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LOW COST AUTOTHERMAL DIESEL REFORMING CATALYST DEVELOPMENT

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ABSTRACT

Catalytic autothermal reforming (ATR) represents an important step of converting fossil fuel to hydrogen rich reformat for use in solid oxide fuel cell (SOFC) stacks. The state-of-the-art reforming catalyst, at present, is a Rh based material which is effective but costly. The objective of our current research is to reduce the catalyst cost by finding an efficient ATR catalyst containing no rhodium. A group of perovskite based catalysts have been synthesized and evaluated under the reforming condition of a diesel surrogate fuel. Hydrogen yield, reforming efficiency, and conversion selectivity to carbon oxides of the catalyst ATR reaction are calculated and compared with the benchmark Rh based material. Several catalyst synthesis improvements were carried out including: 1) selectively doping metals on the A-site and B-site of the perovskite structure, 2) changing the support from perovskite to alumina, 3) altering the method of metal addition, and 4) using transition metals instead of noble metals. It was found that the catalytic activity changed little with modification of the A-site metal, while it displayed considerable dependence on the B-site metal. Perovskite supports performed much better than alumina based supports. Reformula-

INTRODUCTION

In the hunt for alternative energy sources, a considerable amount of attention is given to the use of hydrogen as an energy carrier in fuel cells. Fuel cells are recognized for their clean emissions and considerable efficiency over combustion methods. Unfortunately, providing a pure, practical source of hydrogen has posed a greater concern: though hydrogen may be the most abundant element on earth, air comprises only a few thousandths of a percent of it; the rest is in water and organic molecules [1]. There are various ways of extracting hydrogen from these sources. One of the most effective methods of generating hydrogen from hydrocarbon fuels is fuel reforming, through which a fossil fuel is catalytically broken down to form a mixture containing H₂, CO, CO₂, etc. The hydrogen-rich mixture, also called reformat, can then be used directly as the fuel for various types of fuel cells.

Diesel is one of the most attractive hydrocarbon fuels that can be reformed for fuel cell application. It has the highest volumetric and gravimetric densities for hydrogen content compared to other hydrocarbons, making it ideal for transportation and remote power generation applications. Also, as diesel is used extensively as a fuel source for heavy vehicles, existing distribution networks would still be employed. One of the applications of diesel reforming is to use a hydrogen source for a

Solid Oxide Fuel Cell (SOFC) powered Auxiliary Power Unit (APU). For example, a SOFC based truck APU would supply the constant energy requirements for all non-power train related elements such as air conditioning, electronics, etc, even when the vehicle is idling. A fuel cell powered APU will save a considerable amount of fuel and provide a highly efficient, low noise power source [2].

There has been a considerable amount of research in developing a catalyst for diesel reforming for fuel cell application. The studies [3, 4] have shown that certain rhodium (Rh) based catalysts perform exceptionally well. However, Rh is among the most expensive precious metals with its market price constantly fluctuating between \$1000/oz to \$2000/oz. It is economically unfeasible to produce Rh based catalysts for the mass APU market. To make commercial SOFC APU viable, a low cost alternative material has to be found which can replace the Rh based catalyst [2].

Using the performance of the rhodium catalyst as a benchmark, our group synthesized and tested various catalysts in hopes of identifying a catalyst composition and operating condition that produced similar efficiencies at a cost-effective level. The focus of our catalyst materials were transition metal based perovskite compounds. Several perovskite based catalysts were synthesized and evaluated through a microreactor test plant. Dodecane was chosen as a surrogate for diesel

to provide a better estimation on fuel conversion efficiency and hydrogen yield. Dodecane has a molecular formula similar to the diesel average composition. Also, its overall heat of combustion is comparable to that of high quality diesel.

