Advanced Membrane Reactors in Energy Systems
A Carbon-Free Conversion of Fossil Fuels

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Abstract
The purpose of this project is to develop hydrogen and CO2 selective membranes to allow combination of natural gas reforming with H2 or CO2 separation in separation enhanced reactors, i.e. membrane reactors, for carbon-free hydrogen production or electricity generation. To achieve this, the project comprises three distinct tasks: system and reactor analysis, membrane materials research and catalysis.

Already in an early stage it has been shown that when considering the gas compositions in a Steam Reforming membrane reactor, CO2 selective membranes are no option due to the very low concentration and therefore driving force of CO2. In water gas shift (WGS) reactions or with gas compositions as from a coal gasifier, these membranes perform comparable to H2 selective membranes when used in a membrane reactor. On a system level CO2 selective membranes should have a flux twice that of the H2 selective membranes assuming the same surface area (=cost). They suffer from a larger specific electric loss but produce a purer CO2 stream. Expected future developments only marginally positively affect CO2 selective membranes as compared to their H2 counterpart.

From the outset of the project, hydrotalcites (HTC, Mg_{x}Al_{1-x}(OH)_{2}(CO_{3})_{(1-x)/2}·xH_{2}O) were thought to be good candidates as membrane material for CO2 selective membranes given their high absorption affinity to this gas. Two modes of operation were thought to be possible: as a dense membrane with transport through the water-carbonate layer in this clay like compound, or as a porous membrane via affinity based pore blocking.

In order for a hydrotalcite to be a viable membrane material, it has to be prepared single phase and the behavior as a function of temperature should be known. The Mg/Al ratio needed for obtaining single phase material was determined using neutron diffraction to be 1.8 (x=0.64). Under heating the HTC is established to decompose via 5 steps
involving the evolution of H\textsubscript{2}O and CO\textsubscript{2} eventually yielding a mixed oxide material. Since the diffusion path through the hydrotalcites disappears at operational temperature, the only option left is as an affinity based porous membrane.

Several approaches were investigated to be able to produce small pores, a few kinetic diameters of CO\textsubscript{2}, that have not too strong an interaction with CO\textsubscript{2}; in-situ growing of a hydrotalcitic layer inside the pores or making HTC nanoparticles that can be coated on a porous support yielding the right pore size and having the right i.e. not too strong, affinity to CO\textsubscript{2}. Both options eventually yielded a membrane that could be tested. The large experimental matrix to be tested to obtain the right particles included different precursors, solvents, temperatures, dispersants, pH etc. A glycerol/water 63/37 v/v mixture used for the hydrotalcite synthesis, yielded non-aggregated particles of about 10 nm diameter that could be coated on a tubular porous membrane support. Single gas permeance test have been performed and showed that the CO\textsubscript{2}/H\textsubscript{2} selectivity was larger (0.5) than the Knudsen value (0.21). Mixed gas tests (CO\textsubscript{2}: H\textsubscript{2}O=1:1) showed the same behavior for the coated sample but no selectivity at all for the in-situ impregnated one.

Furthermore supported ionic liquid membranes based on the best candidate, emim-Tf2N, resulting from the work performed at the Technical University of Delft were prepared and tested. Although the absorption selectivity for CO\textsubscript{2} is much larger than for H\textsubscript{2}, permselectivities showed a reduction by a factor of 5 to about 1.3. Larger diffusivity of H\textsubscript{2} or deterioration of the liquid, or both, are the possible causes. Moreover, both CO\textsubscript{2} and water appear to have a detrimental effect on the transport properties. In a supported ionic liquid membrane emim-Tf2N is not the right candidate.

Membrane shift reactors can be operated with a suitable water-gas shift catalyst. Two types of catalysts have been considered candidates, based on prior experience: standard commercial HTS (high temperature shift) catalysts (i.e., based on Fe and Cr) and noble metal shift catalysts developed for fuel processing applications. A total of six catalysts have been selected. All catalysts were tested for their activity, at atmospheric pressure without H\textsubscript{2}S. The noble metal catalysts are more active than the base metal catalysts. Subsequently the catalysts were tested for stability for 200 hours under the expected operating conditions but at atmospheric pressure; most of the catalysts show significant deactivation during the initial stage, followed by more gradual decline in activity. Stability tests have been repeated in the presence of 20 ppmv of H\textsubscript{2}S. The activity of all catalysts is significantly, yet reversibly, affected by H\textsubscript{2}S. Eventually an iron oxide/chromia catalyst proved to be best and was used to also measure the kinetics under sour conditions. The rate equation could successfully be derived and is in accordance with the scarce and rather old literature data.

**Introduction**

A sustainable use of fossil fuels in the future will undoubtedly make use of concepts, where the energy content of the fossil fuel is first transferred to hydrogen, followed by the conversion to the desired energy form. The driving force for these concepts is the possibility of capturing CO\textsubscript{2} elegantly, while using the favorable thermodynamics to increase the efficiencies of fossil fuel conversion. ECN and TU-Delft, have identified membrane reactors as a game changing technology for highly efficient conversion of fossil fuels to carbon free energy carriers.
The purpose of this project is to develop hydrogen and CO\(_2\) membranes to allow combination of natural gas reforming with H\(_2\) or CO\(_2\) separation in separation enhanced reactors, i.e. membrane reactors, for carbon-free hydrogen production or electricity generation. These devices offer multiple advantages, such as eliminating the requirement of water gas shift reactors with associated costs reductions; offering higher conversion efficiencies at lower temperatures; and decreasing primary energy use for CO\(_2\) separation/capture associated with electricity generation.

