Pyrochlore-based fuel reforming catalyst

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Introduction

The National Energy Technology Laboratory (NETL) has been developing reforming catalysts based on the pyrochlore crystal structure to overcome the catalyst deactivation problem. Pyrochlore-based catalysts are of interest primarily due to their refractory nature and their stability in high temperature reducing and oxidative environments. They also have the ability to "atomically-disperse" the active metal catalysts within an oxide framework. This distinguishes them from traditional supported metal catalysts which are more prone to sintering at high-temperature and have less control over particle size and "next nearest neighbor interactions". Also, the pyrochlores crystal structure is accommodating to the partial substitution of numerous dopants, which affords the opportunity to tailor various catalytic properties. Pyrochlores have the ability of increasing oxygen conductivity throughout the lattice framework, which is believed to reduce carbon formation.

The focal point of this study is to develop stable and active pyrochlore-based catalysts to produce a hydrogen-rich syngas via reforming of current infrastructure fuels such as diesel, biodiesel, middle distillates and natural gas. Natural gas and diesel fuels are particularly of interest for this study because they represent the best near term and largest market opportunities for the catalyst (hydrogen and syngas production for refining and solid oxide fuel cells respectively). The catalyst has also shown utility for various emission and waste stream/VOC clean-up applications.

Materials and Methods

The pyrochlore catalysts were prepared using modified Pechini method [1]. The experiments were run in a fixed bed continuous-flow reactor. Oxidative steam reforming (O/C = 1.0, steam/C = 0.5, GHSV = 25,000 scc/g_{cat}/h, 900 °C, and 2 atm) was chosen for the reforming mode to convert diesel fuel into synthesis gas. A wide range of reaction conditions (S/C = 2 to 3, O/C = 0 to 1, 700 to 900 °C, 2 to 25 atm, 50,000 to 200,000 scc/g_{cat}/h) were evaluated to convert natural gas into H₂-rich synthesis gas.

Results and Discussion

A long-term, 1,000-hour catalyst demonstration of oxidative steam reforming (OSR) of diesel fuel was conducted on an optimized Rh-based lanthanum zirconate powder. The diesel fuel used for the test was obtained from a local fuel station. The testing demonstrated remarkably stable, near-equilibrium performance throughout the entire 1,000-hr test. It also demonstrated impressively low, single-digit ppm production levels of >C1 hydrocarbons (the species that could potentially degrade a fuel cell).

The next step in the development was to apply the catalyst used for the 1,000-hr test to a structured material (i.e., monolith, foam, pellet). For this, an alumina monolith (400 cubic channels/sq in) was coated with a zirconia doped ceria (ZDC) oxygen-conducting support the Rh-pyrochlore catalyst phase. Complete hydrocarbon conversion and near equilibrium syngas yields were observed for diesel reforming over the Rh-based pyrochlore containing monolith. There were no signs of catalyst degradation (olefin formation, pressure buildup, etc.) when the run was discontinued after 93 hours due to a crack in the quartz reactor containing monolith. The catalyst yields from this run are shown in Figure 1.

Natural gas is being viewed as a potential replacement feed for the petrochemical industry because it is a cheap and abundant domestic resource. It can be upgraded to a series of chemicals and fuels utilizing catalysts. However, methane, the main component of natural gas, is the most stable paraffinic compound and, therefore, the activation of methane into a reactive intermediate is a major obstacle for reforming catalysts. The composition of a pyrochlore type oxide has been tailored for the conversion of methane at high space velocities as well as to minimize, catalyst deactivation through normal mechanisms observed by conventional supported catalysts (e.g. metal sintering, carbon formation, support collapse, etc.). The NETL formulated catalyst was evaluated at a variety of conditions to produce synthesis gas from natural gas reforming at the conditions that are generally accepted and used in the industry.





Significance

Substitution of Rh into a pyrochlore-based catalyst produces properties of Rh metal for reforming of hydrocarbon fuels ranging from natural gas to diesel fuels. While in the structure, the metal retains high activity, and is less susceptible to deactivation by aromatics and sulfur.

References

(1) Pechini, M. P. Method of preparing lead and alkaline earth titanates and niobates and coating method using the same to form a capacitor United States, 1963.