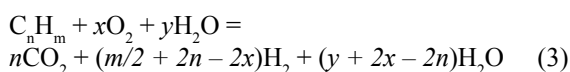
The reactor design employs autothermal reforming (ATR) techniques to generate the hydrogen from the dodecane. The process is the combination of two separate reactions, partial oxidation (POX) and steam reforming (SR). An ideal partial oxidation reaction converts fuel to carbon dioxide and hydrogen, as shown by the following exothermic reaction [5]:



An ideal steam reforming reaction converts fuel with water to carbon dioxide and hydrogen by the following endothermic equation [5]:



Combining POX and SR one obtains the autothermal reforming reaction [6]:



Ideally, the ATR reaction converts all fuel to CO_2 and H_2 . The x coefficient is the oxygen to fuel ratio, y is the steam to fuel ratio. The $(y + 2x - 2n)$ is the excess water, and $(m/2 + 2n - 2x)$ is the hydrogen produced per mole of fuel. The POX and SR reactions are exothermic and endothermic, respectively. Through the ATR mechanism, the heat generated from the POX reaction is used in the SR reaction. Thus, the reaction can be controlled near thermally neutral conditions.

EXPERIMENTAL METHODS

The catalyst is produced using the glycine-nitrate self-combustion synthesis technique, which forms perovskite structured solids [7]. The synthesis involves adding stoichiometric amounts of metal nitrates in a glycine solution. Following heating and vaporization, the solution will gelatinize and self combust to form a very fine powder. The powder is calcined for a few hours in dry air to remove the residual organics and nitrates and to form perovskite micro-crystallites. Most of the catalyst composition during this study period is derived from $LaCrO_3$ based formulation. The A-site and B-site of the perovskite is partially exchanged through the addition of transition or noble metals. This is attained either by adding the metal nitrate to the reaction solution, allowing for structural addition of the metal, or through post-impregnation with the metal nitrate, followed by reduction in hydrogen to remove the metal oxides and nitrates. The powder was collected, pressed, and palletized using sieves for use in the reactor.

Shown in Figure 1 is a simplified schematic of the reactor used to test the ATR capability of the catalyst. The reactants for the reaction are supplied through several parallel lines

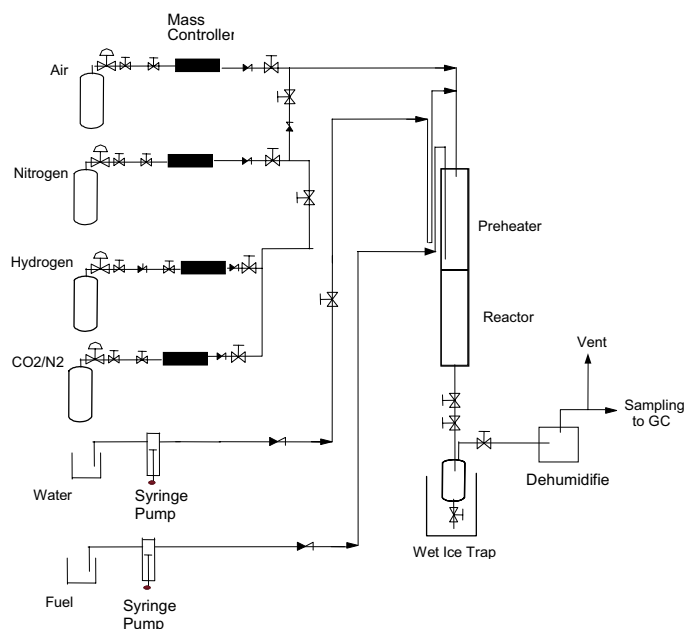


Figure 1: Schematic of diesel autothermal reforming reactor.

outside of the reactor. The gases are regulated by a calibrated mass flow controller. The water and fuel are supplied from two metered syringe pumps. To provide the flexibility of varying input gas mixtures, several other gas lines were constructed, such as CO_2/N_2 to imitate a recycling feed, and nitrogen as a carrier gas in steam reforming. During the experiment, the water input and oxygen input can be changed to simulate different ATR conditions. For example, during ATR the water input is increased in steps from the stoichiometric ratio of H_2O/C of 1 to 3 while holding oxygen flow constant. Similarly, the oxygen is decreased in steps from the stoichiometric ratio of O_2/C of 0.5 to 0.30 while holding water flow constant. During SR, the water input is increased from 3 stoichiometric equivalents to 6 in the absence of air. The reformate product concentration at the exit of the reactor is analyzed by a gas chromatograph (GC) after the steam is removed.

