Advanced Fuel Processing Catalysts for Hydrogen Production and Fuel Cell Systems

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Introduction

- Fuel cells offer an efficient, clean alternative to combustion-based generation of primary power for stationary and mobile applications.
- The lack of a hydrogen (H_2) infrastructure has stimulated research to develop new fuel processing technologies to produce H_2 from hydrocarbon and alcohol fuels.
  - ✓ Fuels of interest include infrastructure fuels, such as natural gas, liquefied petroleum gas, gasoline, or diesel, and renewable fuels such as bioethanol.
  - ✓ The goal is produce H_2 at the "point of application."
- Figure 1 is a flow diagram for a fuel processor for use with a polymer electrolyte fuel cell (PEFC).

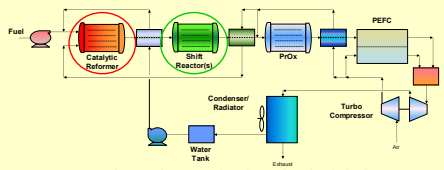


Fig. 1. Fuel processor for polymer electrolyte fuel cell.

- ✓ The first step is to reform the fuel. The reforming processes used include:

Steam reforming (SR): $C_nH_m + nH_2O \rightarrow nCO + (n + m/2)H_2, \quad \Delta H^\circ_{298} > 0$

Partial oxidation (POX): $C_nH_m + (n/2)O_2 \rightarrow nCO + (m/2)H_2, \quad \Delta H^\circ_{298} < 0$

Auto thermal reforming (ATR): $C_nH_m + (n/2 - y)O_2 + 2yH_2O \rightarrow nCO + (m/2 + 2y)H_2,$

$\Delta H^\circ_{298} < 0$ or > 0 depending on air:fuel and water:fuel ratios

- ✓ The fuel gas produced by the reformer can contain 10% or more of CO. Because the PEFC is poisoned by CO concentrations of ~10-100 ppm, additional processing is required. Most processors use a two-step process to reduce the CO concentration to acceptable levels. The two reactions are:

Water-gas shift (WGS): $CO + H_2O \leftrightarrow CO_2 + H_2$

Preferential oxidation (PrOx): $CO + 1/2O_2 \rightarrow CO_2$

Challenges

- The three processes—reforming, WGS, and PrOx—require catalysts. For large-scale industrial H_2 production the catalysts are:
  - ✓ Ni-supported on modified alumina for steam reforming.
  - ✓ Fe-Cr and Cu-Zn oxide for the WGS.
  - ✓ Co and Pt on a refractory oxide; for PrOx pressure-swing adsorption is used to produce high-purity H_2.
- There are issues with using these catalysts in small-scale distributed applications because of the differences in the operating characteristics and performance requirements compared with large-scale H_2 production units:
  - ✓ Ni catalysts are susceptible to coke formation, extremely intolerant to sulfur, likely to form an inactive spinel with Al, and pyrophoric in the reduced state.
  - ✓ Fe-Cr and Cu-Zn catalysts need to be carefully reduced prior to use, are pyrophoric in the reduced state, and deactivate when subjected to temperature excursions and condensation/vaporization cycles.
  - ✓ Precious-metal catalysts have been shown to address most of the issues mentioned above, but cost becomes an issue.
- The objectives of this research are to develop:
  - ✓ Cost-effective reforming and WGS catalysts that overcome the issues related to current catalyst technology.
  - ✓ A better understanding of reaction mechanisms through kinetic and characterization studies.

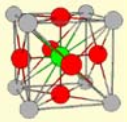
Argonne's Approach

- For the reforming catalysts, we are developing two different classes of materials:
  - ✓ Single-metal and bimetallic formulations that contain oxide-supported transition metals (e.g., Pt, Rh, and Ni) where the support is either an oxide-ion conducting substrate, such as gadolinium-doped ceria, or a refractory oxide, such as alumina.
  - ✓ Mixed non–noble metal oxides with the ABO_3 stoichiometry and the perovskite structure.

The goal is to improve the activity and stability of the catalysts, retard coke formation and improve sulfur tolerance.

- For the water-gas shift catalysts, our approach is to use theoretical chemistry to provide insight into the energetics of the elementary reaction steps in the WGS reaction on different metals—in particular, understanding how to reduce the formation of methane.

