CATALYTIC AUTOTHERMAL REFORMING FOR FUEL CELL SYSTEMS

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Introduction

In the absence of a hydrogen delivery infrastructure, commercial applications of polymer electrolyte fuel cells will depend upon the ability to convert available fuels into high-quality hydrogen. While the production of hydrogen in the chemical process industry is established technology, the constraints (e.g., size, weight, cost, etc.) imposed on the fuel processors for the automotive application require new approaches.

Argonne National Laboratory articulated the merits of autothermal reforming in 1993[1] and suggested a preferable operating temperature for such reformers of about 700°C, based on equilibrium gas compositions [2]. While others had early success with reformer designs using the principles of oxygen-deficient burners [3], we have been exploring catalysts that could accelerate the autothermal reforming reaction:

$$C_8H_{18} + \boldsymbol{x}O_2 + (16-2\boldsymbol{x})H_2O = 8CO_2 + (25-2\boldsymbol{x})H_2 \qquad (1)$$

Catalyst Evaluations

We have had good success with catalysts that consist of various transition metals supported on an oxide ion conducting substrate. To optimize the catalyst for the autothermal reforming of hydrocarbon fuels – where the focus has been primarily on gasoline-type hydrocarbons, we have looked into the effect of the metal and the substrate. These experiments were conducted at 500-800°C in a 12.5-mm diameter micro-reactor, with a feed stream consisting of iso-octane (2,2,4-trimethylpentane, C_8H_{18}), air, and steam, where the O_2/C and H_2O/C ratios were maintained at 0.46 and 1.14, respectively. The reactor was loaded with ~2 g of the catalyst particles and maintained at the desired temperature within an electric furnace. The catalyst formulations were all synthesized in an identical manner. For samples with Gd-doped ceria as the substrate, Figure 1 shows the effect of the metal on the conversion-

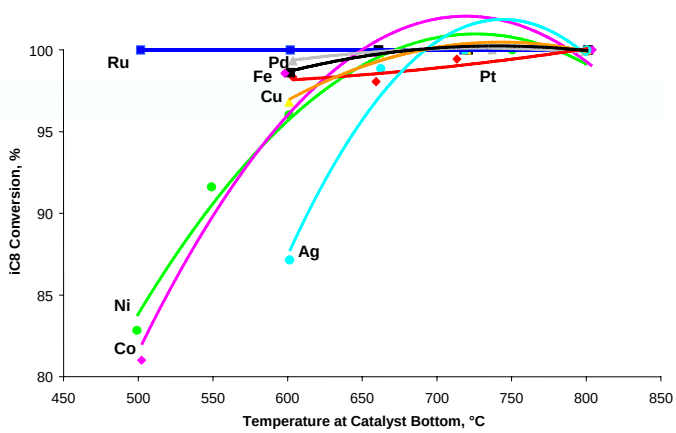

Figure 1. Effect of the metal on the conversion temperature behavior during the autothermal reforming of iso-octane.

[1] Siemens AG, Power Generation, Berlin, Germany

temperature behavior. Above 650°C, the conversion approaches 100% for all the metals. It is notable that at these temperatures, even the non-noble metals are as active as the more expensive platinum- and palladium-containing catalysts. Ruthenium maintains complete conversion of the iso-octane at temperatures as low as 500°C.

Figure 2 shows the change in hydrogen selectivity with temperature for the various metals. The hydrogen selectivity is defined as the mols of hydrogen produced as a percentage of the mols of hydrogen that is theoretically possible per reaction (1) where ***x*** was 3.68. Under those conditions 17.6 mols of hydrogen can be produced per mol of iso-octane. The figure shows that at 800°C, palladium demonstrates very high H_2 selectivity. Ruthenium is the most selective in the temperature range 600-700°C. The selectivity of nickel is comparable to that of ruthenium at 500°C, although it is quite low at less than 60%. In general, the noble metals showed better selectivity than the transition metals. This finding may be related to the total surface area of the different catalysts, since it was found that the transition metal catalysts had lower surface areas. This suggests that alternative synthesis methods, may yield higher surface areas with the transition metal catalysts, and thus lead to more active, selective, and inexpensive catalysts.

