IV.F.7 Water Gas Shift Catalysis

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Objectives

- To develop advanced water gas shift (WGS) catalysts that meet DOE performance requirements for fuel processing catalysts.
- Improve our understanding of the WGS reaction and catalyst deactivation mechanisms.
- Define operating parameters (e.g., steam-to-carbon ratio, temperature, gas-hourly space velocity [GHSV], and catalyst structure) to maximize catalyst performance and lifetime.

Technical Barriers

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

- I.   Fuel Processor Startup/Transient Operation
- L.   Hydrogen Purification/Carbon Monoxide Cleanup
- M. Fuel Processor System Integration and Efficiency

Approach

- Identify metal and metal oxide combinations that promote the elementary reaction steps (e.g., CO oxidation, H_2O dissociation, formate/formyl decomposition) involved in the WGS reaction or improve catalyst stability.
- Synthesize materials based on these metal-metal oxide combinations.
- Evaluate the WGS activity of these materials in a microreactor system.
- Use characterization techniques, such as BET surface area measurement, CO chemisorption, temperature-programmed reduction (TPR), X-ray absorption spectroscopy (XAS), and transmission electron microscopy (TEM), to identify factors needed to improve catalytic activity or to reduce catalyst deactivation.
- Develop kinetic and transport models to aid in the design of fuel processors and to define the operating parameters required to optimize catalyst performance and lifetime.

Accomplishments

- Demonstrated that the addition of rhenium increases the WGS activity of Pt-ceria catalysts by a factor of ~3 on a per-gram-of-Pt basis.
- Demonstrated that there is minimal difference in the performance of the Pt-Re catalyst supported on a metal foam compared with the Pt-Re catalyst supported on a ceramic monolith. The monolith is the preferred support because of lower cost.

- Developed a kinetic rate equation and a reactor simulation model to predict the performance of a WGS reactor that uses the Pt-Re catalyst. Showed that the Pt-Re catalyst could meet the DOE GHSV target of $30,000 \, h^{-1}$.
- Optimized the synthesis procedure for a base metal catalyst that led to a more active and stable catalyst.

Future Directions

- Optimize formulation and synthesis procedures to increase WGS activity and selectivity of base metal and precious metal-base metal catalysts. Address sulfur poisoning of these catalysts.
- Conduct long-term testing to evaluate catalyst durability. Identify approaches to improve catalyst durability.
- Conduct characterization and mechanistic studies aimed at improving catalyst performance and improving our understanding of reaction mechanisms.


Introduction

Steam reforming, partial oxidation, or autothermal reforming of hydrocarbon fuels (natural gas, gasoline, diesel, etc.) produces a H_2-rich product gas, termed reformate, that contains 5-20% CO depending on the steam-to-carbon and air-to-fuel ratios in the reformer inlet. For use in a polymer electrolyte fuel cell, additional processing is required to reduce the CO content to <10 ppm because of the poisoning effect of CO on the Pt-based anode catalyst. The WGS reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$) is used in most fuel processing schemes to convert the bulk of the CO to CO_2 and, as an added benefit, to produce one additional mole of H_2 per mole of CO converted. Since the equilibrium constant for the WGS reaction increases with decreasing temperature, lower reaction temperatures favor higher CO conversion. However, the reaction rate also decreases as the reaction temperature decreases, leading to a larger reactor volume. A critical aspect in designing the WGS reactor for use in automotive on-board fuel processors (and in stationary applications) is the trade-off between achieving a high CO conversion and minimizing the reactor volume.

Two commercial catalysts—an iron-chromium oxide catalyst, which is active at 300-450°C, and a copper-zinc oxide catalyst, which is active at 180-270°C—are used in the industrial production of H_2 via steam reforming of natural gas. The commercial catalysts are designed to operate at a GHSV of 3,000-6,000 h^{-1}, well below the DOE target of 30,000 h^{-1}. These catalysts do not perform well when exposed to

rapid startups and shutdowns, condensing and vaporizing steam, and numerous redox cycles, as is required of WGS catalysts used in fuel processors for automotive and stationary fuel cell applications. The goal of this project is to develop new WGS catalysts to meet the DOE performance, durability, and cost targets and address the operational drawbacks of using commercial WGS catalysts in fuel cell systems.

