Materials for Hydrogen Production with Integrated CO_2 Capture

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Presended that the AESAN Conference, Jakarta, Indonesia, June 2009

ECN-M--09-149 December 2009

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Abstract. Palladium-based membrane reactors and sorption-enhanced water-gas shift are two promising technologies for efficient production of hydrogen with integrated CO_2 capture. This paper discusses material issues of the two crucial materials of these technologies: the membrane and the CO_2 sorbent. For Pd and Pd-alloy membranes the major issues concern the stability of the membrane and the poisoning of the membrane surface by compound such as sulfur and carbon monoxide. Both issues are addressed by research into novel Pd-alloys. For the potassium-promoted hydrotalcite CO2 sorbents used in sorption-enhanced water gas shift, the main challenges are a high CO_2 adsorption capacity, chemical and mechanical stability, and low steam use for sorbent regeneration. Promising results have recently been reported for several of these challenges.

Keywords: hydrogen, CO_2 capture, membranes, palladium, sorption-enhanced water-gas shift, hydrotalcite.
PACS:

INTRODUCTION

Hydrogen is one of the largest industrial processes, with a worldwide annual production of more than 1 billion m^3 per day[1]. Hydrogen is mostly used in ammonia synthesis (0.7 billion m^3 per day) and in hydrotreating of transportation fuels. The role of hydrogen in the energy and transport sector is expected to strongly increase[2]. Hydrogen fueled fuel cell vehicles offer an in principle zero-emission form of road transport. In power production, hydrogen is a carbon free fuel for gas turbines.

One of the advantages of using hydrogen as an energy carrier is that it can be produced from many sources. Renewable electricity sources like photovoltaics and wind can be used for hydrogen production through water electrolysis. From biomass hydrogen can be produced by gasification of biomass. However, at the moment almost all hydrogen is still produced from fossil fuels: approx. 50% from natural gas, 30% from coal and 20% from oil.[3] The CO_2 emitted from hydrogen production is partly used in the food industry, but the bulk is emitted to the atmosphere. The transition to a renewable hydrogen production will take multiple decades and the threat of climate change urges the CO_2 emissions to decrease much sooner than that. The production of hydrogen from fossil fuels with capture and storage of CO_2 offers a possibility to produce large amounts of hydrogen with low impact on the climate.

Hydrogen production from natural gas is conventionally performed by first producing syngas using either methane-steam reforming, autothermal reforming or catalytic partial oxidation.[4] Subsequently the syngas is converted into hydrogen and CO_2 using high-temperature and low-temperature shift reactors in series. For the final steps, the purification of the hydrogen, several technologies are in use. One option is CO_2 removal by either physical or chemical absorption followed by conversion of the remaining CO and CO_2 into methane. In this case the CO_2 produced is relatively pure. Alternatively, pressure swing adsorption (PSA) is used to produce pure hydrogen and a second stream that contains CO, CO_2, CH_4 and hydrogen. This purge stream is used for underfiring of the reformer, so the CO_2 produced is strongly diluted with nitrogen and not suitable for storage.

Coal and oil are converted into syngas by gasification. After the gasifier the syngas has to be cleaned thoroughly to remove heavy metals, halogens and dust. Subsequently, there are two options. In the first one, H_2S is removed in an absorber, the CO is converted with steam to hydrogen and $_{CO2}$ in the water-gas shift reactors, and CO_2 is removed by adsorption or PSA.[4] The second option is to first perform the water-gas shift reaction using so-called sour gas shift catalysts, and subsequently remove H_2S and CO_2 in one absorption step.

These conventional processes can in principle be used for hydrogen production, but the production of a stream of pure CO_2 alongside the hydrogen requires a considerable extra energy input. Cost increases of 19 to 35% for CO2-free hydrogen and electricity compared to conventional hydrogen production have been reported.[5] Several novel concepts for hydrogen production with integrated CO_2 capture are in development, aimed at reducing the costs. One promising concept is so-called separation enhanced reactions. The most important reactions in hydrogen production are two equilibrium reactions: the methane steam reforming reaction (when natural is used as the hydrogen source) and the water-gas shift reactions.