Background

The steam reforming and the water gas shift equilibriums are key reactions for the production of hydrogen from fossil fuels:

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} & \rightleftharpoons \text{CO} + 3\text{H}_2 \\
\text{CO} + \text{H}_2\text{O} & \rightleftharpoons \text{CO}_2 + \text{H}_2
\end{align*}
\]

By removing either CO\(_2\) or hydrogen from the reaction mixture, the equilibrium can be shifted to the product side. Effectively, this can lower the reaction temperature and improve the purity of the product. In conventional, hydrogen production from natural gas, the steam-reforming step is followed by two water gas shift (WGS) reactors. When separating either CO\(_2\) or hydrogen inside the reforming reactor, both the WGS steps can be eliminated. This implies that separation-enhanced techniques can also lead to investment costs reductions. Hydrogen or CO\(_2\) separation is a flexible technique that can be used in hydrogen production from natural gas, but also can replace the WGS section of an IGCC or Biomass gasification plant. These techniques are especially suited for CO\(_2\) capture, because the production of pure hydrogen and CO\(_2\) streams is intrinsic to separation-enhanced reactors.

The combination of separation and reaction, as foreseen in membrane reactors, offers higher conversion of the reforming reactions at lower temperatures due to the removal of hydrogen or CO\(_2\) from these equilibrium reactions, as shown in equations 1 and 2. For instance, in the case of natural gas reforming for carbon free hydrogen production, the use of membrane reactors will result in significantly lower operation temperatures (500 - 600\(^\circ\)C) and higher capture ratios, 85 - 90 instead of 75\%.\[^1\] Membrane reformers or reactors can be integrated in power generation systems. Assessment studies clearly showed that in a more integrated approach of electricity production and CO\(_2\) capture, using high-temperature membrane reactors will result in a substantially lower primary energy use for the CO\(_2\) separation/capture \[^2\]. Besides that, the low operation temperature of the membrane reactor creates possibilities for so-called chemical recuperation, compensating part of the CO\(_2\) capture efficiency penalty.

The tasks defined within this project are:

| Task 1 | System analysis and thermodynamic evaluations | Executed by ECN |
| Task 2 | Hydrogen membrane research and development | Executed by TUD |
| Task 3-a | Hydrotalcite CO\(_2\) membranes research and development | Executed by ECN |
| Task 3-b | Ionic liquids CO\(_2\) membranes research and development | Executed by TUD |
| Task 4 | Catalyst screening | Executed by ECN |
| Task 5 | Reactor modeling and design | Executed by ECN |
Tasks 1, 4 and 5 pertain to both the hydrogen and carbon dioxide membrane cases.

The interaction between the tasks and the outcome anticipated at the outset are depicted in Figure 1. Results from tasks 2 and 3-b are reported separately by the respective PIs Prof. Dr Joop Schoonman and Dr Cor Peters of the Technical University of Delft.

Figure 1 Interaction between the tasks in this project.

**Results**

*System and reactor analysis:*

On a reactor level the viability of both H$_2$ and CO$_2$ selective membranes has been assessed both in SR and WGS processes. Prior to material development it should be clear whether application of the one is preferred to the other. Therefore a fair comparison was made by assigning the same properties (in terms of selectivity, permeability, etc) to a membrane black-box either fit for H$_2$ or CO$_2$ separation.

The results as to the pros and cons for H$_2$ or CO$_2$ separation are the following:

- Separating CO$_2$ from Natural Gas Steam Reforming mixtures has the largest beneficial influence on conversion as compared to H$_2$, since only one CO$_2$ molecule has to be removed whereas for the same effect four H$_2$ molecules have to be taken out. However, the driving force for separation is close to zero in this case (Figure 2) due to the already low CO$_2$ partial pressure in the feed. Therefore CO$_2$ selective membranes cannot be applied in a steam reforming membrane reactor.

- Application of membranes in combination with the Water Gas Shift reaction yields only a slight preference for H$_2$ separation

- Changing to low H$_2$/CO$_2$ ratio feedstock as from coal gasification (Figure 3) makes the applicability of CO$_2$ separating membranes possible in all situations. Detailed overall system and exergy analyses are needed to discern between H$_2$ and CO$_2$ membranes in these cases

- A sensitivity analysis on all important parameters involved (Table I, ), indicate that there is no clear-cut choice for the most important parameter to optimize the system, i.e. the parameter space as a whole should be optimized
Table I Parameters varied in WGS CO\textsubscript{2} selective membrane reactor analysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>minimum</th>
<th>maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>sweep flow/feed flow</td>
<td>0.15</td>
<td>0.40</td>
</tr>
<tr>
<td>steam flow before shift (mimics S/CO)</td>
<td>1.0</td>
<td>1.5</td>
</tr>
<tr>
<td>V/A ratio (m\textsuperscript{3}/m\textsuperscript{2}, mimics catalyst quantity versus membrane area)</td>
<td>0.01</td>
<td>0.00001</td>
</tr>
<tr>
<td>membrane surface area (m\textsuperscript{2})</td>
<td>10,000</td>
<td>2,000</td>
</tr>
<tr>
<td>operating temperature (°C)</td>
<td>400</td>
<td>200</td>
</tr>
<tr>
<td>feed side pressure (bar)</td>
<td>42.2</td>
<td>50</td>
</tr>
</tbody>
</table>

Figure 2 H\textsubscript{2} and CO\textsubscript{2} partial pressure profiles in a membrane reactor for natural gas steam reforming clearly showing that under SR conditions there is no driving force for CO\textsubscript{2} permeation, and only H\textsubscript{2} selective membranes are feasible.

Figure 3 Carbon capture ratio versus CO\textsubscript{2} retentate partial pressure for different upstream syngas generation processes

Figure 4 shows that the syngas generation processes that yield the highest CO\textsubscript{2} partial pressure (after shifting the CO to CO\textsubscript{2}) are the most beneficial for application of CO\textsubscript{2}-selective membrane reactors. In general coal gasification obviously gives the highest CO\textsubscript{2} pressures and also increasing the total pressure is beneficial. The main message
here is that CO$_2$ selective membranes are only viable in WGS membrane reactors and H$_2$ selective membranes also in SR.

