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 CO_2 selective 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. 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, CO_2 selective membranes are no option due to the very low concentration and therefore driving force of CO_2. In water gas shift (WGS) reactions or with gas compositions as from a coal gasifier these membranes perform comparable to H_2 selective membranes when used in a membrane reactor. On a system level CO_2 selective membranes should have a flux twice that of the H_2 selective membranes assuming the same surface area (=cost). They suffer from a larger specific electric loss but produce a purer CO_2 stream. Expected future developments only marginally positively affect CO_2 selective membranes as compared to their H_2 counterpart. Results have submitted to *Chemical Engineering Science*.

From the outset of the project, hydrotalcites were thought to be good candidates as membrane material for CO_2 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 where through affinity based pore blocking H_2 is largely kept out of the pores and CO_2 travels through the membrane via some kind of surface diffusion. Since the diffusion path for hydrotalcites disappears at operational temperature, the only option left is thus as an affinity based porous membrane. Several approaches were investigated to be able to produce small pores, a few kinetic diameters of CO_2, that have not too strong an interaction with CO_2: in-situ growing of a hydrotalcitic layer inside the pores or making hydrotalcite nanoparticles that can be coated on a porous support yielding the right pore size and having the right affinity to CO_2. The first option did not work. The second one was pursued using either co-precipitation or sol-gel processes. Making monodisperse non aggregated particle proved to be hard but finally both routes are really closing in to the right properties! The large experimental matrix to be tested included different precursors,

solvents, temperatures, dispersants, pH etc. In the course of this process one of the particle dispersions was used to coat a tubular porous membrane support. A coating resulted that firstly reduced the permeance as compared to the bare support and secondly yielded a permselectivity (673 K, 1 bar), H_2/CO_2, half of the Knudsen value, evidencing affinity based transport. Particle synthesis and coating procedure clearly have to be optimized but these first results are promising.

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_2S. 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_2S. The activity of all catalysts is significantly, yet reversibly, affected by H_2S. One of the HTS catalysts turned out to be best under all circumstances and is chosen as the ultimate for the GCEP project. Currently the kinetics on this catalyst is being measured.

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_2 elegantly, while using the favorable thermodynamics to increase the efficiencies of fossil fuel conversion. We, 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:

$$CH_4 + H_2O \leftrightarrows CO + 3H_2 \qquad\qquad (1)$$
$$CO + H_2O \leftrightarrows CO_2 + H_2 \qquad\qquad (2)$$

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 rectors, 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 case natural gas reforming for carbon free hydrogen production, the use of membrane reactors will result in significantly lower operation temperatures (400 - 500°C) and higher efficiencies 85 - 90 instead of 75%.[1] In fact membrane reactors allow for low-irreversibility production and conversion of hydrogen to another energy form with integrated CO_2 capture.

Membrane reformers/reactors can be integrated in power generation systems but also in central heating devices. Our 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.

Results
System and reactor analysis:
Two advanced membrane reactor configurations were assessed wit 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. 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.

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. 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 H_2 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.

The results of the system assessments also illustrate that an IGCC with carbon dioxide capture through a carbon dioxide-selective WGS-MR has one important disadvantage compared with the hydrogen-selective WGS-MR, being the higher specific electric loss. 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-MR are expected to benefit slightly more from future developments towards higher operating pressures of dry-fed gasifiers compared with hydrogen-selective WGS-MR. It must be noted that a significant development in carbon dioxide-selective membranes is required to exploit this possible advantage. Moreover, the implementation of membrane reactors is also dependent on developments in water-gas shift catalysts, being lower inlet temperatures and reduced steam/CO-ratios.

This concludes the tasks on system and thermodynamic analyses. The results are submitted for publication in 'Chemical Engineering Science'.

Membrane materials research, Task 3a
In order to find a material that shows not too strong chemisorption of CO_2, 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_{total}= 25 bar, p_{CO2}=6.3 bar, p_{H2}=10.075 bar, p_{N2}=0.525 bar, p_{H2O}=5.225 bar, p_{CO}=2.7 bar, p_{Ar}=0.15 bar. The results obtained are shown in the table I.

