VII.F.2 Catalysts for Autothermal Reforming

Theodore Krause (Primary Contact), Magali Ferrandon, and Jennifer Mawdsley
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439
Phone: (630) 252-4356; Fax: (630) 972-4463; E-mail: krause@cmt.anl.gov

DOE Technology Development Manager: Nancy Garland
Phone: (202) 586-5673; Fax: (202) 586-9811; E-mail: Nancy.Garland@ee.doe.gov

Start Date: FY 1995
Projected End Date: Project continuation and direction determined annually by DOE

Objectives

- Develop advanced fuel processing catalysts that, in conjunction with other technology developments, would enable stationary fuel processors to meet DOE targets for durability, cost, and performance.
- Define operating parameters (e.g., O_2:fuel and H_2O:fuel ratios, temperature, and gas-hourly space velocity [GHSV]) to optimize catalyst performance and lifetime.
- Improve our understanding of reforming reaction mechanisms, catalyst deactivation, and sulfur poisoning.

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 reforming catalysts for producing H_2 from natural gas and liquefied petroleum gas (LPG). Catalysts developed from 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: $250/kW_e$
- Transient Response Time: 1 min

Approach

- Building on past Argonne National Laboratory experience and the technical literature, investigate transition metals supported on refractory or reducible oxide substrates as catalysts for autothermal reforming (ATR) and steam reforming (SR) of natural gas and LPG.
- Determine catalyst performance (H_2 yield, CO_x selectivity, hydrocarbon breakthrough, fuel conversion) and durability as a function of catalyst composition, fuel composition and sulfur content, and operating parameters (e.g., O_2:fuel and H_2O:fuel ratios, temperature, and GHSV).

- Conduct catalyst characterization and mechanistic studies to identify factors influencing activity, product selectivity, causes of deactivation, and how sulfur affects catalyst activity.

Accomplishments

- Demonstrated steady yields of H_2, nearly equal to the yields predicted by thermodynamic equilibria, for ATR of n-butane and natural gas and SR of natural gas with the Rh catalyst over a period of 150 h.
- Determined that the ATR activity of Rh catalyst is proportional to the Rh dispersion and that the oxide support does not influence the activity of Rh.
- Demonstrated that the addition of Ni to Rh catalysts allowed the Rh loading to be decreased while improving catalyst stability and lowering the amount of carbon deposited during ATR of n-butane.

Future Directions

- For bimetallic Ni-Rh catalyst, determine the optimal Ni-Rh ratio and weight loadings, develop a kinetic reaction model and conduct long-term testing of bimetallic Ni-Rh catalyst.
- Investigate Ni- and Co-based bimetallic compositions to lower the catalyst cost by replacing Rh with less expensive metals while maintaining catalytic performance and durability.
- Conduct characterization studies to determine the particle morphology of bimetallic Ni and Co catalysts under ATR and SR reaction conditions to develop a better understanding of reaction mechanisms.
- Investigate the effect of sulfur on the performance of bimetallic Ni and Co catalysts.

Introduction

In FY 2005, the focus of this project changed from developing catalysts for on-board ATR of gasoline to catalysts for stationary ATR and SR of natural gas and LPG. Catalytic ATR or SR of natural gas or LPG is one option being pursued for providing H_2 for stationary fuel cell systems. Nickel catalysts are currently used in the industrial production of H_2 by SR of natural gas. Although Ni catalysts are cost-effective, there are a number of issues that preclude their use in stationary fuel processor-fuel cell systems. They are susceptible to excessive carbon deposition, which can lead to mechanical degradation of the catalyst. Their activity is strongly dependent on the redox environment in the reformer, deactivating if the environment is too strongly oxidizing or reducing. Finally, they are extremely sensitive to sulfur, often present as an odorant. Precious-metal-based catalysts have been shown to address most of these issues; however, such catalysts are more costly.

Bimetallic catalysts can exhibit higher activity or better durability than the corresponding monometallic catalysts. In an attempt to reduce the precious metal loading, we are investigating bimetallic compositions consisting primarily of

nickel and a lesser quantity of a precious metal, such as Rh, Pt, or Pd, as ATR and SR catalysts. Our objective is to reduce the precious metal loading through the use of bimetallic formulations compared with precious-metal-based catalysts, while addressing the issues of carbon deposition, over-oxidation/reduction, and sulfur poisoning.

