sorption capacity than the former. This new evidence found explanation on the reduction in the melting temperature of the eutectic mixture. While single NaNO₃ and NaNO₂ present a theoretical melting point of 308 and 271 °C, respectively, the eutectic mixture of NaNO₃/NaNO₂ exhibits a melting temperature of 185 °C. Thus, the eutectic mixture facilitates the sorption process by providing a molten phase that works like a liquid channel. Ternary doping with NaNO₃, lithium nitrate (LiNO₃) and potassium nitrate (KNO₃) registered an even more accentuated reduction in the eutectic mixture's melting point and an enhanced CO₂ sorption performance. In the case of the ternary doping with LiNO₃, NaNO₃ and Na₂CO₃, the former two form the molten phase in which Na₂CO₃ dissolves along with the bulk MgO to react with the CO₂ molecules [24][31]. It is well accepted that the melting temperature of the eutectic mixture impacts greatly on the CO₂ sorption performance.

The enhancement of Mg-based sorbents carrying capacity boosts its use for SEWGS processes, but current focus is on considering the simultaneous WGS reaction and CO₂ capture are scarce, but promising.

To the best of our knowledge, the first experimental work conducted with Mg-based sorbent in a SEWGS reaction was performed by Abbasi et al. [32]. A partially calcined dolomite impregnated with K₂CO₃ was tested as sorbent/catalyst, at 20 atm, in a simulated syngas atmosphere. The sorbent was shown to be capable of achieving 95% of CO₂ capture and 40% of conversion in the WGS reaction, but both activities decreased with increasing temperature. The results indicated that the pre-breakthrough WGS conversion diminishes as the sorbent is carbonated and CO₂ concentration approaches the inlet concentration, leading to the conclusion that the catalytic activity of MgO is significantly greater than that of MgCO₃. During the SEWGS at 400 °C, the H₂ (dry basis) change from ~60 to ~45%, and CO₂ from ~9 to ~25%, in the pre- and post-breakthrough phases, respectively.

Hu et al. [22] synthesized AMS-promoted MgO-CaCO₃ sorbents and obtained a high CO₂ carrying capacity and stability after 30 cycles, i.e., 0.55 g CO₂/g sorbent (carbonation at 350 °C, 30 min, 1 atm, 50% CO₂; and regeneration at 420 °C, 10 min, 1 atm, N₂). The enhancement of sorbent performance resulted in a high H₂ purity during the SEWGS process. For the optimized conditions, i.e., 12 atm, 300 °C, an initial ratio H₂O/CO molar ratio of 1.5 and a three catalyst/sorbent layered configuration, the H₂ purity was 99.4% for the 1st cycle and 98.2% after 10 cycles. Recently, Hu et al. [33] describes the preparation of K₂CO₃-promoted Cu/MgO-Al₂O₃ by sol-gel method to be used in a SEWGS reaction. Very much promising results were obtained for a sorbent with a K/(Mg + Al) ratio of 0.2 and a Mg/Al ratio of 9. A H₂ yield of 99.9% was registered after 10 SEWGS/regeneration cycles at 300 and 380 °C for SEWGS and for regeneration, respectively.

In another one by Lee et al. [23] reported a Na-Mg double salt-based sorbent that was tested under SEWGS conditions using a commercial catalyst. A divided section packing concept of catalyst/sorbent was prepared and a high pure H₂ was obtained (CO < 10 ppm). The carrying capacity of this Na-Mg double salt-based sorbent was ca. 0.15 g CO₂/g sorbent, so the reactor column was divided into more sections (~10) and packed with increasing amounts of sorbent.

2.1. Effect of Temperature on Mg-Based Sorbents

As shown in **Figure 2**, the MgO carbonation is strongly dependent on temperature, but the sorbent synthesis and properties, such as the use and type of promoters, also had a relevant role on the CO₂ uptake. Wang et al. [26] analyzed the effect of temperature on CO₂ sorption by NaNO₂ and NaNO₃-promoted MgO. It was observed that at low temperatures (240–260 °C), the 0.2NaNO₃/MgO sorbent exhibited relatively low CO₂ uptake. On the other hand, the 0.2NaNO₂/MgO demonstrated faster weight increases, which indicates that the formed MgCO₃ product layer of 0.2NaNO₂/MgO is thicker than that of 0.2NaNO₃/MgO, which increases the CO₂ diffusion resistance. Further increasing the temperature to 280–300 °C, the CO₂ sorption of two sorbents was significantly enhanced since the diffusion process was activated, and values were attained near 0.55 g CO₂/g sorbent after 60 and 120 min for 0.2NaNO₂/MgO and 0.2NaNO₃/MgO, respectively. With the temperature increasing to 320–340 °C, the sorption rates decreased during the initial period, whereas the final uptakes were slightly