Table I Promising materials for CO_2 capture

MnO and MgO	325 and 425 °C, applicable in SEWGS
Hydrotalcite	400-450°C, applicable in SEWGS
BaTiO$_3$	500°C applicable in SEWGS
CaO	800°C applicable in SERP

Included were also the sodium and potassium bicarbonates but their application for a stable membrane coating is limited.

The research on hydrotalcite, $Mg_{0.64}Al_{0.36}(OH)_2(CO_3)_{0.18} \cdot 1H_2O$, as a possible CO_2 selective membrane material with a porous membrane mechanism, has been pursued. The focus of our 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 sol that can be used for coating on γ-alumina membrane supports. Another route to make a CO_2 affinity based porous membrane would be to transform the γ-alumina layer of the support into hydrotalcite by reaction with Mg species.

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 but it usually leads to large agglomerates. In order to break these agglomerates or to not let them create, a few different solvents have been used. The techniques used for the characterization are XRPD, SEM and DLS. The results obtained are shown in table II for comparison.

**Table II** Co-precipitation results as a function of the solvent used

Solvent	crystallite size (Scherrer)	particle size (DLS)
Water only	15 nm	300 nm
Water only in an strong alkaline solution	15 nm	15 nm and 450 nm
25% glycerol in water	15 nm	30 nm
67% glycerol in water	No crystalline HTC	~20 nm
50% octanol in water	15 nm	230 nm
50% hexanol in water	15 nm	100 nm
Water + 10% formamide added	15 nm	65 nm
Water + 10% PSS added	15 nm	250 nm
100% methanol	No crystalline HTC	

In table 2, it is clear that most of the samples show aggregation of the particles in solution. From these results, it also looks clear that of all the solvents tried, the most suitable to obtain a good dispersion seem to be the glycerol/water mixtures and maybe a very alkaline aqueous solution (figure 1, left).
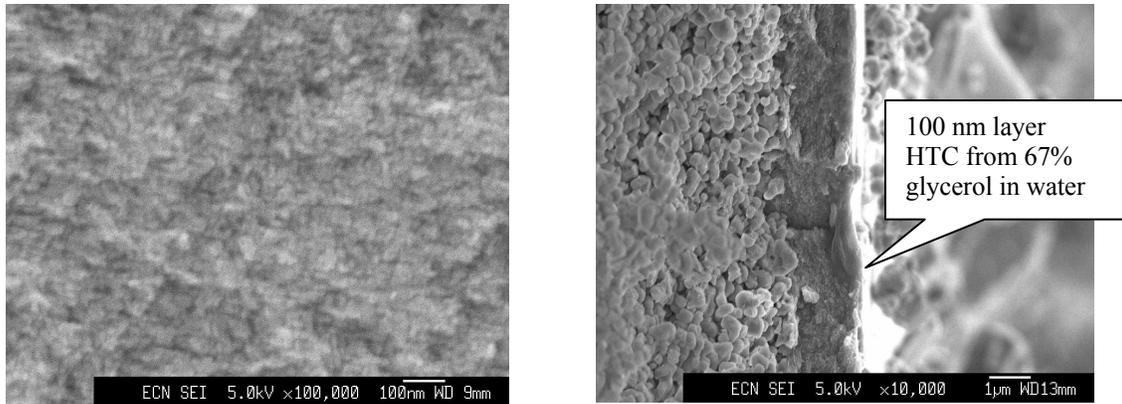
Figure 1 Left: SEM picture of water only 10-15 nm sized hydrotalcite particles, right: SEM picture of the 67% glycerol coating on the membrane support