(1): $H_2O + CH_4 \leftrightarrows CO + 3\,H_2$ $(\Delta H_{298}^0 = 206\ \text{kJ/mol})$

(2): $H_2O + CO \leftrightarrows H_2 + CO_2$ $(\Delta H_{298}^0 = -\ 41\ \text{kJ/mol})$

Both reactions can be enhanced by removing one of the products from the reaction zone. In this paper two separation-enhanced reactions will be discussed.

1. Membrane reforming and membrane water gas shift. Palladium-based membranes separate hydrogen from the reaction zone, and this shifts the equilibrium to the product side. The remaining gas is rich in CO_2.
2. Sorption-enhanced reforming and water-gas shift. A catalyst is mixed with a solid sorbent that removes CO_2 from the reaction zone. The remaining gas is hydrogen rich. The sorbent is regenerated by either pressure swing or temperature swing and in this step CO_2 is released.

This paper provides an overview of the material aspects of key materials in these two technologies: Pd-based membranes and hydrotalcite-bases CO_2 sorbents.

PALLADIUM-BASED MEMBRANES

The principle of membrane reforming is illustrated in Figure 1. Natural gas and steam enter the middle compartment, in which a steam reforming catalyst converts the mixture into hydrogen and CO. The catalyst also catalyses the water-gas shift reaction, but at the temperatures used in steam reforming (above 550°C), the equilibrium lies at the left hand side. Simultaneously, the hydrogen is withdrawn from this compartment through the membrane. This pulls the equilibrium of both the reforming and shift reactions to the product side. The gas leaving the middle compartment, the retentate, consists mainly of CO_2 and steam, with small amounts of unconverted CH_4 and CO and not-permeated hydrogen. The heat for the endothermic steam methane reforming reaction is provided by combustion of a fuel (natural gas or hydrogen) in the top compartment. In the bottom compartment hydrogen that has permeated through the membrane is harvested, the permeate stream. In many cases a sweep gas is used to reduce the partial pressure of the permeate and increase the driving force over the membrane.

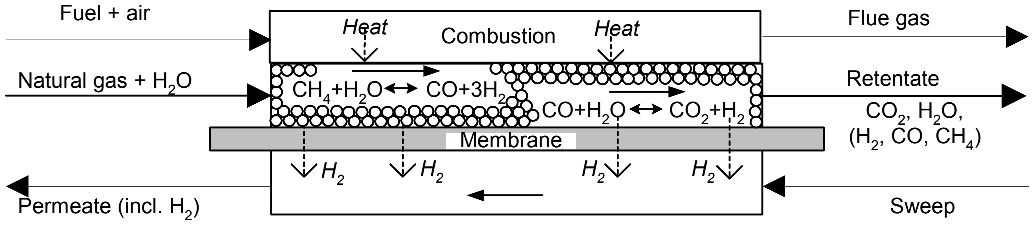

FIGURE 1. Operating principle of a membrane reactor for steam methane reforming.

In the last years, the development of membrane integrated hydrogen production has been pursued in by many. Currently, Tokyo Gas has demonstrated the world's largest scale membrane reformer with a rated H2 production capacity of 40 Nm3/h on natural gas. The membrane units are made by rolling sheets of Pd-alloy to a thickness of about 20µm. A main drawback has been the cost of the membrane material, which is connected to the thickness (>20µm) of existing commercial membranes[6]. It is thus necessary to develop membranes with reduced thickness of the Pd layer. Thin layer (approx. 2µm) Pd membranes always need a stainless steel or ceramic support to provide mechanical strength for the membrane.

The permeation of hydrogen through a palladium-based membrane is illustrated in Figure 2. The hydrogen molecule first adsorbs at the membrane surface and then dissociates. The hydrogen atoms are subsequently transported through the membrane by a solution/diffusion mechanism. At the permeate side, the hydrogen atoms recombine and the hydrogen molecule desorbs from the surface and is transported through the porous support. Depending on the characteristics of the membrane and the reaction conditions, one or more of these steps will be rate determining. The value for the rate of permeation, or flux, through the membrane is given by[7]:

$$J_{H_2} = k_{\text{mem}}\left(p^{n}_{\text{H}_2,\text{reformate}} - p^{n}_{\text{H}_2,\text{permeate}}\right) \quad \left[\text{mol/m}^2\text{s}\right]$$