The reactor is divided into two sections, preheater and reactor. The preheater is filled with inert, alumina pellets, used to distribute the heat. The preheater also contains the air and water inlet, allowing for vaporization and mixing before entering the reactor. The preheater is surrounded by a furnace operating at a set temperature. The fuel line passes through the preheater into the reactor and mixes with the now vaporized fuel with the air and steam. The reactor zone is packed with inert materials and the pelletized reforming catalyst. The catalyst may comprise the total composition or it may be diluted with alumina. The reactor is surrounded by a second furnace operating at a temperature that is usually higher than that of the preheater.

The reformate travels along the rest of the reactor tube and into a condenser surrounded by a wet ice trap to remove the majority of the steam. The trap also collects unreacted fuel and heavier residual hydrocarbons with boiling points greater than $\sim 0^\circ C$. The reformate mixture subsequently enters a dehumidifier that removes the rest of the steam before it is directed to a

vent and an extraction tube for GC analysis. Moisture must be removed from the reformat as it would interfere with the GC analysis, resulting in a drift of hydrocarbon peak timing and inaccurate intensity measurement.

The reformat is analyzed for key components (H_2 , CO , CO_2 , CH_4 , N_2) and residual hydrocarbons (C_2H_6 , C_3H_6 , C_4H_{10} , C_6H_6 , etc) in the gas chromatograph. The GC shows relative amounts of the various hydrocarbons and hydrogen, which can be qualitatively calculated and translated into important catalyst performance parameters such as hydrogen yield, fuel conversion efficiency, selectivity toward CO_x , etc. The datum is input into a spread sheet for comparison and analysis. The efficiencies and hydrogen yield of the catalyst per mole of fuel is compared.

In addition to testing the catalyst for ATR capability, the reactor also tests the steam reforming ability of the catalyst, by using nitrogen instead of air. Nitrogen in the ATR and SR functions as a constant mass balance for which to base the calculations of the hydrogen and hydrocarbon productions of the reaction. Nitrogen does not react in the reactor, and so, by specifying the input, the output can be easily quantified.

The fuel used is 99% purity dodecane from Aldrich Chemicals. Dodecane was chosen because its molecular formula closely represents the overall composition of diesel.

RESULTS

Figure 2 and Figure 3 are a comparison of hydrogen yields during ATR of dodecane over a rhodium doped perovskite catalyst, PV-Rh, and an in-house developed perovskite catalyst, ANL-PV1, as the functions of steam-to-carbon (H_2O/C) ratio and oxygen-to-carbon (O_2/C) ratio. The hydrogen yield is defined as the mole of hydrogen produced over the mole of fuel input. H_2O/C is increased by increasing the water flow while the air flow is held constant. Likewise, O_2/C is decreased by reducing the air flow while the water flow is held constant. Figure 2 shows the increase of hydrogen yield with the increase of the H_2O/C whereas Figure 3 shows the slight decrease of hydrogen yield with increase of O_2/C .

Figure 4 and Figure 5 are a comparison of fuel conversion efficiency to H_2 and CO as a function of H_2O/C and O_2/C during the reforming of dodecane over the same catalysts