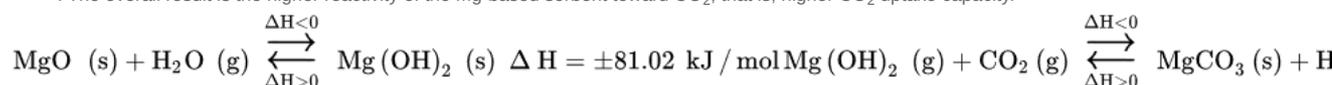
improved. It was justified by the increased CO₂ equilibrium concentration in the molten salts and the enhanced diffusivity of CO₂ in the product layer with increasing temperature. Hiremath et al. [34] synthesized KNO₃-LiNO₃/MgO-TiO₂ sorbents and observed that the CO₂ uptake initially increases with increasing temperature from 250 to 300 °C, and started to decrease for higher temperatures (325, 350 and 375 °C), which is in line with previous results. The kinetics of CO₂ uptake showed an interesting behavior at a lower temperature (250 °C): the CO₂ uptake was fast at the beginning (<10 min), but at 300 °C the initial 10 min showed a slight increase in CO₂ uptake followed by a fast transition leading to a higher CO₂ uptake, although the initial sorption kinetics was slower. Wang et al. [35] found similar behavior with the sorption temperature, i.e., during the initial stage of the CO₂ absorption process, the lower the temperature (275 vs. 375 °C) the higher the rate, which was justified by the higher CO₂ concentration in the molten salt at a lower temperature. With the progress of CO₂ absorption, the disadvantage of slow kinetics at low temperatures is more prominent, and a low CO₂ uptake after 120 min of absorption was observed. Pozzo et al. [29] analyzed the cyclic performance of MgO promoted by 10% of (Li,Na,K)NO₃ for different carbonation temperatures, 250, 275 and 300 °C, with a partial pressure of CO₂ of 0.2 atm. At 275 °C, the CO₂ uptake was higher, which was explained by the higher thermodynamic driving force at lower carbonation temperatures. It was stated that the eutectic mixtures become particularly important, as the low melting point broadens the operating window of the material.

Then, the temperature affects the kinetics that is a relevant aspect of the in situ CO₂ uptake. The Mg-based sorbent carbonation should be quick enough to produce high-purity H₂ during the SEWGS process.

2.2. Effect of Steam on Mg-Based Sorbents

The SEWGS process requires the presence of high quantities of steam for the WGS reaction, which justifies the understanding of the steam effect on the Mg-based sorbents performance. Zarghami et al. [36] investigated the effect of the presence of H₂O on the reactivity of Mg-based sorbents. The experimental results demonstrated that the existence of steam in the sorption step had a positive influence in the rate of the carbonation reaction. Several tests were carried out using reactant gas mixtures containing 50% CO₂ and increasing concentrations of steam (10, 20 and 30%), in a pressurized system (20 bar) at 430 °C. A positive relationship was observed between the steam increase and the CO₂ uptake, attaining values near 100% of CO₂ uptake with 30% of steam, after 15 min.

Water is believed to work as a co-sorbent that boosts CO₂ chemical reactivity, by creating a new carbonation pathway consisting of two mechanisms [25]. The primary mechanism forms an alternative transient compound, Mg(OH)₂, with a larger molar volume than that of MgO (the following Equation). The secondary mechanism acts at the pore structural level, by expanding the inner pore volume and, thus, diminishing the resistance through diffusion in its inside (the following Equation) [21][25]. The overall result is the higher reactivity of the Mg-based sorbent toward CO₂, that is, higher CO₂ uptake capacity.



