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Hydrogen production from E85 fuel with ceria-based catalysts

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ABSTRACT

The use of renewable (crop-derived) fuels to produce hydrogen has considerable environmental advantages with respect to reducing net emissions of carbon dioxide into the atmosphere. Ethanol is an example of a renewable fuel from which hydrogen can be derived, and E85 is a commercially available ethanol-based fuel of increasing importance. The distributed production of hydrogen from E85 fuel is one potential way of assuring availability of hydrogen as PEM fuel cells are introduced into service. NexTech Materials is collaborating with the U.S. Army Construction Engineering Laboratory (CERL) on the development of a hydrogen reformation process for E85 fuel. This paper describes the technical status of E85 fuel reforming process development work using Rh/ceria catalysts. Reforming results are compared for steam reforming and oxidative steam reforming of ethanol (the primary constituent of E85 fuel), isooctane, ethanol/iso-octane fuel mixtures (as a surrogate to E85), and commercially available E85 fuel. Stable reforming of E85 at 800 °C and a space velocity of 58,000 $\mathrm{scm^3\,g_{cat}^{-1}\,h^{-1}}$ over a 200-h period is reported.

1. Introduction

As oil supplies dwindle, other sources of energy need to be developed to support the growing energy needs of the world. There is no single energy solution for the future, with coal, solar, wind, nuclear and fuel cells all having their place. The use of liquid fuels, such as ethanol, produced from renewable resources, is an attractive intermediate approach for energy production which reduces near-term reliance on fossil fuels, while alternative energy technologies are being established.

The U.S. military is in a unique position to support the demonstration of emerging renewable energy technologies. With a large number of military bases and installations throughout the world, there is opportunity for significant cost savings, as well as environmental stewardship. Further, highly trained personnel are available to support implementation of new energy technologies as they are introduced. The Army has been at the forefront of this trend. In 2005, the *Army Energy Strategy for Installations* was established [1,2], with the goal of: (1) eliminate/reduce energy and water usage in existing facilities, (2) increase energy efficiency in renovation and new construction, (3) reduce dependency on fossil fuels, (4) conserve water resources, and (5) improve energy security.

Fuel cells offer a promising approach for achieving these goals. Fuel cells efficiently generate power from hydrogen or hydrocarbon fuels and greatly reduce emissions of pollutants. Fuel cells offer a near-term solution for conserving fossil fuels, and a long-term solution for generating power from renewable fuels. Of the various types, the proton exchange membrane (PEM) fuel cell operates at low temperature with pure hydrogen as fuel. PEM fuel cells are being developed for both stationary and transportation applications; the technology has matured to the point that systems are entering the demonstration phase of commercial acceptance. However, lack of availability of low-cost hydrogen limits the widespread use of PEM fuel cells.

Even before implementation of the *Army Energy Strategy for Installations*, the U.S. Army has been supporting its goals with a program aimed at demonstrating stationary fuel cells at military installations. In one such program, being led by the Army's Construction Engineering Research Laboratory (CERL), 93 PEM fuel cells have been installed at 56 different military sites. These fuel cells operate on hydrogen, which was either stored in cylinders or produced via on-site reformation of fossil fuels (natural gas or propane). A logical next step in development of fuel cell technology for stationary and transportation applications is the operation of fuel cells on hydrogen derived from renewable fuels. A partially renewable fuel of increasing importance is E85, which

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is a blend of 85% ethanol (produced from corn) and 15% gasoline. Future commercial availability of E85 fuel is assured, given that this is the primary alternative fuel for “Flex-Fuel” vehicles that are being produced worldwide in ever increasing numbers. Although pure ethanol may be a more logical fuel choice for fuel cell systems, E85 was examined because of its widespread commercial availability.

To produce hydrogen from E85 fuel, the fuel must be reformed with steam and/or oxygen to produce a hydrogen-rich gas mixture that can be purified and collected. Reforming is a challenge because E85 fuel consists of two distinct types of hydrocarbons (ethanol and gasoline) and because the gasoline fraction contains sulfur that is a poison to most reforming catalysts. The demonstration of a suitable reforming catalyst and process is the first and most critical step toward demonstrating hydrogen production from E85 fuel.

In general, the level of difficulty for the reforming of hydrocarbon fuels increases with the complexity of the hydrocarbon fuel. Thus, ethanol with two carbon atoms in its structure is more difficult to reform than methane or methanol (both of which have one carbon atom in their structures). Gasoline is especially difficult to reform, given the multitude of different hydrocarbon species in gasoline and average carbon number of 7–8. It is particularly noteworthy that E85 is a fuel that contains two distinctly different components (ethanol and gasoline). Thus, a catalyst that works well for reforming of ethanol needs to work equally well for reforming of gasoline. The biggest challenge to designing catalysts for reforming of E85 fuel is the presence of sulfur in the fuel. This further limits the scope of available catalysts.