Approach

Bimetallic formulations of Ni and Rh supported on refractory oxide supports such as lanthanum-modified alumina (LAO), or reducible oxide supports such as ceria-zirconia (CZO), are prepared using the incipient wetness technique from aqueous solutions of salt precursors mixed at the desired Ni to Rh atomic ratio. The catalysts are tested in a microreactor system for ATR and SR of natural gas and LPG, as well as methane and n-butane, which are single-component surrogates for natural gas and LPG, respectively. Catalyst performance is evaluated by measuring the fuel conversion, H_2 yield, CO_x selectivity, and hydrocarbon breakthrough as a function of operating parameters (O_2:fuel and H_2O:fuel ratios, reactor temperature, and GHSV) and the Ni-to-Rh ratio. Monometallic Ni or Rh catalysts at weight loadings similar to their weight loadings in the bimetallic formulations are

also prepared and tested for ATR and SR. Catalyst samples are characterized before and after microreactor studies to gain a better understanding of the relationship between the catalyst composition and morphology and its performance in terms of its activity and durability. Among the characterization techniques employed are BET surface area measurement, CO chemisorption, temperature-programmed reduction (TPR) and oxidation (TPO), X-ray absorption spectroscopy (XAS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

Results

Rh/LAO ATR catalyst

The Rh/LAO catalyst was shown to produce steady yields of H_2, nearly equal to the yields predicted by thermodynamic equilibria, for ATR of n-butane and natural gas and SR of natural gas over of period of 150 hours, as shown in Figure 1. A study of the ATR of *i*-butane catalyzed by a series of catalysts consisting of Rh supported on a number of different refractory and reducible oxide supports indicated that the rate of H_2 production was correlated to the Rh dispersion, as shown in Figure 2. The function of the oxide support was to stabilize the dispersed Rh; there was no evidence that the oxide support influenced catalytic activity.
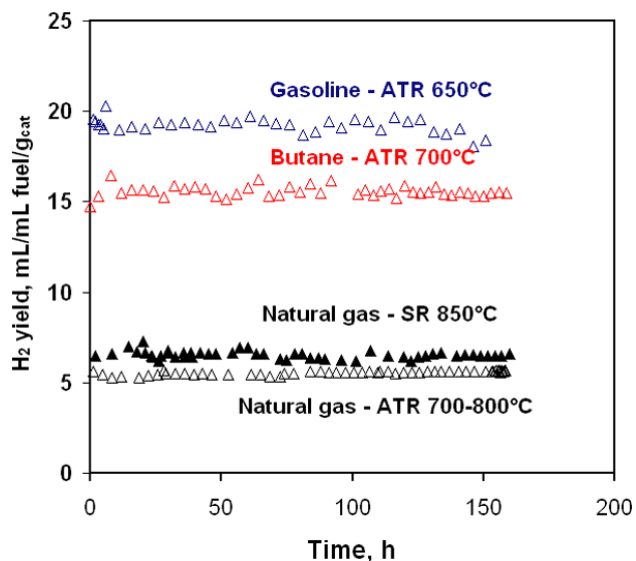

Figure 1. H_2 Yields From the ATR of Gasoline (<1 ppm S), n-Butane, and Natural Gas and SR of Natural Gas Catalyzed by Rh/LAO Catalyst
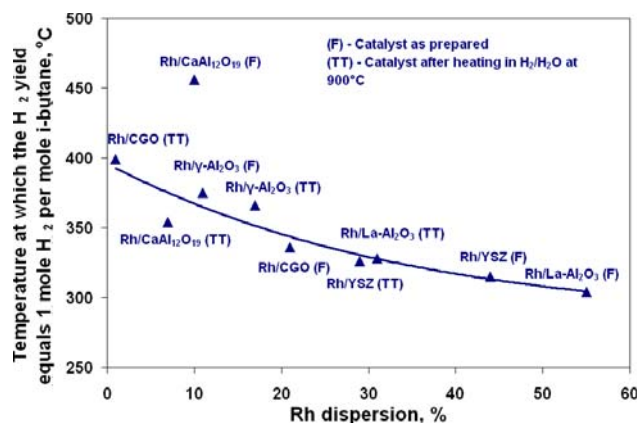

Figure 2. Relationship Between Rh Dispersion and the Temperature at Which the H_2 Production Rate Equals 1 mole H_2 per mole *i*-Butane

Bimetallic Ni-Rh catalysts

The effect of the ratio of Ni:Rh on the reforming activity and durability of Ni-Rh catalysts was determined by monitoring the H_2 yield for the ATR of n-butane using Ni-Rh catalysts with different Ni-Rh atomic ratios but constant total weight loading. The H_2 yields produced by the Ni-Rh catalysts were compared with the H_2 yields produced by monometallic Ni or Rh catalysts at similar weight loadings. As shown in Table 1, near-equilibrium H_2 yields were observed with all bimetallic Ni-Rh catalysts and monometallic Rh catalysts tests. The Ni catalyst produced considerably less H_2, probably

Table 1. Comparison of the H_2 yield, deactivation rate, and the wt% of carbon on the catalyst after testing for the ATR of n-butane catalyzed by monometallic Ni and Rh and bimetallic Rh catalysts. The units are mL/mL fuel/g_{cat} for the H_2 yield and h^{-1} for the deactivation rate.

