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# Critical Issues in Catalytic Diesel Reforming for Solid Oxide Fuel Cells

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**Developing low-cost diesel-reforming catalysts and improving fuel mixing prior to catalytic reforming were addressed as two critical issues under the current study. Ruthenium-doped lanthanum chromite and aluminite were explored as catalysts for the autothermal reforming of diesel fuel. Dodecane was used as a surrogate fuel. Both catalysts yielded nearly 20 moles of hydrogen per mole of dodecane at oxygen-to-carbon ratios of 0.5 and steam-to-carbon ratios of 2 at space velocities near 100,000/h$^{-1}$. Both catalysts were shown to have good S tolerance when tested with a fuel mixture containing 50 parts per million S in the form of dibenzothiophene. Parallel to catalyst development, the impact of fuel mixing and vaporization through improved liquid injection also is under investigation.**

**Keywords** catalytic diesel reforming, fuel injection, perovskite, solid oxide fuel cell

## 1. Introduction

Solid oxide fuel cell (SOFC) auxiliary power units (APU) for heavy-duty vehicles could reduce emissions and conserve fuel on the North American continent where engines are kept running while drivers rest. An SOFC APU must generate enough power for cabin comfort and may also have to supply electricity for the refrigeration of the load. It is highly desirable that an SOFC APU consumes the same type of diesel fuel used by the main engine.

Converting diesel fuel into a hydrogen-rich gas that is suitable for SOFC is more challenging than converting gasoline due to the multicyclic aromatics and the aromatic S compounds in diesel fuel. To break down these compounds, the reformer must operate at elevated temperature and the reforming catalyst needs to have a significant tolerance for S. In making these statements, it is assumed that an autothermal reactor (Ref 1) is used, and that the S in the diesel fuel is not completely removed at the refinery.

When the operating temperature of the autothermal reforming (ATR) exceeds about 800 °C, catalyst stability becomes an issue. Noble metal catalysts such as Rh, Pd, or Pt on alumina or ceria not only lose some activity due to the adsorption of $H_2S$ on the metal surface, but also are further affected by evaporation and agglomeration of the metal.

In an earlier work, it was noticed that noble metals interact with supports containing oxide ion vacancies as shown in the following equation:

$$\mathrm{Pt} + \mathrm{V_O} + \mathrm{O_2} = \mathrm{Pt^{4+}} + 2\mathrm{O^{2-}} \quad \text{(Eq 1)}$$

Under oxidizing conditions, none of the Pt loaded onto a Gd-doped ceria surface was present as metal but instead had formed Pt(IV)-Pt$^{+4}$ ions. The latter are known to activate carbon hydrogen bonds, and the autothermal reforming of the hydrocarbon molecules is catalyzed by a redox reaction with Pt (IV). It stands to reason that the partial oxidation of hydrocarbon molecules might also be occurring on perovskite surfaces with B-site elements that can undergo redox reactions. Such catalysts would be expected to be more thermally stable than finely dispersed noble metals on alumina.

To be useful as an ATR catalyst, the perovskite must, of course, be chemically stable in both oxidizing and reducing conditions. Lanthanum chromite and lanthanum aluminite meet that requirement. The former has some redox properties on the B site, while the latter does not. However, doping with other transition metal elements on the B site can make the surface more active. In this article, results are reported on doping chromite and aluminite with Ru.

Another critical aspect of diesel reforming is fuel mixing and vaporization before entering the catalyst bed. Diesel has a higher average boiling point and viscosity than does gasoline, and is known to be difficult to mix uniformly with other reactants such as air and steam in the gas phase. Inadequate mixing and poor dispersion often cause coke formation and localized hot spots, both of which affect reforming efficiency and hydrocarbon conversion. For better catalytic reforming, it is highly desirable that complete vaporization and mixing of diesel occur, using existing commercial injector components.

## 2. Results and Discussion

### 2.1 ATR Reforming Catalyst Development

Perovskites were made by mixing nitrate solutions of the transition metals with glycine followed by drying and a self-combustion process (Ref 2). The perovskite powders were subsequently calcined and pelletized, followed by testing in a plug-flow reactor using a sample size of ~0.5 g. Dodecane was used as the diesel surrogate fuel in this first phase of the study. To evaluate S tolerance, dibenzothiophene (DBT) was added to

