Water-Gas Shift Catalysis

Sara Yu Choung (Primary Contact), John Krebs, Magali Ferrandon, Razima Souleimanova, Deborah Myers, Theodore Krause
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439
Phone: (630) 252-3420; Fax: (630) 972-4454; E-mail: choung@cmt.anl.gov

DOE Technology Development Manager: Nancy Garland
Phone: (202) 586-5673; Fax: (202) 586-1637; E-mail: Nancy.Garland@ee.doe.gov

Objectives

Develop water-gas shift (WGS) catalysts for on-board fuel processing that meet the DOE targets for performance [gas-hourly space velocity (GHSV) ≥30,000 h⁻¹, CO conversion ≥90%, CO selectivity ≥99%], durability [lifetime >5000 h], and cost [<$1/kWe]. Eliminate the drawbacks of commercial WGS catalysts, CuZn and FeCr oxides, for on-board fuel processing, including the need for well-controlled in situ activation, the loss of activity due to temperature excursions, and the need to sequester the catalysts during shutdown to prevent deactivation.

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 R,D&D Plan:

- J. Durability
- L. Hydrogen Purification/Carbon Monoxide Cleanup
- N. Cost

Approach

- Explore metal/metal oxide combinations that exhibit the bifunctional mechanism where the metal adsorbs CO, CO is oxidized by the metal oxide, and the metal oxide is then reoxidized by water.
- Metals (e.g. Pt, Ru, Co, Cu) that have CO adsorption energies of 20-50 kcal/mol
- Metal oxides that exhibit redox activity under WGS reaction conditions

Accomplishments

Pt Catalysts

- Improved the activity and stability of Pt/doped ceria catalyst with a bimetallic formulation.
- Identified Zr and Gd as dopants for ceria that can improve WGS activity at temperatures >300°C compared to undoped Pt/ceria.
- Demonstrated that 5 ppm H₂S does not enhance deactivation of Pt/doped ceria catalyst at 300°C but does promote deactivation at 400°C.

Cu Catalysts

- Investigated Re, Ni-Re, and Mn as promoters to enhance the activity of Cu catalysts.
Future Directions

Pt Catalysts
- Optimize bimetallic formulation to increase activity while decreasing Pt loading to achieve DOE cost target.
- Retard Pt sintering.
- Address H$_2$S poisoning at 400°C.
- Evaluate catalyst performance on monolith.

Cu Catalysts
- Increase low temperature (230-300°C) activity.
- Reduce Cu sintering through the addition of promoters to improve stability.
- Improve sulfur tolerance.

- Conduct characterization studies (SEM/TEM and EXAFS/XANES) to improve activity and reduce deactivation.

Introduction

On-board reforming of hydrocarbon fuels for H$_2$ generation for fuel cell-powered vehicles produces reformate containing ≤10% CO. The CO content in reformate must be reduced to <100 ppm because it poisons the polymer electrolyte fuel cell (PEFC). The water-gas shift (WGS) reaction (CO + H$_2$O = CO$_2$ + H$_2$) converts CO to CO$_2$. Commercial WGS catalysts, CuZn and FeCr oxides, have a number of drawbacks, including the need for a well-controlled in situ activation process, the loss of activity due to temperature excursions, and the need to sequester the catalysts during shutdown to prevent reoxidation. All of these factors make the commercial WGS catalysts undesirable for use in on-board fuel processing. The goal of this project is to develop new WGS catalysts that overcome these drawbacks and meet the DOE performance, durability, and cost targets.

Approach

Metal/metal oxide combinations that exhibit bifunctional mechanisms are being explored where the metal active sites adsorb CO and the oxide support provides the oxygen for CO oxidation and is reoxidized by water. Pt and Cu are being studied because their CO adsorption energies are 20–50 kcal/mol, which is considered to be optimal for WGS catalysts [1]. Gadolinia and zirconia doped ceria are being investigated as supports because they exhibit redox chemistry under WGS reaction conditions. Kinetic studies on Pt/ceria catalysts have shown that the rate is zero order in CO and one-half order in H$_2$O (i.e., the CO conversion rate is proportional to P$_{CO}^0$ P$_{H2O}^{0.5}$) [2,3], suggesting that the Pt surface is saturated with CO and the reaction is controlled by the reoxidation rate of ceria by water, the oxygen transfer rate from the ceria to the metal interface, or the metal dispersion and surface area. Our approach is to improve ceria redox/oxygen transfer rates by cation doping, improve water dissociation on the Pt surface by addition of a second metal, and stabilize Pt against sintering.

