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# *n*-Dodecane reforming over nickel-based monolith catalysts: Deactivation and carbon deposition

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## Abstract

The carbon deposition behavior of Ni-based monolith reforming catalysts was studied during *n*-dodecane autothermal reforming, partial oxidation, and steam reforming. One catalyst formulation was nickel deposited on cerium zirconium oxide (CZO) coated monolith, while the second formulation was nickel directly deposited on bare monolith. In both formulations, a series of catalysts with a range of nickel loadings (0–16 wt.%) were prepared to examine the influence of nickel loading on carbon deposition and to elucidate the benefits of the reducible oxide support CZO on carbon deposition. Carbon deposition was generally more pronounced at higher nickel loadings and on catalysts lacking CZO. Nickel supported on bare monolith suffered from excessive carbon deposition and carbon-induced monolith disintegration. The morphologies of carbon were determined by scanning electron microscopy (SEM). Temperature programmed oxidation (TPO) indicated the presence of two types of carbon. The low-temperature TPO peak can be attributed to coating carbon, while the high-temperature peak corresponds to filamentous carbon structures, including large whiskers and smaller filaments. Accumulation of whisker carbon had a deleterious effect on the monolith substrate resulting in the physical destruction of some samples. X-ray diffraction (XRD) gave no evidence for the presence of graphite or carbide species in carbon-deposited catalysts. The experimental results of this study are used to diagnose the causes for nickel catalyst deactivation during autothermal reforming and for proposing strategies to mitigate the deactivation.

*Keywords:* Dodecane; Carbon; ATR; Nickel; Monolith; Ceria; TPO; TGA; SEM; Jet fuel

## 1. Introduction

Currently, liquid hydrocarbons because of their availability and cost are the most plausible feedstock for hydrogen and carbon monoxide generation onboard of a vehicle. Onboard-generated hydrogen and carbon monoxide have great utility as a feed for solid oxide fuel cells or as reductant for lean $NO_x$ emission control systems. In order to make onboard fuel processing a reality, durable fuel reforming catalysts must be developed because current reforming catalysts are incapable of processing commercial fuels without deactivation. Carbon deposition represents a significant technological challenge to the development of a viable fuel reforming catalyst. It is common practice in stationary methane steam reformers to control carbon formation by increasing the steam to carbon ratio in the feed. However, onboard applications have additional constraints. The production of large quantities of steam is impractical for onboard applications because water would have to be carried onboard the vehicle or obtained from the fuel cell anode recycling stream [1,2]. Therefore, novel catalyst formulations or reactor schemes must be developed to process the fuel effectively under conditions prone to carbon formation, i.e. conversion of large hydrocarbons at low steam to carbon ratios.

Reforming reactions primarily take place over supported metal catalysts at elevated temperatures. Traditionally, nickel has been used industrially as a catalyst for methane steam reforming and is attractive because of its relatively high activity and low cost [3–6]. Both nickel and precious metals have been examined for liquid hydrocarbon autothermal reforming [7–14]. Precious metals, particularly Ru, Rh, Pt and Pd generally have greater autothermal reforming activity than Ni. Interestingly, ruthenium and rhodium are also some of the most active catalysts for methane steam reforming. The relationship between methane steam reforming activity and liquid hydro-

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carbon autothermal activity remains unclear, but it seems logical that the two should be related at least qualitatively. Autothermal reforming of liquid hydrocarbons over precious metals has shown significant problems with carbon deposition, except for rhodium, which gives low amounts of carbon formation even during the reforming of heavy hydrocarbon fuels [15]. Temperature programmed oxidation of the carbon deposited on Pt-based catalysts showed the existence of two types of carbon species: carbon associated with the support and carbon on the precious metal [16].

Although nickel catalysts are much more affordable than precious metal catalysts, nickel catalysts are thought to be more prone to carbon deposition than precious metal catalysts [16]. Nickel catalysts suffer from the formation of carbon deposits on the catalyst, particularly filamentous carbon, which deactivate the catalyst and foul the reactor [17]. The literature on the subject of filamentous carbon formation on nickel is vast and spans many applications including steam reforming to hydrogen storage [17–22]. Many papers focus on the growth of filamentous carbon from various hydrocarbons, and on carbon nanotube synthesis. Currently, there is some debate as to the mechanism of filament growth. One mechanism proposes that filament growth is initiated by diffusion of carbon through the nickel particles and is sustained through deposition of additional carbon at the base of the nickel particle [23,24]. Carbon diffusion through the nickel bulk is thought to be the rate-limiting step in this mechanism. The other proposed mechanism is that growth is initiated by surface diffusion of carbon to the edges of the nickel particle and proceeds from the edge upward [25]. In both cases the carbon filaments lift the nickel particles off the surface of the support with nickel particles ending up at the tip of the growing carbon filaments.