The effect of the oxide-ion conducting material was investigated by changing the substrate, while platinum was used as the metal. The experiments were conducted at 800°C, and a gas hourly space velocity of 2600/h, with an O_2/C=0.5 and H_2O/C=1.14. As shown in Figure 3, the catalyst with the samarium-gadolinium doped ceria yielded a reformate containing the highest hydrogen concentration, and the least "total hydrocarbon" which was primarily methane. As expected, the total hydrocarbon content in the product gas was higher with the materials that produced less hydrogen. These materials also produced more of the higher hydrocarbons (C_2-C_4).

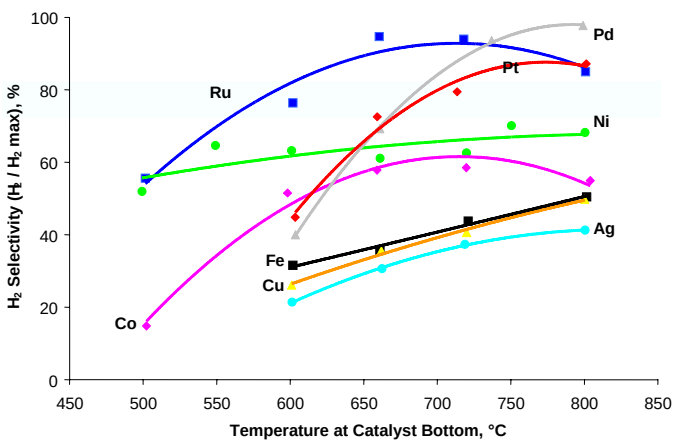

Figure 2. Effect of the metal on the Hydrogen Selectivity-Temperature behavior during the autothermal reforming of iso-octane.

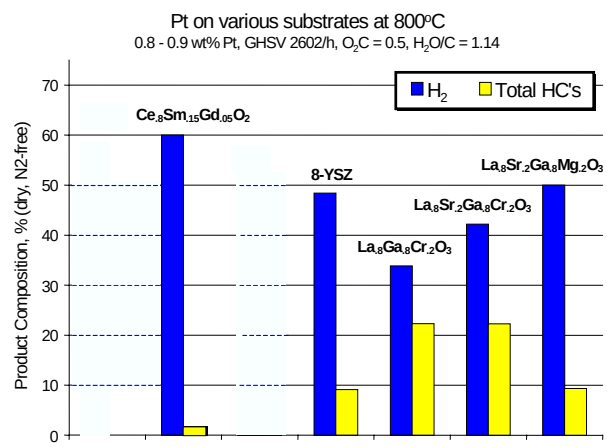

Figure 3. Effect of the oxide ion conducting substrate on the product gas composition.

Long-Term Performance

In order to address the question of durability, long-term experiments have been conducted with a reforming catalyst, composed of a noble metal on a Gd-doped ceria substrate. A microreactor similar to the one described above was operated for over 80 days with numerous start/stop cycles to emulate the thermal cycling typical of actual automotive operating conditions. For the fuel, several pure hydrocarbons (iso-octane, 74 wt%; 1-pentene, 1%; methylcyclohexane, 5%; dimethylbenzene, 20%) were blended to represent the key components in gasoline. The fuel blend was spiked with 50 ppm (by weight) of sulfur in the form of dibenzothiophene. The sulfur did not show any poisoning effect, and in fact upon comparing these data with those from a similar experiment but without sulfur in the fuel, we found the hydrogen concentrations to be actually higher when the fuel contained sulfur. Further details are provided in J. P. Kopasz's paper [4].

Microchannel Catalysts

It has been determined that the reforming step in the fuel processor (that is, conversion of the hydrocarbon fuel into H_2, CO, and CO_2) at temperatures of ~700°C takes place through very fast

reactions. As such, the reactions catalyzed by the use of pellets are not reaction limited but mass transfer limited. To take advantage of the fast kinetics, we have structured our catalyst in the form of monoliths containing microchannels and evaluated its performance. Figure 4 compares the hydrogen yield obtained from the catalyst in the form of pellets and microchannel as a function of the fuel feed rate. The microchannel catalyst is clearly more effective, and at 0.6 ml/min of iso-octane yields more than three times as much hydrogen. This confirms our estimates that, by using our catalyst in microchannel form, the autothermal reforming zone will account for a very small fraction of the total fuel processor volume.