There has been a significant amount of reported work devoted to reforming of gasoline, diesel and logistic fuels, both for on-board fuel processing in automotive applications and for military fuel cell systems. Rhodium-based catalysts, and especially Rh/ceria catalysts, have been found to be extremely effective for reforming of these higher hydrocarbons with respect to obtaining high hydrogen yields without carbon deposition [3–7]. There also is a wide body of recent literature describing the steam reforming of ethanol for use in PEM fuel cell systems. Of the various catalysts evaluated, Rh/ceria catalysts were found to be extremely active for ethanol reforming, and more selective toward hydrogen [8–14], without formation of methane, ethylene and other undesired by-products of the ethanol decomposition reaction. Another potential advantage of Rh/ceria catalysts for steam reforming of ethanol is their high water-gas-shift activity, which leads to a reformed product gas with higher hydrogen and less carbon monoxide depending on temperature and steam content.

In this work, the activity, selectivity, and long-term stability of Rh/ceria catalysts for reforming of ethanol, iso-octane, mixtures of the two, and real E85 are examined. The affect of sulfur in the fuel on catalyst performance is also observed. Based on the demonstrated high performance of Rh/ceria catalysts for E85 steam reforming and oxidative steam reforming, the catalysts appear to be an excellent material for distributed hydrogen production systems under development.

2. Experimental/materials and methods

2.1. Design and construction of liquid-fuel reforming reactor

Carefully designed fuel and steam delivery is necessary to demonstrate long-term catalyst performance when using liquid reactants under neat conditions. Oscillations in fuel to liquid ratio can cause carbon formation that ultimately leads to reactor failure. A liquid reforming test reactor was therefore designed and constructed for use in this research. The primary reactor components included: HPLC pumps for steady delivery of liquid reactants (water and fuel); mass flow controllers for delivering gaseous reactants (e.g., air); heated vaporization using NexTech’s custom-built vaporizer design, a mixing chamber to dampen oscillations in vaporization and ensure even mixing of reactants; a packed bed catalyst chamber, a condensing system for removal of water and partially reacted condensable gases in the reformed product, and a gas chromatograph fitted with a thermal conductivity detector for product gas analysis. The reactor system allowed for testing catalysts under neat conditions (fuel and steam only) to simulate a real reforming system. The gas chromatograph (with helium carrier) was set up to detect the possible gaseous products, including: CO, CO_2, H_2, methane, ethane, and ethylene. The product analysis was further verified with a MKS Cirrus mass spectrometer.

2.2. Catalyst synthesis and characterization

Catalyst testing was performed using NexTech’s 2-wt% Rh/ceria reforming catalyst, prepared by proprietary methods. The doped ceria catalyst support was prepared by a hydrothermal synthesis process that provides a thermally stable high surface area ceria-based mixed oxide support. Proprietary metal deposition and reduction methods were used to maximize rhodium dispersion and uniformity. The catalyst has a BET surface area of $64\,m^2\,g^{-1}$, after deposition of rhodium. All catalysts were calcined at 800 °C prior to testing.

2.3. Catalyst testing

The catalyst was tested at various temperatures (700–800 °C), steam-to-carbon ratios (3–6), and oxygen-to-carbon ratios (0–0.25) with ethanol, ethanol/iso-octane, or E85 as the fuel. An outline of the test conditions reported in this study is shown in Table 1. The sulfur content of the commercial E85 was estimated based on sulfur exiting the reactor, detected by a mass spectrometer. Tests were carried out at steady-state over hundreds of hours to observe signs of catalyst deactivation (visible by breakthrough of unreformed hydrocarbons) or carbon formation (causing increased pressure drop and reactor failure). Space velocities were chosen to achieve

Table 1
Breakdown of long-term testing conditions for 2% Rh/ceria catalyst.

Fuel	T (°C)	SV ($scm^3\,g^{-1}\,h^{-1}$)	Steam/carbon ratio	O_2/carbon ratio	Sulfur content in fuel (ppmw)	Test duration (h)	Figure(s) showing results
Ethanol	700	20,000–50,000	3–5	0	0	100	1
Iso-octane	800	18,000–55,000	5–6	0.00–0.13	0	50	2
E85 surrogate	800	68,000–80,000	5–6	0.00–0.25	0	50	3–4
E85 surrogate	750–800	48,000	5	0	0	80	5
E85 surrogate	800	58,000	6	0	5	40	6
E85 surrogate	800	58,000	6	0	20	75	7
Commercial E85	800	58,000	6	0	~10	100	8
Commercial E85	800	48,000–58000	5–6	0.00–0.13	~10	125	9–10
Commercial E85	800	58,000	6	0	~10	200	11