Catalyst-free ceramic-carbonate dual phase membrane reactor for hydrogen production from gasifier syngas

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Abstract

Ceramic-carbonate dual phase dense membranes are a new group of inorganic membranes with perm-selective to CO₂ at high temperatures. This paper reports a new catalyst-free tubular membrane reactor to shift CO from the hot gasifier syngas to H₂ and CO₂ with simultaneous separation of CO₂. The membrane reactor is based on a samarium-doped ceria (SDC)-carbonate dual phase membrane which removes CO₂ facilitating conversion of CO to H₂ at high temperatures. The results show that catalytic-free membrane reactor can convert CO to H₂ and CO₂ with removal of CO₂ at temperatures above 800 °C. At 900 °C, the membrane reactor gives CO₂ flux of $2.7 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$, CO conversion and CO₂ recovery of 26.1% and 18.7%, respectively, much higher than the conventional fixed bed reactor under identical conditions. Temperature, steam to CO ratio, and syngas feed flow rate are key parameters to control the reaction performance. Increase of the feed pressure (reaction side) is an effective strategy to improve the reactor performance and CO₂ recovery. The membrane reactor shows high thermal and chemical stability under syngas WGS reaction environment. This work demonstrates potential of using catalyst-free SDC-carbonate dual phase membrane reactor for water gas shift reaction to convert CO to H₂ with CO₂ capture.

Keywords: Gasification; Syngas; Membrane reactor; CO₂ separation; Hydrogen

1. Introduction

As one of the promising strategies to effectively reduce carbon dioxide (CO₂) emissions, pre-combustion CO₂ capture in the integrated gasification combined cycle (IGCC) power plant has attracted considerable interest from both academia and industry [1-3]. In this process, carbonaceous fuels are gasified at high temperature (may exceed 1500 °C) to produce high pressure (20-40 bar) syngas [4], comprised mainly of hydrogen (H₂), carbon monoxide (CO) and CO₂, which is further converted to more H₂ through the water gas-shift (WGS) reaction, resulting in high pressure CO₂ and H₂. Separation of these two components allows for the storage of CO₂, while H₂ can be used for power generation.

Membrane technology has great potential for both H₂ and CO₂ separation within this gasification process [5-8]. Several types of H₂ selective membranes, such as palladium-based metallic membranes [9,10], proton-conducting dense ceramic membranes [11,12], silica membranes [13,14] and zeolite membranes [15,16], have been studied as membrane reactors for simultaneously shift reaction and H₂ separation. In this type of membrane reactors, H₂ permeates through the membrane reactor and is collected as a low pressure stream. Considering that WGS is an exothermic reaction, traditional two-stage WGS membrane reactors always operate at relatively low temperature (<400 °C) to achieve high CO conversion. However, the low operation temperature imposes a considerable cooling penalty on the gasifier syngas, which is a formidable economic disadvantage [5]. To avoid the cooling of syngas to a large extent, the high temperature WGS reaction was proposed by the researchers at US National Energy Technology Laboratory (NETL) [17-18]. WGS reaction was operated in a Pd-Cu membrane reactor at 900 °C. High CO conversion can be obtained at a relatively long residence time [19]. However, the poor stability of the metallic membrane at such high reaction temperature limited its practical application.

Besides the in-situ separation of H₂, CO₂ removal has been confirmed as another promising route to promote the WGS reaction for H₂ production. Typically, CO₂ sorbents were used for in situ CO₂ removal to enhance the reaction performance [20-22]. It is also highly desirable to use a CO₂-selective membrane for the WGS reaction because CO₂-selective membrane reactors have the potential to achieve higher H₂ recovery [5].

Moreover, CO₂ removal through the membrane retains H₂ at high pressure, maximizing the efficiency of the combustion turbine. Scholes et al. [5] also stated that if CO₂-selective WGS membrane reactors can be adapted to operate at high temperatures and pressures they will present an attractive option for the IGCC process.

