VII.F Fuel Processing

VII.F.1 Water-Gas Shift Catalysis

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Start Date: FY 1998
Projected End Date: Project continuation and direction determined annually by DOE

Objectives

- Develop advanced water-gas shift catalysts which, in conjunction with other technology developments, would enable stationary fuel processors to meet the DOE targets for durability, cost, and CO content in product stream.
- Define operating parameters [e.g., steam-to-carbon ratio, temperature, gas hourly space velocity (GHSV), and catalyst structure] to maximize catalyst performance and lifetime.
- Improve our understanding of the water-gas shift (WGS) reaction and catalyst deactivation mechanisms.

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:

- A. Durability
- B. Cost
- F. Fuel Cell Power System Integration

Technical Targets

This project is developing advanced water-gas shift catalysts that reduce the CO content in reformates produced from natural gas and liquefied petroleum gas (LPG). Catalysts developed under this project will be incorporated into fuel processors being developed for stationary fuel cell systems that meet the following DOE 2010 stationary fuel processor targets:

- Durability: 40,000 h
- Cost: $250/kW$_e$
- CO content in product stream: 1 ppm (steady-state), 25 ppm (transient)

Approach

- Identify metal and metal oxide combinations that promote the elementary reaction steps involved in the WGS reaction (i.e., CO oxidation, H_2O dissociation, formate/formyl decomposition), inhibit undesirable competing reactions (e.g., methanation), or improve catalyst durability.

- Synthesize materials based on these metal-metal oxide combinations.
- Evaluate the performance of these materials in a microreactor system by determining the effect of operating parameters (e.g., steam-to-carbon ratio, temperature, GHSV) on the WGS reaction rate, CO to CO_2 selectivity, and catalyst durability.
- Use characterization techniques [e.g., N_2 adsorption surface area measurement, CO chemisorption, temperature-programmed oxidation (TPO) and reduction (TPR), x-ray absorption spectroscopy (XAS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM)] to identify the factors needed to improve catalytic activity, inhibit competing reactions, or improve catalyst durability.

Accomplishments

- Initiated development of Co and Ru catalysts as a low-cost alternative to Pt catalysts.
- Demonstrated that the CH_4 selectivity exhibited by Co and Ru catalysts could be reduced by adding modifiers, such as Cu or Re, which inhibit selected elemental reaction steps involved in the formation of CH_4. The addition of Re to Ru reduced the CH_4 selectivity by ~60% at 400°C.
- Determined that the addition of Re to Pt catalysts leads to a synergistic effect between Pt and Re that enhances the activity of the Pt catalysts.

Future Directions

- Continue development of modified Co and Ru catalysts, focusing on inhibiting the methanation reaction.
- Conduct molecular modeling studies to better understand the mechanistic pathways of the WGS and methanation reactions and the role of additives in inhibiting the methanation reaction.
- Conduct lifetime testing to evaluate the durability of modified Co and Ru catalysts.

Introduction

Steam reforming (SRM) or autothermal reforming (ATR) of infrastructure fuels (i.e., natural gas, LPG, gasoline, diesel, etc.) produces a H_2-rich fuel gas, termed reformate, that contains 5-20 vol% CO depending on the steam-to-carbon and air-to-fuel ratios in the reformer feed. For use in a polymer electrolyte fuel cell (PEFC), reformate must be further processed to reduce the CO concentration 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.

Two commercial catalysts—an iron-chromium oxide (Fe–Cr) catalyst, which is active at 300–450°C, and a copper-zinc oxide (Cu–Zn) 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 for the operating conditions encountered in industrial H_2 production (i.e., controlled start-ups and shutdowns, steady-state operation, minimal

turndown/turn-up cycles) and do not perform well when exposed to the rapid start-ups and shutdowns, condensing and vaporizing steam, and numerous redox cycles that WGS catalyst will experience during the operating lifetime of a stationary fuel processor–fuel cell system. The goal of this project is to develop advanced WGS catalysts that are more active than the commercial catalysts, address the operational drawbacks of using commercial WGS catalysts in fuel cell systems, and can enable stationary fuel processors to meet the DOE performance, durability, and cost targets.