Ni wt%	Rh wt%	H_2 Yield	Deactivation Rate	Carbon wt%
2.0	-	5.4	0.0007	0.2
1.6	0.4	13.6	0.0005	0.2
1.3	0.7	14.0	0.0013	0.1
-	0.7	13.8	0.0028	0.4
0.7	1.3	14.0	0.0002	2.8
-	1.3	13.8	0.0017	4.2
-	2.0	13.8	0.0007	0.1
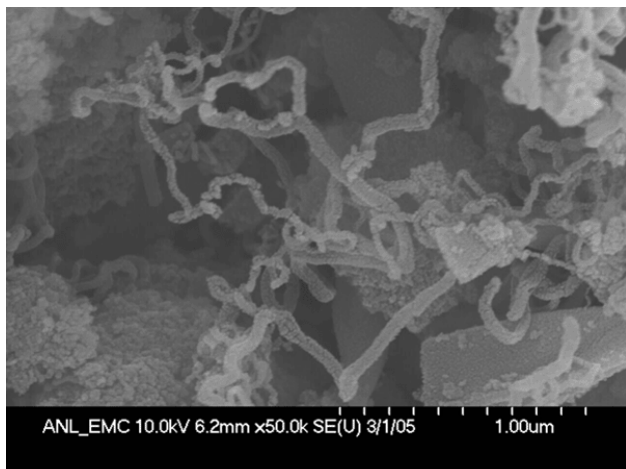
Figure 3. SEM Showing the Presence of Carbon Whiskers on a Ni-Rh Catalyst After ATR of n-Butane

Figure 4. The Magnitude of the Fourier Transformed EXAFS at the Rh *K*-edge for Ni-Rh and Rh Catalysts Treated Under Oxidizing Conditions at 900°C

due to the formation of inactive Ni-Al spinels, which were identified by X-ray diffraction (XRD), when the Ni catalyst was heated above 500°C in air. From these results, it is apparent that the addition of Ni to Rh did not enhance the reaction rate. However, it does appear that addition of Ni to Rh improved the catalyst stability since the Ni-Rh catalysts were observed to deactivate at a lower rate than the Rh catalysts, as shown in Table 1. Furthermore, elemental carbon analyses of the catalysts after ATR testing indicated that there was significantly less carbon deposited on the Ni-Rh catalysts compared with the Rh catalysts, as shown in Table 1. Using SEM, carbon whiskers were observed on the Ni-Rh catalyst after ATR testing, as shown in Figure 3, indicative of carbon formation on Ni particles [1], suggesting that monometallic Ni particles were present even in the bimetallic catalyst.

XAS, was used to determine if Ni and Rh in the bimetallic Ni-Rh catalysts were interacting during ATR and SR to form binary compounds, such as alloys, or if they were not interacting and were segregated as monometallic Ni and Rh particles. Samples of bimetallic Ni-Rh and monometallic Ni and Rh catalysts were treated under oxidizing or reducing conditions at 900°C to simulate the environment a catalyst would experience located at the inlet or exit of catalyst bed in an ATR reformer, respectively. The treated samples were then characterized by XAS using extended x-ray absorption fine structure (EXAFS) analysis. Under oxidizing conditions, as shown in Figure 4, the
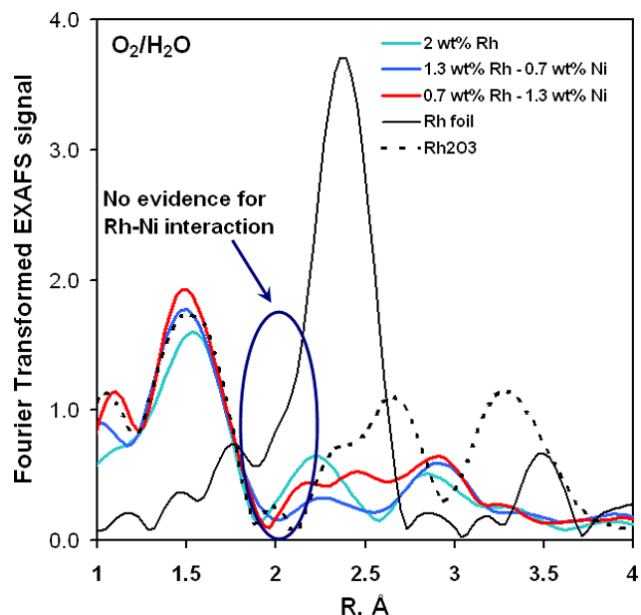
magnitude of the Fourier transformed EXAFS signal results at the Rh *K*-edge for the bimetallic Ni-Rh and monometallic Rh catalysts are similar, suggesting that Ni and Rh are segregated and probably do not interact in the bimetallic catalyst. However, under reducing conditions as shown in Figure 4, a peak is observed in the magnitude of the Fourier transformed EXAFS signal at the Rh *K*-edge for the bimetallic Ni-Rh catalyst at ~2Å, which has been attributed to a Ni-Rh interaction [2]. A peak is not observed at ~2Å in the radial distribution function for Rh in the monometallic Rh catalyst. Although there is evidence for a Ni-Rh interaction in the bimetallic catalyst under reducing conditions, the majority of the Rh and the Ni still appear to be segregated (Figure 5). Currently, we have not been able to discern the role, if any, of the Ni-Rh interaction in decreasing the deactivation rates and increasing resistance to carbon deposition displayed by the bimetallic Ni-Rh catalysts compared with the monmetallic Rh catalysts.

