

Heavy Hydrocarbon Reforming Deactivation Pathways Over Nickel-based Monolith Catalysts

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Introduction

Catalyst deactivation is one of the major technical barriers facing the processing of liquid hydrocarbons into syn-gas streams to power solid oxide fuel cells onboard of vehicles. Possible pathways for deactivation during heavy hydrocarbon reforming include: coke formation, sulfur poisoning, thermal sintering, physical attrition and volatilization of the metal phase. Problems associated with coke formation from heavy hydrocarbon reforming can be traced back to decades ago[1]. Nickel, a widely used industrial catalyst for methane reforming, is particularly susceptible to coke formation. Coke can exist in different morphologies (whiskers, encapsulated and pyrolytic carbon, and even carbide) [2]. However, catalyst supports with oxygen storage capacity like ceria have attracted attention for their enhanced activity and coking resistance during reforming [3,4]. In this work Ni and Ni/Ce-Zr-O₂ catalysts with various Ni loadings supported on Ce-Zr-O washcoated cordierite monoliths have been examined for deactivation during ATR. The influences of nickel metal loading, reaction conditions, and calcination temperatures on coke formation and thermal stability were examined. The insights gained from a multi-faceted characterization approach were used to postulate probable pathways of deactivation in relation to catalyst structure.

Materials and Methods

A series of monolith catalysts with different Ce_{0.75}Zr_{0.25}O₂ (0-23 wt%) and nickel (0-16 wt%) loadings were prepared by a washcoating method developed in our lab and wet impregnation, respectively. Briefly, the washcoating of monoliths was carried out by multiple immersions of the monolith into an aqueous solution of Ce(NO₃)₃ and ZrOCl₂, and the loading of the nickel phase was accomplished by impregnating the CZO coated monolith with the Ni(NO₃)₂ solution, followed by drying at room temperature and at 110 °C, followed by final calcination at 600 °C. The CZO coating and nickel loading procedures were repeated until a desired weight loading was reached. Prior to reaction, the monoliths were reduced in a 5%H₂/N₂ 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 (INSTECH) 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 catalysts were characterized for surface area, pore size distribution, metal dispersion, and crystallographic phase after experiencing different thermal and chemical environments. The following characterization techniques were used: N₂ physisorption, CO chemisorption (ASAP2020) and X-ray powder diffraction (Rigaku).

Carbon morphology and amount were examined by SEM with EDAX (FEI Nova) and TGA (TA Q500), respectively.

Results and Discussion

The amount of carbon deposition was strongly influenced by the nickel weight loadings on the monolith. There appears to be a transition between 2 wt% and 4 wt% nickel where coke formation becomes significant. Coke formation was found to lead to destruction of the monolith, especially at the higher Ni weight loadings. SEM micrographs of the monoliths and downstream fines showed that deposited carbon took the form of carbon filaments. The TGA of post reaction monoliths in air showed two types of carbon, with peaks centered at 450 °C and 600 °C. In low nickel loading samples the low temperature feature is most significant, while in the high Ni loading samples the 600 °C is the dominant feature. The probable linkage between carbon formation and catalyst structure will be also discussed in this work.

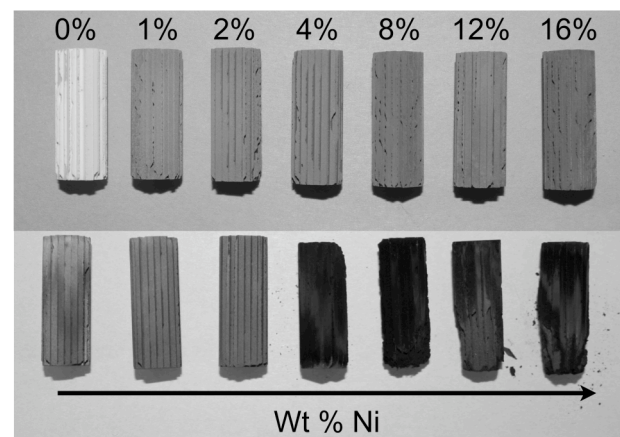


Figure 1. Photo comparison of Ni/CZO/monoliths pre (top) and post (bottom) autothermal reforming (O/C = 0.6, H₂O/C = 2.0, feed temperature = 550 °C, and 60,000 hr⁻¹).

Significance

The development of stable catalysts for kerosene fuel reforming is needed for the development of auxiliary power units for the military and freight industry.

References

1. M. Flytzani-Stephanopoulos, G. E Voecks, *Energy Progress*, 1 (1981) 53-58
2. J. R. Rostrup-Nielsen, "Catalysis: Science and Technology", Vol. 5, chap. 1 *Catalytic Steam Reforming*, Springer-Verlag, 1984.
3. M. Krumpelt, T.R. Krause, J.D. Carter, J.P. Kopasz, S. Ahmed, *Cat. Today* 77, 3 (2002).
4. X. Wang, R.J. Gorte, *App. Cat. A: Gen.* 224, 209 (2002).