However, the development of membranes that can retain the small molecular H₂ but permeate the larger CO₂ is a significant challenge. Many polymeric membranes show CO₂ perm-selectivity [7,23,24]. However, these membranes are not stable in the membrane reactor environments at elevated temperature. Inorganic membranes exhibit better thermal and chemical stability and have been studied in recent years for CO₂ separation [25-28]. The separation process is controlled by the preferential adsorption mechanism of CO₂. Several inorganic membranes exhibit high CO₂ perm-selectivity at room temperature, but at higher temperatures (>400 °C) their selectivity diminishes due to the low CO₂ adsorption. Consequently, there is a compelling need for CO₂ separation membranes that can operate under more extreme conditions while providing a high performance for sustainable CO₂ capture.

In an effort to develop CO₂ perm-selective membranes, Lin and co-workers were the first to report synthesis and CO₂ permeation of a metal-carbonate [29] and ceramic-carbonate [30] dual-phase membranes for CO₂ separation. These dual-phase membranes have high CO₂ permeance with theoretically infinite selectivity for CO₂ over all other gases in 700-900 °C [29-41]. A typical dual-phase membrane is composed of a ceramic phase and a molten carbonate phase. The ceramic phase serves as a porous support and also an oxygen ion (O²⁻) conductor, while the molten carbonate phase is infiltrated into the porous support as a carbonate-ion (CO₃²⁻) conductor. At high temperatures, CO₂ combines with O²⁻ to be CO₃²⁻ which transports through the membrane under the driving force of CO₂ partial pressure gradient.

Inspired by the striking property of dual-phase membranes, here we proposed a new membrane reactor to convert CO from the hot gasifier syngas to H₂ and CO₂ with simultaneous separation of CO₂, as shown in **Figure 1**. The in situ removal of CO₂ from reaction zone can break the thermodynamic equilibrium limitation and significantly enhance the CO conversion of the WGS reaction. Moreover, at high temperatures (above 700 °C) the

homogeneous WGS reaction rate could be sufficiently high to avoid the use of a WGS catalyst for the CO conversion. The catalyst-free WGS membrane reactor could result in substantial saving in the capital cost and great simplification in membrane reactor design. To the best of our knowledge, this unique idea has never been attempted. The successful implementation of this new technology could open the door for innovative process designs for high-efficiency IGCC power plant with CO₂ capture. The present work is aimed at demonstration of the feasibility of this idea.

Figure 1: Schematic of catalyst-free ceramic-carbonate dual phase membrane reactor for syngas WGS reaction.

2. Experimental

2.1 Tubular dual phase membrane synthesis and characterization

Sm_{0.2}Ce_{0.8}O_{1.9} (SDC) powder was synthesized via the citrate method from the metal nitrates [34,35]. Stoichiometric amounts of Ce(NO₃)₃·6H₂O (Alpha Aesar) and Sm(NO₃)₃·6H₂O (Alpha Aesar) were mixed into deionized water, followed by the addition of citric acid (mole ratio of total metal ions to citrate is 1:2) with stirring. The solution containing the complex precursor was then heated on a hot plate to 200-300 °C. Upon heating, the solution boiled and formed a gel. The gel underwent a dehydration and decomposition process and produced a foam-like solid, which ignited to produce a soft and fluffy product.

Finally, the products were calcined in air at 550°C for 5 h to prepare SDC oxide.

SDC tubular substrate was prepared using a centrifugal casting method as reported in our previous work [34]. About 50 wt% SDC, 50wt% water and a few drops of PVA solution were mixed and ball milled at 175 rpm for 3h to prepare homogeneous SDC slurry. The SDC slurry was poured into the stainless steel mould with an inner diameter of 1.2-1.3 cm. After centrifugation on a homemade machine for 20 min at the spin rate of 4000 rpm, the green tubes were dried in a humidity chamber at 40 °C with a relative humidity of 60% for 12 h. Then, the tubes were sintered at 1420 °C for 12h. The thickness of the SDC tube could be controlled by the amount of the added SDC slurry. SDC tubular supports with the thickness of 1.5 mm were prepared.