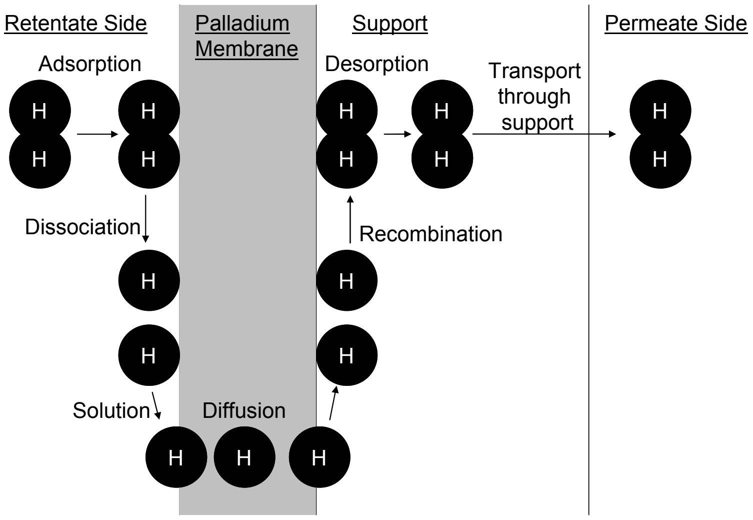

FIGURE 2. Schematic representation of hydrogen diffusion through a Palladium membrane.

The value of *n* in the flux equation reflects the nature of the rate-determining step. In a relatively thick membrane (>20μm), the hydrogen flux is described by a combination of dissociation/dissolution and diffusion. According to Fick's law for diffusion of atomic hydrogen and Sievert's law for dissociation of a diatomic gas, the value of *n* is equal to ½ for thick membranes. For thinner membranes the distance for bulk diffusion will become increasingly short and other processes may become rate limiting, such as surface effects, gaseous flow through defects, or transport resistance through the substrate. This causes an increase in the observed value for *n*, eventually approaching 1. For palladium membranes with a thickness ranging from 0.35 to 244 μm, Rothenberger et al.[7] summarise literature data with *n* ranging from 0.5 to 1.0.

The two major routes for the production of thin supported membranes are electroless plating and microwave sputtering. Electroless plating involves the submersion of a ceramic support in a plating batch consisiting of Pd-salts, EDTA, ammonia and hydrazine.[8] Subsequently, a thermal treatment is applied to form the Pd layer. Pd-alloy membranes, e.g. Pd-Ag membranes are produced by submersing the Pd-membrane in a second plate bath containing silver salts and subsequently alloying the two metals by heat treatment.[9] The microwave sputtering method developed by SINTEF in Norway makes a very homogenous and very thin layer of the desired Pd-alloy on a waver. Subsequently, this thin layer is wrapped on a support.[10] Both membrane types have very high selectivities and fluxes: Peters et al. reported a H_2 flux of more than 1200 $\text{mL}\cdot\text{cm}^{-2}\cdot\text{min}^{-1}$ for highly selective (permselectivity typically > 2000) membrane prepared by microwave sputtering operating under 25 bar pressure difference at 400°C.[11]

Materials Issues for Palladium-Based Membranes

Many issues exist for the production of stable supported Pd-based membranes with high selectivities and fluxes. The membrane layer should be strongly connected to the support to prevent disconnection, but the interaction with the support should not negatively affect the hydrogen permeation. Also the thermal expansion of the support and the membrane layer should be matched, to prevent cracking of the membrane layer and loss of selectivity. The membrane should be stable at the operating temperature, and in the case of Pd-alloys, segregation of the two (or more) metals should be prevented. In some applications, like membrane methane steam reforming, the temperatures are relatively high (up to 700°C) and the membranes should retain there strength and selectivities in those conditions. The interaction between the membrane and the catalyst should not lead to poisoning of either one. Two other issues are dealt with in some more detail below.