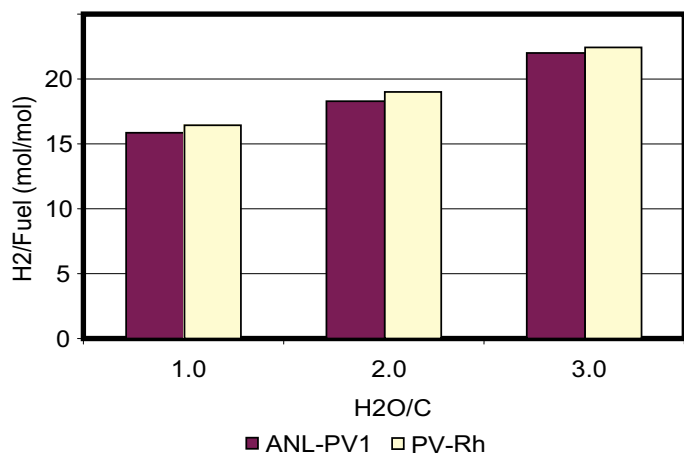


Figure 2: ANL-PV1 and rhodium doped perovskite: hydrogen yield per mole of fuel at increasing water input.

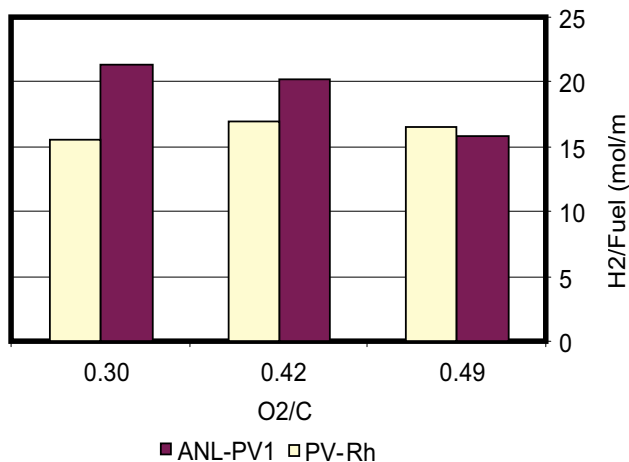


Figure 3: ANL-PV1 and rhodium doped perovskite: hydrogen yield per mole of fuel at decreasing oxygen input.

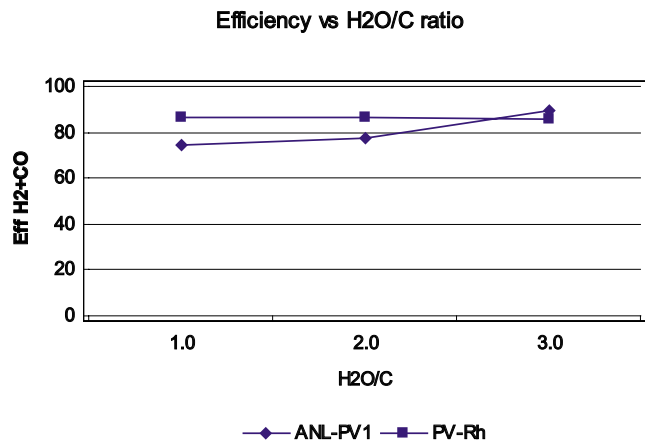


Figure 4: ANL-PV1 and rhodium on perovskite support: efficiency of hydrogen and CO production at increasing water input.

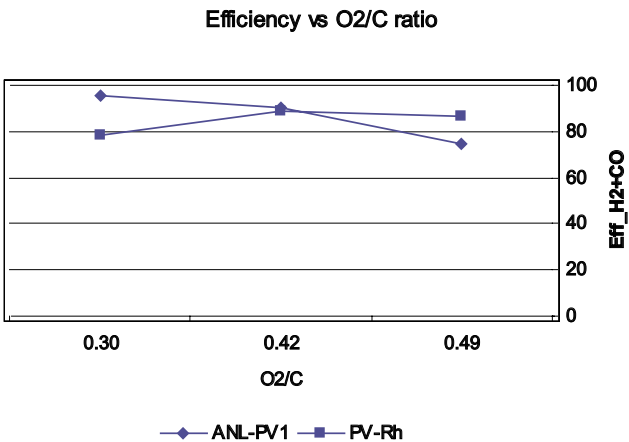


Figure 5: ANL-PV1 and rhodium on perovskite support: efficiency of hydrogen and CO production at decreasing oxygen input.

