II.D.5 The Integration of a Structural Water-Gas Shift Catalyst with a Vanadium Alloy Hydrogen Transport Device

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Objectives

- Develop structural water-gas shift (WGS) catalysts capable of withstanding compressive forces.
- Select vanadium (V)-based alloy hydrogen separation membranes for fabrication of devices by brazing.
- Integrate the WGS catalyst and metallic membranes and testing the integrated device under gasifier conditions.
- Fabricate a modular WGS/membrane integrated device capable of producing 10,000 liters/day of hydrogen from coal-derived synthesis gas (syngas).
- Complete testing of scaled integrated membrane devices based on performance data for testing under coal gasification.
- Develop and test WGS catalyst-membrane modular devices capable of being commercialized.

Technical Barriers

This project addressed the following technical barriers from the Production section of the Hydrogen, Fuel Cells, and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(K) Durability
(P) Flux
(Q) Testing and Analysis

Technical Targets

The project contains three separate and important investigations to aid membrane scale-up and integration. Project targets were to meet the DOE goals for hydrogen separation membranes while completing these technical objectives:

- Develop ceramic-based WGS catalysts appropriate for inclusion in pressurized systems undergoing pressure and thermal cycling.
- Develop bonding practices for sealing vanadium alloy membranes to structural alloy components for manufacturability.
- Design integrated systems suitable for scaling to large structures containing monolithic WGS catalysts and metallic vanadium membranes.

TABLE 1. Progress toward Meeting Technical Targets for Hydrogen Separation Membranes

Goal	2010 DOE Target	Project 2009 Estimates
Membrane flux	250 scfh/ft^2	100 scfh/ft^2
Selectivity	99.99	99.999
Pressure	400 psi	400 psi
Recovery	80%	60%
Cost	\$1,000/ft^2	\$600/ft^2

Accomplishments

This project is 95% complete, and the final report is currently being drafted. Two different viable integrated WGS/vanadium membrane device designs were fabricated that should meet scalability issues and performance criteria.

The focus of the chemistry of the WGS catalyst has been on iron (Fe)-aluminum (Al)-chromium (Cr)-copper (Cu)-cerium (Ce)-based systems, including:

- Tested catalysts by impregnation into porous mullite substrates and cordierite monoliths.
- Highest activity and stability have been shown for 75Fe-15Al-8Cr-2Cu.
- Among Fe-Cr-Cu-Ce-oxygen (O) catalysts, those with 4 wt% ceria are the most active and stable for WGS.
- Producing high surface area monoliths of this catalyst series may be problematic due to sintering at higher operational temperatures.
- Obtained and tested multiple vanadium alloys for brazing performance with Cu.
- Developed guidelines based on the brazing tests and analysis of the literature to anticipate the performance of vanadium alloys with respect to hydrogen transport and fabricability based on alloying elements.
- Elements that are potentially positive to both hydrogen transport performance and brazing performance include Ce, Cu, Fe, manganese (Mn), molybdenum (Mo), nickel (Ni), and zinc (Zn).
- Additional alloying elements may be sufficiently advantageous to transport characteristics to overcome their detrimental effect on brazing.
- Brazing results for vanadium and structural alloys, including mild steel, 304 stainless steel, and 9Cr 1Mo steel, were generally excellent.
- Among Fe-Cr-Cu-Ce-O catalysts, those with 4 wt% ceria are the most active and stable for WGS.
- Produced a physical model with three layers of vanadium foil (2.25-inch diameter), and 304 stainless steel, capable of being used as an integrated device (Figure 1).

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Introduction

This project responds to a requirement for a system that combines WGS technology with separation technology for coal-derived syngas. The justification of such a system would be improved efficiency and lowering cost for hydrogen production. By removing hydrogen from the syngas stream, the WGS equilibrium would force more carbon monoxide (CO) to carbon dioxide (CO_2) and maximize the total hydrogen produced. Additional benefit would derive from the reduction in capital cost of the plant due to the removal of one step in the process by integrating WGS with the membrane separation device.

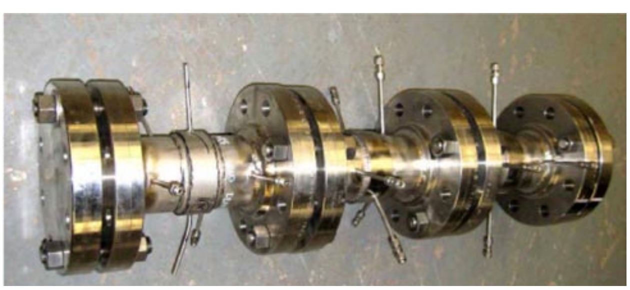

FIGURE 1. Three-Module Integrated WGS/Membrane Device

Approach

The primary goal of this project was to design, fabricate, and test a modular component that integrates the WGS catalyst and the vanadium-based hydrogen selective membrane capable of producing 10,000 liters of hydrogen per day. Modular and integrated WGS/vanadium membrane devices capable of producing hydrogen from coal-derived syngas will be fabricated and tested.