The kinetics of the reaction between CO₂ and Mg(OH)₂ described in above Equation is faster than that of the reaction between CO₂ and MgO. The capture of CO₂ with Mg(OH)₂ is an exothermic reaction with a ΔH value much lower than that of the reaction of MgO with CO₂, i.e., -19.7 vs. -100.9 kJ/mol. Moreover, the capture of CO₂ with Mg(OH)₂ at a high temperature is faster than with MgO. Researchers deduce that the presence of water provokes the rearrangement of surface oxide to hydroxide over MgO molecules, producing Mg(OH)₂. This transient species have weaker lattice bonds when comparing to MgO, which smooths the transfer ability of OH⁻ more than O²⁻.

At atmospheric pressure, the Mg(OH)₂ registered an absorption capacity of 0.148 g CO₂/g sorbent (1 bar), but its operation is limited to the temperature window of 200–315 °C and requires the rehydroxylation of MgO in the sorbent regeneration [26][28]. In addition, the existence of water decreases the operating temperature. Thus, the regeneration of MgCO₃ into Mg(OH)₂ can be achieved at lower temperatures [21][31][32].

Yang et al. [24] also found that the presence of H₂O during the sorption step improved the kinetics of sorption rates. In addition, it is also reported that the introduction of H₂O at the desorption step could have benefits in the improvement of both regeneration rate and efficiency of Mg-based sorbents. These results support the idea that the steam will be beneficial to the performance of SEWGS process when Mg-based sorbents are used for CO₂ capture, especially at high pressures.

2.3. Effect of Pressure on Mg-Based Sorbents

Currently, SEWGS processes take place at high pressures [24]. Thus, a CO₂ separation unit of a SEWGS process demands Mg-based sorbents to keep its cyclic CO₂ uptake capacity stable at high pressures. Hwang et al. [37] investigated the effect of the operation pressure in the CO₂ uptake capacity of a Mg-based sorbent impregnated with alkali metal nitrates under multiple cycles. The obtained experimental results showed a general upward profile of the CO₂ uptake capacity with increasing operation pressure: the CO₂ uptake capacity increased dramatically from 1 to 20 atm, while a more discreet increase was registered from 20 to 30 atm. This fact was attributed to gaseous diffusion being mainly controlled by Knudsen

diffusion at higher pressures. A Mg-based sorbent impregnated with 5% of NaNO₃ plus 5% of KNO₃ was able to maintain its CO₂ uptake capacity at 0.40 g CO₂/g sorbent after five cycles at 300 °C and 20 atm. It was concluded it was an adequate sorbent to be used in a SEWGS process at high pressures.

Hu et al. [22] analyzed the pressure effect on the outlet gas composition at the pre-breakthrough stage of a SEWGS process, using an AMS-Mg₉₅Ca₅ sorbent and increasing the total pressure from ambient pressure to 12 atm. It was observed that the outlet concentration of CO₂ during the pre-breakthrough period decreases, whereas those of H₂ and CO increase, which is reasonable because the driving force for CO₂ sorption increases with total pressure (Figure 2). For 1, 4, 8 and 12 atm, the measured CO₂ concentrations during pre-breakthrough were 13.6%, 3.3%, 1.9% and 0.8%, respectively, while the equilibrium values were 5.2%, 1.3%, 0.6% and 0.4%, respectively. Therefore, the higher the pressure, the nearer the concentration approaches the equilibrium value. At the post-breakthrough stage, where the sorbent is completely saturated, no CO₂ sorption occurs and only WGS takes place. At this stage, the outlet concentrations of H₂, CO₂ and CO at different pressures tend to the equilibrium values (46.3%, 46.3% and 7.4%, respectively)

Ryu et al. [38] examined the CO₂ absorption properties of MgO-based sorbents loaded with K₂CO₃ according to the pressure (1, 10 and 20 atm). The MgO-based sorbent loaded with K₂CO₃ showed improved CO₂ capture capacity at higher pressures, which was attributed also to the reaction of MgO and K₂CO₃ in the presence of water vapor at 20 atm, namely, due the formation of structures, such as MgCO₃·H₂O and K₂Mg(CO₃)₂. Hence, a positive effect of the high pressure on the CO₂ uptake during the SEWGS process is expected.

In agreement with the MgCO₃ thermodynamic equilibrium relative to CO₂ partial pressure, it was reported [24] that working at a higher desorption pressure results in a higher desorption temperature needed for the regeneration of the sorbent. Hwang et al. [37] investigated the regeneration capacity of an AMS-promoted Mg-based sorbent at a high pressure and 100% CO₂ condition. It was observed that the CO₂ gas was desorbed at temperatures above 575 °C, with a peak at about 620 °C for CO₂ desorption at 20 atm and 100% CO₂. Based on this result, it was concluded that the optimum regeneration temperature was greatly shifted from 430 to 620 °C when regeneration conditions of 100% CO₂ were used, compared to when N₂ gas was used.