Transition Metal on Oxide-Ion Conductors



Perovskites

Reforming Catalyst Development

- Effect of support for Rh catalysts:
  - ✓ Small particles (1-5 nm) are of particular interest because they have a high surface-to-volume ratio of atoms with a significant fraction of the total number of atoms being coordinately unsaturated sites (CUS).
  - ✓ We have shown that the turnover rate for hydrocarbon reforming increases as the size of Rh clusters decreases, or as the dispersion of Rh increases (Fig. 2), suggesting that CUS activate C-H bonds.
  - ✓ The role of the support studied here was limited to how it affects metal dispersion (Fig. 2).

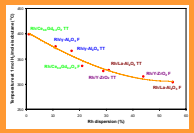


Fig. 2. Activity for reforming of C_2H_{10} related to particle size (dispersion) of Rh onto different supports before (F) and after thermal treatment at 900˚C for 24 h in steam/H_2 (TT).

- Sulfur poisoning during the reforming of gasoline:
  - ✓ The presence of ~30 ppm sulfur in gasoline poisoned the Rh/La-Al_2O_3 catalyst, with the effect being more pronounced at 700ºC than at 800ºC (Fig. 3).
  - ✓ SEM analysis of the tested catalysts showed the presence of bead-like coke (Fig. 4).

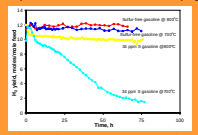


Fig. 3. Effect of temperature on the activity for reforming of gasoline without and with ~ 30 ppm sulfur.

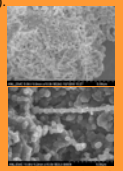


Fig. 4. SEM images of catalyst tested for reforming at 700ºC without (above) and with S-free gasoline (below).

- Stability of the perovskite structure:
  - ✓ Neutron scattering showed that Ni "leached" out of the perovskite structure during ATR (Fig. 5).
  - ✓ Activity improved after the catalyst had been "activated" (Fig. 6).

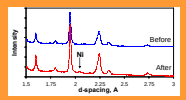


Fig. 5. Neutron scattering of $La_{0.8}Sr_{0.2}Cr_{0.9}Ni_{0.1}O_3$ perovskite before and after the reforming of isooctane.

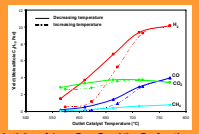


Fig. 6. Activity of $La_{0.8}Sr_{0.2}Cr_{0.9}Ni_{0.1}O_3$ for the reforming of isooctane with increasing and decreasing temperature.

Water-Gas Shift Catalyst Development

- There are two competitive pathways for CO conversion: WGS reaction and methanation:
  - ✓ Water-gas shift (WGS): $CO + H_2O \leftrightarrow CO_2 + H_2$
  - ✓ Methanation: $CO + 3H_2 \rightarrow CH_4 + H_2O$
- Thermodynamic calculations show that the CO equilibrium concentration is considerably lower when methane formation is allowed to occur (Fig. 7).

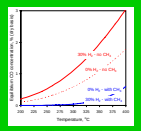


Fig. 7. CO Equilibrium with and without methane formation and with 0-30% H_2.

- Ru is a known catalyst for producing methane from synthesis gas but it also shows good WGS activity (Fig. 8). The CH_4 yield decreases as the H_2 concentration decreases (Fig. 9).

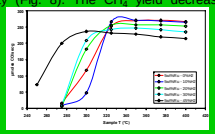


Fig. 8. CO concentration as a function of temperature and H_2 concentration.

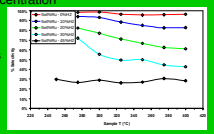


Fig. 9. CH_4 production as a function of temperature and H_2 concentration.

- The critical issue is whether CO adsorption is associative (favoring WGS reaction) or dissociative (favoring methanation). Using theoretical modeling [Vienna *ab initio* Program (VASP) software], we are trying to gain a better understanding of what influences each reaction pathway.
- Modeling suggests that associative CO adsorption ($M + CO_{(g)} \rightarrow M\text{-}CO_{(a)}$) compared to dissociative CO adsorption ($2M + CO(g) \rightarrow M\text{-}C(a) + M\text{-}O(a)$) (Fig. 10) is
  - ✓ Favored on Cu, Pt, and Ag and
  - ✓ Unfavored on Co, Ni, and Ru.
- We will run simulation cases to see if a second metal can make CO dissociation less favored on Co, Ni, and Ru.

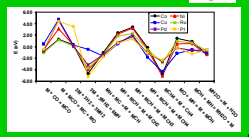


Fig. 10. Energetics of different reaction steps on various transition metals.

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