Two advanced membrane reactor configurations were assessed on a system level with respect to implementation in an Integrated Gasification Combined Cycle (IGCC) with pre-combustion CO$_2$ capture. The advanced membrane reactors comprise a H$_2$- and CO$_2$-selective Water-Gas-Shift Membrane Reactor (WGS-MR), in which the separation enhances the equilibrium limited water-gas-shift reaction. Dry-fed coal gasification was selected for these detailed system assessments (Figure 4, Figure 5). The assessments were performed with AspenPlus combined with the in-house developed membrane model [3], as well as ‘Exercom’ that facilitates second law analysis. The final results lead to the following conclusions (see also Figure 6).

Figure 4 Coal based power generation with a H$_2$ selective membrane
Both a hydrogen and a carbon dioxide selective WGS-MR should preferably be operated at relatively low overall steam/CO-ratios of 1.30, to obtain the lowest specific electric losses. Hydrogen-selective WGS-MR should be swept with the nitrogen at a pressure level equal to the gas turbine pressure ratio. In this case shift conversion and hydrogen recovery are not 100%. However, when combined with an additional cryogenic distillation step, this appears more beneficial than the pursuit of a near 100% carbon monoxide conversion as well as hydrogen recovery factor (using a low permeate pressure in combination with H₂ recompression). At equal membrane surface areas, a carbon-dioxide WGS-MR requires a target permeance which is approximately twice as high as the target permeance for hydrogen-selective WGS-MR. This is attributable to the fact that the theoretically obtainable hydrogen partial pressure on the feed side is approximately two times higher than the carbon dioxide partial pressure. Application of low pressure steam as membrane sweep flow in carbon dioxide-selective WGS-MR appears to result in the lowest efficiency penalties in comparison with intermediate pressure steam and expanded steam.

Figure 7 shows that for hydrogen-membrane reactors decreasing the sweep pressure from 23 bar (right-hand side of the lines) to 1 bar (left-hand side) strongly decreases the electric efficiency, while the carbon capture ration increases only slightly. For CO₂-selective membranes changing the sweep steam flow from 0.77 kmol/s (right-hand side of the lines) to 3.08 kmol/s (left-hand side) results in a higher capture ratio, but a lower electric efficiency. Comparison of hydrogen and CO₂-selective membranes under the same conditions (40 bar pressure, 90% CO₂ capture and target permeance) shows that the efficiency for a hydrogen-selective membrane reactor (40.6%) is higher than for a CO₂-
selective membrane reactor (39.7%). In general CO$_2$-selective membranes need a higher permeance to reach high CO$_2$ capture ratios. However, advantages of the carbon dioxide-selective WGS-MR are the high carbon dioxide purity and the absence of combustible compounds in the carbon dioxide product stream. Carbon dioxide-selective WGS-MRs are expected to benefit slightly more from developments towards higher operating pressures of dry-fed gasifiers compared with hydrogen-selective WGS-MR.

It can be concluded that both hydrogen and CO$_2$-selective membranes have the potential to reach high CO$_2$ capture ratios at relatively low efficiency penalties. It must be noted that to reach these numbers, the membranes must fulfill stringent criteria. Both membranes were assumed to be 100% selective. Lower selectivities directly lead to lower CO$_2$ capture ratios. Also very high permeances are required (the target permeance is equal to the permeance of a state-of-the-art Pd-Ag-membrane). Moreover, the high electric efficiencies also dependent on developments in water-gas shift catalysts, being lower inlet temperatures and reduced steam/CO-ratios.

![Figure 6 Carbon capture ratios at variable membrane feed pressure, membrane sweep pressure (H$_2$-selective WGS-MR), membrane sweep flow and permeance (CO$_2$-selective WGS-MR); the specific electric loss is depicted by the diagonal lines (steam/CO-ratio: 1.30)](image)

Membrane materials research

In order to verify the assumption used in the project proposal that hydrotalcite based membranes are indeed a challenging option for use in advanced membrane reactors, an inventory has been made on CO$_2$ membranes and membrane materials for CO$_2$ separation. This study yields the following general conclusions:
Existing polymer and polymer-hybrid materials are no options for water-gas shift CO\(_2\) membrane reactors due to loss of selectivity at operating temperatures higher than 100-200\(^\circ\)C.

Porous or dense ceramic membranes with or without promoters like alkali carbonates, zirconates etc. are viable options that have to be explored further. They comprise among others porous or dense hydrotalcites and alumina impregnated with hydrotalcites.

Systems based on molten carbonate like concepts require too high an operating temperature to ensure reduction of energy use and CO\(_2\) emissions.

Exotic new, scarcely investigated, compounds like calixarenes cannot a priori be excluded, but are too far out with respect to our established competences and skills. Production is still on the milligram scale and the possible use as a membrane material only speculative. Any progress in the development of this kind of materials will be monitored. At present an avalanche of results in HOIF research suggest that also in this class of compounds, promising candidates can be found. It remains to be seen if these materials eventually can be made on a scale needed for equipping most of the power plants with capture technology.

The structural aspect of water and carbonate bearing layers in between sheets of magnesium-aluminium hydroxide in hydrotalcites leads to the assumption that both dense and porous membranes may be produced from this compound. They have already proven their applicability as CO\(_2\) sorbent in sorption enhanced reaction processes [4].

**Membrane materials research, Task 3a**

Mg/Al based hydrotalcites (HTC), Mg\(_x\)Al\(_{1-x}\)(OH\(_2\))(CO\(_3\))(1-x)/2\cdot xH\(_2\)O, have proven their applicability in CO\(_2\) absorption and have a crystal structure that may shows a transport pathway for CO\(_2\) transport through the carbonate and water bearing inter layers. This means that there are in principle two membrane transport mechanisms operable for the HTC to function as a CO\(_2\) selective membrane: bulk and affinity based through preferred absorption (Figure 7).