3. Medium-Temperature Catalyst–Sorbent: Hybrid/Mixed Materials and Sequential Arrangement

The application of WGS catalyst—Mg-based sorbents—during the SEWGS reaction is recent, and few experimental studies contemplate its use. Lee et al. [23] studied the influence of the catalyst packing method in the CO₂ removal of a WGS reaction, using a Na-Mg double salt as sorbent and a commercial catalyst (Cu/ZnO/Al₂O₃). In a first attempt, it was successfully synthesized a one-body hybrid solid by ball-milling, consisting of both catalyst and sorbent. However, it exhibited low sorption capacity when compared to that of single materials. The XRD analysis shows that the characteristic peaks for NaNO₃ in the one-body hybrid solid disappeared after the SEWGS reaction. Since the NaNO₃ crystalline structure was not recovered after cooling, the formation of the molten phase was inhibited, resulting in poor CO₂ sorption. It may be possible that the reduced Cu reacted with oxygen, converting NaNO₃ to NaNO₂. Subsequently, a multi-section concept was adopted for the reactor that minimized the contact between the catalyst and the sorbent. This attempt generated high-purity H₂ by SEWGS. Moreover, higher production of high-purity H₂ (>98%) was registered when using a higher ratio of sorbent-to-catalyst, as higher concentrations of CO₂ were being captured. It was also observed that the SEWGS performance improved with the increasing number of the reactor sections. The effluent gas composition from the SEWGS reaction in a ten-section reactor and a total catalyst-to-sorbent ratio of 1 (1 g of catalyst or sorbent) were alternately loaded in each section. It showed that the pre-breakthrough of CO₂ and CO was ~25.5 min. Further investigations using a reactor packing method with different catalyst-to-sorbent ratios were proposed.

The SEWGS experiment performed in a fixed bed reactor using AMS-promoted MgO-CaCO₃ as sorbent and Cu/Ce_{0.6}Zr_{0.4}O₂ as catalyst is reported by Hu et al. [22]. Four catalyst/sorbent layered configurations were investigated: mode I with one layered configuration (2 g/2 g), mode II and III with two layered configurations (2 g/2 g–2g/2g and 2 g/2 g–0.5g/0.5g) and mode IV (2 g/2 g–0.5g/0.5g–0.125g/0.125g), catalyst/sorbent, respectively. The optimum condition was a reaction temperature of 300 °C, a total pressure of 12 atm and an initial H₂O/CO molar ratio of 1.5 with a three catalyst/sorbent layered configuration. This optimum condition yielded a H₂ purity as high as 99.4% (dry basis) at the first SEWGS cycle, which was stabilized at 98.2% after 10 consecutive cycles, demonstrating good cyclic stability. Recently, they [33] prepared a hybrid material, K₂CO₃-promoted Cu/MgO–Al₂O₃ by a sol–gel method. It was observed that the K/(Mg + Al) and Mg/Al atomic ratios affect the physicochemical properties of hybrid materials, especially in the morphology and the basicity distribution, which in turn affected the CO₂ adsorption performance. In addition, it was found that the regeneration temperature of hybrid materials influences the SEWGS performance, 380 °C being the most favorable temperature since at higher temperatures the CO conversion at the post-breakthrough stage decreases with the number of cycles, but it does not happen for the material regenerated at 350 or 380 °C. The best performance was obtained for the hybrid material composed by a K/(Mg + Al) ratio of

0.2 and a Mg/Al ratio of 9, since the CO was completely converted and a yield >99.9% of H₂ was attained in 10 consecutive SEWGS cycles at 300 °C, and regeneration at 380 °C.

The performance of hybrid materials is not consensual, further attention are needed. In relation to the sequential arrangement, both show an enhanced performance of SEWGS process with the increase in catalyst–sorbent layers. As mentioned above, also for sorbents at medium temperature, the preparation of catalysts and sorbents using wastes as precursors should be evaluated. In case of Mg-based materials, the potential of Mg recovered from magnesite mines sludges or from desalination reject brine [\[39\]](#) is an interesting alternative.

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