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HEXAALUMINATE COMBUSTION CATALYSTS FOR FUEL CELL FUEL REFORMERS

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HEXAALUMINATE COMBUSTION CATALYSTS
FOR FUEL CELL FUEL REFORMERS

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1. INTRODUCTION

Fuel cells may offer significant advantages over conventional diesel generator sets for mobile military electric power applications. Fuel cells can provide quiet, flexible, and fuel-efficient operation, making them suitable for use in "stealth" vehicles or quiet portable power systems. A key requirement for the deployment of fuel cells is the conversion of logistics fuels into hydrogen.

Logistics fuels can be converted into hydrogen through steam reforming -- a reaction which requires heat input. When heat is produced by combustion of logistics fuel in an open-flame or radiant burner, the rate of hydrogen production in the steam reforming reactor is generally limited by the rate of heat transfer from the burner. The rate of heat transfer from the burner into the reforming catalyst bed is limited by wall film and bed resistances. Catalytic combustion of logistics fuel can increase the heat transfer rate by eliminating these resistances. Fuel combustion can be carried out using a catalyst coated on a thin metal channel wall, with steam reforming catalyst coated on the other side of the wall. In this way heat is transferred by conduction directly from the source to the sink, allowing for faster hydrogen production in a more compact catalytic reactor. This approach, however, requires the development of active, stable combustion catalysts that can be coated directly onto metal supports.

Metal-substituted hexaaluminates are currently being developed for use as combustion catalysts in high temperature lean natural gas turbines in order to reduce NO_x emissions. Unlike standard γ-alumina supported catalysts, they maintain substantial surface areas at temperatures exceeding 1000 °C and thus are well-suited for high temperature catalytic combustion. They have the general formula $AM_xAl_{12-x}O_{19}$ where A is a large ion from the alkaline earth metals or the lanthanides and M is a transition metal ion close in size to the Al^{3+} ion. The A ion creates a layered structure which inhibits sintering. The M ion catalyzes combustion.

Experiments were performed to select an optimal hexaaluminate combustion catalyst. Different catalyst formulations were synthesized as granules and tested in a 12-inch long, 0.188-inch ID packed bed reactor for propane/air catalytic combustion activity and high-temperature stability. A catalyst formulation with superior activity and stability was then tested as a washcoat on a 12-inch long, 0.125-inch wide metal support. Haynes 214 alloy was chosen as the support material because of its excellent high-temperature stability and resistance to oxidation and metal dusting. The performance of the hexaaluminate coating was characterized by studying its activity in propane/air combustion tests.

2. RESULTS AND DISCUSSION

Catalyst surface area measurements for the $AM_xAl_{12-x}O_{19}$ catalysts are listed in Table 1. As transition metal substitution increases, surface area tends to decrease. For $x = 0.5$, surface area ranges from 65 to 78 m^2/g; for $x = 1$ surface area ranges from 46 to 70 m^2/g; for $x = 2$ surface area ranges from 27 to 62 m^2/g; and for $x = 3$ surface area ranges from 12 to 44 m^2/g.

Light-off curves for the catalysts are shown in Figure 1. Gas flow rates were 94 sccm air, 3 sccm propane, and 3 sccm neon internal standard. Catalysts with 1-3 manganese atoms per hexaaluminate unit are the most active. They have the lowest light-off temperatures and completely oxidize propane to carbon dioxide and water. The high manganese content of $BaMn_3Al_9O_{19}$ provides it with a higher intrinsic activity than the other catalysts and thus the highest conversion at low temperatures. Near full conversion, however, mass transfer limitations between the gas bulk and the catalyst surface become more important and the catalyst's low surface area causes its light-off curve to lag. $LaMnAl_{11}O_{19}$ reaches complete conversion at the lowest temperature.

Catalysts with 0.5 manganese atoms per hexaaluminate cell are less active. $LaCo_{0.5}Mn_{0.5}Al_{11}O_{19}$ and $LaMg_{0.5}Mn_{0.5}Al_{11}O_{19}$ reach full conversion at temperatures about 50 °C higher than the best catalysts. $La_{0.5}Mn_{0.5}Al_{11}O_{19}$ is competitive with the best catalysts, but only because of its exceptionally high surface area. All three generate hydrogen as a partial oxidation product.

Catalysts without manganese are poor. They have high light-off temperatures and produce substantial amounts of hydrogen, carbon monoxide, and ethylene as partial oxidation products. Of the metals tested, iron is best, followed by cobalt and cerium.