discussed in Figure 2 and 3. The fuel conversion efficiency is defined as the sum of the combustion heats from the H_2 and CO produced over the combustion heat of dodecane input. This is a parameter commonly used to gauge the reforming efficiency. Figure 4 shows a slight increase of efficiency for the ANL-PV1 catalyst with the increase of H_2O/C while the efficiency remains nearly constant for the Rh based catalyst. Figure 5 shows a slight decrease of reforming efficiency with the increase of O_2/C for ANL-PV1 catalyst while the efficiency reaches a maximum at $O_2/C = 0.42$ for Rh based catalyst.

Figure 6 and Figure 7 show hydrogen yield comparisons of three perovskite catalysts as functions of H_2O/C and O_2/C , respectively. The A-site of these catalysts is partially doped by three different elements from the lanthanide group, A_1 , A_2 and A_3 , whereas the composition of the B-site remains the same. Within the experimental error, no clear distinction between the three catalysts was observed.

Figure 8 and Figure 9 show the hydrogen yield during the reforming of three perovskite catalysts as the functions of H_2O/C and O_2/C , respectively. The B-site of these catalysts is doped by B_1 , B_2 and Rh, whereas the composition of the A-site remains the same. B_1 and B_2 are elements from Group VIA and

VIIIA known for their excellent POX and SR activities. As shown in these figures, the catalyst doped with B_2 has a similar performance to that of Rh in the H_2O/C experiment and even a better performance in the O_2/C experiment. The catalyst doped with B_1 has generally poorer activity in comparison with the other two.

Figure 10 and Figure 11 show the hydrogen yields during the reforming of catalysts M/Al_2O_3 and M-PV as the functions of H_2O/C and O_2/C , respectively. M/Al_2O_3 is a catalyst in which the metal M is dispersed over the high surface area alumina while M-PV is a catalyst with M doped on the B-site. The results show that in both figures that perovskite based supports perform much better than the alumina based supports.

Figure 12 and Figure 13 are hydrogen yield comparisons during the reforming over catalysts Rh-PV and Rh/PV as the functions of H_2O/C and O_2/C , respectively. Rh-PV is the perovskite catalyst where Rh was incorporated into the lattice through one-step process. Rh/PV is the catalyst where Rh was added through post-impregnation method. The two methods of addition perform about the same.

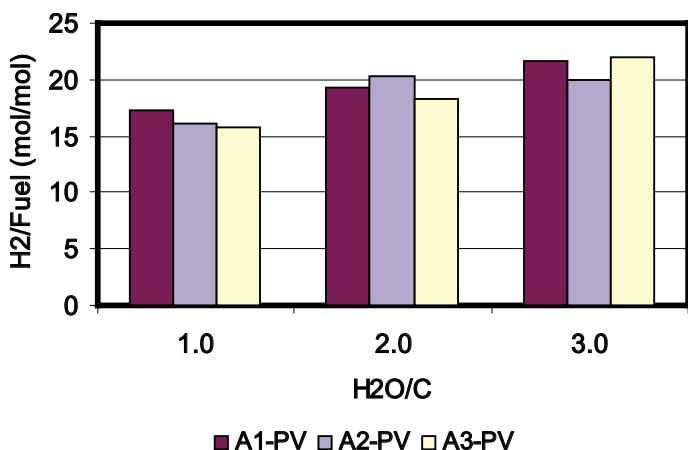


Figure 6: A-site variation hydrogen yield per mole of fuel at increasing water input.