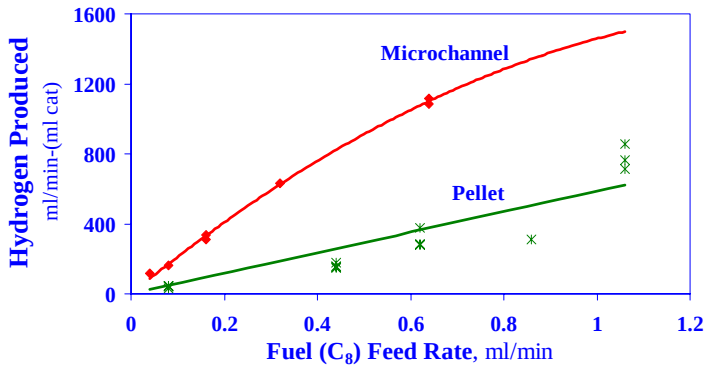

Figure 4. Hydrogen yield obtained from pellet and micro-channel catalysts after the autothermal reforming of iso-octaine.

Integration of Fuel Processor Components

The fuel processor for low temperature fuel cells such as the polymer electrolyte fuel cell requires a reformate gas that is not only rich in hydrogen, but has very strict restrictions on the amount of carbon monoxide and sulfur. In addition, the fuel processor must be highly efficient and capable of rapid start and load changes. Because of these requirements, the fuel processor needs to incorporate several catalytic reactors and unit operations, preferably, within one enclosure.

Argonne National Laboratory has designed and tested an integrated fuel processor that incorporates a reformer, a sulfur trap, and a water-gas shift reactor. It accepts air, fuel, and water, where they react in the reforming section to produce H_2, CO, and CO_2. Because of the sulfur tolerance of the reforming catalyst, the sulfur comes out of the reforming catalyst section in the form of H_2S. The gas is then cooled and trapped in a zinc oxide bed, before passing through the water gas shift reactor containing an ANL developed catalyst, that is active in the temperature range of 250-400°C. The temperature in the shift reactor decreases as the reformate gas travels downstream. The reformate gas cooling is by countercurrent heat exchange with the cooler incoming reactant streams (viz., fuel, steam, and air).

Figure 5 is a picture of the integrated unit with a volume of 7 liters, and is capable of delivering sufficient hydrogen for a 5-10 kW(e) fuel cell stack. Figure 6 shows the product gas composition from the integrated unit, with iso-octane as the fuel feed, as it exits the shift reactor zone.

Figure 5. Photograph of 7-L fuel processor rated for a 5- to 10-kWe fuel cell system.

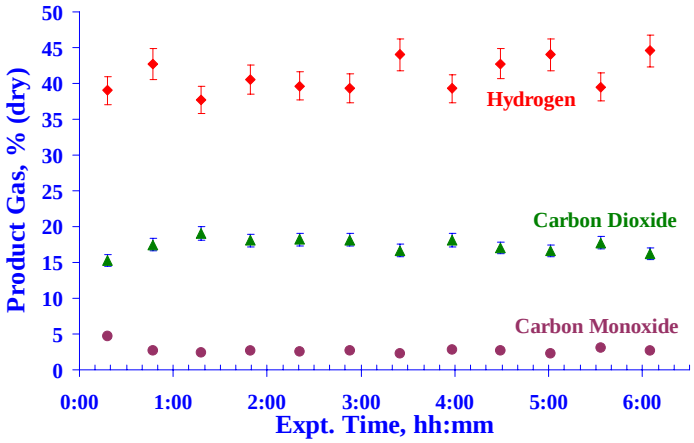

Figure 6. Product gas composition from the integrated unit as a function of time.

Conclusions

Fuel processors that can be incorporated into vehicles hold the key to successful near-term commercialization of low temperature fuel cells. Argonne National Laboratory has favored catalytic autothermal reforming and has developed catalysts for the reforming and shift reactors. The Argonne-developed reforming catalyst is active, selective for hydrogen, and sulfur tolerant. Our research program has focused on advancing the catalyst and reactor technology toward low cost materials and forms that will lead to compact, lightweight, efficient fuel processors that can meet the goals of rapid start and dynamic load following. These materials and concepts have been verified in laboratory tests, as well as in tests with engineering-scale hardware.

Acknowledgment

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