Approach

Metal and metal oxide combinations are identified that promote one or more elementary reactions, e.g., CO oxidation, H_2O dissociation, and formate/formyl decomposition, which collectively make up the WGS reaction. Catalysts based on these metal-metal oxide combinations are synthesized using a number of different techniques, including incipient wetness and deposition-coprecipitation. These catalysts are evaluated for WGS activity in a microreactor system over a temperature range of 200-500°C using gas compositions representative of the reformate produced by an autothermal reformer. Samples of the catalysts are examined before and after testing using a variety of characterization techniques, e.g., N_2 adsorption, CO chemisorption, TPR, XAS, and TEM, to identify factors needed to improve WGS activity and minimize catalyst deactivation. Reaction rates are measured, and kinetic models are developed for the most active and stable catalysts. The kinetic models are then incorporated with heat and mass transport models to aid in the design of the fuel processor and to define the operating parameters that optimize catalyst performance and lifetime.
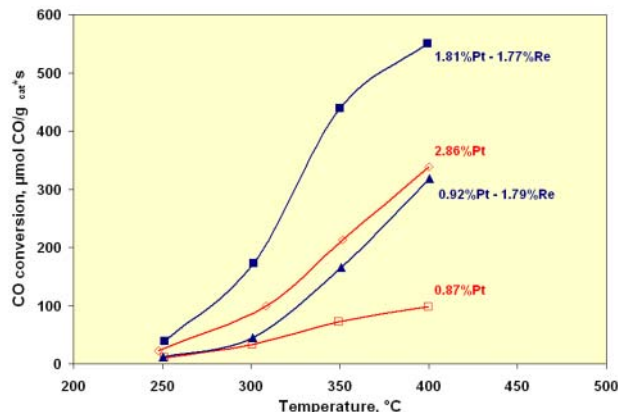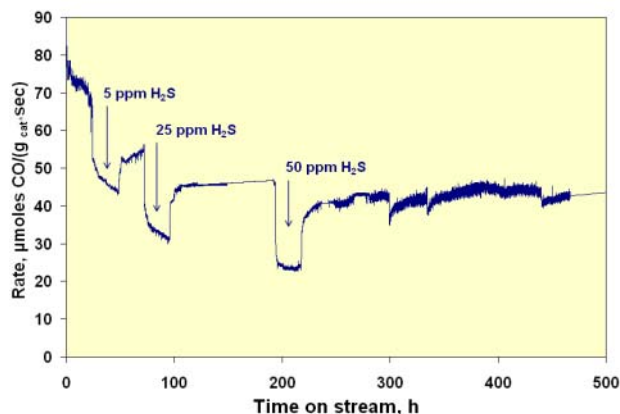
Figure 1. Comparison of the WGS Activity of Pt and Pt-Re Catalysts at Various Pt Loadings

Figure 2. Long-Term Performance of Pt-Re Catalyst

Results

We have shown that catalysts consisting of Pt supported on either zirconia- or gadolinium-doped ceria exhibit high WGS activity and overcome many of the problems associated with using commercial catalysts in fuel processors designed for on-board automotive applications.[1] However, the high cost of Pt makes it very difficult to meet the DOE targets for catalyst cost ($1/kW$_e$) and catalyst activity (GHSV of 30,000 h^{-1}). Our research has focused on identifying a promoter that would allow us to decrease the Pt loading without sacrificing performance. The addition of Re has been shown to significantly improve the WGS activity of Pt catalysts, as shown in Figure 1. The WGS activity of Re was negligible under these reaction conditions. A theoretical study suggests that Re enhances the rate of dissociation of water, which is one of the elementary steps in the WGS reaction mechanism.[2] In our work, the results from TPR and XAS suggest that Re stabilizes Pt, inhibiting it from sintering under reaction conditions. Loss of metal surface area due to sintering has been identified as one reason for loss of activity for ceria-supported precious metal catalysts.[3]

A 500-hour test conducted to evaluate the stability of the Pt-Re catalyst showed that the catalyst lost about 50% of its initial activity during the first 250 hours but then stabilized, with no further loss in activity over the next 250 hours, as shown in Figure 2. Characterization studies are in progress to determine

the reasons for the initial deactivation. During the test, the catalyst was exposed to reformate containing 5, 25, or 50 ppm of H_2S. The catalyst was poisoned by H_2S at all three concentrations, but the activity recovered almost completely when the H_2S was removed from the reformate. The ability of the Pt-Re catalyst to recover its activity when the H_2S is removed suggests that the absorption of sulfur on this catalyst is reversible.

The reaction kinetics data were used to develop a power-law rate equation for the WGS on the Pt-Re catalyst. The reaction orders were zero for CO, 0.40 for H_2O, –0.58 for H_2, and –0.17 for CO_2. The activation energy, E_a, was 16 kcal/mol. A reactor model based on these kinetic data was used to determine the steam-to-carbon ratio and the inlet temperature needed to reduce the CO concentration to 1% in a single-stage adiabatic reactor operating at a GHSV of 30,000h^{-1}. Based on the initial activity of the Pt-Re catalyst, a steam-to-carbon ratio of >3 and a reactor inlet temperature of >300°C are required, as shown in Figure 3. Assuming a 50% loss in activity over time, the Pt-Re catalyst can still reduce the CO concentration to 1% if the steam-to-carbon ratio is >3.7 and the reactor inlet temperature is >340°C.