**Mechanisms of separation:**
- Thermal assisted hopping of ions or atoms through the bulk lattice:
- Molecular sieving:
- Affinity based
  - Dissolution-diffusion
  - Preferred adsorption and exclusion:

**Figure 7 Main membrane transport mechanisms**

Molecular sieving is commonly done with e.g. zeolites, the dissolution-diffusion mechanism occurs in polymer membranes and supported liquid membranes. Whatever
the mechanism, it is prerequisite to know what the real composition or compositional window of the HTC is (x in the molecular formula), and what the behavior as a function of temperature in order to choose the right thermal treatment and to know what happens under operating conditions in a WGS process. Literature is not conclusive on this point, probably because no membrane applications are envisioned. It was observed that for different Mg/Al ratios different impurities were formed. For an HTC with a high Mg content (e.g., Mg90) hydromagnesite and for an HTC with a low Mg content (e.g., Mg25) Boehmite was formed (Figure 8).

Figure 8 XRD patterns of HTC for different % of total metal content (Mg + Al); the Mg% is indicated by Mgxy. Non marked peaks are HTC

To actually determine the Mg/Al ratio, neutron powder diffraction was used to be able to distinguish between Mg and Al, since X-ray powder diffraction is not able to distinguish between Mg$^{2+}$ and Al$^{3+}$ because of their very similar electronic configuration. A complicating factor to neutron diffraction experiments is the fact that the sample contains a lot of hydrogen atoms in the form of both water and hydroxide, which gives rise to a very high background due to incoherent scattering. Three samples were prepared hydrothermally: Mg25, Mg50 and Mg90. In the Mg25 sample the excess of Al crystallizes in a poorly crystalline boehmite phase. In the Mg90 sample the excess of Mg crystallizes in a poorly crystalline hydromagnesite phase which is, moreover, the majority phase. Both the Mg25 and the Mg90 samples yielded very poor refinement results (Figure 9 and Figure 10). Trying to refine the Mg/Al ratio led to diverging behavior.
The Mg50 sample contains the least impurity phase, in this case boehmite. The Mg50 diffraction pattern could be refined (Figure 11), and it was possible to extract the expected structural information. Lattice parameters can be determined rather accurately but the other, atomic, parameters really suffer from the moderate quality of the diffraction patterns. Indeed the Mg/Al ratio is close to 2 and was refined to be 1.8.
As starting values for the refinement, crystallographic data for hydrotalcite from Costantino et al.[5], for boehmite from Christoph et al. [6], and for hydromagnesite from Akao et al. were taken [7,8]. Using rigid bodies for carbonate ions and water molecules, the Mg\(^{2+}/\)Al\(^{3+}\) ratio was found to be 0.64(1)/0.36(1) = 1.8 (R\(_{wp}\)=0.02, \(\chi^2\)=6.2). The composition of the hydrotalcite phase of the hydrothermally synthesized Mg50 is thus found to be: Mg\(_{0.64}\)Al\(_{0.36}\)(OH)\(_2\)(CO\(_3\))\(_{0.18}\)•1.0H\(_2\)O. The remainder of the aluminium-nitrate used in the synthesis forms the boehmite phase.

The behavior upon thermal treatment of Mg61 shows that there are several decomposition steps involving water and carbon dioxide loss (Figure 12).
Experiments performed on the TGA-MS with different heating rates from room temperature till 1000 °C have permitted to establish the activation energies related to each decomposition step (Figure 13). The activation energy can be determined by plotting \( \ln(\beta/T_{\text{max}})^2 \) vs \( 1/T_{\text{max}} \), the slope yields the activation energies, as described in [9], where \( \beta \) is the heating rate and \( T_{\text{max}} \) the temperature of maximum desorption.

![Figure 13: Hydrotalcite decomposition steps using different heating rates.](image)

The values of the activation energies, i.e. in this case equal to the decarbonation or dehydration energies, are close to the values found for similar compounds. With these results it was then possible to propose a five-step decomposition path that gives more insight firstly on the decomposition itself and secondly on what could be the active species responsible for the \( \text{CO}_2 \) adsorption behavior of this material:

a) 150-230°C: \((\text{Mg}_4\text{Al}_2\text{(OH)}_2\text{CO}_3\cdot x\text{H}_2\text{O}) \rightarrow (\text{Mg}_4\text{Al}_2\text{(OH)}_2\text{CO}_3) + x\text{H}_2\text{O}\)

b) 230-320°C: \((\text{Mg}_4\text{Al}_2\text{(OH)}_2\text{CO}_3 \rightarrow "\text{Mg}_4\text{Al}_2\text{O}_3\text{(OH)}_6\text{CO}_3" + 3\text{H}_2\text{O}\)

c1) 320-450°C: \("\text{Mg}_4\text{Al}_2\text{O}_3\text{(OH)}_6\text{CO}_3" \rightarrow 0.5"\text{Mg}_2\text{Al}_4\text{O}_7\text{CO}_3" + 0.5\text{MgCO}_3 + 3\text{H}_2\text{O} + 2.5\text{MgO}\)

c2) 400-450°C: \(0.5\text{MgCO}_3 \rightarrow 0.5\text{MgO} + 0.5\text{CO}_2\)

d) 450-600°C: \("0.5\text{Mg}_2\text{Al}_4\text{O}_7\text{CO}_3" \rightarrow "\text{Mg}_4\text{Al}_2\text{O}_3" + 0.5\text{CO}_2\)

Below 150°C only physisorbed water is evolved. The most obvious conclusion for membrane development is that a dense membrane is not possible since under operating conditions the interlayer no longer exists.

**Membrane preparation**

The research on hydrotalcite, \( \text{Mg}_{0.64}\text{Al}_{0.36}(\text{OH})_2(\text{CO}_3)_0.18\cdot 1\text{H}_2\text{O} \), as a possible \( \text{CO}_2 \) selective membrane material for a porous membrane, has been pursued. The focus the research is on preparing nano-particles of hydrotalcites by two different routes, co-
precipitation and sol-gel synthesis, in order to obtain a very well dispersed particulate sol that can be used for coating on γ-alumina membrane supports. Another route to make a CO₂ affinity based porous membrane would be to impregnate the γ-alumina layer of the support with hydrotalcite by in-situ letting the salts react with the basic ingredients inside the pores so as to form HTC.