WGS rates were measured in a microreactor using synthetic reformate (6.9% CO, 10.4% CO$_2$, 31.1% H$_2$, 31.0% H$_2$O, and 20.7% N$_2$) on powder samples at a catalyst temperature of 250–400°C. High space velocities were used (GHSV=200,000–1,500,000 h$^{-1}$) to maintain differential reactor conditions (i.e., conversion ≤15%) at the lower temperatures (250–300°C).

Results

The effect of Pt loading on WGS activity was investigated. The WGS activity (per gram catalyst) increased with Pt loading (0.87–2.86%) while the CO conversion rates (per mole Pt) were nearly identical...
(Figure 1), indicating that WGS rates (per mole Pt) are independent of Pt loading. Therefore, the CO conversion per unit volume of reactor can be increased by increasing the Pt loading to achieve the volume/weight targets.

Pt bimetallic formulations were investigated in an attempt to reduce the amount of Pt while enhancing its activity. Bimetallic formulations were selected on the basis of theoretical studies of the energetics of H₂O dissociation and reactions between COₐds + OHₐds on Pt-mixed metal clusters [4]. The WGS activities (per mole Pt) of different Pt bimetallic formulations (Pt+M) are compared to Pt in Figure 2. Pt+A and Pt+B showed higher rates than Pt, indicating that the addition of A and B is favorable for promoting the WGS reaction. On the other hand, the addition of C and D seemed to have inhibiting effects on WGS because lower rates were observed on Pt+C and Pt+D than with Pt. The activities of Pt+A and Pt+B are compared to Pt at 300°C with time on stream in Figure 3. Pt lost half of its activity after ~40 hours and Pt+B deactivated more rapidly than Pt and lost half of its activity after ~2 hours. Pt+A was more stable than Pt and had a half life of ~217 hours. Wang et al. reported that deactivation observed during WGS on Pt/ceria and Pd/ceria catalysts is caused by metal surface area loss [5]. The Pt+A bimetallic formulation may inhibit the sintering of Pt, resulting in enhanced stability.

Co, Sn, Ni, Re, and Mn promoters were added to Cu-based WGS catalysts to try to improve the air stability. The activity decreased when Co and Sn were added, and these were subsequently dismissed as potential promoters. Rhenium was selected because it improved the air stability of Co-based WGS catalysts. Rhenium and copper do not form a solid solution or alloy of definitive stoichiometry. Nickel forms a solid solution with both Cu and Re and was used to increase their interaction. The Cu-Re catalyst is significantly more active than the Cu-Ni-Re catalyst (Figure 4). The selectivity to H₂ is considerably reduced with the presence of Ni because nickel is a very efficient methanation catalyst, particularly under WGS conditions. As shown in Figure 4, the Cu-Mn catalyst showed higher activity than the Cu catalyst at temperatures >275°C. However, the air stability of the Cu-Mn catalyst was poor; 10–20% of the initial activity was lost after a single exposure to dry air at 400°C. The promoted samples were more active than Cu at the higher temperatures (>375°C) after exposure to air. Preliminary powder x-ray diffraction studies were
inconclusive regarding the extent of interaction of the promoters (Re, Mn) with Cu in these catalysts. Manganese is expected to form a spinel phase with Cu, based on available CuO-Mn$_2$O$_3$ phase diagrams.

**Conclusions**

- WGS activity (per gram catalyst) increased with Pt loading while CO conversion rates (per mole Pt) were similar, indicating that rates (per mole Pt) are independent of Pt loading (0.87–2.86 wt%).
- Activity and stability of Pt/doped ceria catalysts increased with bimetallic formulations.
- Ni, Re, and Mn promoters enhanced WGS activity of Cu/γ-Al$_2$O$_3$, but promoted samples were less stable after air exposure.

**References**


**FY 2002 Publications/Presentations**