SDC-carbonate dual-phase membranes were obtained via a direct infiltration of molten carbonates into the SDC supports by the method described in our previous work [34]. Lithium (Li), sodium (Na), and potassium (K) carbonates from Alpha Aesar (Li_2CO_3 , 99.2%; Na_2CO_3 , 99.9%; K_2CO_3 , 99.8%) were mixed in the mole ratio of 42.5%: 32.5%: 25% and heated to 600 °C in a box furnace. The porous SDC supports were preheated in the furnace, then vertically dipped into the molten carbonate and held for 1h. After removing the excess carbonate on the surface, the dual-phase membranes were obtained.

The morphologies of the substrates and membranes were examined by scanning electron microscopy (SEM) (Philips FEI XL-30) after gold deposition. The gas-tightness of the dual-phase membranes was tested before the high temperature gas permeation. In testing the gas-tightness, the membrane was assembled into a tubular permeation cell sealed with epoxy resin. N_2 was fed to the tube side and the shell side was connected to a soap bubble flowmeter. The feed pressure was 0.3MPa. If no obvious N_2 flow rate was observed on the soap bubble flowmeter in 3 h, the membrane was considered to be gas tight. Only gas tight membranes (without defects) was used for CO_2 separation and membrane reactor experiments. The crystal phases of the samples were determined by X-ray diffraction (XRD) with Cu Ka radiation (Bruker, AXS-D8,). Diffraction patterns were collected at room temperature in the range of $20^\circ < 2\theta < 80^\circ$, with a step width of 0.05° and a scan rate of 0.2 s per step.

2.2 Syngas water gas shift reaction

The tubular dual-phase membranes with the thickness of 1.5 mm and length of around 2.5 cm were used. The schematic diagram of the set-up was shown in **Figure 2**. N₂ as a carry gas took water and simulated syngas (49.5% CO, 36% CO₂, 10% H₂ and 4.5% N₂) into the tube side of the membrane. CO₂ permeated through the membrane to the outer side and was swept out by helium. Although no catalyst was used, WGS reaction occurred during the removal of CO₂ to produce more H₂ and CO₂. The compositions of feed-out and sweep-out gases were analyzed using a gas chromatography (GC, Agilent 6890 N with a column of HayeSep DB 100/120, AllTech). The flow rates of both feed-out and sweep-out gases were measured by a soap film flow meter. The CO conversion (X_{co}) was calculated as follows.

$$X_{co} = \frac{F_{CO}^{feed\ in} - F_{CO}^{feed\ out} - F_{CO}^{sweep\ out}}{F_{CO}^{feed\ in}} \times 100\% \quad (1)$$

where $F_{co}^{feed\ in}$, $F_{co}^{feed\ out}$, and $F_{co}^{sweep\ out}$ are CO flow rates of feed-in stream, feed-out stream and sweep-out stream, respectively. The CO₂ recovery (R_{co2}) was calculated as follows.

$$R_{co2} = \frac{F_{CO2}^{sweep\ out}}{F_{CO2}^{feed\ out} + F_{CO2}^{sweep\ out}} \times 100\% \quad (2)$$

where $F_{co2}^{feed\ out}$, and $F_{co2}^{sweep\ out}$ are CO₂ flow rates of feed-out stream and sweep-out stream, respectively.

For traditional reactor, the membrane in Figure 2 was replaced by a dense alumina tube with the same size. The reaction occurred under the identical conditions with the syngas and steam. The leaked gas, if present, could be swept out by He. The CO conversion was calculated as Eq. 1.

Figure 2: Schematic diagram of tubular SDC-carbonate dual phase membrane reactor for high temperature syngas WGS reaction.