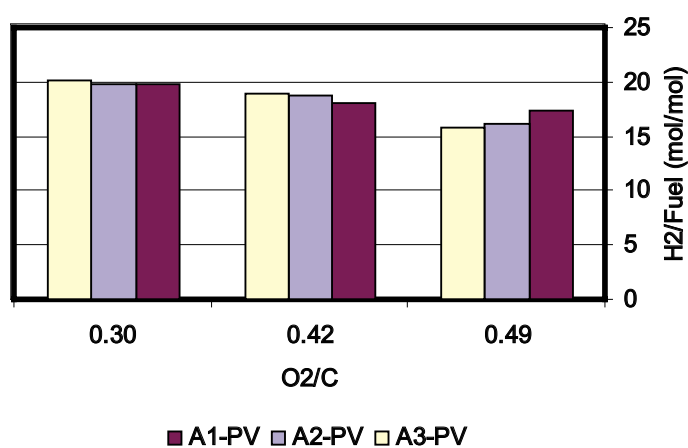


Figure 7: A-site variation hydrogen yield per mole of fuel at decreasing oxygen input.

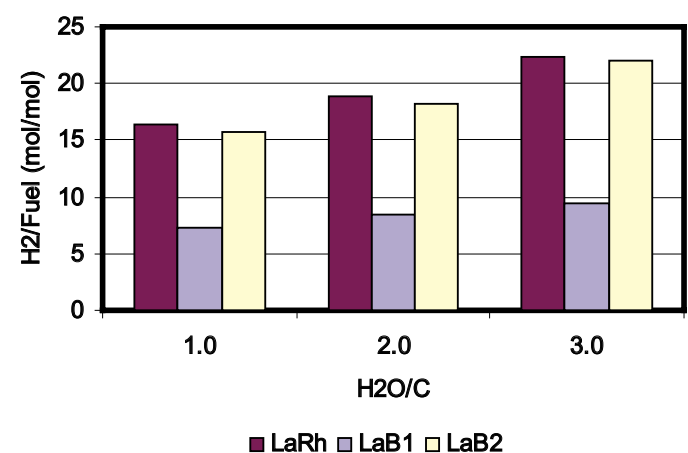


Figure 8: B-site variation hydrogen yield per mole of fuel at increasing water input.

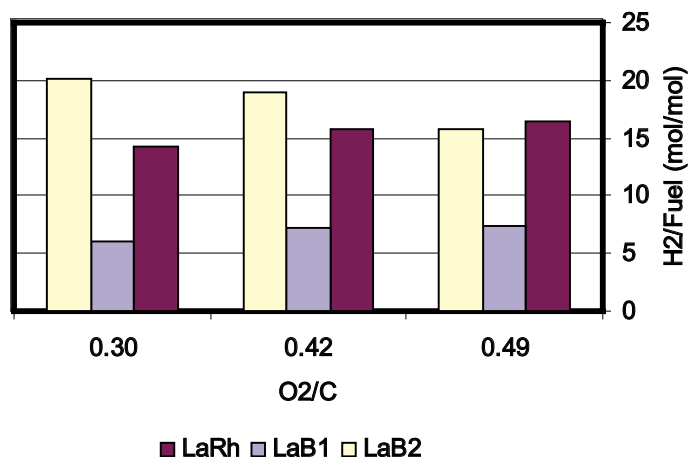


Figure 9: B-site variation hydrogen yield per mole of fuel at decreasing oxygen input.

DISCUSSION AND CONCLUSION

As stated beforehand, the goal of this experiment is to develop a catalyst that is cheaper than rhodium based catalysts but as efficient in reforming. The new catalyst has to be effective under the normal operating condition and over the range of input mixtures. In a catalytic ATR reaction, two key operating variables are steam and oxygen contents. The effects of steam and oxygen concentration on the ATR reaction were tested by holding one variable constant while varying the other. In Figures 2, 3, 4, and 5 the influence of air and steam on a rhodium based catalyst and on a new, cheaper, in-house developed catalyst (ANL-PV1) is compared.