Industrial reforming catalysts have been modified by alkali metal oxides (MgO and KO), metal alloys, and selective sulfur poisoning of active carbon producing sites to reduce carbon deposition [5,26–28]. Filamentous carbon growth has also been demonstrated to be a strong function of nickel particle size [25,29–32]. Nickel particles smaller than 7 nm are thought to be unable to form filamentous carbon [18,29,33]. The support material has also been identified as an important factor in preventing carbon formation. The use of reducible oxide supports has been suggested as a way to decreased carbon deposition. Cerium–zirconium oxide has been shown to lower carbon deposition during tetradecane partial oxidation [34]. Experiments have demonstrated that during methane partial oxidation, carbon deposition was strongly related to the ion conductivity of the support, with gadolinium doped cerium oxide and zirconium doped cerium oxide depositing far less carbon than alumina [35].

In this follow-up paper of previous work [36], nickel-based catalysts supported on monoliths were examined for deactivation during autothermal reforming, the amount of carbon deposition produced during autothermal reforming, and the morphologies of the carbon species. The influence of nickel weight loading on carbon deposition was determined in order to find an optimal nickel loading. The behavior of the monolith catalysts with and without a cerium–zirconium oxide support was compared in an attempt to understand the influence of reducible oxide supports on carbon deposition. The amount and types of carbon deposition were compared post-autothermal reforming, partial oxidation, and steam reforming of *n*-dodecane. The objective of this work was to elucidate the deactivation behavior due to carbon deposition in order to further the development of non-precious metal-based catalysts capable of reforming commercial fuels without detrimental carbon deposition.

## 2. Experimental

### 2.1. Catalyst synthesis

Nickel-based catalysts solution-coated on cordierite monoliths were prepared and tested for autothermal reforming (ATR) activity. The detailed synthetic procedure is presented in the previous work [36], but briefly it involves the immersion of bare monoliths into various solutions of precursor salts followed by drying and calcination to produce the desired oxide species. Nickel deployed on the bare monolith (Ni/monolith) and supported on cerium–zirconium oxide ($Ce_{0.75}Zr_{0.25}O_2$) deployed on monolith (Ni/CZO/monolith) were both synthesized using the above method. Nickel loadings on a monolith basis ranging from 0 wt.% to 16 wt.% were prepared on both catalysts and a 23 ± 2 wt.% CZO loading was used as support. Each sample was given a corresponding sample ID, with MCZO series catalyst corresponding to monolith with cerium–zirconium oxide and the MN series corresponding to the nickel on bare monolith catalysts. In the text the catalysts are described by their nominal weight loadings rounded to the nearest percent.

### 2.2. Reforming experiments

The series of nickel-based catalysts were tested for autothermal reforming activity, catalyst durability, and carbon deposition. Autothermal reforming reactions were performed in a quartz flow reactor at a low oxygen to carbon ratio, $O/C = 0.6$; a steam to carbon ratio, $H_2O/C = 2.0$; and a low feed temperature, 550 °C, to enhance the rate of carbon deposition on a laboratory accessible timescale. Selected catalysts were tested for steam reforming (SR) and partial oxidation (POX) behavior. SR reactions were carried out at $H_2O/C = 2.0$, with a $N_2$ feed equal to the total flow of air during ATR conditions to keep the concentration of $H_2O$ constant between ATR and SR. POX experiments were performed at $O/C = 0.6$, with a $N_2$ feed equal to the total flow of $H_2O$ during ATR and SR to keep the concentration of $O_2$ the same as ATR. The details of the quartz reactor dimensions, experimental start up procedure, and catalyst pre-treatment are provided elsewhere [36]. All catalysts were reduced in 100 sccm of 5% $H_2/N_2$ at 600 °C for 1 h prior to each individual reaction run. The flow reactor system was composed of an Instech peristaltic pump for water delivery, an Isco syringe pump for fuel delivery, a 10 m section of stainless steel tubing wrapped with heating tape to mix and vaporize the liquids, and a 200 ml ice-water-cooled condenser