# Catalytic Autothermal Reforming Of Hydrocarbon Fuels For Fuel Cells<sup>†</sup>

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#### Introduction

Fuel cell development has seen remarkable progress in the past decade because of an increasing need to improve energy efficiency as well as to address concerns about the environmental consequences of using fossil fuel for producing electricity and for propulsion of vehicles [1]. The lack of an infrastructure for producing and distributing  $H_2$ has led to a research effort to develop on-board fuel processing technology for reforming hydrocarbon fuels to generate  $H_2$  [2]. The primary focus is on reforming gasoline, because a production and distribution infrastructure for gasoline already exists to supply internal combustion engines [3]. Existing reforming technology for the production of  $H_2$ from hydrocarbon feedstocks used in large-scale manufacturing processes, such as ammonia synthesis, is cost prohibitive when scaled down to the size of the fuel processor required for transportation applications (50-80 kWe) nor is it designed to meet the varying power demands and frequent shutoffs and restarts that will be experienced during normal drive cycles. To meet the performance targets required of a fuel processor for transportation applications will require new reforming reactor technology developed to meet the volume, weight, cost, and operational characteristics for transportation applications and the development of new reforming catalysts that exhibit a higher activity and better thermal and mechanical stability than reforming catalysts currently used in the production of H<sub>2</sub> for large-scale manufacturing processes.

The conversion of hydrocarbon fuels to  $H_2$  can be carried out by several reaction processes, including steam reforming (SR), partial oxidation (PO), and autothermal reforming (ATR). *Steam reforming* involves the reaction of steam with the fuel in the presence of a catalyst to produce  $H_2$  and CO. Since steam reforming is endothermic, some of the fuel must be burned and the heat transferred to the reformer via heat exchangers. *Partial oxidation* involves the reaction of oxygen with fuel to produce  $H_2$ and CO when the oxygen-to-fuel ratio is less than that required for total combustion, i.e., complete conversion to  $CO_2$  and  $H_2O$ . Partial oxidation can be conducted with a catalyst (catalytic partial oxidation) or without a catalyst (non-catalytic partial oxidation). The reaction rates are much higher for partial oxidation than for steam reforming, but the  $H_2$  yield per carbon in the fuel is lower. Non-catalytic partial oxidation requires reaction temperatures above 1000°C to achieve rapid reaction rates. Although the reaction is exothermic, some of the fuel must be combusted because the amount of heat generated by the reaction is not sufficient to preheat the feed to achieve optimal rates [4]. Recently, there has been an interest in catalytic partial oxidation since it operates at lower temperatures than the non-catalytic route. The lower operating temperatures provide better control over the reaction, thus minimizing coke formation and allowing for a wider choice of materials of construction for the reactor. *Autothermal reforming* involves the reaction of oxygen, steam, and fuel to produce  $H_2$  and  $CO_2$ , and can be viewed as a combination of partial oxidation and steam reforming.

The choice of the reaction process for on-board reforming depends on the operating characteristics (e.g., varying power demand, rapid startup, frequent shutdowns) for transportation applications. Steam reforming is heat transfer limited and as such does not respond rapidly to changes in the power demand (i.e., "load following"). When power demand rapidly decreases, the catalyst can overheat, causing sintering, which in turn results in loss of activity. Autothermal reforming can overcome the load following limitations of steam reforming since the heat required for the endothermic reactions is generated within the catalyst bed, a property that allows for more rapid response to changing power demands and faster startup [5]. The lower operating temperature of catalytic autothermal reforming has several advantages including less complicated reactor design, wider choice of materials of construction, and lower fuel requirements during startup over the higher operating temperature of partial oxidation or the endothermic steam reforming for transportation applications [6].

At Argonne National Laboratory, we are developing new catalysts for autothermal reforming [7]. Our catalysts are derived from solid oxide fuel cell technology, where a transition metal is supported on an oxide-ion-conducting substrate, such as ceria, zirconia, or lanthanum gallate that has been doped with a small amount of a non-reducible element, such as gadolinium, samarium, or zirconium. Ceria-based materials are being investigated as potential catalysts for CO and hydrocarbon oxidation reactions because of the redox and oxygen storage/release properties of ceria [8]. The catalytic activity of ceria can be further enhanced by the addition of dopants, such as  $Gd^{3+}$  or  $Sm^{3+}$ , which have been shown to increase the number of oxygen vacancies, improve the oxygen mobility and oxygen ion conductivity, and enhance the redox and oxygen storage/release properties of ceria. The role of defect chemistry and the surface oxygen vacancies in determining the catalytic behavior of these metal/mixed oxide systems is well known [9].

#### Results and Discussion

Figure 1 compares the yields for the primary reaction products ( $H_2$ , CO, CO<sub>2</sub>, and CH<sub>4</sub>) produced from reforming isooctane (2,2,4-trimethylpentane), which is used as a