**Table 1.** Catalyst compositions and surface areas

Catalyst	X	Surface Area (m^2/g)
$La_{0.5}Mn_{0.5}Al_{11}O_{19}$	0.5	78
$LaMg_{0.5}Mn_{0.5}Al_{11}O_{19}$	0.5	65
$Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$	1	70
$LaCo_{0.5}Mn_{0.5}Al_{11}O_{19}$	1	67
$BaMnAl_{11}O_{19}$	1	62
$LaMnAl_{11}O_{19}$	1	53
$LaCoAl_{11}O_{19}$	1	46
$BaFe_2Al_{10}O_{19}$	2	62
$BaFeMnAl_{10}O_{19}$	2	27
$BaCe_3Al_9O_{19}$	3	44
$BaMn_3Al_9O_{19}$	3	12
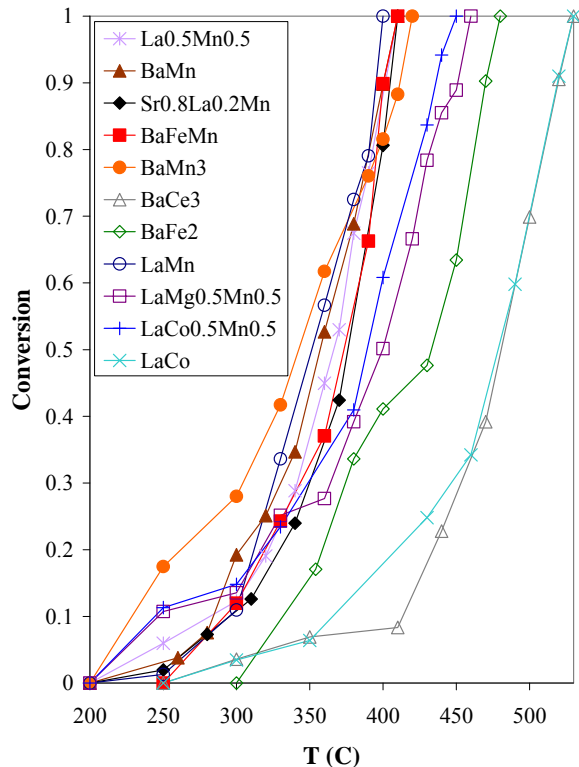
Figure 1. Light-off curves for propane combustion

The high-temperature stability of $LaMnAl_{11}O_{19}$ was tested by running a self-sustained combustion reaction in the packed bed with gas flow rates of 238 sccm air and 10 sccm propane. A red-hot spot formed at the entrance of the reactor and remained stationary over 14 cumulative hours of operation and four start-ups. Light-off curves (using the same gas flow rates as in Figure 1) from before and after the test are displayed in Figure 2 and are essentially identical. As the reactor was not within a tube furnace for these experiments, the reactor was not isothermal and the measured exit temperatures are lower than the reactor temperatures in Figure 1. Figure 2 also contains light-off curves for a Haynes 214 strip coated on one or both sides with $LaMnAl_{11}O_{19}$. Gas flow rates were the same as those of the packed bed light-off curves. The coating was adherent and withstood thermal cycling, but could not sustain combustion without external heating due to excessive reactor dead volume.
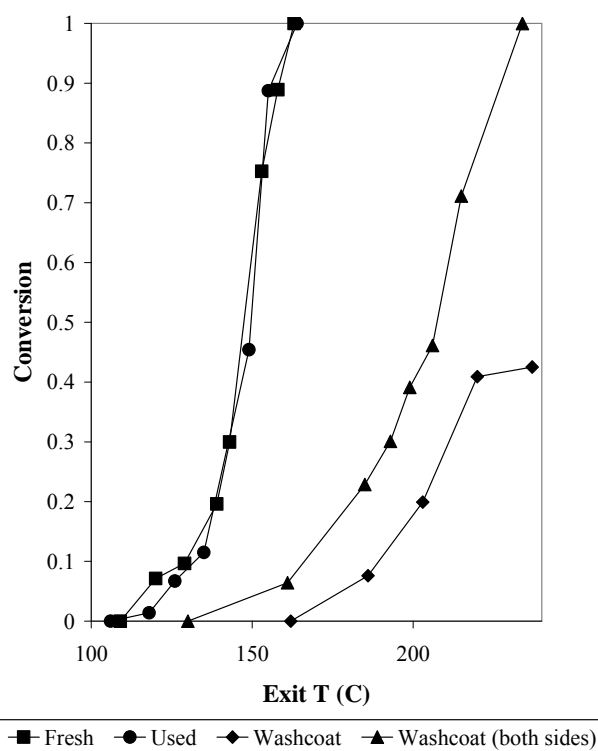
Figure 2. Light-off curves for $LaMnAl_{11}O_{19}$ used in high-temperature stability test and washcoat on Haynes 214 strip

CONCLUSION

$LaMnAl_{11}O_{19}$ is the most active hexaaluminate catalyst tested. N_2-BET analysis revealed that the catalyst remained porous (53 m^2/g) after calcination at 1100°C. It can form adherent washcoats on aluminum-containing superalloys such as Haynes 214 and should therefore be appropriate for use in a compact flat plate logistics fuel reformer system. This will allow the development of mobile military electric power generators with greater mobility, efficiency, and reliability and smaller signatures than currently available.