The 67% glycerol in water sample has been coated on a membrane support and tested for H_2 and CO_2 permeabilities. Figure 1 (right) shows the SEM picture of the layer deposited on the γ-alumina support. It seems that some solvent has entered the support layer. 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 selectivity towards CO_2. The pore size is still too large and the layer contains some larger defects. The fact that as a function of temperature the permeance shows the same behavior as the absorption capacity is a strong indication that affinity based transport is taking place. This is a first step on the right track.
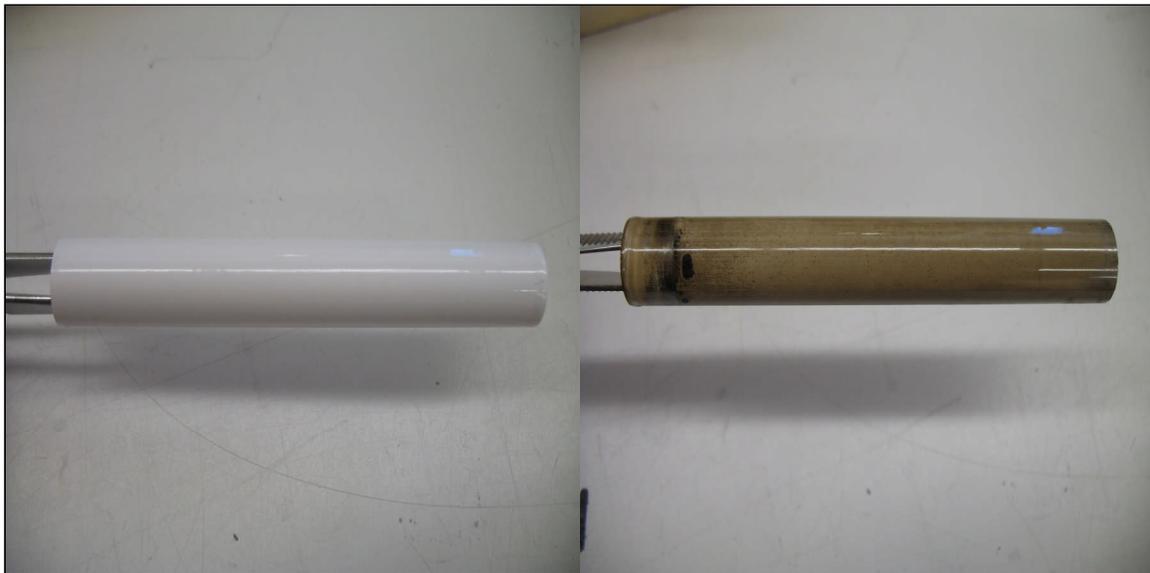
Figure 2 HTC membrane from "67% glycerol particles": on the left, before and on the right, after testing.

Figure 2 shows the coated membrane before and after permeability tests. It seems that during the test the membrane got carbonated, in line with the observation that maybe part of the glycerol is still 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.

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 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 with ethanol as a solvent; however they till now did not yield a coating.

It can be concluded from the materials research that we were able to produce very small well dispersed hydrotalcite particles that could be coated on a membrane support. The membrane test was positive: affinity clearly plays a role in the separation. The next step is to improve the pore size distribution of the separating layer in order to enhance the selectivity. Recipes for sol preparation will have to be optimized as well as the formulation of the coating solution.

Ionic liquids CO_2 membranes research and development Task 3-b
Task performed by TU Delft (to be reported by Dr Cor Peters under the Delft contract). ECN participates in this task through Dr Haije who had a supported IL membrane made and tested at ECN with single gas permeance measurements using H_2 and CO_2. The permselectivity appeared to be half of the absorption selectivity because of the higher diffusivity of H_2. Joint publications on high pressure absorption behavior of various gasses and membrane performance are currently being written.

