II.I.6 Robust Low-Cost Water-Gas Shift Membrane Reactor for High-Purity Hydrogen Production from Coal-Derived Syngas

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Contract Number: DE-FC26-05NT42452

Start Date: May 20, 2005
Projected End Date: May 31, 2007

Objectives

- Develop a water-gas shift (WGS) membrane (Figure 1) that replaces multiple process units with a single catalytic membrane reactor, has high process efficiency realized by improving hydrogen yield at low steam to carbon rations, and produces a high-pressure CO_2–rich stream potentially suitable for sequestration.
- Develop a lower cost, robust WGS membrane reactor that can be used to process coal-derived syngas for the production of high-purity hydrogen.
- Develop and demonstrate a contaminant-tolerant, highly active WGS catalyst.
- Develop and demonstrate a selected Pd/Cu coated Ta membrane with improved durability.
- Construct and demonstrate a bench-scale WGS membrane reactor.
- Demonstrate the scalability of the technology by constructing a 500 L hydrogen/hr production capacity unit.
- Perform a study on the economic feasibility of the WGS membrane reactor.
- Analyze cost benefits of the demonstrated WGS membrane reactor technology.

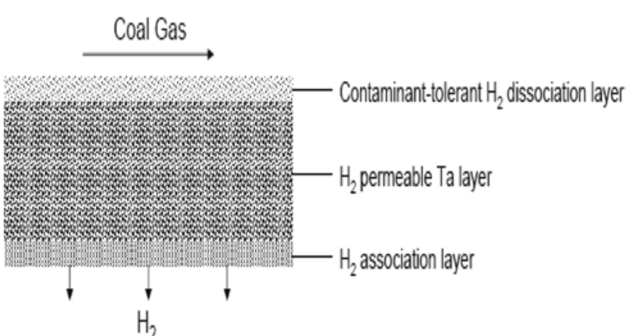

FIGURE 1. Membrane Design

Introduction

There exists a need to develop a lower cost, robust WGS membrane reactor that can be used to process coal-derived syngas for the production of high-purity hydrogen. The required characteristics of this WGS membrane reactor are a contaminant-tolerant, highly active WGS catalyst and a selective Pd/Cu coated Ta membrane with improved durability. Such a membrane reactor should be constructed and demonstrated at the bench-scale to demonstrate the scalability of the technology, preferably at 500 L hydrogen/hr production capacity. WGS membrane reactors incorporating a highly selective H_2-permeable membrane offer the advantages of: 1) generating more hydrogen in a single reactor, instead of conventional two-stage (high-temperature and low-temperature) shift process, 2) simplifying or completely eliminating downstream hydrogen separation and purification processes, and 3) producing a high-pressure stream of predominantly CO_2 for cost-effective capture and sequestration. However, despite these obvious advantages, H_2 generation from syngas employing WGS membrane reactors has not been commercialized in any significant scale, primarily due to the unavailability of reliable, high-performance and economical membrane reactors and WGS catalysts. This project will address these technical barrier issues.

Approach

Initial work will be directed towards the development of a contaminant-tolerant, highly active WGS catalyst (MoS_2-based with added modifiers). A suitable Pd/Cu coated Ta membrane, capable of promoting H_2 dissociation/association reactions in the presence of S and Cl, with improved durability, will then be selected for development and demonstration. Both the WGS catalyst and the H_2-selective membrane must be capable of operating at 300-500ºC, 300-500 psig and remain tolerant of high concentrations of H_2S and HCl. Using data from these tests, a bench-scale WGS membrane reactor will then be constructed and demonstrated. Finally, to show that the WGS membrane reactor technology is scalable, a 500 L hydrogen/hr system will be built and an economic feasibility study of the WGS membrane reactor will then be performed.

Accomplishments

- Completed preparation of 10-16 samples of both alumina-supported and unsupported nano-sized Mo_2C and sulfided Mo, MoCo and CoCr catalysts and completed characterization of the catalysts by investigating the structural properties and determining their surface area, pore size, agglomerate size, composition, and crystallinity.
- Completed evaluation of the catalysts prepared in Q1 and compared with commercial high-temperature WGS catalysts for their WGS activity and stability in a high-pressure fixed-bed catalyst testing system. Identified and selected the most active and stable WGS catalysts and the best operating conditions.
- Completed the development of Pd/Cu-coated Ta tubular H_2 membrane elements and studied the use of an electroless plating method to fabricate Pd/Cu-coated Ta membrane tubes with different wall thicknesses.
- Identified contaminant-tolerant WGS catalysts with high activity over a wide temperature range (300-500°C). The catalysts demonstrated excellent durability in the presence of 3,000 ppm H_2S and 350 ppm HCl for over 220 hours (see Table 1).

TABLE 1. Result Summary – WGS Catalyst

Performance Criteria	Current Status	Targets		This Work
		2010	2015	
Catalyst Form	Pellets	Advanced configurations – TBD		Pellets
Active Metal	Cu/Zn or Fe/Cr or Co/Mo	Advanced configurations – TBD		Mo
Feed Temperature (°C)	200-300	>250	>400	>250
Feed Pressure (psia)	450-1150	>450	>750	415
Approach to Equilibrium (°C)	8-10	<6	<4	<4
Min. H_2O/CO Ratio	2.6	<2.6	<2	<2
Sulfur Tolerance (ppm_v)	varies	>20	>100	3000
COS Conversion	varies	Partial	Total	-
Chloride Tolerance (ppm_v)	varies	>3	>100	350
Durability (y)	3-7	>7	>10	-
Catalyst Cost ($/lb)	~5	<5	<5	-

- Identified dense metal membranes with high H_2 permeability and selectivity. The membranes maintained high permeability in the presence of 2,000 ppm H_2S and 33% H_2O.

Future Directions

- Complete characterization and testing for H_2 separation (see Table 2) in order to identify and select the most stable and efficient membranes and associated membrane preparation parameters for building a WGS reactor and scale-up.

TABLE 2. Result Summary – Hydrogen Separation

Performance Criteria	Current Status			Targets			This Work
	Microporous	Cermet	Dense Ceramic	2007	2010	2015	
Flux (scfh/ft²)	20-100	~300	2	100	200	300	20
Temperature (°C)	300-600	300-400	900	400-700	300-600	250-500	350-550
S Tolerance (ppm_v)	Yes	~20	-	-	20	>100	2000
Cost ($/ft²)	150-200	<200	-	150	100	<100	-
WGS Activity	No	-	-	Yes	Yes	Yes	Yes
ΔP Capability (psig)	100	1000	-	100	400	800	400
CO Tolerance	Yes	Yes	-	Yes	Yes	Yes	-
H_2 Purity (%)	90-98	>99.999	-	95	99.5	99.99	>99.9
Durability (y)	-	0.9	-	1	3	5	-

- Quantify performance and stability of membrane in contaminant-laden syngas.
- Examine membrane microstructure in order to relate permeability to structure and synthetic parameters.
- Fabricate and demonstrate integrated WGS membrane reactor.
- Conduct cost analysis.