

**Title:** REFORMULATION OF COAL-DERIVED TRANSPORTATION FUELS: SELECTIVE OXIDATION OF CARBON MONOXIDE ON METAL FOAM CATALYSTS

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**Objectives.** Coal-derived transportation fuels must be reformed in a series of steps to provide hydrogen for use in proton exchange membrane (PEM) fuel cells. In the preferential oxidation (PROX) reaction step, carbon monoxide is selectively oxidized to less than 10 ppm in the presence of ~40% hydrogen, and steam, to prevent poisoning of the fuel cell anode. This process requires an active, selective, and stable catalyst.

Structured catalyst supports, such as ceramic monoliths and ceramic foams, have been used for a variety of applications. One of the most prominent examples is the washcoated, straight-channel ceramic monolith in the catalytic converter for gasoline-powered automobiles. An alternative to this ceramic monolith is a structured metal foam. These metal foams offer a number of advantages over the traditional ceramic monolith: higher thermal conductivity, radial mixing and heat transport, and a durable, low density, high strength structure. Our research examines the viability of catalyzed metal foams for PEM fuel cell-powered automotive applications, and compares these materials to ceramic monoliths.

**Accomplishments to Date.** Using 5% platinum and 0.5% iron catalysts,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> washcoated metal foams, 2” in length and 1” in diameter, with varying pores per inch and density were tested for their activity and selectivity on a CO PROX reaction in the presence of a H<sub>2</sub>-rich gas stream. The activity and selectivity of these metal foams were measured in an adiabatic flow reactor, and the catalysts were characterized by pulse chemisorption and temperature programmed desorption (TPD).

Tests on an unwashcoated, uncatalyzed blank metal foam and blank reactor show no CO uptake. Tests on washcoated supports reveal that the Fe,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> washcoat, or surface impurities, weakly adsorb CO, causing an elongated tail during pulse chemisorption.

In our TPD measurements, we observe a similar desorption temperature peak of ~160°C for CO linearly adsorbed on Pt, as shown by Manasilp and Guilari<sup>1</sup>. The TPD results are lower than the pulse chemisorption results because the latter accounts for CO adsorption on the Fe,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> washcoat, surface impurities, or a combination of the three, in addition to the Pt.

For Fe-promoted Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts, Liu et al. used TEM and HRTEM to show dispersed Pt particles with an average size of ~ 2 nm<sup>2</sup>, while Sakamoto et al. determined the average  $d_{Pt}$  to be ~ 20 nm using both XRD and dark field TEM<sup>3</sup>. Our  $d_{Pt}$  results, using a spherical model, are higher than Liu and Sakamoto, indicating possible sintering of the catalysts by agglomeration. Liu et al. and Sakamoto et al. agree that Fe enriches the Pt surface, decreasing the CO uptake by chemisorption and TPD because the Fe blocks CO adsorption on the Pt surface. We speculate that the supports with higher CO activity and selectivity will have lower CO uptake because the Fe is dispersed on the Pt particles<sup>2,3</sup>.

**Future Work.** The work planned for the remaining months of this research grant includes some of the following tasks:

- Other catalyst characterization techniques (SEM w/ EDAX, TEM, XPS, ICP) that are destructive to our catalytic supports.
- In-house washcoating of catalytic supports.
- Testing of different metals (Au, Ru) and/or promoters (Mn, Sn).
- Publications of the results acquired in these investigations.

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<sup>1</sup> Manasilp, A. and E. Gulari, *Applied Catalysis B – Environmental*, **37** (1, 2002), 17-25.

<sup>2</sup> Liu, X., O. Korotkikh and R. Farrauto, *Applied Catalysis A - General*, **226** (2002), 293-303.

<sup>3</sup> Sakamoto, Y., et al., *Applied Catalysis B – Environmental*, **23** (2-3, 1999), 159-167.

