

# Nickel-based Monolith Catalysts for Autothermal Reforming of n-Dodecane

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## Introduction

Autothermal reforming (ATR) of liquid hydrocarbons is a promising process to produce syn-gas streams onboard a vehicle for solid oxide fuel cell auxiliary power units [1]. An auxiliary power unit is a device that provides electrical power to a vehicle thereby displacing load from the engine and ultimately increase fuel savings. Autothermal reforming combines exothermic partial oxidation with endothermic steam reforming, and is considered one of the most attractive options for onboard reforming of liquid fuels. Recently, many efforts have been made to optimize catalyst formulations and deployment on engineered substrates to enhance reforming activity and coking resistance [2,3]. Although, great progress has been made in recent years in the field of fuel reforming, better catalytic materials are still needed to process kerosene-based fuel. Towards this goal, we investigated the reaction characteristics of ceria-zirconia (CZO) washcoated Ni-based monolith catalysts for ATR of n-dodecane. The monolith catalysts were also tested for partial oxidation and steam reforming activity in an attempt to elucidate the specific roles that nickel and ceria-zirconia play in the monolith catalysts during ATR.

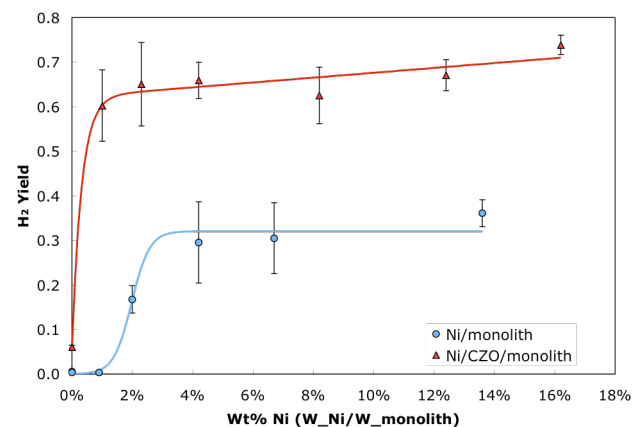
## Materials and Methods

A series of monolith catalysts with different CZO (0-23 wt%) and nickel (0-16 wt%) loadings were prepared by a washcoating method developed in our lab. Typically, the washcoating of monoliths was carried out by multiple immersions of the monolith into an aqueous solution of  $\text{Ce}(\text{NO}_3)_3$  and  $\text{ZrOCl}_2$ . Between immersions, the excess solution was blown out with compressed air, followed by drying at room temperature and at 110 °C, followed by final calcination at 600 °C. The coating procedure was repeated until a target CZO weight loading was reached. The loading of the nickel phase was accomplished by impregnating the CZO coated monolith with the  $\text{Ni}(\text{NO}_3)_2$  solution followed by drying and calcination at 600 °C in air. Prior to reaction, the monoliths were reduced in a 5% $\text{H}_2/\text{N}_2$  flow at 600 °C.

Reaction experiments were carried out using a continuous flow quartz reactor (ID= 10 mm). Reaction temperatures were monitored by thermocouples located upstream and downstream of the monolith. The oxygen supply was provided by a flow of air into the reactor, which was metered using a mass flow controller (MKS). Water and n-dodecane were delivered using a peristaltic pump (INSTTECH) and a syringe pump (Isco), respectively. Product analysis was conducted using a gas chromatograph (Varian CP-3800) equipped with both thermal conductivity and flame ionization detectors. The surface area, pore size distribution, metal dispersion, and crystallographic phase of catalysts were characterized by  $\text{N}_2$  physisorption, CO chemisorption (ASAP2020) and X-ray powder diffraction (Rigaku).

## Results and Discussion

Syn-gas formation was favored by increasing nickel loadings in both the Ni and Ni/CZO catalysts (Figure 1). The addition of ceria-zirconia to the monoliths significantly increased hydrogen yield under ATR conditions. This can be attributed to an increase in steam reforming activity, which was verified during pure steam reforming experiments. The conversion of n-dodecane was strongly influenced by the reaction feed temperature, as well as the availability of oxygen in the system. The mechanistic insights gained from the reaction experiments suggest that thermal cracking reactions upstream of the monolith contribute to overall conversion of n-dodecane. Surface area characterization showed a decrease in active surface area with increased nickel loading. The activity trends will be discussed in the context of structural parameters such as metal dispersion.



**Figure 1.** Hydrogen yield comparison for ATR of n-dodecane over Ni-based monolith catalysts with and without the washcoat of CZO ( $\text{O}/\text{C} = 0.6$ ,  $\text{H}_2\text{O}/\text{C} = 2.0$ , feed temperature = 550 °C, and  $\text{SV} = 60,000 \text{ hr}^{-1}$ ).

## Significance

The development of stable active catalysts for onboard diesel and kerosene reforming is needed for the deployment of auxiliary power units for the military and freight industry.

## References

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