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. If the metal and metal oxide combination also promotes undesirable competing reactions, such as methanation (CO $+ 3H_2 \leftrightarrow CH_4 + H_2O$), additives are incorporated to inhibit these reactions. Catalysts

based on these metal-metal oxide combinations, including additives, are synthesized using a number of different techniques, including incipient wetness and deposition-coprecipitation. These catalysts are evaluated for WGS activity, CO to CO_2 selectivity, and catalyst lifetime in a microreactor system using gas compositions representative of reformate compositions produced by ATR or SRM reformers over a temperature range of 200-500°C. Samples of the catalysts are examined before and after testing using a variety of characterization techniques, including BET surface area measurement, CO chemisorption, TPR, TPO, XAS, SEM, and TEM. The objective is to identify methods to improve WGS activity, inhibit undesirable competing reactions and improve catalyst durability. Reaction rates are measured and kinetic models are developed for the most active and stable catalysts.

Results

Ru-Co catalysts

We have previously reported on the development of a ceria-supported Pt-Re bimetallic WGS catalyst that exhibits a higher activity and better stability than the commercial Fe-Cr and Cu-Zn catalysts [1]. Because of concerns over the high cost of Pt, we have directed most of our effort in FY 2005 towards developing WGS catalysts that use less expensive metals, such as Co and Ru. These metals were selected because they both have been shown to exhibit higher intrinsic rate for the WGS reaction than Pt in the absence of CO_2 and H_2 [2]. Figure 1 shows that the rate of CO conversion as a function of temperature exhibited by Ru catalysts is comparable to that of our Pt–Re catalyst and much higher than that of the commercial Fe-Cr catalysts.

In addition to the WGS reaction, Co and Ru also catalyze the methanation reaction, however. For these metals, inhibiting the dissociative adsorption of CO to generate carbon [3] or promoting gasification of carbon [4] plays a critical role in inhibiting CH_4 formation. For Ru, additives such as Cu or Re were selected based on their ability to block active sites on the Ru surface that dissociatively adsorb CO or enhance the activation of water, which promotes the gasification of carbon, respectively. Figure 2 shows that the addition of Cu or Re to Ru reduces CH_4
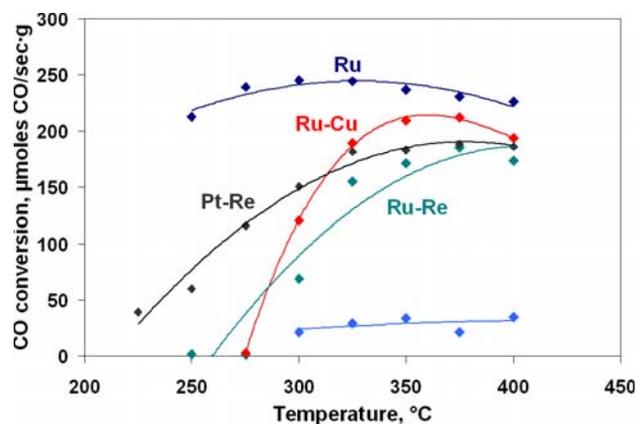