surrogate for gasoline, using Pt supported on doped ceria and Rh supported on doped ceria at 500 and 700°C. The experiments were conducted in a microreactor system using ~1 g of powder catalyst. The product gas was analyzed by gas chromatography. The space velocity for these experiments was  $\sim 20,000 \text{ h}^{-1}$ . The experiments were conducted using an O<sub>2</sub>:C<sub>8</sub> ratio of 4 and a H<sub>2</sub>O:C<sub>8</sub> ratio of 9. At 700°C, the yields of 11.4 moles H<sub>2</sub> per mole of isooctane in the feed for the Pt catalyst and 10.9 moles of H<sub>2</sub> per mole of isooctane in the feed for the Rh catalyst are close to the 12.2 moles of  $H_2$  per mole of isooctane in the feed predicted by thermodynamic equilibrium. The isooctane conversion was 94% for the Pt catalyst and 100% for the Rh catalyst. At 500°C, the H<sub>2</sub> yield for the Rh catalyst is greater that of the Pt catalyst (10.7 moles of H<sub>2</sub> vs. 4.5 moles of H<sub>2</sub> per mole of isooctane, respectively). The isooctane conversion was 73% for the Pt catalyst and 99% for the Rh catalyst. At 500°C, various C<sub>3</sub>-C<sub>5</sub> hydrocarbons and isooctane were detected in the product gas for the Pt catalyst, whereas only methane and isooctane were the only hydrocarbons detected in the product gas for the Rh catalyst. There was no evidence of coke formation for either catalyst. The higher H<sub>2</sub> yield for the Rh catalyst compared to the Pt catalyst at 500°C can be attributed to Rh catalyst being more active for steam reforming. No O<sub>2</sub> was detected in the product gas suggesting that the reactions involving O<sub>2</sub> are extremely rapid for both catalysts.



Figure 1 Comparison of the yield of H<sub>2</sub>, CO, CO<sub>2</sub>, and CH<sub>4</sub> for autothermal reforming of isooctane (O<sub>2</sub>:C<sub>8</sub>=4 and H<sub>2</sub>O:C<sub>8</sub>=9) at 500°C and 700°C for Pt and Rh supported on doped ceria catalysts.

Figure 2 compares the H<sub>2</sub> yield as a function of gas-hourly space velocity (GHSV) for the Pt and Rh catalysts. H<sub>2</sub> is produced by the Pt and Rh catalysts at 600°C at GHSV as high as 150,000  $h^{-1}$ . Of particular note is that at a GHSV of 190,000  $h^{-1}$ , the Rh catalyst produces 9.9 moles of H<sub>2</sub> per mole of isooctane in the feed, evidence of the high steam reforming activity of this catalyst.



Figure 2 Comparison of the  $H_2$  yield as a function of gas-hourly space velocity (GHSV) for the reforming of isooctane ( $O_2:C_8=4$  and  $H_2O:C_8=9$ ) for Pt and Rh supported on doped ceria catalysts.

Because of concerns over the cost of a noble metal reforming catalyst, there is considerable interest to develop a non-noble metal reforming catalyst. Figure 3 shows the product yields of H<sub>2</sub>, CO, CO<sub>2</sub>, and CH<sub>4</sub> produced from reforming isooctane over the temperature range of 500-800°C using a Ni supported on a doped ceria catalyst. Similar to the Rh catalyst, the Ni catalyst exhibits good steam reforming activity at 500°C based on the production of 9 moles of H<sub>2</sub> per mole of isooctane in the feed. The conversion of isooctane ranged from 75% at 500°C to >99% at 800°C. At 500°C, C<sub>3</sub>-C<sub>5</sub> hydrocarbons, methane, and isooctane are present in the product gas. As the reforming temperature is increased to 800°C, the concentration of C<sub>3</sub>-C<sub>5</sub> hydrocarbons in the product gas decreases; however, the concentration of CH<sub>4</sub> increases. There was no evidence of coking under these reaction conditions.

Sulfur tolerance is an important issue for reforming catalysts being developed for on-board reforming of gasoline. Despite new EPA regulations that will lower the average sulfur content in gasoline to 30 ppm with a maximum of 80 ppm, many reforming catalysts will still be poisoned by sulfur at these levels. As shown in Figure 4, the presence of 300 ppm sulfur added as benzothiophene to isooctane does not degrade the performance of the Pt catalyst over a period of 48 h. In long-term testing, the vol.% of H<sub>2</sub> in the product gas generated from reforming a benchmark fuel mixture consisting of isooctane, pentene, methylcyclohexane, and xylenes, which contains 50 ppm S added as benzothiophene decreased by only 5% over a 1700 h period for the Pt catalyst. Experiments are in progress to determine the sulfur tolerance of the Rh supported on doped ceria catalyst. For comparison, commercial nickel steam reforming catalysts for show evidence of sulfur poisoning when the sulfur content of the gas is 50 ppm [4].



Figure 3 Comparison of the yield of  $H_2$ , CO, CO<sub>2</sub>, and CH<sub>4</sub> for autothermal reforming of isooctane (O<sub>2</sub>:C<sub>8</sub>=4 and H<sub>2</sub>O:C=9) for Ni supported on doped ceria. GHSV=19,000 h<sup>-1</sup>.



Figure 4 Effect of 300 ppm S in isooctane on the vol% of  $H_2$ , CO, CO<sub>2</sub>, and CH<sub>4</sub> in the product gas over a Pt supported catalyst on doped ceria.

## Conclusions

Platinum, Rh, and Ni supported on doped ceria catalyze the autothermal reforming of isooctane to produce a H<sub>2</sub>-rich product gas at temperatures ranging from 500-800°C. At 500°C, the H<sub>2</sub> yield for the Rh and Ni catalysts, 10.7 and 9 moles of H<sub>2</sub> per mole of isooctane, respectively, is higher than the H<sub>2</sub> yield for the Pt catalyst (4.5 moles of H<sub>2</sub> per mole of isooctane) which is attributed to the higher steam reforming activity of the Rh and Ni catalysts. At 700°C and a GHSV of ~20,000 h<sup>-1</sup>, the Pt catalyst exhibited the

highest  $H_2$  yield, 11.4 moles of  $H_2$  per mole of isooctane. There was no evidence of coke formation for any of the catalysts in these reactor studies. The Pt catalyst exhibits excellent sulfur tolerance with minimal loss in activity over 1700 h when reforming a benchmark fuel containing 50 ppm S as benzothiophene.

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