Hydrogen Production from Simulated Gasoline using Nickel-Based Catalysts

Andrew Tadd, Ben Gould, Johannes Schwank
Chemical Engineering Department, University of Michigan, Ann Arbor Michigan

Introduction

Fuel cells, which produce electricity directly from hydrogen and oxygen, offer a clean and efficient potential alternative to internal combustion engines for generating power for portable and transportation applications. However, there currently is no infrastructure for the wide scale production and distribution of hydrogen to the transportation market. Instead of building new infrastructure, it is possible to produce hydrogen on-demand from common hydrocarbon fuels. [1] Several catalytic processes can be used to produce hydrogen from hydrocarbons. The most common are partial oxidation (POX), steam reforming (SR), and autothermal reforming (ATR), all of which produce primarily hydrogen, carbon monoxide, and some carbon dioxide. In partial oxidation the fuel is combusted with a sub-stoichiometric quantity of oxygen. Steam reforming uses water to reform the fuel, is highly endothermic and requires a significant heat input, usually provided by combusting some amount of the fuel. Autothermal reforming combines POX and SR by reacting the fuel with both steam and oxygen. In ATR the operating temperature is moderated, and the addition of extra heat through fuel combustion may be eliminated. Since there is no external heat transfer limitation, it seems that ATR would be more responsive to transients in operation than SR. ATR produces higher hydrogen yields than POX, since hydrogen is produced from both steam and fuel, as opposed to just the fuel.

A key to implementing any ATR system is an active, stable catalyst. Of primary concern is a resistance to coking. In practice, SR and ATR systems usually employ excess steam to avoid coking and prolong the catalysts' activity. [2] A resistance to coking would allow for lower steam to carbon ratios and more efficient operation. Ceria is a key component of three-way automotive emission control catalysts and has the ability to store and release oxygen under different reaction conditions. Doped and mixed oxides of ceria have been widely studied in the literature. [3-9] It has also been proposed that ceria can have a bifunctional action in steam reforming and water gas shift reactions. [7] Ceria can donate oxygen to react with carbon on active metal sites, and then be re-oxidized by water. This could improve coking resistance when used as a catalyst in ATR or SR.

In this work catalysts prepared as nanopowders via flame-spray pyrolysis and using traditional precipitation techniques are compared. The effects of reaction temperature, space velocity, steam to carbon ratio, oxygen to carbon ratio, and metal loading on activity and coking behavior have been investigated. Partial oxidation and steam reforming experiments of single components and mixed feeds have also been undertaken to investigate the rates and potential mechanisms of the overall autothermal reforming process. Washcoat formulations of some of the catalysts were developed and tested for autothermal reforming using a planar microreactor.