Hydrogen Embrittlement

One of the major issues for Pd membranes is hydrogen embrittlement. In pure Pd, an α-to-β hydride phase transition may occur in H_2 below approximately 290°C, and only a few transitions give a brittle material and must therefore be avoided. This is especially important during start-up and shut-down of the membrane reactor. By alloying Pd with different elements, the phase transition temperature can be suppressed. In particular alloys with 20–30 wt% Ag are resistant to hydrogen embrittlement. However, PdAg membranes also have drawbacks: the silver evaporates at temperatures above 600°C and PdAg is very susceptible to sulfur poisoning. Novel membrane compositions are being investigated, including ternary alloys, that have α-to-β hydride phase transition at low temperature and are more sulfur tolerant than PdAg.[12]

Influence of Other Gas Components on Hydrogen Flux

Much of the investigations on Pd membranes have been performed in pure hydrogen, but in a real life membrane reactor other gases, like methane, steam, nitrogen, carbon monoxide and sulfur compounds may be present. Two effects will influence the membrane flux in such a case. The first is concentration polarization, which is visible when hydrogen is mixed with an inert gas like nitrogen. The rate of withdrawal of the hydrogen is so high, that the concentration of hydrogen close to the membrane becomes lower and reduces the driving force for transport through the membrane. This transport phenomenon can be influenced by the design of the membrane reactor, the superficial gas velocity, and the presence of a catalyst.

The second effect is adsorption of the gas component onto the Pd layer and thereby blocking sites for hydrogen dissociation. Methane usually has little effect on the hydrogen flux.[13] Depending on the temperature, CO2, CO, steam and higher hydrocarbons reduce the flux of hydrogen through Pd and PdAg membranes. For membranes thicker the 10 micron, this effect has been found to disappear at temperatures above 600°C.[13] The negative effect of CO on hydrogen flux is particularly strong, and it may be assumed that the value of n in the flux equation above, is 1 when CO is present. This means that the flux is determined by the surface reaction of hydrogen, which is strongly inhibited by co-adsorption of CO. It has also been reported that the presence of CO in the hydrogen can lead to the formation of carbon on the membrane.[8]

For the use of membrane reactors in coal gas, sulfur resistance is an import issue. The sulfur content at the inlet of the water-gas shift section in a coal gasifier based hydrogen production system is approx. 20 ppm for the clean shift case and more than 2000 ppm for the sour shift case. Tests with PdAg membranes at ECN have shown that introducing 50 ppm H_2S to the feed mixture leads to a complete blockage of the H_2 flux and also pure Pd membranes loose their hydrogen transport properties due to sulfidization of the Pd.[14] It has been long known that PdCu and PdAu alloys are less susceptible to embrittlement and sulfur poisoning. The sulfur compound tolerance of PdCu membranes increases with increasing Cu content, 70mol% PdCu membranes show much less sensitivity to sulfidization, but are not entirely immune.[14] Unfortunately, for PdCu H_2 permeability decreases rapidly in with increasing Cu content. The latter possibly can be counteracted by adding a third metal.[12]

SORPTION-ENHANCED WATER-GAS SHIFT

Sorption-enhanced reactors are another form of a separation-enhanced process. In sorption-enhanced reforming (SER) or water-gas shift (SEWGS) reactors, one of the products is extracted from the reaction zone, thus shifting the reaction equilibrium to the product side. In SER and SEWGS the SMR or WGS catalyst is mixed with a CO_2 sorbent (“acceptor”). The CO_2 produced during the reaction is adsorbed and the reverse reaction cannot occur (Figure 3). The hydrogen stream also contains unconverted methane and CO. For production of pure hydrogen an extra hydrogen purification step is needed; for application of SER in pre-combustion CO_2 capture for power generation, the gas can be fed directly to the gas turbine. The two major sorbents examined for sorption-enhanced reforming are CaO-based materials and hydrotalcites. Work on these and other sorbents for SER has recently been reviewed by Harrison.[15] In this paper materials issues for hydrotalcite-based CO_2 sorbents for SEWGS will be discussed.

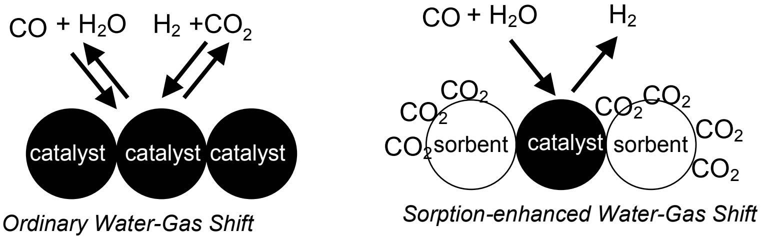

FIGURE 3. Schematic representation of ordinary and sorption-enhanced water-gas shift.

