

# Catalysts and Fuel Mixing for Diesel Reformer in Fuel Cell Auxiliary Power Unit

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The high energy density and existing refueling infrastructure of petroleum-derived heavy hydrocarbon fuels, such as diesel and JP8 fuel, have made them popular in transportation, military, and industrial power generations. Recent development in the prospects of on-board or remote solid oxide fuel cell (SOFC) power plants has created a great demand for reforming diesel-type fuels to produce reformat, a gas mixture containing hydrogen, carbon oxides, and light hydrocarbons as the fuel gas. The conversion of diesel fuel to reformat can be achieved through a catalytic reformer which can be coupled with a SOFC unit to produce electric power with high efficiency, low noise and reduced emissions. The advantage of such combination is highly attractive in many applications. One of the examples is the auxiliary power unit (APU) of truck or aircraft in which combined generation of power and heat is of particularly beneficial during the shutdown of the main engine.

At Argonne National Lab, we have been focusing on developing technology solutions for some of the key challenges for commercially viable diesel reformer. One of our focus areas is the low-cost diesel reforming catalyst. We selected autothermal reforming (ATR) as our choice of catalytic conversion. The state-of-the-art diesel ATR catalyst contains rhodium as the key active ingredient. Although the catalyst has a good hydrogen yield and reforming efficiency, it is expensive due to the high cost of raw material, rendering it unattractive for large-scale commercial production. There is clearly an urgent need to find an alternative, low-cost ATR catalyst that performs equally well or better than the benchmark Rh catalyst. Another focus area is fuel mixing for diesel injection. Diesel is known for its difficulty to be uniformly mixed in the gas phase with other reactants such as air and steam. Inadequate mixing and poor dispersion often cause coke formation and self-ignition; both affect the reforming efficiency and hydrocarbon conversion. It is highly desirable that a completely vaporization and mixing of diesel can be accomplished for better catalytic reforming using the existing commercial injector components.

## Development of Perovskite ATR Reforming Catalysts

We have been investigating new perovskite type of metal oxide materials as potential low-cost catalysts for ATR reforming. Perovskite-related metal oxides are known for their good catalytic activities in the partial oxidation (POX) and, to a lesser degree, in the steam reforming (SR) reactions. Shown in Figure 1 is a single lattice cell structure of perovskite. Both the A- and the B- site in a perovskite can be partially substituted by different types of cations, A' and B', while maintaining a stable crystal structure, it is therefore relatively easy to alter the formulation from  $ABO_3$  to  $A_{1-x}A'_xB_{1-y}B'_yO_{3-e}$ , where the ionic radii and the charges in A' and B' can be the same or different from A and B. This enables us not only to reformulate the

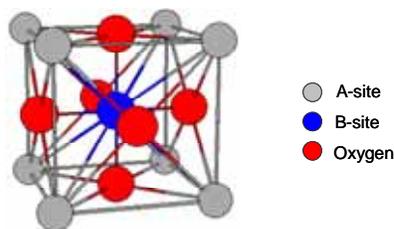


Figure 1. Lattice structure of a single cell in perovskite.

composition by properly incorporating the transition metals with strong POX or SR activities to create an effective ATR site, but also to synthesize material with designed charge deficiency and lattice distortion. The charge imbalance due to partial doping can lead to either oxidation state adjustment of the counter cation or the oxygen vacancy, either of which could result in new redox property and the surface morphology preferred for ATR reaction.

We have based our work on lanthanum chromite and lanthanum aluminite perovskites since both are stable in reducing and oxidizing environments, and have then made partial substitutions on the “A” and “B” sites. The perovskites were made by mixing nitrate solutions of the transition metal with the organic compound followed by drying and a self-combustion process [1]. The perovskite powder were subsequently pelletized and evaluated in a plug-flow reactor test plant. Dodecane was used as the diesel surrogate fuel in this study. To evaluate the catalyst deactivation due to sulfur, we also prepared S-contaminated surrogate fuel by adding a representative organic sulfur compound, dibenzothiophene (DBT), into the dodecane so that that the final fuel mixture contained 50 ppm sulfur by weight. During the catalytic activity test, dodecane was mixed with air and steam to form input mixtures with various pre-defined oxygen-to-carbon ratios,  $O_2/C$ , and steam-to-carbon ratios,  $H_2O/C$ . In our 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 between different catalysts, relatively high space velocities were used, with a typical velocity of GHSV  $>100,000 \text{ hr}^{-1}$ . The reactor temperature was maintained either at  $700 \text{ }^\circ\text{C}$  or  $800 \text{ }^\circ\text{C}$  through 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) reforming efficiency,  $\eta_{H_2+CO}$ , which is

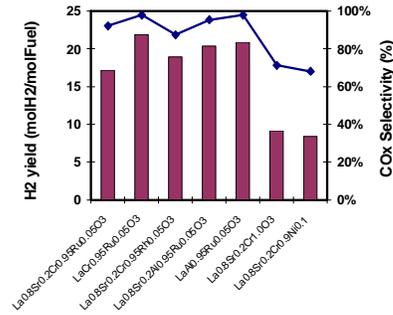


Figure 2. Hydrogen yields and CO<sub>x</sub> selectivities measured for several perovskite catalysts during ATR reforming.