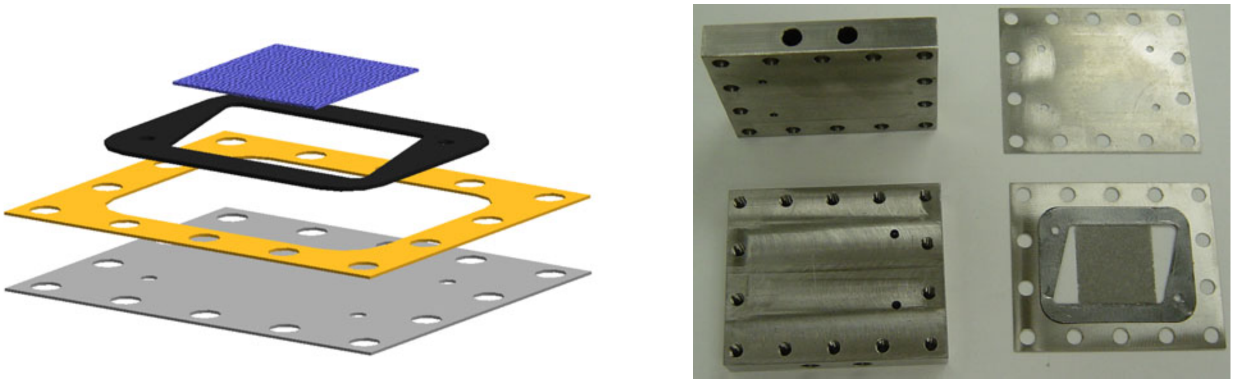
Experimental

The ceria-zirconia supports used in this work ($Ce_{0.75}Zr_{0.25}O_2$) were prepared in our laboratory using co-precipitation. Aqueous solutions of $Ce(NO_3)_3 \cdot 6H_2O$ and $ZrOCl_2 \cdot 8H_2O$ were prepared and precipitated by addition of 2M NH_4OH. After precipitation, the slurry was aged overnight while stirring, then recovered by filtration. The precipitate was dried overnight in air at 110 ºC, crushed, and calcined in air for one hour. Yttria-stabilized zirconia (Y:Zr = 8:92) was prepared using the same method, starting with $Y(NO_3)_3{\cdot}6H_2O$ and $ZrOCl_2{\cdot}8H_2O$. Following preparation, supports were characterized using X-ray diffraction and single point BET area.

Catalysts were prepared by wet impregnation of the previously prepared supports with a solution of $Ni(NO_3)_3{\cdot}6H_2O$ in ethanol. Following impregnation, the pre-catalysts were dried in air at 110 ºC. Finally the pre-catalysts were calcined by ramping from room temperature to 600 ºC in air and holding for one hour. Following calcination, catalysts were characterized primarily by single point BET area and pulse chemisorption of hydrogen. Weight loadings in the range 5 and 20 wt% nickel were prepared. Nanopowder $Ni/Ce_{0.75}Zr_{0.25}O_2$ catalysts were prepared via liquid feed flame spray pyrolysis. [10] Some finished and post-reaction catalysts were characterized with X-ray diffraction.

Catalysts were tested in both conventional packed beds, as well as in a planar microreactor (see Figure 1). For testing in the microreactor, catalyst were prepared as washcoats and deposited on FeCrAlloy foam carriers. First, a binder solution was prepared from pure $Ce_{0.75}Zr_{0.25}O_2$ support by ball milling the support and deionized water in a plastic container with zirconia grinding pellets overnight. Then a catalyst powder was combined with deionized water, polyvinyl alcohol, and the ceria-zirconia binder in the same ball mill and milled overnight. The resulting washcoat mixture was placed in a Petri dish and foam carriers were submerged and removed. The wet foams were placed on a quartz rack and dried at 110 ºC for approximately 30 minutes. Multiple applications of the washcoat mixture were made until a desired loading was achieved, about 125 mg of washcoat. The foams were then calcined in air for one hour at 600 ºC on the same quartz rack.

Figure 1. Planar microreactor schematic, and the actual device with a single metal foam.