These three different routes will be described with a special attention on the dispersion of the different sols obtained as a function of the solvent used for the co-precipitation route and on the different parameters that can vary for the sol-gel route.

Co-precipitation route:
This is the easiest and most employed route to form hydrotalcite consisting of just putting all ingredients (Mg and Al nitrate, sodium carbonate and Sodium hydroxide dissolved in water) in a beaker within seconds a precipitate is formed. It usually leads to large agglomerates. In order to break these agglomerates or to prevent their formation, a number of different solvents and dispersants have been used instead of the usual “pure water” method (Figure 14). Using glycerol/water as a solvent provided the best results. XRD analysis indicates that the primary particle size (strictly: coherence length) should be around 15 nm. The dip-coated membranes were not calcined before testing but during the temperature dependent permeance measurements.

Sol-gel route:
The sol-gel route has been selected as a possible route to produce very well dispersed particles as is known from the literature. Many parameters can play a role in this synthesis route as to the precursors, the solvent, the acid used for the hydrolysis, the base

Figure 14 Examples of particle size distributions for different solvents. Clearly glycerol/water performs best.
used for the condensation of the species, the temperature as well as the concentration of the reactants. From earlier experiments, it has been suggested to try longer alcohols in order to reduce the interfacial tension and check whether it will be possible to decrease both the particle size and the size distribution. The sols obtained were characterized by DLS and the powders by XRD and SEM. The results obtained were comparable with those of the co-precipitation route. The best sols obtained were prepared using ethanol as a solvent. However, problems during the coating step hampered membrane production using this technique.

The in-situ impregnation route:
This route consists in making the hydrotalcite particles grow into and onto the membrane support. The adhesion between the support and the particles should not be a problem as the support is made of alumina and the HTC material also contains alumina. The process consists of two steps. First the support is rendered basic with soaking it into a basic solution containing both sodium hydroxide and sodium carbonate. Then, the outer surface of the tubular membrane is placed into a solution of the metal nitrates. After the reaction has taken place the membrane is calcined at 450˚C and tested for its permeance. Some of these membranes were also promoted with potassium carbonate as this latter is known to enhance the CO$_2$ adsorption in hydrotalcites.

Membrane tests: Hydrotalcite
Coating supports is the most employed route to form membranes. The nanoparticles formed in 67% glycerol-33% water are from the size point of view the most promising ones. SEM analysis of the coating obtained (Figure 15) did not show large defects and this was confirmed by permoporometry (Figure 16) and the membrane was therefore tested with single gas permeation and mixed gas permeation tests.

![Figure 15, SEM picture of the HTC from 67% glycerol 33% water coating on the membrane support](image)
Figure 16 Permporometry results of the HTC from 67/33 glycerol/water mixture coated membrane before testing (before testing, i.e. uncalcined)

Figure 17 shows the coated membrane before and after permeability tests. It seems that during the test the membrane got carbonized, which may be due to decomposition of the glycerol still present in the support. Furthermore, the collapse of the HTC structure upon heating may have changed the porous structure in such a way that the pore size increased, explaining the low selectivity. The average pore size measured by permporometry was about 1 nm but the pore size distribution was still rather large (from 0.5 to 4 nm). This is clearly too large to obtain a good CO$_2$ selectivity, apart from the presence of defects in the separating layer.

![Figure 17 HTC membrane from “67% glycerol particles”: on the left, before (green: uncalcined) and on the right, after testing (calcined during measurement).](image)

The permeabilities tests were done as a function of temperature, pressure and pressure difference. The ideal permselectivity for Knudsen diffusion is CO$_2$/$H_2$ equals 0.21. From our measurements, the permselectivity was calculated to be 0.43 which shows some deviation from the Knudsen diffusion, showing some affinity based selectivity towards CO$_2$. 
Likewise, in-situ prepared membranes have been measured for their membrane properties. The permeance results of both types of membranes are shown in Table II.

Table II Permselectivities measured on the differently prepared membranes (last column is selectivity from mixed gas measurements, for comparison)

<table>
<thead>
<tr>
<th>Membrane</th>
<th>CO$_2$/H$_2$ single gas</th>
<th>CO$_2$/He single gas</th>
<th>CO$_2$/N$_2$ single gas</th>
<th>CO$_2$/H$_2$ mixed gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coated</td>
<td>0.43</td>
<td></td>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td>In-situ</td>
<td>0.53</td>
<td>1.3</td>
<td>1.7</td>
<td>1</td>
</tr>
<tr>
<td>In-situ promoted with K</td>
<td>0.6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As can be seen from Table II, the in-situ prepared membranes show an indication of enhanced affinity based selectivity towards CO$_2$ although far too small i.e. CO$_2$/H$_2$ should at least be larger than one. A clear explanation for the larger permselectivity for CO$_2$/He has not been found yet. There are indications that hydrogen reduces the ‘hydrotalicite’ Mg oxides to Mg. Mixed gas experiments on a 50-50 mixture of CO$_2$ and H$_2$ however, did not show any selectivity for the ‘in-situ’ sample, probably due to the sintering and decomposition process the pores are simply too large.

In order to find other materials that show reversible chemisorption behavior of CO$_2$ in a small temperature range, preferably without a decomposition trajectory, thermodynamic calculations were performed. The thermodynamic calculations were performed with FactSage (Version 5.5), assuming the following static conditions: T= 300-1000 K in steps of 25 K, p$_{\text{total}}$= 25 bar, p$_{\text{CO}_2}$=6.3 bar, p$_{\text{H}_2}$=10.075 bar, p$_{\text{N}_2}$=0.525 bar, p$_{\text{H}_2}\text{O}$=5.225 bar, p$_{\text{CO}}$=2.7 bar, p$_{\text{Ar}}$=0.15 bar (Figure 18).