The SEWGS process has initially been developed by Air Products in the US.[16] A SEWGS-reactor contains a high-temperature shift (HTS) catalyst and a CO_2 sorbent. The HTS catalyst is a commercially available Iron-Chromium catalyst. The CO_2 sorbent used in the system developed by Air Products is a potassium-carbonate promoted hydrotalcite (K-HTC). The K-HTC material has a relatively low working capacity (approx. 0.6 mmol CO_2 per gram of K-HTC)[17], but the great strength of the material is that it can be regenerated at the same temperature as the adsorption takes place (between 350 and 500°C).

The SEWGS cycle contains several different steps. During the feed step, syngas is fed to a SEWGS reactor, the CO_2 is captured and hydrogen is produced. At some point before breakthrough of CO_2, the reactor is rinsed to remove the hydrogen gas still present in the reactor. Subsequently the pressure is released in several (usually three) steps. Then the bed is at low pressure and a counter current steam purge is applied. To be able to produce a continuous stream of hydrogen and CO_2, multiple beds are necessary. Also, by cleverly using pressurized gas released in the equilibration steps to re-pressurize reactors at low pressure after the purge step, the hydrogen yield is being maximized. In total six to eight reactors, all connected with valves, are needed for the most efficient SEWGS cycle.

The SEWGS process poses several demands on the sorbent:

- The CO_2 adsorption capacity should be as high as possible. High capacities lead to smaller reactor sizes, which reduces the capital costs of the process. It also leads to smaller amounts of rinse gas, which improves the thermal efficiency of the process.
- The steam used for the purge step (sorbent regeneration) should be as low as possible. Especially when the hydrogen produced is used for power production in a gas turbine combined cycle, all steam used in for purgeing cannot be used in the steam cycle anymore, which represents a direct los of electric efficiency.
- The sorbent should be chemically stable: it should have at least the same life time as the water-gas shift catalyst, which is more than three years.
- The sorbent should be mechanically stable: in the SEWGS reactor the sorbent is present in the form of pellets, to assure an acceptable pressure drop. Powdering of the pellets leads to increase of the pressure drop and pollution of downstream parts of the SEWGS installation with sorbent powder.
- The sorbent should be selective for CO_2 adsorption. Co-adsorption of other components like steam, CO or hydrogen may reduce the capacity for CO_2.

CO_2 Sorption on Potassium-Promoted Hydrotalcites

The potassium-promoted hydrotalcite CO_2 sorbent is based on the hydrotalcite (HTC) structure. The HTC is a layered structure with layers of $(Mg,Al)OH_6$ octahedra in between layers containing water molecules and carbonate ions. It should be noted that this hydrotalcite structure decomposes at temperatures above 300°C, both in steam and in a steam and CO_2 mixture[18]. So in the SEWGS process, which operates at temperatures higher than 350°C, a decomposed hydrotalcite operates as CO_2 sorbent. The hydrotalcite is promoted with potassium carbonate, which boosts the CO_2 adsorption capacity with a factor seven.[19] The exact role of K_2CO_3 and the interaction with the decomposed hydrotalcite is not exactly known yet. Ritter and co-workers proposed a reaction mechanism involving several species all including both Mg and Al[20], but experimental evidence for the different reactive species proposed was not presented. The knowledge on the mechanism is important, especially for modeling the SEWGS process, which is indispensable for the design of efficient SEWGS cycles.[21]