3. Results and discussion

3.1 Membrane morphology and CO₂ permeation

Figure 3 shows the morphology of tubular SDC supports and SDC-carbonate membranes. Using the centrifugal casting method, tubular SDC supports with different size can be prepared. SDC supports are porous with the porosity of about 35-40% (Figures 3b and 3c). After infiltration with molten carbonates, the dense SDC-carbonate membranes are formed (Figures 3d and 3e). Clear dual-phase structure can be observed from the cross section (Figure 3f). The SDC and carbonate phases are well mixed.

Figure 3: (a) Photo of SDC substrates with different sizes; SEM images: (b) outer and (c) inner surfaces of SDC substrate sintered at 1420 °C for 12h; (d) outer and (e) inner surfaces of SDC-carbonate membrane after infiltration; (f) cross section of SDC-carbonate membrane.

First of all, the CO₂ permeation flux of the dual phase membrane during the syngas WGS reaction was measured (**Figure 4**). CO₂ permeation flux increases with temperature. At 900°C, the flux is $2.7 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$. For comparison, the CO₂ fluxes of the same membrane with CO₂/N₂ (1:1 in volume, or 50% CO₂) feed were also provided. Compared with the CO₂ flux in CO₂/N₂ system, the relatively low flux in reaction process is attributed to the lower feed CO₂ concentration [34]. In that temperature range, the CO₂ concentration in the feed was 12% and in the feed-out was 12.5% - 14.8% in 800-900°C, with average CO₂ concentration lower than 50% in the case with CO₂/N₂ feed. In the membrane reactor, the activation energy for CO₂ permeation is estimated to be $90.8 \text{ kJ} \cdot \text{mol}^{-1}$, which is a little bit higher than that in CO₂/N₂ system ($83.3 \text{ kJ} \cdot \text{mol}^{-1}$). This is caused by the fact that the average CO₂ concentration in the feed, and hence the driving force for CO₂ permeation, increases slightly with temperature. The higher apparent activation energy for permeation flux reflects contribution of the change in the driving force as temperature increases.

Figure 4: Arrhenius plots of the CO₂ permeation flux of SDC-carbonate tubular dual-phase membranes in syngas WGS reaction system and CO₂/N₂ system. For syngas WGS reaction system, feed side: syngas flow rate $20 \text{ mL} \cdot \text{min}^{-1}$, N₂ flow rate $10 \text{ mL} \cdot \text{min}^{-1}$, and H₂O (steam) to CO molar ratio is 3.0; sweep side: He flow rate $60 \text{ mL} \cdot \text{min}^{-1}$. For CO₂/N₂ system, feed side: CO flow rate $25 \text{ mL} \cdot \text{min}^{-1}$, N₂ flow rate $25 \text{ mL} \cdot \text{min}^{-1}$; sweep side: He flow rate $60 \text{ mL} \cdot \text{min}^{-1}$. The pressure at feed and permeate sides are both 1 atm

3.2 WGS Reaction in Membrane Reactor

For the high temperature syngas WGS reaction in the membrane reactor, temperature, steam to CO molar ratio and syngas flow rate are three critical parameters [42]. Accordingly, the effects of these parameters on the reaction performance were investigated. **Figure 5** shows the temperature dependence of reaction performance of the dual phase membrane reactor. CO conversion and CO₂ recovery increase from 15.1% to 26.1% and 9.6% to 18.7%, respectively, as the temperature increase from 800 to 900 °C. WGS reaction is an exothermal reaction, thus the high temperature is adverse for the conversion of CO. However, the in-situ removal of CO₂ by the dual-phase membrane greatly promotes the shifting of the reaction equilibrium.

Figure 5: Performance of dual phase membrane reactor (MR) and traditional reactor (TR) for high temperature syngas water gas shift reaction as a function of temperature without catalyst. Feed side: simulated syngas flow rate 20 mL·min⁻¹, N₂ flow rate 10 mL·min⁻¹, and H₂O (steam) to CO molar ratio is 3.0; Sweep side: He flow rate 60 mL·min⁻¹. The pressure at feed and permeate sides are both 1 bar.