Figure 2 shows that as the steam-to-carbon ratio increases, the hydrogen yield increases. Le Chatelier's Principle would suggest that, by reaction (2), the hydrogen yield would adjust to compensate for the increase of steam. Higher steam content in the input fuel mixture also has an additional benefit of reducing carbonaceous material, or coke, formation. During catalyst testing, a discernible amount of carbon deposit forms downstream of the reactor. Coke that forms on the surface of the catalyst tends to block the active sites on the catalyst, consequently reducing the overall activity. High temperature

steam is a weak oxidant which oxidizes carbon deposit on the catalyst, thereby maintaining a higher activity. However, in practical applications there is a limit to the amount of water that can be stored on-board. Therefore it is desirable to minimize water usage for the ATR reaction. Our study suggests that no significant benefit will be achieved when the steam-to-carbon ratio exceeds three. Figure 3 shows that hydrogen production varies with oxygen-to-carbon ratio. The hydrogen yields decline slightly at higher O_2/C , in part, due to consumption of the hydrogen by the excess of oxygen, forming water. Defining a correct O_2/C window is important to reforming. POX reactions will not perform as well when the oxygen content is too low, but too much oxygen will over-oxidize the fuel and the hydrogen to carbon dioxide and water, resulting in a complete combustion instead of partial oxidation.

Figure 4 shows that the efficiency of the rhodium catalyst is fairly consistent throughout the steam variation. The new ANL-PV1 catalyst, however, increases in efficiency to a point that it is above that of rhodium. Figure 5 shows a striking increase in ANL-PV1 efficiency as the amount of oxygen decreases, allowing a range from about 96% efficiency to 75%. The rhodium catalyst maintains 80-90% efficiency. From this, the new catalyst shows promise as a replacement for rhodium.

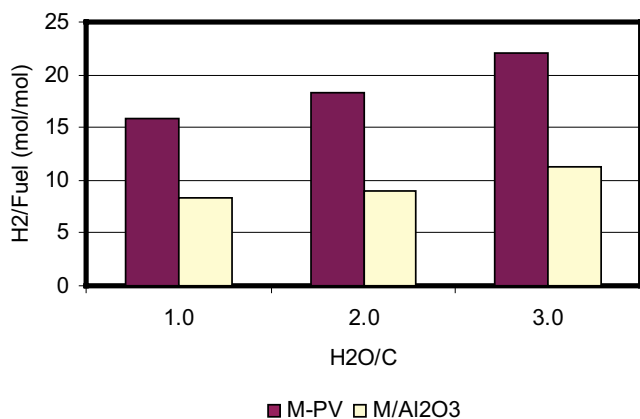


Figure 10: Metal M on alumina and perovskite support: hydrogen yield per mole of fuel at increasing water input.

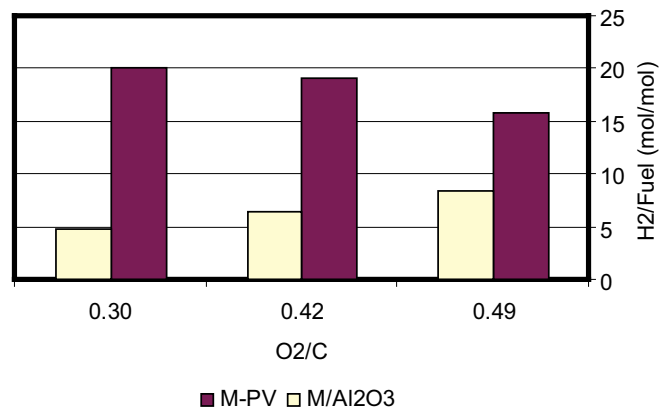


Figure 11: Metal M on alumina and perovskite support: hydrogen yield per mole of fuel at decreasing oxygen input.

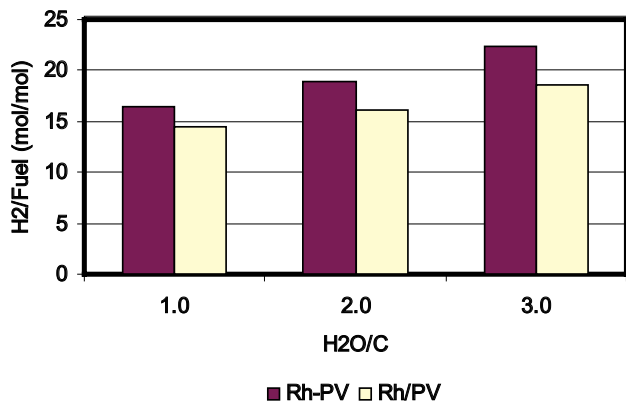


Figure 12: Rhodium addition by structure and post-impregnation: hydrogen yield per mole of fuel at increasing water input.