Catalyst screening
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 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 ($Fe_2O_3/Cr_2O_3/CuO$)   'HTS1'
- B. Commercial HTS catalyst (Fe_2O_3/Cr_2O_3)   'HTS2'
- C. Noble metal   'NM1'
- D. Noble metal   'NM3'
- E. Noble metal (tolerates up to 10 ppmv of H_2S)   'NM2'
- F. Noble metal (needs about 50 ppmv of H_2S)   'NM4'

HTS catalysts (i.e., HTS1 and HTS2) are active as Fe_3O_4, which could be oxidized (during H_2 removal) or reduced (during CO_2 removal) in situ to inactive oxides, according to:

$$2\ Fe_3O_4 + H_2O \quad = \quad 3\ Fe_2O_3 + H_2$$
$$Fe_3O_4 + CO \quad = \quad 3FeO + CO_2$$

However, thermodynamic calculations have shown that no stability problems are expected even for high recovery of H_2 or CO_2 since, with $(H_2O/CO)_{in} = 2$ and at 450°C:

- $[H_2O]/[H_2] = 113$ (equilibrium at 99% H_2 recovery) while Fe_3O_4 is stable for $[H_2O]/[H2] < 24 \cdot 10^3$; and
- $[CO_2]/[CO] = 7.8$ (equilibrium at 99% CO_2 recovery) while Fe_3O_4 is stable for $[CO_2]/[CO] > 0.62$.

All catalysts were tested for their activity, at atmospheric pressure without H_2S. 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. This agrees with previous tests. 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_2S. The activity test of NM4 have therefore been repeated in the presence of 20 ppmv of H_2S, effectively eliminating 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 3a 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 of H_2S. Catalysts NM2 and NM4 performed identical with 20 ppmv of H_2S 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 3b. The activity of all catalysts is significantly, yet reversibly, affected by H_2S. In presence of sulphur, HTS2 retains a higher activity than HTS1. NM1 looses all activity in presence of H_2S and was therefore eliminated. The activity of NM2 was reduced significantly by H_2S. Measured after 178 hours on stream (150 hours with H_2S) 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.

Kinetics are currently being measured for catalyst HTS2 in compositions representative of membrane enhanced WGS. Data will be fitted to a power law model, with explicit incorporation of the influence of H_2S in the range of 10–30 ppmv.
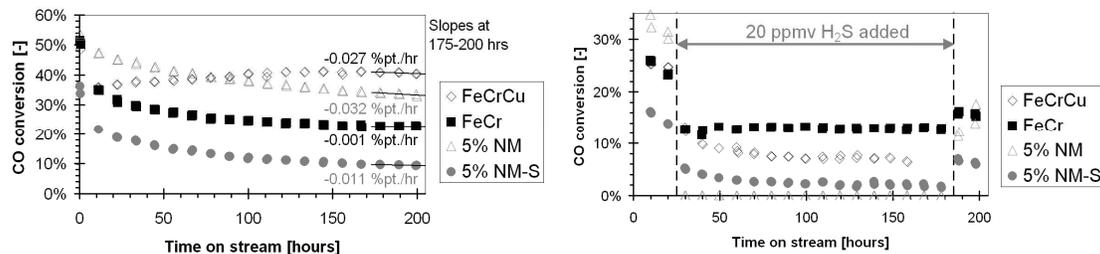
Figure 3 WGS catalyst stability tests left) clean, right) with 20 ppmv H_2S. Experimental conditions: 10% CO, 19%H_2O, 20% CO_2, 20% H_2, 31% N_2; GHSV 30,000 hr-1 (HTS) or 70,000 hr-1 (5%NM diluted in alumina); deactivation at 450°C, intermittently measuring activity at 400°C; 20 ppmv of H_2S added from 25 hours to 185 hours on stream in 2nd experiment.