Figure 1. Comparison of the CO Conversion Rate for Selected Modified Ru Catalysts and the Rate for Pt-Re and Fe-Cr Catalysts
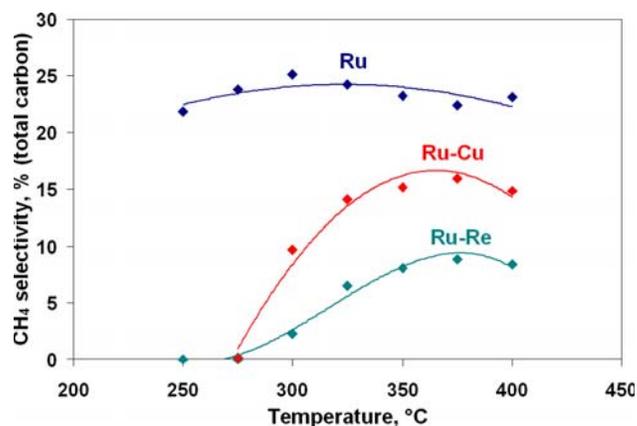

Figure 2. Effect of the Addition of Cu or Re to Ru on CH_4 Selectivity

selectivity; however, the CH_4 yield is still unacceptably high for fuel cell applications. Co catalysts, including unmodified Co and Co modified with additives such as Re, exhibit CO conversion rates similar to those exhibited by the Ru catalysts. However, the CH_4 selectivity exhibited by the Co catalysts (2–6% at 400°C) is lower than that exhibited by the modified Ru catalysts. The effect of modifiers, such as Re, on reducing the CH_4 selectivity exhibited by Co catalysts is not as pronounced as it was on that exhibited by the Ru catalysts.

Pt-Re catalysts

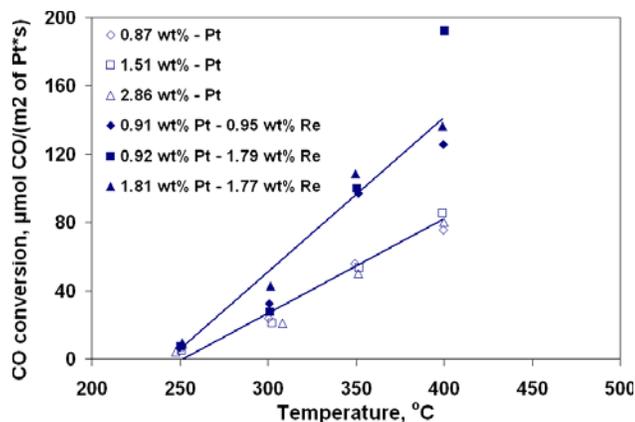We have shown that the addition of Re enhances the WGS activity of ceria-supported Pt WGS

Figure 3. Comparison of the CO Conversion Rate per m^2 of Pt for Pt-Re and Pt Catalysts at Different Pt and Re Loadings

Figure 4. Oxidation State of Re in Pt-Re Catalyst During TPR as Determined by XAS

catalysts [1]. To better understand the role of Re in enhancing the WGS activity of Pt, the effect of Re on the Pt dispersion was measured using CO chemisorption, and the reducibility of Pt and Re was investigated using TPR and XAS.

CO chemisorption measurements showed that the Pt dispersion was higher on the Pt–Re catalysts than on the Pt catalysts at similar Pt weight loadings, suggesting that Re improves the Pt dispersion. Based on the dispersion measurements, the rate of CO conversion per m^2 of exposed Pt was higher on Pt–Re than on Pt catalysts, as shown in Figure 3, indicating that the role of Re in enhancing the WGS reaction is more complicated than simply increasing the Pt dispersion.