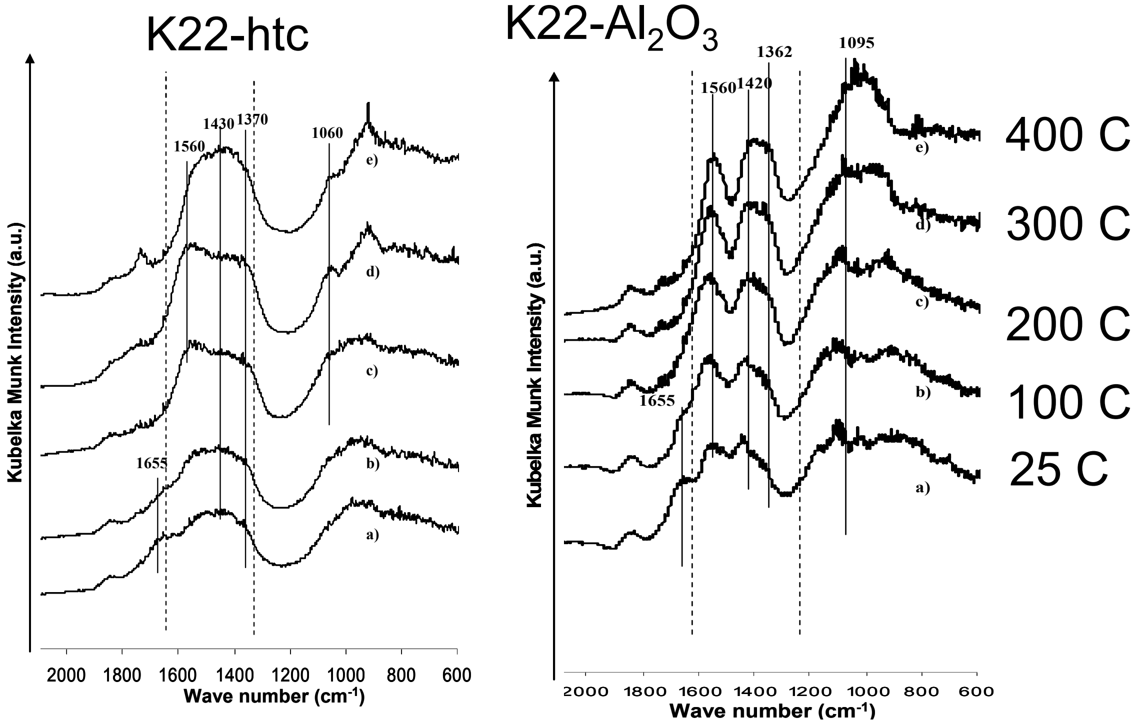

FIGURE 4. DRIFT spectra of HTC promoted with 22wt% K_2CO_3 (Left) and γ-Al_2O_3 promoted with 22 wt% K_2CO_3 (Right) in the carbonate region. From Walpurger et al.[18] Copyright: Wiley.

Recently, Walspurger et al.[18] has shown that also γ-Al_2O_3 promoted with K_2CO_3 shows CO_2 adsorption capacity at 400°C, albeit somewhat lower than HTC. This is remarkable while non-promoted alumina has no CO_2 adsorption capacity at 400°C whatsoever. Figure 4 shows infrared spectra for K_2CO_3 promoted alumina and HTC. The bands in the carbonate region are very similar in both cases and it was postulated that a K-O-(CO)-O-Al species plays an important role in the CO_2 sorption mechanism on both K_2CO_3-promoted γ-Al_2O_3 and hydrotalcite.

Recent work at ECN, has shed some new light on the role of magnesium in the K_2CO_3-promoted HTC.[17] Experiments were performed in a two meter tall reactor, at realistic process conditions (30 bar, 400°C). In a breakthrough experiment, depicted in Figure 5a, it was shown that after sharp breakthrough after and initial fast uptake of CO_2, CO_2 uptake continued for several hours in a slow process. Subsequently, the set-up was run in cyclic mode: CO_2 adsorption at 30 bar until breakthrough, rinse with steam at 30 bar, blowdown, steam purge at 1 bar. One cycle lasts approx. 10 minutes and the steam used in the purge step is 2.5 mol per mol of CO_2. Figure 5b shows that there is no CO_2 in the product gas for the first 200 cycles, after which the CO_2 concentration increases up to cycle 500 and stabilizes for the last 900 cycles. This shows that the sorbent is chemically stable for this period. The appearance of the CO_2 slip in the product gas is believed to be related with the slow process observed in Figure 5a. During the adsorption step of the cycle a CO_2 sorption front moves quickly through the column, as was observed by a temperature increase measured by thermocouples along the length of the bed (the adsorption of CO_2 is an exothermic process). During the first 200 cycles also a second CO_2 adsorption front moved slowly in the reactor. After 200 cycles this slow front reached the top of the reactor and CO_2 appeared as slip in the product.