![Figure 18 Calculated reaction mixtures as a function of temperatures: Carbonation plus WGS equilibrium](image)

From these thermodynamic calculations and taking into account the WGS process conditions, some materials are found to be suitable. Suitable materials must have a carbonation/decarbonation temperature between 250 and 650°C for CO$_2$ pressures between 1 and 10 bar. These materials are shown in Figure 19. Most of these materials do not suffer from decomposition like HTC.
In order to confirm those findings, experiments are currently being performed on a high pressure DSC and on an atmospheric pressure TGA-MS. These should give indication on whether these materials behave as predicted and with reasonable kinetics.

**Membrane tests: Supported ionic liquid**

Task 3a performed at Delft University of technology yielded two ionic liquid (IL) candidates to be used in a supported IL membrane: Emim-Tf2N and Bmim-Tf2N. The better candidate Emim-Tf2N (Fluka, purum > 97.0 %; H2O< 0.5%, Figure 20), has been impregnated in the top layer, the γ-alumina layer, of a tubular porous asymmetric membrane support [10], having a pore size of about 4 nm. The thickness of the impregnated layer is about 1-2 µm

Single gas permeabilities have been measured on this supported ionic liquid membrane (SILM) in a standard gas permeation set-up with He (quality test), H2 and CO2, the gasses to be separated in a water-gas-shift membrane reactor. Temperatures used were 25°C and 80°C. The feed pressure of each of the gasses was 8 barg, the pressure at the permeate side was constant, 1.11 barg. The permeance was derived from the flow needed to keep the feed pressure at 8 barg. Feed and permeate gasses were in all cases chosen to be equal, so no sweep gas was used. The measurement sequence was He at 25°C, CO2 at 25°C, He at 25°C, H2 at 25°C, He at 80°C, CO2 at 80°C, He cooling down to 25°C and again up to 80°C(flat horizontal part is 25 °C), H2 at 80°C and finally He cooling down to
25°C (see also Figure 21). The permselectivity is defined as the ratio of the single gas permeances.

![Figure 21: Permeances of the different gasses at different temperatures during the whole experiment](image)

The results of the permeance measurements are depicted in Figure 21, the average plateau values at stable temperature of the single gas permeances are listed in Table III. The figure clearly shows that equilibration takes a very long time after switching gasses and that the permeances measured are quite low. At 25°C the membrane is well behaved: permeances reaching a stable value and the He level returning to its original value. At 80°C however things are quite different: the baseline of He at 25°C increases as compared to the original value and also the 80°C He permeance increases over time. The calculated CO₂/H₂ permselectivities are 1.45 and 1.25 for 25°C and 80°C respectively. It is not completely clear whether this reduced value at higher temperature is due to a higher mobility of H₂ or deterioration of the membrane, probably both. Solinas et al [11] found a dramatic increase in H₂ solubility when this IL is pressurised under CO₂. Anyhow these values are definitely lower than the absorption selectivity of pure gasses in the IL by a factor of at least 5. This means that the higher diffusivity of hydrogen is making up for the difference in absorption selectivity. The permselectivity is still higher than for the bare γ-alumina layer. The Knudsen diffusion based value is about 0.2.

Table III Average plateau values of the single gas permeances at stable temperature

<table>
<thead>
<tr>
<th>Condition (°C)</th>
<th>He 25</th>
<th>CO₂ 25</th>
<th>He 25</th>
<th>H₂ 25</th>
<th>He 80</th>
<th>CO₂ 80</th>
<th>He 80/25/80</th>
<th>H₂ 80</th>
<th>He 80/25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average plateau permeancy (10⁻⁸ mol/m²sPa)</td>
<td>1.2</td>
<td>2.5</td>
<td>1.1</td>
<td>1.7</td>
<td>1.4</td>
<td>4.2</td>
<td>1.9</td>
<td>3.3</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Based on the absorption selectivity for CO₂ as compared to the other gasses, CH₄, CO and H₂, varying between 5 and 15 in a temperature window between 50 and 180°C, Emim-Tf₂N is not the right IL for pre-combustion carbon capture processes, especially since these processes, either water gas shift or steam reforming, take place at even much...
higher temperatures. From the equilibration times found in this study (larger than half an hour, see Figure 21), also post combustion application of this IL as a scrubbing liquid will not be feasible.

It has been reported that the presence of water strongly reduces the CO$_2$ solubility in ILs [12] and also negatively influences the surface tension [13] having a detrimental effect on the allowable pressure drop over the liquid membrane. Since the SILM has to operate in a steam environment at high T, > 250$^\circ$C, and p, about 20 bar., also the stability against water vapor of the SILM has been determined.

![He permeance through an EmimTf2N SILM, under increasing RH at 303 K](image)

Figure 22 Increasing permeance of He with increasing relative humidity of the He-stream.

Clearly (Figure 22) with increasing relative humidity the permeance of an inert gas, i.e. He increases. Also this adds to the doubt concerning applicability. Furthermore, the non negligible vapor pressure of the ILs [14] is a point of concern for any membrane application.

In conclusion it may be stated that, although Emim-Tf2N turns out not to be applicable as a CO$_2$-selective membrane, the results presented by no means constitute a final ‘no’ to the application of ILs in pre- or post-combustion CO$_2$ capture, either as a scrubbing liquid or applied in a membrane.