Kinetic studies have shown that the activation of water is the rate-determining step for ceria-supported Pt catalysts. A TPR study of ceria-supported Pt-Re and Re catalysts using XAS to monitor the oxidation state of Re as a function of temperature showed that Re is initially present as Re_2O_7 (Re^{7+}) and that it undergoes a reduction to yield a mixture of ReO_3 (Re^{6+}) and ReO_2 (Re^{4+}). For the Pt-Re catalyst, this reduction occurs at ~150°C, as shown in Figure 4. In contrast, for the Re catalyst, this reduction did not occur until ~350°C. A TPR study of ceria-supported Pt-Re and Pt catalysts using XAS to monitor the oxidation state of Pt showed that Pt undergoes a reduction from $Pt^{2+/4+}$ to Pt^0 at temperatures below 150°C on both catalysts. Based on these
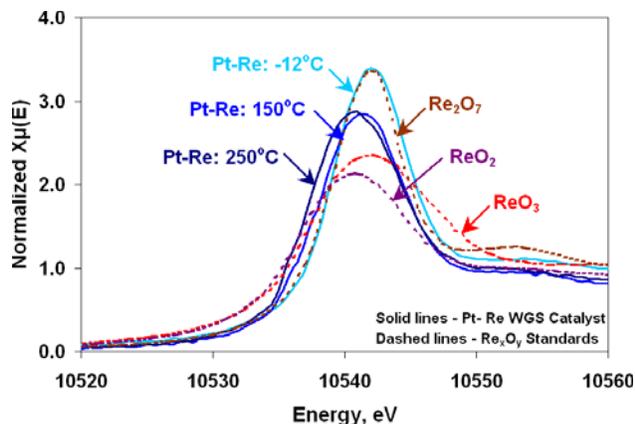
observations, it is suggested that "hydrogen spillover" from Pt^0 may be responsible for promoting the reduction of Re in the Pt-Re catalyst. We hypothesize that the ability of Re to undergo partial reduction may enhance the activation of water on the Pt-Re catalyst, leading to the higher intrinsic activity. TPR studies have shown that oxidized Ru and Co reduce at higher temperatures than oxidized Pt. Because oxidized Ru and Co are more stable than oxidized Pt, the ability of Re to enhance the activity of Ru and Co catalysts will probably be less pronounced.

Conclusions

- Co and Ru are active catalysts for both the WGS and methanation reactions at 200-500°C.

- The addition of modifiers such as Cu, which blocks dissociative adsorption of CO, and Re, which promotes gasification of carbon, reduces the CH_4 selectivity exhibited by Ru catalysts. The addition of modifiers has a less pronounced effect on reducing the CH_4 selectivity exhibited by Co catalysts than it has on the Ru catalysts.

- For ceria-supported Pt catalyst, the addition of Re leads to a synergistic effect between Pt and Re. Re increases the Pt dispersion, and Pt promotes the reduction of Re^{7+} to $Re^{4+/6+}$. We hypothesize that the ability of Re to undergo partial reduction enhances the activation of water on the Pt-Re catalyst, leading to its higher intrinsic activity.

References

1. T. Krause, R. Souleimanova, J. Krebs, and M. Castagnola, "Water-Gas Shift Catalysis," 2004 Annual Progress Report, U.S. DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Program.

2. D.C. Grenoble, M.M. Estadt, and D.F. Ollis, *J. Catal.*, 67 (1981) 90.

3. S.Y. Lai and J.C. Vickerman, *J. Catal.*, 90 (1984) 337.

4. W.Y. Wen, *Catal. Rev. Sci. Eng.*, 22 (1980) 1.

FY 2005 Publications/Presentations

1. "Pt-Re bimetallic supported on CeO_2-ZrO_2 mixed oxides as water-gas shift catalysts," S.Y. Choung, M. Ferrandon and T. Krause, *Catal. Today*, **99** (2005) 257-262.

2. "Catalyst development and engineering considerations for reducing the size of the shift reactor in fuel processors," T. R. Krause, S.Y. Choung, D.D. Papadias, and R. Souleimanova, Presented at the 2004 Fuel Cell Seminar, San Antonio, Texas, November 1-5, 2004.

3. "Effect of doping CeO_2 with Gd_2O_3 or ZrO_2 on the reducibility of Pt and Ce in Pt-CeO_2 water-gas shift catalysts," M.J. Castagnola, M. Ferrandon, A.J. Kropf, and T.R. Krause, Presented at the 2005 Users Meeting for the Advanced Photon Source and the Center for Nanoscale Materials, Argonne, Illinois, May 2-6, 2005.