The increase of CO₂ permeation flux with temperature results in the relatively high CO

conversion at high temperature. For comparison, the results of a traditional reactor (a dense alumina tube with the same size) measured at the identical conditions are also provided in **Figure 5**. CO conversion of the traditional reactor is much lower than that of the membrane reactor. Furthermore, it decreases first and then increases upon increasing the temperature, which may be caused by the fact that the WGS reaction rate increases with temperature whereas the equilibrium conversion decreases from 74.1% at 800 °C to 68.7% at 900 °C. These results indicate that using SDC-carbonate dual phase membrane reactor for high temperature syngas WGS reaction with simultaneous CO₂ removal is technical feasible, and high temperature is favorable for the reaction.

Figure 6 presents the effect of steam to CO molar ratio (H₂O/CO ratio) on the reaction performance at 900 °C. Upon increasing the H₂O/CO ratio, the CO conversion increases, while the CO₂ recovery shows an opposite trend. When the H₂O/CO ratio is 4.0, the CO conversion reaches 27.8% but the CO₂ recovery is 17.4 %. The enhancement of CO conversion is more significant at the H₂O/CO ratio of 1.0-3.0. However, further increase of H₂O/CO results in a relatively slow increase of CO conversion. This is attributed to that high H₂O/CO ratio reduces the residence time of the feed gases in the reactor since the CO flow rate is fixed. As is well known, short residence time is unfavorable for both CO conversion and CO₂ recovery. In addition, excessive steam for the relatively high H₂O/CO ratio reduces the partial pressure of CO₂ in the reaction side, resulting in the low CO₂ permeation flux and low CO₂ recovery. Therefore, in following experiments, the H₂O/CO ratio is fixed as 3.0.

Figure 6: Performance of dual phase membrane reactor as a function of steam to CO ratio at 900 °C. Feed side: simulated syngas flow rate 20 mL·min⁻¹, N₂ flow rate 10 mL·min⁻¹; Sweep side: He flow rate 60 mL·min⁻¹. The pressure at feed and permeate sides are both 1 bar.

Figure 7 shows the effect of syngas flow rate on the reaction performance at 900 °C. Both CO conversion and CO₂ recovery decrease upon increasing the syngas flow rate. When the flow rate is 10 mL·min⁻¹, the CO conversion and CO₂ recovery are 37.4% and 33.5%, respectively. However, the higher syngas flow rate increases the space velocity and reduces the residence time for WGS reaction, resulting in the decrease of CO conversion. Enick and coworkers [19] also observed that during the WGS reaction the CO conversion could be seriously reduced from 99.7% to 55% by decreasing the residence time from 2s to 0.7s. Additionally, the higher syngas flow rate has negative effect on CO₂ removal through the membrane. Too much unreacted CO and steam in the feed greatly reduces the CO₂ partial pressure, leading to the low CO₂ permeation flux and decrease of CO₂ recovery. In other words, the significant role of dual-phase membrane in the membrane reactor is restrained at high syngas flow rate. Therefore, the match between the syngas flow rate and the WGS reaction rate, and match between the CO₂ production rate from the reaction and the CO₂ removal rate through the membrane are critical.

Figure 7: Performance of dual phase membrane reactor as a function of syngas flow rate at 900 °C. Feed side: simulated syngas flow rate 10-30 mL·min⁻¹, N₂ flow rate 10 mL·min⁻¹, steam to CO ratio is 3.0; Sweep side: He flow rate 60 mL·min⁻¹. The pressure at feed and permeate sides are both 1 bar.