**Published/Submitted Journal Articles, and Completed Presentations** (Speaker Underlined)

*NC State*

1. Chin, P., Sun, X., Roberts, G.W., Spivey, J.J., “Selective Oxidation of CO in H<sub>2</sub>-containing Gases using Metal Foam Catalyst Supports”, Southeastern Catalysis Society Fall Symposium, Asheville, NC, September 30, 2002.
2. Sun, X., Roberts, G.W., Spivey, J.J., Chin, P., “Selective Oxidation of CO in H<sub>2</sub>-containing Gases using Metal Foam Catalyst Supports”, AIChE 2002 Annual Meeting, Indianapolis, IN, November 6, 2002.
3. Roberts, G.W., Spivey, J.J., Chin, P., Sun, X., “On Choosing a Catalyst Support: Applications to Fuel Cell Technology”, AIChE 2003 Spring Topical Conference Presentation Publication Session 98: Fuel Cell Technology – An Overview, New Orleans, LA, March 31, 2003.
4. Roberts, G.W., Spivey, J.J., Chin, P., Sun, X., “On Choosing a Catalyst Support: Applications to Fuel Cell Technology”, AIChE 2003 Spring Topical Conference Presentation, New Orleans, LA, March 31, 2003.
5. Chin, P., Sun, X., Roberts, G.W., Spivey, J.J., “Considerations for Catalyst Support Selection in Fuel Cell Applications” poster, Southeastern Catalysis Society Spring Symposium, Asheville, NC, April 13, 2003.
6. Chin, P., Sun, X., Roberts, G.W., Spivey, J.J., “Selective Oxidation of CO on Metal-foam Supported Pt-Fe Catalysts” poster, 18th North American Catalysis Society Meeting, Cancun, Mexico, June 4, 2003.
7. Roberts, G.W., Spivey, J.J., Chin, P., Sun, X., “*Preferential oxidation of carbon monoxide with Pt/Fe monolithic catalysts: interactions between external transport and the reverse water-gas-shift reaction.* Applied Catalysis B - Environmental, 2003. **46**(3): p. 601-611.
8. Chin, P., Sun, X., Roberts, G.W., Spivey, J.J., “CO Preferential Oxidation Supports Study for Fuel Cell Applications”, DOE NETL UCR/HBCU/OMI contractor’s meeting, Pittsburgh, PA, June 3, 2003.

*Clemson*

1. A. Sirijaruphan, J. G. Goodwin. Jr., and R. W. Rice, “Investigation of the Initial Rapid Deactivation of Platinum Catalysts during the Selective Oxidation of Carbon Monoxide,” Southeastern Catalysis Society symposium, Spring 2003 meeting, April 2003.
2. A. Sirijaruphan, J. G. Goodwin. Jr., and R. W. Rice, “Investigation of the Initial Rapid Deactivation of Pt Catalysts during the Selective Oxidation of CO,” the 18<sup>th</sup> North American Catalysis Society Meeting, Cancun, Mexico, June 2003.

3. A. Sirijaruphan, J. G. Goodwin. Jr., and R. W. Rice, "Investigation of the Initial Rapid Deactivation of Platinum Catalysts during the Selective Oxidation of Carbon Monoxide," International Conference 2003, Chulalongkorn University, Bangkok, Thailand, July 2003.
4. A. Sirijaruphan, J. G. Goodwin. Jr., and R. W. Rice, "Deactivation of Pt-Fe Catalysts for the Selective Oxidation of CO," ACS 2003 Regional Meeting, Atlanta, Georgia, USA, November 2003.
5. A. Sirijaruphan, J. G. Goodwin. Jr., and R. W. Rice, "Deactivation of Pt-Fe Catalysts for the Selective Oxidation of CO," AIChE Annual Meeting, San Francisco, California, USA, November 2003.
6. A. Sirijaruphan, J. G. Goodwin, Jr., and R. W. Rice, "Investigation of the Initial Rapid Deactivation of Platinum Catalysts during the Selective Oxidation of Carbon Monoxide," *J. Catal.* **221** (2004) 288-293
7. A. Sirijaruphan, J. G. Goodwin, Jr., and R. W. Rice, "Effect of Fe promotion on the surface reaction parameters of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for the selective oxidation of CO," in press in Journal of Catalysis (2004).
8. A. Sirijaruphan, J. G. Goodwin, Jr., and R. W. Rice, D. Wei. K. Butcher, G W. Roberts and J. J. Spivey, "Use of Metal Foams to Support Pt Catalyst for Selective CO Oxidation," prepared to submit to Applied Catalysis A: General.

#### **Students Receiving Financial Support from Grant**

- Paul Chin (North Carolina State University)
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