For on-board automotive applications, it is preferred that the catalyst be dispersed on a structured support, such as a metal form or a ceramic monolith, to prevent degradation due to vibration-induced grinding. The results of both experimental and modeling studies showed that there is little difference
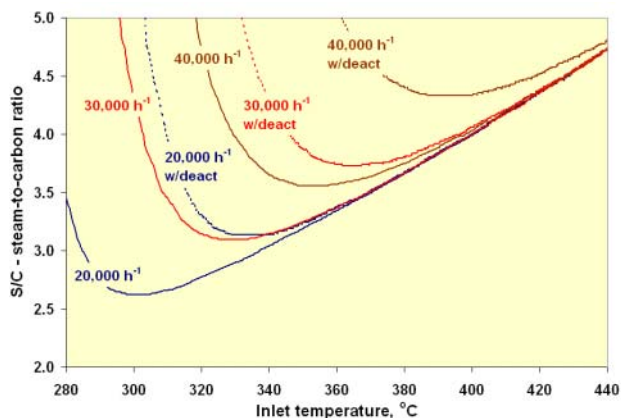
Figure 3. Modeling Study Showing the Reactor Operating Parameters Needed to Reduce the CO Concentration to 1%
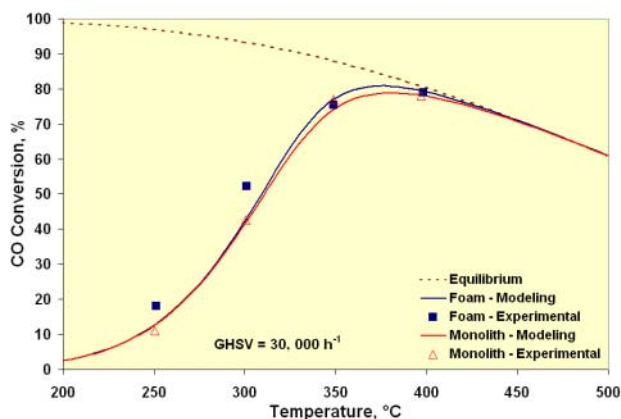
Figure 4. Comparison of the Performance of the Pt-Re Catalyst Supported on a Metal Foam and on a 600-cpi Ceramic Monolith

in performance, whether the catalyst is supported on a metal foam or on a 600-cpi ceramic monolith (see Figure 4). The monolith is preferred because it is significantly less expensive than the foam.

In addition to our work on Pt-ceria catalysts, we are also working on developing less-costly base metal catalysts because it is still challenging for the Pt-Re catalyst to meet the cost target. Initially, we focused on Cu-containing catalysts, but difficulty in stabilizing Cu at high temperature has led us to focus on other base metals. We have identified one base metal that shows promise. For this metal, our studies have shown that the rate of CO conversion depends
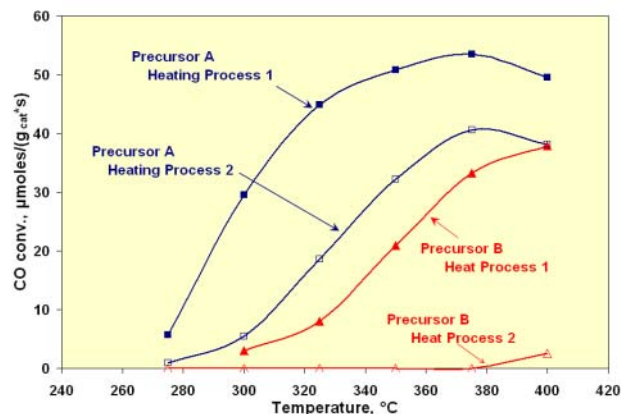
Figure 5. Effect of Precursor and Heating Process on the WGS Activity of Base Metal Catalyst

on the nature of the precursor (i.e., chloride, nitrate, etc.) and the heating process used to prepare the catalyst, as shown in Figure 5. TPR studies suggest that heating processes that promote the interaction of the metal with the support to form complexes, such as spinels, result in less active catalysts. Unlike the Pt-based catalysts, the base metal catalyst promotes CO methanation ($CO + 3H_2 \leftrightarrow CH_4 + H_2O$), with about 20% of the CO converted being converted to CH_4. The addition of a small amount of precious metal to the base metal has been shown to significantly increase the catalyst's activity at >350°C. Work is focusing on optimizing the formulations of the base metal and precious metal-base metal combinations to improve their activity and reduce CO methanation.

Conclusions

- Addition of Re significantly improves the activity of Pt-ceria catalysts.
- There is little difference in the performance of the Pt-Re catalyst when supported on a metal foam or on a 600-cpi ceramic monolith.
- Modeling studies suggest that the Pt-Re catalyst can meet the DOE target for GHSV; however, meeting the cost target may still be challenging.
- The WGS activity of the base metal catalyst depends on the precursor and heat treatment process used to prepare the catalyst.

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