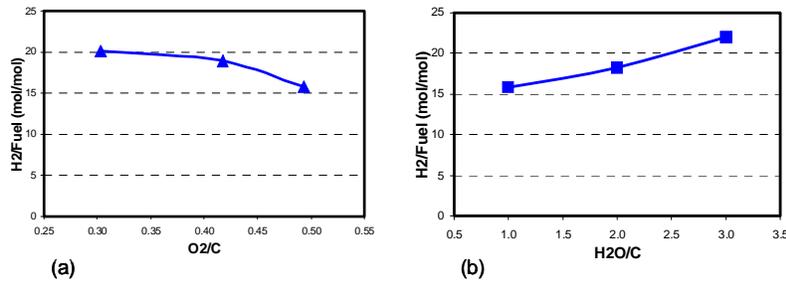


Figure 3. The changes of hydrogen yield as the function of oxygen-to-carbon ratio (a) and steam-to-carbon ratio (b) during ATR reforming over  $La_{0.8}Sr_{0.2}Co_{0.95}Ru_{0.05}O_3$ .

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) CO<sub>x</sub> selectivity, which is calculated based on the molar sum of CO and CO<sub>2</sub> produced in the reformat over the total moles of carbon in the fuel.

## Results

One of the key discoveries in our experiment is that the ATR reforming activity increases substantially when small amount of ruthenium is exchanged into the B-site of the perovskites, particularly chromite and aluminite. Shown in Figures 2 is an example of hydrogen yields and CO<sub>x</sub> selectivities obtained during the study of ATR reforming activities of several Ru doped perovskite catalysts. For comparison, we also included one Rh doped and other none-doped materials. In general, the ruthenium exchange perovskites performed equally well or better than that doped with rhodium. The performance also much exceeded that of none-doped or nickel doped perovskites. To evaluate the impact of reforming input on overall ATR activity, we also studied the change in hydrogen yield and reforming efficiency of the reformat by systematically varying the composition of the input mixture. Shown in Figure 3a and 3b are the change of hydrogen yield as the function of O<sub>2</sub>/C and H<sub>2</sub>O/C during the catalytic reaction over La<sub>0.8</sub>Sr<sub>0.2</sub>Cr<sub>0.95</sub>Ru<sub>0.05</sub>O<sub>3</sub> catalyst, respectively. The hydrogen production clearly favors higher steam and lower oxygen content. In an adiabatic reactor, however, a balance has to be optimized so that the thermal energy consumed by the endothermic SR reaction and the heat loss can be compensated by that produced through exothermic POX path.

The catalyst deactivation from sulfur poisoning represents a major issue in diesel reforming because of the high S content in the commercial fuel. To evaluate the impact of sulfur on ATR catalytic activity, we added DBT as a representative organic sulfur contaminant to the surrogate fuel. DBT is a well-known compound existing in a commercial low sulfur diesel fuel. It contains two phenyl group coupled by a sulfur and a C-C bond. Due to the spatial hindrance from the two phenyl groups, it is very difficulty to remove this compound and its derivatives from the hydrocarbon fuels through the hydro-desulphurization process during refining. We conducted the S-tolerance study for a series of perovskite catalyst by first subjecting the catalyst with the reforming input containing S-free dodecane mixed with air and steam at GHSV ~ 100,000 with

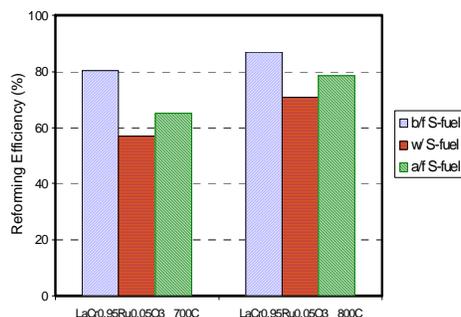


Figure 4. Comparison of total reforming efficiencies before and after S-contaminated fuel exposure at 700 °C and 800 °C for LaCr<sub>0.95</sub>Ru<sub>0.05</sub>O<sub>3</sub> catalyst.

O<sub>2</sub>/C = 0.5 and H<sub>2</sub>O/C = 1. After the catalytic reforming activity reached to a steady state and established a baseline, the fuel was switched to the sulfur contaminated surrogate mixture for an extended period of exposure. At the end of the S-deactivation process, the fuel input was switched back to clean dodecane to continue run briefly until the recovery baseline was established. Catalytic reaction temperatures of both 700 °C and 800 °C were used for the study. Shown in Figure 4 are the reforming efficiencies taken for one of our benchmark catalysts, LaCr<sub>0.95</sub>Ru<sub>0.05</sub>O<sub>3</sub>, under the both reaction temperatures before, during and after sulfur exposure.

The catalyst performance improved at every level when the catalytic temperature was raised just by 100 degree; especially notable is the increase of efficiency under the influence of sulfur. Furthermore, the catalyst activity recovered much better at 800 °C as is demonstrated by the relative ratio before and after the exposure of sulfur contaminated fuel. We attribute the improved catalyst performance to the following factors; first, the binding of sulfur is significantly weakened