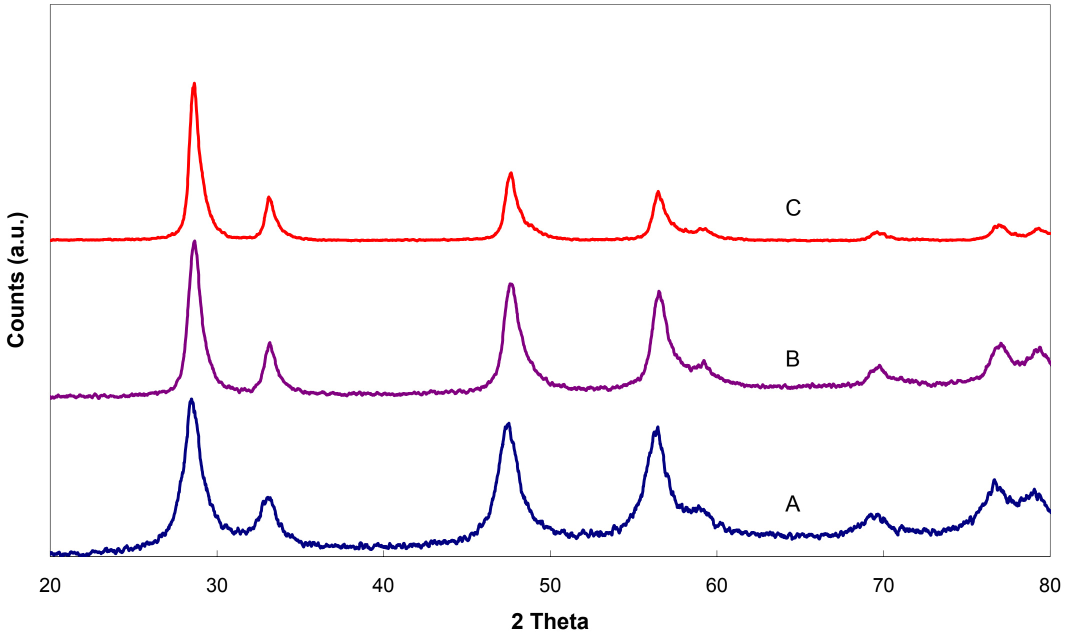
Catalytic reactions were carried out using a flow reactor setup. Air was metered using mass flow controllers while fuel and water were delivered using peristaltic pumps. Gases and liquids were vaporized and mixed in a heated stainless steel line, then flowed into a 14 mm diameter quartz tube situated in a vertical, high-temperature electric furnace where the catalyst sample is loaded on top of a quartz wool plug. Water and unreacted fuel were condensed in a cold-water condenser, and then collected in an ice temperature cold trap. The non-condensable gases continued from the cold trap to a gas chromatograph for analysis.

In packed bed runs, the gas hourly space velocity (GHSV) was varied between 100,000 hr^{-1} and 500,000 hr^{-1}, and the furnace temperature between 350 and 650 ºC. Generally between 100 mg and 1000 mg of catalyst were used depending on whether differential or total conversion was desired. Catalyst washcoats deposited on foams were tested using the microreactor housing and the flow reactor feed system. The effluent from the microreactor is carried to the cold trap and then to the chromatograph. For microreactor test runs, the number of catalyst coated foams was varied. For these runs the oxygen to carbon ratio was held at 1:1 and the steam to carbon ratio was held at 2:1. The furnace was set to a constant temperature of 600 ºC.

Results and Discussion

After calcination, XRD indicated that the desired oxide phases were obtained for both YSZ and $Ce_{0.75}Zr_{0.25}O_2$. The surface area of the YSZ, which was calcined to 800 ºC, was approximately 10 m^2/g. The surface area of the $Ce_{0.75}Zr_{0.25}O_2$ was highly dependent on calcination temperature. Surface areas for the $Ce_{0.75}Zr_{0.25}O_2$ before calcination were greater than 130 m^2/g, and generally greater than 60 m^2/g after calcination at 600 ºC. After calcination at 800 ºC, the $Ce_{0.75}Zr_{0.25}O_2$ had a surface area of less than 30 m^2/g. Figure 2 presents the XRD patterns of $Ce_{0.75}Zr_{0.25}O_2$ as prepared and calcined at 600 and 800 ºC. In all cases, the $Ce_{0.75}Zr_{0.25}O_2$ XRD indicates the oxide structure. Catalysts prepared using the low surface area supports (< 30 m^2/g) had very low nickel dispersion.

Figure 2. XRD of $Ce_{0.75}Zr_{0.25}O_2$ (A) as prepared (B) calcined in air for 2 hours at 600 ºC and 800 ºC.