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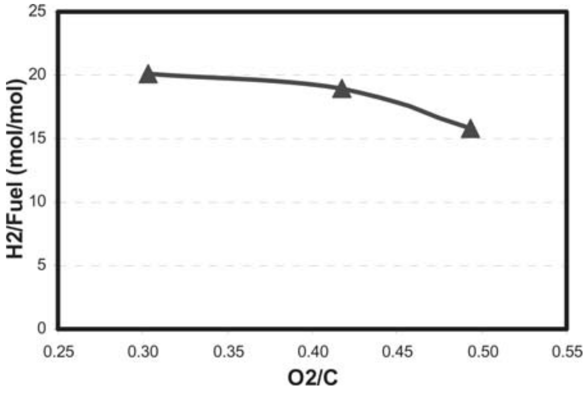

**Fig. 1** Hydrogen yield as a function of $O_2/C$ during the reforming of dodecane over $La_{0.8}Sr_{0.2}Cr_{0.95}Ru_{0.05}O_3$

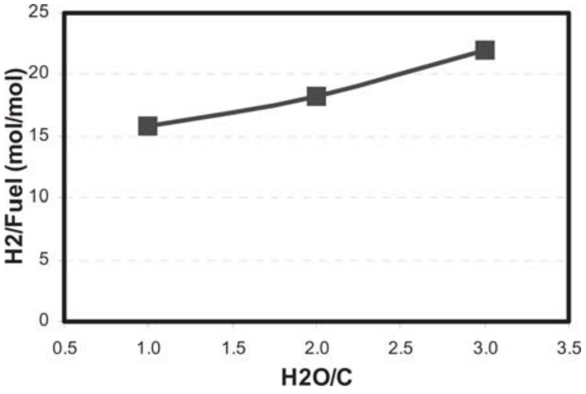

**Fig. 2** Hydrogen yield as a function of $H_2O/C$ during the reforming of dodecane over $La_{0.8}Sr_{0.2}Cr_{0.95}Ru_{0.05}O_3$

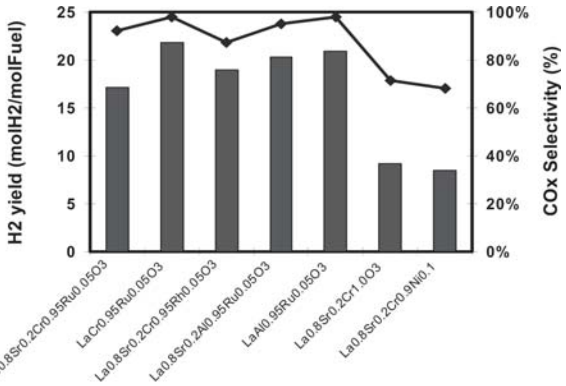

**Fig. 3** Hydrogen yield (bar) and COx selectivity (line) obtained for several perovskite catalysts during ATR reforming

the dodecane so that the total S content was 50 parts per million (ppm) by mass.

During the catalytic activity test, the surrogate fuel was mixed with air and steam to form input mixtures with various predefined oxygen-to-carbon ratios ($O_2/C$) and steam-to-carbon ratios ($H_2O/C$). In this study, $O_2/C$ was generally in the range of 0.3 to 0.5, while $H_2O/C$ was in the range of 1 to 3. To differentiate the performance of various catalysts, relatively high space velocities were used with a typical velocity of gas hourly space velocity (GHSV) >100,000/h. The reactor temperature was maintained near 700 °C using a tube furnace. The reformate produced from the catalytic reaction was analyzed by gas chromatography after water was removed from the product through a condenser and a moisture trap. The ATR reforming activity was typically measured by: (a) hydrogen yield, which represents the mole of hydrogen produced over the mole of input fuel; (b) total reforming efficiency, $\eta_{H2+CO}$, which is defined as the heat of combustion produced by hydrogen and carbon monoxide in the reformate over the heat of combustion of the input fuel; and (c) COx selectivity, which is calculated based on the molar sum of the CO and $CO_2$ produced in the reformate over the total moles of carbon in the fuel.

Shown in Fig. 1 is an example of the $H_2$ yield obtained during the investigation of one of the perovskite catalysts, $La_{0.8}Sr_{0.2}Cr_{0.95}Ru_{0.05}O_3$, at three different $O_2/C$ ratios by gradually increasing airflow while maintaining $H_2O/C$ at one. The increase of $H_2$ yield with the decrease of air input can be attributed to reduced hydrogen oxidation due to a lower amount of oxygen and improved fuel conversion at lower space velocity. Corresponding to the change of $H_2$ yield, a similar trend was observed for the total reforming efficiency under these experimental conditions.

Parallel to the oxygen-to-carbon ratio experiment, the $H_2$ yield and the total fuel reforming efficiency was investigated as a function of $H_2O/C$, by gradually increasing the water injection while maintaining the $O_2/C$ at 0.5. The $H_2$ yields under these experimental conditions are plotted in Fig. 2. Clearly, the production of $H_2$ favors high steam content even when the space velocity is raised substantially as a result. It was also found that very good $H_2$ yield and total reforming efficiency can be achieved after removing the air from the mixture. This suggests that the material is also a very good steam-reforming catalyst.