When all the CO_2 was removed from the sorbent used in the cyclic experiment, in total 11.6 mmol/g sorbent was recovered from the material. This is much higher than the measured breakthrough capacity of 1.4 mmol/g. The rest of the desorbed CO_2 could be explained by formation of $MgCO_3$. With the sorbent used (Mg:Al ratio is 70:30), a full conversion of all Mg into $MgCO_3$ would give 9.5 mmol/g of CO_2 adsorbed, which is close to the amount of CO_2 desorbed from the bed added to the breakthrough capacity. A breakthrough test using a 'cleaned' sorbent that had undergone approx. 5000 adsorption/desorption and SEWGS cycles showed that the CO_2 capacity was still equal to that of the fresh sorbent.

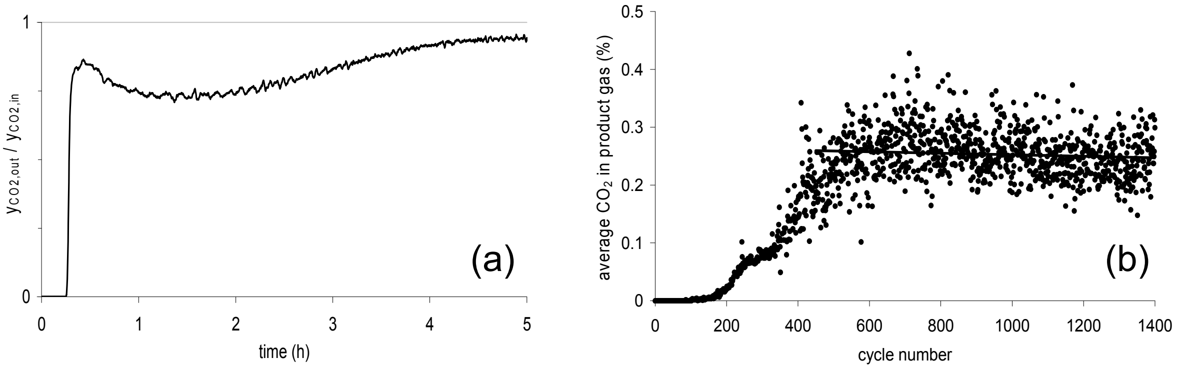

FIGURE 5. (a) breakthrough experiment for CO_2 adsorption on K_2CO_3-promoted HTC (Mg:Al = 70:30). (b) Cyclic experiment on the same HTC: average CO_2 content in the product gas per cycle. From van Selow et al.[17] Copyright: ACS.

Combining the two observations presented above, it may be tentatively postulated that the fast uptake of CO_2 is related to reaction with the K-O-(CO)-O-Al species and the slow uptake is related to the formation of $MgCO_3$. The $MgCO_3$ has a more than double molar volume than MgO, which is expected to have negative consequences for the mechanical stability of the sorbent.

CONCLUSIONS AND RECOMMENDATIONS

Materials issues for two technologies for hydrogen production with integrated CO_2 capture have been discussed: Pd-based membrane reactors and sorption-enhanced water-gas shift.

Pd and Pd-alloy membranes have shown to be both highly selective and have high hydrogen permeation rates. Important research items are the stability of the membranes, especially de development of alloys that are not prone to hydrogen embrittlement upon thermal cycling. A second R&D item is the interaction of the Pd or Pd-alloy layer with other components in the gas, most notably carbon monoxide and hydrogen sulfide. Here also the development of novel alloys, e.g., based on PdCu, offer opportunities for membranes with high hydrogen fluxes, that are not compromised by the presence of H_2S or CO.

Potassium-promoted hydrotalcite-based sorbents have been tested in the sorption-enhanced water-gas shift process. Experimental evidence shows that this sorbent has a relatively low CO_2 adsorption capacity, but also a relatively low steam use for purge and is chemically stable for several thousand cycles. It was discovered that two CO_2 adsorption process occur: a fast process possibly associated with a K-Al-carbonate active site and a slow process postulated to be caused by the formation of $MgCO_3$. The formation of this latter compound may lead to reduced mechanical strength of the sorbent. Future research should focus on elucidating the mechanism of CO_2 sorption by this type of sorbent and on increasing the capacity and reducing the steam use even further. Furthermore, the formation of $MgCO_3$ should be prevented.

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