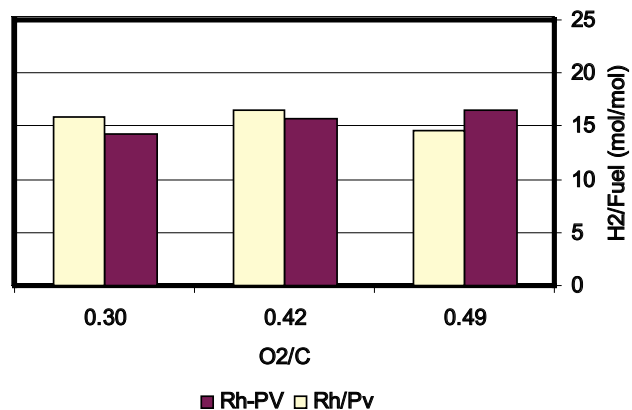


Figure 13: Rhodium addition by structure and post-impregnation: hydrogen yield per mole of fuel at decreasing oxygen input.

ANL-PV1 is a perovskite structured (ABO_3) catalyst, of which both the A and the B site in the unit-cell structure can be partially substituted by other metals to form $A_xA'_{1-x}B_yB'_{1-y}O_3$. By this structure, the A-site metals maintain the charge balance on the unit-cell and can allow for the creation of vacancies. These vacancies can be filled with a B-site metal, which affects the reaction activity of the catalyst. The A-site may also affect oxygen conductivity, which would affect oxidizing potential of a catalyst. Figures 6 and 7, however, show little change when the A-site of the perovskite PV was doped with different cations A1, A2, or A3. More research will be conducted in this area.

Partial exchange of the B-site on the catalyst has demonstrated considerable dependency on the metal used. In Figures 8 and 9 the perovskite doped with B_2 (Group VIIIA) showed exceptional performance compared with that doped with B_1 (Group VIA). We believe that the difference is mainly attributed by the catalytic activity in the B_2 metal. More studies will be continued.

Generally speaking, the catalyst support has a strong impact on the catalytic activity. The support can provide either a promotion or deactivation effect to the reaction. Figures 10 and 11 compare two catalysts supported over alumina and perovskite. The perovskite support performs better than alumina. The promotion effect from the perovskite can be due to a) the transition metal based perovskite support also participates in the catalytic reaction, and b) less coke formed on the perovskite catalyst means less deactivation.

One alternative approach to reduce catalyst cost is to use less of the B-site metal and selectively incorporate it on the surface instead of the bulk of the catalyst. Figure 12 and Figure 13 show that the catalyst prepared through surface impregnation performs nearly as well as the catalyst with the Rh in bulk phase. The Rh/PV, however, contains only 1/5 of the metal in comparison with Rh-PV. This will translate into significant savings in catalyst cost. We plan to explore a similar approach with other metals currently being investigated.

Throughout this study, we have evaluated several catalysts, each containing metals that are substantially cheaper than Rh. New catalyst formulations and synthesis techniques were explored in an attempt to derive a catalyst with performance equivalent or superior than that of rhodium catalysts. Significant progress was made through this research and we have identified several catalysts with promising ATR activity. For example, the catalysts discussed in Figures 2 through 9 have shown to perform admirably compared to the rhodium catalysts. They were only slightly less efficient in ATR and more efficient in SR, while the costs of the metals were ten to a hundred fold less than that of rhodium. Future research activities include continuous optimization of the reforming activity, evaluation of long term catalyst stability, and catalytic sulfur tolerance.

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