The catalyst activity for diesel reforming depends, of course, on the formulation. Shown in Fig. 3 are the $H_2$ yields and COx selectivities of several new catalysts obtained under ATR reforming conditions of $O_2/C = 0.5$ and $H_2O/C = 2$. The Ru-doped lanthanum chromite is clearly much more active than the undoped chromite or the Ni-doped chromite. It was surprising that Sr substitution on the A-site seems to diminish the activity slightly. Similarly, the aluminite-based perovskites with Ru doping on the B-site performed very well, proving that the activity is associated with the B-site doping and not the B-site host. It was also found that Ru-doped chromite has catalytic activity, as measured by the $H_2$ yield and COx selectivity, similar to that of Rh-doped perovskite during the reforming of dodecane. This is rather enlightening, considering the significant difference in raw material cost. Further study is necessary to verify whether comparable performance can be achieved under a wider range of catalytic conditions or types of fuels.

One may ask whether the Ru or the Rh is in fact substituted for Cr or Al in the perovskite lattice or is present as metal or oxide on the surface. Efforts are underway to answer this question using extended x-ray spectroscopy absorption fine structure. Preliminary results indicate that the majority of the Ru and Rh is anchored in the lattice.

One of the key challenges in diesel reforming is deactivation from S poisoning. The current low-S diesel standard has S content targeted at 50 ppm. The organic S compounds in diesel, unlike those in gasoline, are mainly from polyaromatic molecules, such as DBT and methyl-DBT. These compounds are even harder to desulfurize and are expected to cause the deactivation of reforming catalysts. Shown in Fig. 4 are the total

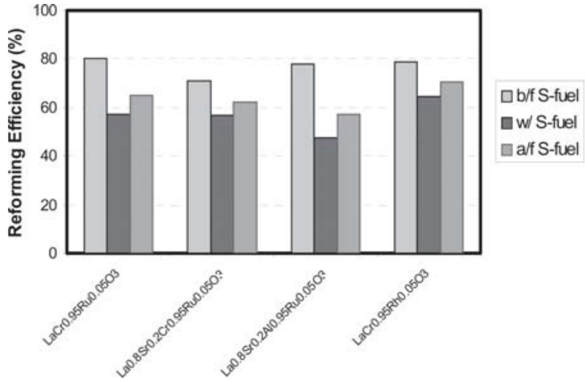

**Fig. 4** Total reforming efficiencies before, during, and after exposure to DBT

reforming efficiencies of the ATR reaction over four perovskite catalysts before, during, and after exposure to the fuel containing the organic S for 150 min. (The maximum reforming efficiency ranges from 81 to 87% depending on the product distribution between $H_2$ and CO.) The deactivation occurs over all the catalyst samples tested, although the degree of poisoning is different. However, a significant recovery was also observed after the S-contaminated fuel was replaced by S-free fuel.

### 2.2 Fuel Injection/Mixing Study

In an ATR diesel reformer, fuel should be mixed with air and steam as thoroughly and uniformly as possible prior to reaching the catalyst bed to minimize the hot spot and coke formation. Preferably, the fuel injection can be accomplished through a low-cost, commercially available fuel injector. To better understand how to maximize fuel vaporization and the mixing, a laboratory test facility has been constructed. The facility consists primarily of a diesel-fuel injection system, a fuel-steam mixing apparatus, and a fuel-reforming chamber. The injection system is a single-injector system designed for a G-2 diesel fuel injector supplied by International Truck and Engine Corporation (ITEC, Warrenville, IL). Diesel fuel is fed to the injector through two stages of pressurization in a fuel accumulator and at the common rail holding the injector. The fuel injection rate is controlled by the ITEC control system. The injection and mixing processes can be examined and recorded by a charge coupled device (CCD) camera. Figure 5 shows the typical diesel fuel spray pattern from the G-2 injector. Fuel droplet size, the homogeneity of the fuel/steam mixing, and the effects on the autothermal reforming process will be examined in the future. The optimal injection and mixing parameters will then be determined.

**Fig. 5** Image of the fuel-spraying pattern obtained through a CCD camera

## 3. Conclusions

Excellent $H_2$ yield and reforming efficiency were observed for Ru-doped chromite and aluminite under catalytic ATR reaction conditions at different $O_2$/C and $H_2O$/C for diesel surrogate fuel. The catalytic activity improved substantially over that of nondoped material and performed equally as well as the Rh-doped perovskite. The catalysts also demonstrated good S tolerance and robust recovery when tested with S-contaminated fuel.

### Acknowledgments

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