Thermocatalytic CO_2-free Production of Hydrogen from Hydrocarbon Fuels

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Objectives

- Develop an economically viable process for centralized and distributed production of hydrogen from hydrocarbons with minimal CO_2 emissions
- Improve the catalytic activity of carbon catalysts and process sustainability
- Increase the yield of high-value carbon products and reduce the cost of hydrogen production

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Fuel Processor Capital Costs
- D. Carbon Dioxide Emissions

Approach

- Produce hydrogen-rich gas via thermocatalytic decomposition of hydrocarbons utilizing a part of the carbon product as a catalyst for the process
- Improve the catalyst activity and process efficiency by continuous activation of carbon particulates in presence of activating agents
- Design, fabricate and test 3-kW_{th} thermocatalytic reactor for CO/CO_2-free production of hydrogen-rich gas and a carbon product from hydrocarbon fuels

Accomplishments

- Demonstrated that the catalyst activity and the process sustainability could be improved by activation of carbon particulates in the presence of small amounts of steam and/or CO_2
- Determined the effect of impurities potentially present in commercial hydrocarbon feedstocks (e.g., H_2S, N_2, moisture, high hydrocarbons) on the process efficiency and the catalyst activity and stability
- Demonstrated the efficient removal of small amounts of CO/CO_2 and olefins from the hydrogen gas via catalytic hydrogenation processes
- Designed, fabricated and tested 3-kW_{th} thermocatalytic reactor using commercial hydrocarbon fuels (pipeline natural gas, commercial propane)
- Conducted reactor modeling and scaling-up studies (in cooperation with industry)
- Evaluated potential markets and new application areas for carbon products

Future Directions

- Optimize the performance of a pyrolytic reformer for distributed production of hydrogen gas with the CO and H_2S content below 10 ppm using commercial hydrocarbon fuels
- Increase the yield of high-value carbon products (>$0.3 per kg) and reduce the cost of hydrogen production (for distributed production applications)
- Conduct system integration studies to increase power density of the pyrolytic reformer and reduce its capital cost

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Introduction

Conventional hydrogen production processes (e.g., steam methane reforming) produce large amounts of CO_2 emissions. One alternative to conventional processes is a single-step thermocatalytic decomposition (TCD) (or pyrolysis) of natural gas (NG) or other hydrocarbon fuels into hydrogen and carbon:

$$CH_4 \rightarrow C + 2H_2 \quad \Delta H^o = 75.6 \text{ kJ/mol } (CH_4)$$

Due to the absence of oxidants (e.g., H_2O and/or O_2), no carbon oxides are formed during the process, thus obviating the need for water gas shift and CO_2 removal stages, which significantly simplifies the process. Pure carbon is produced as a valuable byproduct that can be marketed, thus reducing hydrogen production cost. The technical goals of this research effort are to (1) determine efficient carbon catalysts for methane decomposition process; (2) conduct process engineering development studies, including reactor modeling and scale-up; and (3) characterize carbon byproducts of the process and evaluate their market value.

Approach

The approach is based on TCD of hydrocarbon fuels over high surface area carbon catalysts. The important feature of the process is that the reaction is catalyzed by carbon particulates produced in the process (no external catalyst is required, except for the start-up operation). Carbon catalyst particles circulate between a reactor and a heater, both operating in a fluidized bed regime (similar to industrial fluid coking process). Carbon catalysts exhibit high temperature and sulfur resistance. Due to low endothermicity of the process, the overall CO_2 emissions from the process could be drastically reduced (compared to conventional processes).

Results

The effect of carbon catalyst activation (with small amounts of steam) on the rate of methane decomposition was determined. Figure 1 illustrates the effect of steam treatment of carbon catalyst on its catalytic activity toward methane decomposition. It is evident that the steam treatment of carbon particles resulted in a drastic increase in both catalyst surface area and methane decomposition rate.

It was determined that the presence of small amounts of impurities (H_2S/CH_3SH, CO_2, nitrogen and moisture) potentially present in industrial hydrocarbon fuels is not detrimental to the catalyst activity and process efficiency. These impurities may result in contamination of hydrogen with trace

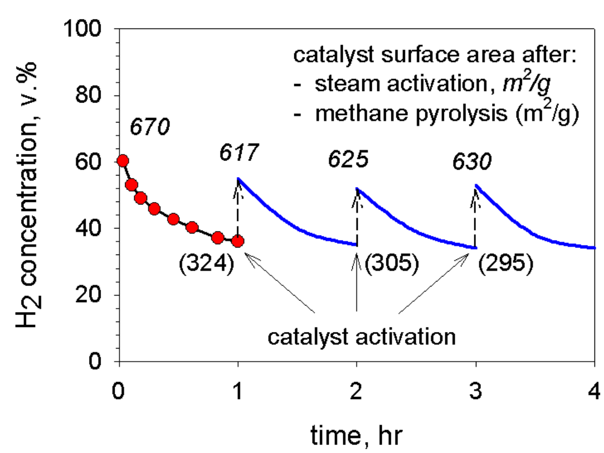

Figure 1. TCD of Methane over Carbon Catalyst in Cyclic Pyrolysis-Activation Process. $T_{pyr.}$=850^o, $T_{act.}$=900^{o}C (*x*-axis shows pyrolysis time only)

amounts of CO and H_2S that can be efficiently removed from hydrogen gas via catalytic methanation and ZnO scrubbing techniques.