The goal of testing of the scale-up device was to ensure long-term stability of the membrane separation assembly. Short- and long-term performance tests were conducted in the WRI fluidized bed gasifier. This 35 lbs/hr steam/oxygen blown gasifier operates with western coals to produce 175 scfh of hydrogen in a syngas mixture. Additional tests were conducted in a second gasifier producing an alternate range of gas composition and conditions.

Some economic analysis was conducted and data was collected based on predicted cost of manufacturing the scaled membrane unit and the performance data recording hydrogen shift and hydrogen separation. This data is being used to calculate the predicted capital cost of installation and operation of the integrated unit in a commercial facility on a per unit of hydrogen basis.

Results

Significant progress has been made with two different integrated devices. The first device, fabricated with the assistance of Chart Energy and Chemicals, Inc used flat circular membranes of vanadium-palladium alloy supported by porous stainless steel structures (see Figure 1). Each module contained a section of monolithic WGS catalyst and two 4.5-inch diameter membranes. Four modules were required to provide sufficient surface area to supply 10,000 liters/day of hydrogen from a coal gasification source. With the multiple modules, there was some flexibility in the operation of the device to arrange individual pairs of membranes in series or in parallel. Scale-up to larger devices would include both larger diameter membranes and more modules. The largest part of each module was the high-pressure flanges due to the 600-psig application. Permanent fittings would eliminate these flanges and reduce total volume of each module.

The second scale-up unit was based on a "disc and doughnut" design produced by R. Buxbaum of REB Research and Consulting (Figures 2 and 3). In this design, the vanadium alloy membranes were joined in pairs into a structural component capable of withstanding differential pressure. Under a subcontract from WRI, Dr. Buxbaum prepared an integrated, two-membrane unit to contain the monolithic catalyst component. Scale-up of this stackable unit appears straightforward up to a certain number of membranes per module. In this design, all membranes were operated in series. The two-membrane unit were completed and tested in a coal gasifier. Initial pressure tests with helium indicated that the membrane system was leak-free. The first separation tests were conducted in pure hydrogen at 100 psi before moving to the gasifier.

WGS catalyst development was completed with the addition of ceria to the conventional Fe-Cr-Cu oxide catalysts. Since the series of catalysts with small amounts of ceria (2 wt% to 8 wt%) were not as effective as the initial ~4 wt% ceria catalyst, apparently due to slight differences in the preparation technique, adjustments were made to the synthesis procedure to attempt to duplicate the original ceria-containing catalyst and to determine if more active and stable catalysts could be produced. WGS catalysts prepared with low levels of ceria was comparable to the improved 15% alumina containing catalysts developed earlier in the project. Ceramic monoliths were developed containing 15% alumina WGS catalyst and incorporation into the two integrated devices described previously. These experiments used a honeycomb mullite structure with multiple coast of the alumina containing WGS catalyst.

FIGURE 2. The Scale-Up Unit Based on a "Disc and Doughnut" Design

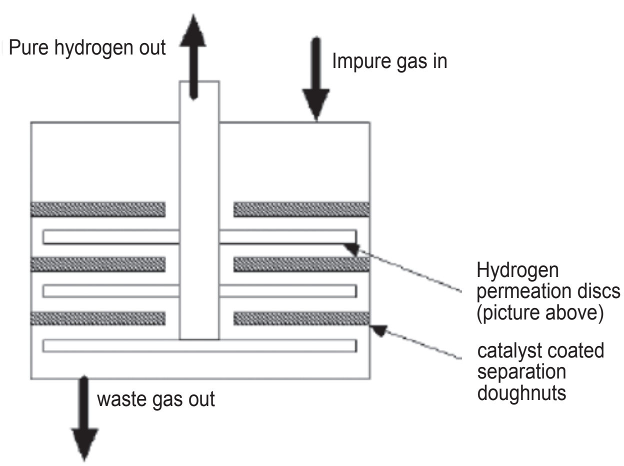

FIGURE 3. Disc and Doughnut Schematic

Conclusions and Future Directions

- Catalysts have been tested by impregnation into porous mullite substrates.
- Highest WGS activity and stability has been shown for 75Fe-15Al-8Cr-2Cu.
- Small additions of cerium oxide (CeO_2) up to 4% look promising.
- The best catalysts were prepared on mullite monoliths and incorporation into integrated devices.
- Two integrated WGS/membrane devices capable of 10,000 liters/day of hydrogen separation were fabricated and were tested for hydrogen production.
- After preliminary testing under pure hydrogen, both integrated devices were tested on the WRI fluidized bed coal gasifier.

Future work will focus on:

- Commercialization of the WGS catalyst monolith will be pursued with the assistance of a catalyst manufacturer.
- Improvement of vanadium alloy membrane production for large-scale manufacturing.
- Design and fabrication of the 10x assembly based on the economic and performance data for testing under coal gasification conditions.

FY 2009 Publications/Presentations

1. DOE Annual Hydrogen Review Meeting, Washington, D.C., May, 2009; T. Barton.

2. PhD Thesis, Metal Oxide Catalysts for Green Applications, T. Popa, Summer 2009.