3.3 Membrane reactor stability

For practical application of dual phase membranes, high thermal and chemical stability under harsh syngas WGS reaction environment is required. Therefore, the long-term stability of the SDC-carbonate membrane reactor was studied. First, the membrane was continuously operated for 30 h at 900 °C and then slowly cooling down to room temperature. After resealing, the membrane was heated to 900 °C for next test. Such a thermal cycle measurement was carried out for four times (0-30h; 30-58h; 58-84h; 84-112h). As shown in **Figure 8**, the CO conversion, CO₂ recovery and CO₂ flux maintain at around 26.2%, 18.4% and 2.7×10^{-3} mol·m⁻²·s⁻¹, respectively. After long-term testing, the morphology of the membrane was analyzed (**Figure 9**). The surface of sweep side is slightly eroded, which may be caused by the minor decomposition of carbonate under the low CO₂ partial pressure at high temperature. However, the thickness of the eroded layer is only 1-2 μm. In contrast, the surface of reaction side is still dense and the corrosion of syngas and steam atmospheres to

the membrane is not obvious.

Figure 8: The long-term stability of SDC-carbonate tubular dual phase membrane reactor for syngas water gas shift reaction at 900 °C without catalyst. Thickness of the membrane is about 1.5 mm. Feed side: simulated syngas flow rate 20 mL·min⁻¹, N₂ flow rate 10 mL·min⁻¹, and H₂O (steam) to CO molar ratio is 3.0; Sweep side: He flow rate 60 mL·min⁻¹. The pressure at feed and permeate sides are both 1 bar.

Figure 9: SEM images of the SDC-carbonate membrane after long-term syngas water gas shift reaction: (a) outer surface (sweep side) and (b) inner surface (reaction side).

Figure 10: XRD pattern of membrane after long-term syngas water gas shift reaction: (a) fresh membrane; (b) outer surface (sweep side); (c) inner surface (reaction side).

The crystal structures of the membrane before and after long-term reaction were also analyzed (**Figure 10**). Both reaction side and sweep side maintain full fluorite structure and no obvious impurity phases are observed. These results indicate that the SDC-carbonate dual phase membrane is stable under the syngas WGS reaction environment. Accordingly, we can

conclude that SDC-carbonate dual phase membrane has high potential for practical applications in high temperature CO₂ separation.

For industrial application of this new proposed process, further improvement of CO conversion and CO₂ recovery is desired. The WGS reaction in the membrane reactor is also influenced by other experimental conditions such as feed pressure and membrane surface area to reaction zone volume ratio, which could not be studied due to the constraint in experimental conditions (e.g., sealing issue prevented experiments at higher temperature). Considering the membrane reactor feature, one of the possible routes for the improvement is to increase the feed pressure. WGS reaction equilibrium itself will not be affected by pressure because it is a constant volume reaction. However, in the dual phase membrane reactor, high operation pressure at the reaction side (feed side) is beneficial for the transport of the produced CO₂ through the membrane, resulting in the shift of the reaction equilibrium toward H₂ and CO₂ production, promoting the CO conversion and CO₂ recovery. Experimental tests on WGS reaction on a disk SDC-carbonate membrane reactor using graphite seal [35] (with CO and H₂O feed at 700 °C) show an increase in CO conversion and CO₂ recovery respectively by 52% and 454% as the feed pressure increase from 1 atm to 5 atm. It is worth noting that the pressure of practical coal gasification gas may be higher than 20 bar. Such a high feed pressure is of great benefit to the CO₂ removal through SDC-carbonate membrane, therefore facilitating the improvement of both CO conversion and CO₂ recovery.

4. Conclusions

This work demonstrates a new process for hydrogen production from high temperature syngas WGS reaction in a SDC-carbonate dual phase membrane reactor with simultaneously CO₂ removal. The membranes show good CO₂ permeation flux and high thermal and chemical stability under syngas WGS reaction environment. The removal of CO₂ by dual phase membrane from reaction process promotes the conversion of CO at high temperatures without a catalyst. Further improvement of CO₂ separation performance in practical application is possible by increasing the feed pressure. This work also confirms the reliability of SDC-carbonate dual phase membranes for high temperature CO₂ removal from industrial processes, such as IGCC.

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