A 3-kW_{th} thermocatalytic reactor for production of hydrogen-rich gas and carbon from industrial-grade feedstocks (pipeline NG and commercial propane) was fabricated and tested (Figure 2). The average concentration of hydrogen in the pyrolysis gas was 45-72 v.% (the balance, predominantly methane), depending on the feedstock and temperature. After methanation, CO/CO_2 concentrations in H_2 dropped to <10 ppm level.

The studies on modeling and scale-up of the fluidized bed reactor were conducted (in cooperation with Reaction Engineering International—REI). A three-phase model to describe bubbling fluidized bed reactor containing carbon particles was developed (Figure 3). The model predictions were in reasonable agreement with the experimental measurements.

Collaborative efforts with industry (MER Corporation, Universal Oil Products—UOP) and national labs (Lawrence Livermore National Laboratory—LLNL) in evaluating markets and identifying potential application areas for carbon products were conducted. The market for carbon products was estimated at 4-5 million ton/year level with carbon selling price at approximately $300/ton.

Figure 2. Experimental Set-up with 3-kW_{th} Thermocatalytic Reactor

Conclusions

It was demonstrated that the catalyst activity toward methane decomposition and process sustainability could be significantly improved via continuous activation of carbon catalysts in the presence of small amounts of steam (the activation occurs outside the pyrolyzer). The process was designed where carbon particulates circulate between a hydrocarbon pyrolyzer and a catalyst heater, both operating in fluidized bed regime (similar to industrial fluid coking process). The impurities (CO_2, H_2S/CH_3SH, moisture) present in commercial hydrocarbon fuels are not detrimental to catalyst activity and process efficiency, and could be efficiently removed from hydrogen gas. A 3-kW_{th} thermocatalytic reactor for CO/CO_2-free production of hydrogen-rich gas was designed, fabricated and tested using pipeline NG and commercial propane as feedstocks. The market for carbon products was estimated at 4-5 million ton/year level with carbon selling price at approximately $300/ton. FSEC participated in several collaborative research efforts with industry, national labs and universities (MER

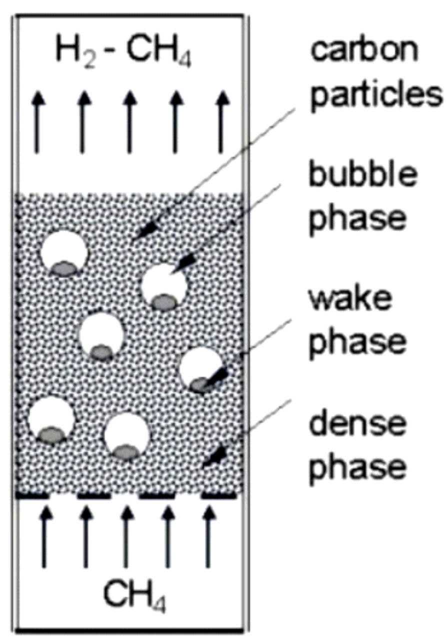

Figure 3. Modeling of Three-Phase Bubbling Fluidized Bed Reactor Containing Carbon Particles

Corporation, REI, National Renewable Energy Laboratory, UOP, LLNL, Florida Institute of Technology).

FY 2003 Publications/Presentations

1. Muradov, N. "Emission-free Fuel Reformers for Mobile and Portable Fuel Cell Applications", *Journal of Power Sources*, v.118, 1-2, 320-324 (2003)
2. Muradov, N. "On-site Production of Hydrogen from Hydrocarbon Fuels with Minimal Greenhouse Gas Emissions", *Symposium: Hydrogen Energy for 21st Century, Amer. Chem. Soc. Meeting*, New Orleans, 2003
3. Muradov, N. "Catalytic Conditioning of Sulfurous Hydrocarbon Fuels for Fuel Cell Applications", *Symposium: Fuel Clean-up Considerations for Fuel Cells, Amer. Chem. Soc. Meeting*, New Orleans, 2003
4. Muradov, N., T-Raissi, A. "Hydrogen Production via Catalytic Reformation of Low-quality Methane Containing Feedstocks", *HYPOTHESIS*, Italy, 2003
5. Muradov, N., Smith, F. "Thermocatalytic Hydrogen Production from Natural Gas with Drastically Reduced CO_2 Emissions", *HYPOTHESIS*, Italy, 2003
6. Muradov, N. and Schwitter, A. "Formation of Conical Carbon Structures on Vapor-grown Carbon Filaments", *Nano Letters*, v.2, 673 (2002)
7. Muradov, N. "Low-emission Fuel Reformers for Fuel Cell Applications", *14th World Hydrogen Energy Conference*, Montreal, Canada, 2002
8. Muradov, N. "Emission-free Fuel Reformers for Fuel Cell Applications", *Fuel Cells, Science and Technology 2002*, Amsterdam, Netherlands, 2002
9. Muradov, N. "Thermocatalytic CO_2-free Production of Hydrogen from Hydrocarbon Fuels", *DOE Annual Hydrogen Prog. Rev. Meeting*, Golden, 2002

Special Recognitions & Awards/Patents Issued

1. University of Central Florida Research Incentive Award, 2003
2. Muradov, N. *U.S. Patent Application No. 60/194,828* "Thermocatalytic Process for CO_2-free Production of Hydrogen and Carbon from Hydrocarbons" (2002)
3. Linkous, C., Muradov, N. *U.S. Patent No. 6,572,829 B2* "Closed Cycle Photocatalytic Process for Decomposition of Hydrogen Sulfide to its Constituent Elements" (2003)