Despite the low nickel dispersion, the $Ni/Ce_{0.75}Zr_{0.25}O_2$ catalysts were active for autothermal reforming of isooctane. When reduced in hydrogen prior to reaction, feed temperatures of 325 ºC were sufficient to light off reaction. If no pre-reduction was carried out, catalysts were still able to light off, but higher pre-heat temperatures were required. Conversions of isooctane to CO, CO_2, and CH_4 were greater than 90%, and the overall product composition closely matched thermodynamic equilibrium predictions calculated using ASPEN®. It was also possible to operate the catalyst adiabatically by insulating the catalyst bed, and using the preheated feed to light off the catalyst instead of the electric furnace.

Different results were obtained when the $Ni/Ce_{0.75}Zr_{0.25}O_2$ catalyst was deployed as a washcoat in the planar microreactor. Packed bed testing of the washcoat indicated similar performance to the catalyst powder alone. When tested on a foam carrier in the microreactor, however, conversions were much lower in general. CO_2 production was similar, but CO and H_2 production were much lower. Oxygen conversions were almost always 100%, indicating that oxidation was taking place. We hypothesize that the metal housing of the microreactor caused extensive heat loss from the catalyst, resulting in lower rates of steam reforming and subsequently lower CO and H_2 production. While the housing is heated to 650 ºC, peak temperatures in the packed beds operating adiabatically have been estimated at 900 ºC. In the packed bed experiments the heat from oxidation is carried through the catalyst bed, supporting the steam reforming reaction. In the microreactor, the heat from oxidation is both carried through the catalyst and conducted away by the housing, probably causing the reduced performance. The design of the microreactor and materials of its construction are subjects of ongoing investigation.

References

1. A. Docter and A. Lamm, Journal of Power Sources, Vol. 84, 1999, pp. 194-200.
2. J. R. Rostrup-Nielsen, in: J. R. Anderson, M Boudart (Eds.), Catalysis, Science and Technology, Vol. 5, Springer, Berlin, 1984, p. 1.
3. R. Craciun, B. Shereck, and R. J. Gorte, Catalysis Letters, Vol. 51, 1998, pp.149-153.
4. J. B. Wang, Y.- L. Tai, W.- P. Dow, and T.- J. Huang, Applied Catalysis A: General, Vol. 218, 2001, pp. 69-79.
5. T. Zhu and M. Flytzani-Stephanopoulos, Applied Catalysis A: General, Vol. 208, 2001, pp. 403-417.
6. S. Pengpanich, V. Meeyoo, T. Rirksomboon, and K. Bunyakiat, Applied Catalysis A: General, Vol. 234, 2002, pp. 221-233.
7. X. Wang and R. J. Gorte, Applied Catalysis A: General, Vol. 224, 2002, pp. 209-218.
8. W.-S. Dong, K.- W. Jun, H.- S. Roh, Z.-W. Liu, and S.- E. Park, Catalysis Letters, Vol. 78, 2002, pp. 215-222.
9. E. Ramiriez-Catrera, N. Laosiripojana, A. Atkinson, and D. Chadwick, Catalysis Today, Vol. 78, 2003, 433-438.
10. S. Kim, J. J. Gislason, R. W. Morton, W. Q. Pan, H. P. Sun, and R. M. Laine, Chemistry of Materials, Vol. 16, 2004, pp. 2336-2343.

What we said…

- **Catalysts comprised of nickel supported on the yttria-stabilized-zirconia (an oxygen ion conductor) and on Ce-ZrO_2 mixed oxides (an OSC material) have been prepared and evaluated for autothermal reforming of simulated gasoline.**
- **Catalysts prepared as nanopowders via flame-spray pyrolysis and using traditional precipitation techniques are compared.**
- **The effects of reaction temperature, space velocity, steam to carbon ratio, oxygen to carbon ratio, and metal loading on activity and coking behavior have been investigated.**
- **Partial oxidation and steam reforming experiments of single components and mixed feeds have also been undertaken to investigate the rates and potential mechanisms of the overall autothermal reforming process.**
- **Washcoat formulations of some of the catalysts were developed and tested for autothermal reforming using a planar microreactor.**