**Catalyst screening**

Next to a membrane, a membrane water-gas shift reactor also needs a suitable water-gas shift catalyst. Two types of catalysts have been considered candidates, based on prior experience: standard commercial HTS catalysts (i.e., based on Fe and Cr) and noble metal shift catalysts developed for fuel processing applications. A total of six catalysts have been selected:

A. Commercial HTS catalyst (Fe$_2$O$_3$/Cr$_2$O$_3$/CuO) 'HTS1'
B. Commercial HTS catalyst (Fe$_2$O$_3$/Cr$_2$O$_3$) 'HTS2'
C. Noble metal 'NM1'
D. Noble metal 'NM3'
E. Noble metal (tolerates up to 10 ppmv of H$_2$S) 'NM2'
F. Noble metal (needs about 50 ppmv of H$_2$S) 'NM4'
HTS catalysts (i.e., HTS1 and HTS2) are active as Fe$_3$O$_4$, which could be oxidized (during H$_2$ removal) or reduced (during CO$_2$ removal) in situ to inactive oxides, according to:

\[
2 \text{Fe}_3\text{O}_4 + \text{H}_2\text{O} = 3 \text{Fe}_2\text{O}_3 + \text{H}_2 \\
\text{Fe}_3\text{O}_4 + \text{CO} = 3\text{FeO} + \text{CO}_2
\]

However, thermodynamic calculations have shown that no stability problems are expected even for high recovery of H$_2$ or CO$_2$ since, with (H$_2$O/CO)$_\text{in}$ = 2 and at 450°C:

- \([\text{H}_2\text{O}]/[\text{H}_2] = 113\) (equilibrium at 99% H$_2$ recovery) while Fe$_3$O$_4$ is stable for \([\text{H}_2\text{O}]/[\text{H}_2] < 24\cdot10^3\); and
- \([\text{CO}_2]/[\text{CO}] = 7.8\) (equilibrium at 99% CO$_2$ recovery) while Fe$_3$O$_4$ is stable for \([\text{CO}_2]/[\text{CO}] > 0.62\).

All catalysts were tested for their activity, at atmospheric pressure without H$_2$S. The noble metal catalysts are more active than the base metal catalysts. Due to this difference in activity, the noble metal catalysts have been measured in a 5% (w/w) dilution throughout. HTS1 and HTS2 perform similar, as was expected from tests in previous projects. Of the noble metal catalysts, NM1 is by far the most active while NM3 and NM2 perform similar. NM4 shows the lowest CO conversion, while it is also the only showing significant methanation, starting already at 310°C. The tendency for methanation could be related to the absence of H$_2$S. The activity test of NM4 have therefore been repeated in the presence of 20 ppmv of H$_2$S, which effectively eliminated methanation. The effect of total pressure on the CO conversion has been assessed by repeating the activity tests at 3 bar(a). Both HTS catalysts showed a higher conversion and hence a positive effect of total pressure. The conversion of CO over noble metal catalysts (NM1–4) was not significantly effected. Based on these activity measurements, catalyst NM3 was eliminated as it was always outperformed by NM1.

Subsequently the catalysts were tested for stability for 200 hours at the expected operating temperature of 450°C, at atmospheric pressure, shown in Figure 23 (left) for four of the catalysts. Except for HTS1, all catalysts show significant deactivation during the initial stage, followed by more gradual decline in activity. This agrees with previous tests, as well as literature data on commercial HTS catalysts. HTS1 is activated during approximately the first 100 hours but then deactivates as well. Possibly, it was not pre-reduced properly.

Stability tests have been repeated in the presence of 20 ppmv H$_2$S. Catalysts NM2 and NM4 performed identical with 20 ppmv of H$_2$S and therefore NM2 was preferred over NM4 because of possible methanation problems at lower sulphur concentrations. The results of the four remaining candidates are shown in Figure 23 (right). The activity of all catalysts is significantly, yet reversibly, affected by H$_2$S. In presence of sulphur, HTS2 retains a higher activity than HTS1. NM1 looses all activity in presence of H$_2$S and was therefore eliminated. The activity of NM2 was reduced significantly by H$_2$S. Measured after 178 hours on stream (150 hours with H$_2$S) at 400°C, NM2 is only a factor 5 more active than HTS2. The catalytic activity has also been compared with
representative (hydrogen) membrane fluxes from literature, showing that the expected hydrogen fluxes are relatively low compared to the catalytic hydrogen production rates, even for HTS2. The latter has therefore been selected as the preferred catalyst for the GCEP project.

Figure 23 WGS catalyst stability tests left) clean, right) with 20 ppmv H\textsubscript{2}S. Experimental conditions: 10\% CO, 19\% H\textsubscript{2}O, 20\% CO\textsubscript{2}, 20\% H\textsubscript{2}, 31\% N\textsubscript{2}; GHSV 30,000 hr\textsuperscript{-1} (HTS) or 70,000 hr\textsuperscript{-1} (5\%NM diluted in alumina); deactivation at 450\textdegree C, intermittently measuring activity at 400\textdegree C; 20 ppmv of H\textsubscript{2}S added from 25 hours to 185 hours on stream in 2\textsuperscript{nd} experiment.

Kinetics have been measured for catalyst HTS2 in compositions representative of membrane enhanced WGS. Data have been fitted to a power law model, with explicit incorporation of the influence of H\textsubscript{2}S in the range of 10–30 ppmv. The commercial iron oxide/chromia catalyst HTS2 has been chosen for the determination of the WGS kinetics under low H\textsubscript{2}S content. It has been measured at atmospheric pressure, between 375–475\textdegree C, and with 11–35 ppmv of H\textsubscript{2}S. Nonlinear regression was carried out based on 176 experimental runs, resulting in the following rate equation:

\[
R = (3.2 \pm 1.3) \times 10^{-6} \exp\left(-\frac{(112 \pm 2) \times 10^3}{R} \left(\frac{1}{T} - \frac{1}{678}\right)\right)
\times \rho_{CO}^{0.84 \pm 0.04} \rho_{H_2O}^{1.17 \pm 0.12} \rho_{CO_2}^{-0.36 \pm 0.05} \rho_{H_2}^{0.99 \pm 0.03} \rho_{H_2S}^{-0.30 \pm 0.03} (1 - \beta_{WGS}) \left[\text{mol} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}\right]
\]

Based on the characteristics of the experiments, the pre-exponential term and the exponents for H\textsubscript{2}O and H\textsubscript{2}S are confounded and this results in a relatively large confidence interval for these parameters. The resulting equation compares well with the scarce literature data [15] and indicate a transition in the observed kinetics between 0 and 75 ppmv H\textsubscript{2}S. Figure 24 shows that the agreement between model and experiment under the conditions used is pretty good.
Overall conclusions