Conclusions

- The Rh catalyst is able to produce steady yields of H_2, nearly equal to the yields predicted by thermodynamic equilibria, for the ATR of n-butane and natural gas and SR of natural gas over a period of 150 h.
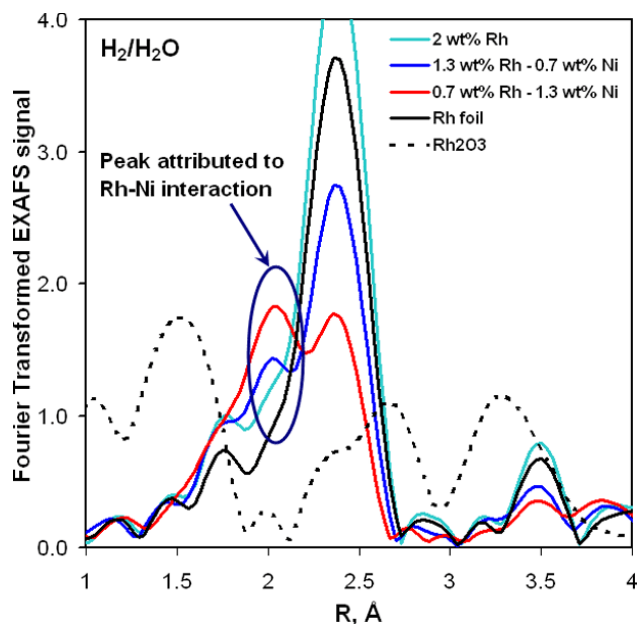
Figure 5. The Magnitude of the Fourier Transformed EXAFS at the Rh *K*-edge for Rh in Ni-Rh and Rh Catalysts Treated Under Reducing Conditions at 900°C

- The activity of Rh is proportional to the Rh dispersion. The oxide support stabilizes the Rh dispersion but does not appear to influence the activity of Rh.
- The addition of Ni to Rh catalysts allows the Rh loading to be decreased while providing better stability and increased resistance to carbon deposition.

- Under reducing conditions, there is evidence for Ni-Rh interactions; however, most of the Ni and Rh is present as segregated monmetallic particles. Under oxidizing conditions, the Ni and Rh are segregated.

FY 2005 Publications/Presentations

1. "Effect of Sulfur on the Performance of Reforming Catalysts for Hydrogen Generation," M. Ferrandon, J. Mawdsley, J. Ralph, and T. Krause, presented at the American Institute of Chemical Engineers 2004 Annual Meeting, Austin, Texas, November 7-12, 2004.

2. "Reforming Catalyst Development for Distributed Hydrogen Production," T. Krause, M. Ferrandon, J. Kopasz, L. Miller, and D. Applegate, presented at the 19th Meeting of the North American Catalysis Society, Philadelphia, Pennsylvania, May 21-28, 2005.

References

1. H. S. Bengaard, J. K. Nørskov, J. Sehested, B.S. Clausen, L. P. Nielsen, A. M. Molenbroek, and J. R. Rostrup-Nielsen, *J. Catal.*, 209 (2002) 365.

2. K. Nagaoka, A. Jentys, and J. A. Lercher, *J. Catal.*, 229 (2005) 185.