

Autothermal Reforming of Liquid Fuels with Ni/CZO Catalysts

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Introduction

Reforming of liquid fuels is an attractive option for solid-oxide fuel cell powered auxiliary power unit (APU) applications in heavy-duty vehicles, [1] and is also of interest for selective catalytic reduction (SCR) of NO_x in automotive emission control systems. A major technological barrier, however, is the susceptibility of reforming catalysts to deactivation by carbon and sulfur. This is especially of concern in on-board applications where logistic fuels such as JP-8 contain significant amounts of sulfur. In this contribution, the effect of carbon deposition and exposure to sulfur compounds is explored for nickel catalysts, and strategies for developing deactivation resistant catalysts are discussed.

Materials and Methods

Three series of catalysts were prepared, with nickel loadings ranging from 1 wt% to 16 wt%. The first series consisted of conventional powder catalysts, prepared by incipient wetness impregnation of Ce_{0.75}Zr_{0.25}O₂ (CZO) support. The second series consisted of nickel deposited on CZO coated cordierite monoliths, while the third formulation was nickel directly deposited on bare monolith. The catalysts were extensively characterized, including BET surface area, chemisorption, X-ray diffraction, temperature-programmed reduction (TPR), scanning electron microscopy, analytical electron microscopy, and XPS. The performance of Ni-based catalysts was studied in flow reactors during autothermal reforming, partial oxidation, and steam reforming of probe molecules such as isooctane, n-dodecane, and tetralin. The carbon deposits were characterized using x-ray diffraction (XRD), scanning electron microscopy (SEM), and temperature programmed oxidation (TPO). The effect of sulfur compounds was investigated by co-feeding 4 ppmv of H₂S, SO₂, or thiophene, respectively. Selected monolith-based Ni catalysts were tested under actual JP-8 feed.

Results and Discussion

Carbon deposition was generally more pronounced at higher nickel loadings and on catalysts lacking CZO. The carbon deposition behavior correlated with nickel particle size, with small average particle size associated with low carbon deposition rates. Multiple reduction features observed in TPR indicated the presence of different types of NiO present in the catalyst, depending on overall nickel loading. TPO indicated the presence of two types of carbon giving rise to low temperature and high temperature oxidation peaks, and the relative concentration of these carbon types depended on nickel loading. Based on SEM images, the low temperature TPO peak was attributed to coating carbon, while the high temperature peak corresponded to filamentous carbon structures, including large whiskers and smaller filaments. Accumulation of whisker carbon had a deleterious effect on the monolith catalysts, causing the physical disintegration of the monoliths at high Ni loadings. The rate of coating carbon formation appeared to be independent of nickel particle size, while the rate of formation of filamentous carbon increased with nickel particle size [2]. Nickel on bare monolith suffered from excessive carbon deposition causing monolith disintegration. Using low nickel loadings with small nickel particle size mitigated carbon deactivation. The CZO support also facilitated

the oxidative removal of carbon. An alternative strategy for minimizing carbon deposition is the use of Sn-Ni surface alloys [5,6,7].

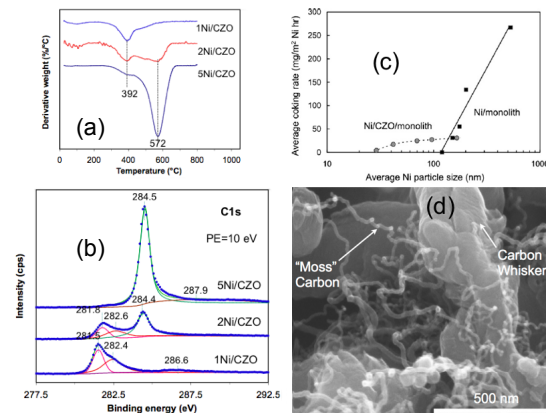


Figure 1. TPO (a) and XPS (b) of carbon deposited on Ni/CZO post iso-octane ATR; carbon formation rate (c) and SEM images of carbon on Ni/CZO/Monolith post n-dodecane ATR (d).

During n-dodecane ATR, homogeneous cracking and oxidative cracking contributed to the overall conversion, whereas partial oxidation of n-dodecane and steam reforming of smaller hydrocarbons played a key role in the formation of H₂, CO, and CO₂ [3]. There were significant differences in the effect of H₂S, SO₂, and thiophene. Most notably, co-feeding of sulfur species changed the temperature profile in the catalyst bed and altered the degree of carbon deposition in a sulfur-compound specific way. Among all the catalysts examined, the 2 wt.% Ni/CZO/monolith showed the best balance between carbon deposition and long-term activity.

Significance

The systematic investigation of nickel-based reforming catalysts has provided important insight into critical factors affecting the performance and durability of catalysts for on-board liquid fuel reforming applications.

References

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