During the project period new insights in different fields have been obtained:

- Behavior of H$_2$ or CO$_2$ selective membrane reactors for different processes i.e. WGS and SR,
- Preference for H$_2$ or CO$_2$ selective membrane reactors in power generating systems,
- Catalysts to be used in these H$_2$ or CO$_2$ selective membrane reactors especially for coal fired plants (sour shift), including determination of the kinetics
- Material properties and behavior as a CO$_2$ selective membrane of the ‘preferred candidate material’ hydrotalcite.
- Behavior of SILMs

At the start of the project it was not obvious what would be the best choice for a membrane, a H$_2$ or CO$_2$ selective one, and in what process it would be applicable, WGS or SR. It turned out that the driving force, i.e., the partial pressure difference between feed and permeate side, for permeation is the decisive parameter. The partial pressure of CO$_2$ at the feed side in a SR process is far too low and thence the required surface area or equivalently the required permeance too high for a viable system. This means that CO$_2$ selective membranes can only be applied in high carbon content mixtures like the water-gas shift step in a coal gasifier, which makes them especially interesting for coal based power production. Hydrogen selective membranes can in principle be used for both WGS and methane steam reforming.

From process analysis of the use of hydrogen and CO$_2$-selective membranes in a dry-fed IGCC can be concluded that both hydrogen and CO$_2$-selective membranes have the potential to reach high CO$_2$ capture ratios at relatively low efficiency penalties. It must be noted that to reach these numbers, the membranes must fulfill stringent criteria. Both membranes were assumed to be 100% selective. Lower selectivities directly lead to lower CO$_2$ capture ratios. Also very high permeances are required (the target permeance is equal to the permeance of a state-of-the-art Pd-Ag-membrane). Moreover, the high
electric efficiencies also dependent on developments in water-gas shift catalysts, being lower inlet temperatures and reduced steam/CO-ratios.

Conventional iron oxide-chromia based WGS catalysts in these novel systems encounter quite different gas compositions than in conventional reactors due to the fact that components are withdrawn from the mixtures (H₂ or CO₂) leading to a change of reductive or oxidative behavior along the membrane’s dimensions. Moreover since coal based power plants will significantly increase in number in the near future, sulphur tolerance is also a real issue. Calculations and experiments have lead to the conclusion that neither of the mentioned threats will hamper the use of iron oxide-chromia based catalysts in membrane reactors. In addition the kinetics of mentioned catalyst has been determined under sour conditions and fills a serious gap in existing knowledge.

A literature survey confirmed that Mg-Al-hydrotalcites were the best membrane materials to start with. It was considered prerequisite that in membrane preparation phase pure starting materials should be used as well as the behavior upon heating to the WGS process conditions. The hitherto unknown optimal Mg/Al ratio for phase pure HTC material has been determined using neutron diffraction to be 1.8. Careful examination of the thermal decomposition of this claylike material has led to a new clear insight in the reactions and species involved. At the outset both bulk and porous CO₂ transport mechanisms seemed to be possible. From the decomposition results it was obvious that only porous membranes may do the job. To this end a thorough investigation into how to make a separating layer has been performed. The most obvious way is to make a coating based on a dispersion of small hydrotalcite particles. To this end particles in the nano size range are required for the affinity based separation mechanism to be operable. A second option is to reduce the pore size of the outer layer of the support by in-situ forming HTC inside these pores. Both methods have been pursued. Extensive experimental effort has been needed to find a way to prevent aggregation of these nano particles. Glycerol/water mixtures appear to do the trick.

Single gas permeation measurements show a slight enhancement of CO₂ permeation as compared to Knudsen behavior. These results have been confirmed in mixed-gas measurements. Although the measured higher CO₂ permeance over hydrogen permeance is higher than has been reported in literature, it is still very far from what is needed for successful application of CO₂-selective membranes in a water-gas-shift reactor. The final stage of the PhD research will be devoted to solve this problem.

The research performed at the Technical University Delft (Dr. Cor Peters) into the possibility to use ionic liquids to make CO₂ selective membranes has resulted in the choice for 1-ethyl-3-methyl-imidazolium-bis-(trifluoromethylsulphonyl) imide(Emim-Tf2N) as the best candidate. It has the best absorption selectivity for CO₂ in a WGS mixture. Single gas permeation measurements revealed that the diffusivity of H₂ is so high that it more than counter balances the absorption selectivity which makes the membrane effectively a H₂ selective one. Furthermore both the presence of CO₂ and that of water clearly influence the behavior of the IL in a detrimental way. These changes
should be clearly understood before embarking at trying other more appropriate compositions and structures.

In reference to Figure 1, in which quite some deliverables were promised at the time of writing the proposal, it can be stated that the major interactions were there but that the fact that no proper membranes could be produced as yet, hampered progress in e.g. cost evaluation, reactor design, reactor tests. This also stood in the way of iterative materials development.

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- Feuillade, V.C., S. Walspurger and W.G. Haije, Synthesis and characterisation of well dispersed hydrotalcite nano particles, Poster presentation, Meeting solid state chemistry and materials science NWO-CW, Lunteren April 2008
- Feuillade, V.C., Haije, W.G., CO₂ capture in power plants: structural and thermal integrity of hydrotalcites as membrane materials, TrondheimCO₂ capture, transport and storage conference, 27 October 2007
- Feuillade, V.C., Haije, W.G., CO₂ capture in power plants: structural and thermal integrity of hydrotalcites as membrane materials, American Institute of Chemical Engineers (AIChE) Fall meeting, Salt Lake City, USA, 1 November 2007

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- Carbo, Michiel C., Daniel Jansen, Wim G. Haije, Adrian H.M. Verkooijen, *Optimisation of advanced membrane reactor operating conditions implemented in IGCC power plants with pre-combustion CO₂ capture*, Submitted to Journal of Hydrogen Energy

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