Progress
- Thermodynamic calculations were performed with Factsage (Version 5.5), yielding especially MgO and MnO as good membrane materials for affinity based separations. MgO is also the main constituent of hydrotalcite under process conditions.
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- Making monodisperse non aggregated particle proved to be hard but finally both routes are really closing in to the right properties! The large experimental matrix to be tested included different precursors, solvents, temperatures, dispersants, pH etc. In the course of this process one of the particle dispersions was used to coat a tubular porous membrane support. A coating resulted that firstly reduced the permeance as compared to the bare support and secondly yielded a permselectivity (673 K, 1 bar), H_2/CO_2, half of the Knudsen value, evidencing affinity based transport. Particle synthesis and coating procedure clearly have to be optimized but these first results are promising.
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- Catalyst stability tests have been performed in the presence of 20 ppmv of H_2S. The activity of all catalysts is significantly, yet reversibly, affected by H_2S. One of the HTS catalysts turned out to be best under all circumstances and is chosen as the ultimate for the GCEP project. Currently the kinetics on this catalyst is being measured.
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- In a Steam Reforming membrane reactor, CO_2 selective membranes are no option due to the very low concentration and therefore driving force of CO_2. In water gas shift (WGS) reactions or with gas compositions as from a coal gasifier these membranes perform comparable to H_2 selective membranes when used in a membrane reactor. On a system level CO_2 selective membranes should have a flux twice that of the H_2 selective membranes assuming the same surface area (=cost). They suffer from a larger specific electric loss but produce a purer CO_2 stream. Expected future developments

only marginally positively affect CO_2 selective membranes as compared to their H_2 counterpart. Results have submitted to Chemical Engineering Science.
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- ECN is actively participating in the GCEP R&D at the TU Delft. Considering the ALD work for H_2 selective porous membranes of Prof. Joop Schoonman, Dr. Wim Haije is present once a week in the lab in Delft to co-supervise the PhD student and Post Doc working on this project. Considering the Ionic Liquids part of Dr Cor Peters, he has performed permeance measurements on supported ionic liquids. The permselectivity appeared to be half of the absorption selectivity because of the higher diffusivity of H_2. Joint publications on high pressure absorption behavior of various gasses and membrane performance are currently being written.
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- Two bachelor and one master students are or have been involved in the recent GCEP research at ECN.

Future Plans

Task 1 The systems and thermodynamic analyses are finished. We are waiting for the referees report on the submitted paper.

Task 3 Developments are promising but in an early stage. Particle synthesis and dispersion has to be optimized, coating recipes tuned to this material and the pore size distribution of the support reduced in both width and median value.

Task 4 The kinetics measurements will be finalized, the kinetic model described and all catalysis results published in a peer reviewed journal.

Task 5 See Task 1.

Publications
1. Haije, W.G. Schoonman, J., Peters, C., Advanced Membrane Reactors in Energy Systems Development of novel membranes for membrane reactors, presentation at the annual GCEP symposium at Stanford university, October 2007
2. Feuillade, V.C., Haije, W.G., CO_2 selective membranes for carbon capture in water-gas-shift reactions, presentation and proceedings at The Fourth Trondheim Conference on CO_2 Capture, Transport and Storage, Trondheim, October 2007
3. Feuillade, V.C., Haije, W.G., CO_2 selective membranes for carbon capture in water-gas-shift reactions, presentation and proceedings at the American Institute of Chemical Engineers (AIChE) annual meeting, Salt Lake City, November 2007
4. Haije, W.G., Materials science as a basis for future technologies for CO_2 Capture and storage. Presentation at a meeting of the Chemical Dispute of Leiden University (CDL), Leiden, February 2008
5. Stoitsas, K., Tran, Y., Haije, W.G., Schoonman, J., Synthesis, characterization and separation potential for H_2/CO_2 mixtures of primary Alumina and Silica membranes (Before the modification with Atomic Layer Deposition). Presentation at the Annual meeting of the Dutch Science Foundation, Chemical Sciences: Solid State Chemistry and Materials Science, Lunteren, April 2008

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1. Bredesen, R., Jordal, K., Bolland, O., High temperature membranes in power generation with CO_2 capture, Chemical Engineering and processing, 43, 1129-1158, 2004

2. Lowe, C., CO_2 capture Project: Pre-combustion technology Overview. Third Annual conference on Carbon Capture and sequestration, May 3- 6, 2004, Alexandria, Virginia USA

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