Evaluation of the possibility to decrease the Rh loading of autothermal reforming catalysts for commercial diesel by adding promoters

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Introduction

It is estimated that a heavy-duty vehicle is idling approximately 6 hours per day, 290 days annually, to supply the vehicle with electricity for cabin comfort during periods of sleep and rest [1]. The fuel to electricity efficiency during idling is just a few percent [2]. In addition to this a considerable part of the total emissions are generated during idling [3]. There are several options available for reducing the idling emission such as truck stop electrification and diesel-fueled auxiliary power systems (a.k.a genset) [4]. For vehicles operating in remote areas where the electric grid is limited the truck stop electrification is not an option. The diesel-fueled auxiliary power system, on the other hand, decreases the total emission but the efficiency leaves much to be desired.

An idling emission reduction option that solves these limitations and in addition introduces hydrogen onboard vehicles are fuel cell auxiliary power units (FC APU). Introduction of hydrogen onboard would open up for other aftertreatment strategies, such as HC-SCR and lean NO_x traps, where hydrogen is a necessity to reach high conversions. However, to make FC APU a viable option, the materials needs to be cheaper at the same time as the performance is retained.

The catalytic material in the reformer usually has a high Rh loading (\sim 3 wt. %) in order to reach the H₂ yield and fuel conversion required. Finding less expensive metals that can make up for the losses in activity due to lower Rh loading is essential. In this evaluation three possible promoter candidates are thoroughly investigated in combination with 1 wt. % Rh supported on CeO₂-ZrO₂ for reforming of commercial diesel.

Materials and Methods

The catalyst samples were prepared by the incipient wetness method with 1 wt. % Rh and 6 wt. % promoter. The catalytic powders were coated onto cordierite monoliths (l = 20 mm, $\emptyset = 20$ mm). The catalysts were evaluated with commercial diesel (MK1). The process parameters were GHSV ~ 50,000 h⁻¹, H₂O/C ~ 2.5 and O₂/C ~ 0.45. The temperature was ramped from 700 °C to 950 °C in 50 °C steps with a dwell of approximately 45 min before each measurement point. Both the fresh and aged materials were thoroughly characterized with TEM, SEM, XRD, H₂-TPR, TPO, CO chemisorption, and BET measurements.

Results and Discussion

The H_2 yield and fuel conversion of the catalysts with time on stream are given in Figure 1. The results for the promoted catalytic materials are comparable with previous results

using 3 wt. % Rh on CeO₂-ZrO₂ [5]. The La-promoted sample showed significantly lower selectivity towards coke precursors such as ethene in the activity experiments. This could also be correlated to a much lower amount of coke deposited on the surface measured by TPO for this catalyst. The Co-promoted material, showing the highest conversion, contained alloys between Rh and Co visible in TEM. These crystals were of the same size as the CeO₂-ZrO₂ crystals, meaning that these alloys of Rh and Co were unsupported.



Figure 1. H_2 yield and fuel conversion for the evaluated promoters. The dashed line shows the performance of Rh(3)/CeO₂-ZrO₂ catalyst.

Significance

The experiments presented are based on reforming of commercial diesel fuel using catalytic materials coated on monoliths, in order to mimic real conditions in automotive applications. A stable reforming catalyst with high hydrogen yield enables improved vehicle efficiency and lower total emissions. By promoting the rhodium catalyst with lanthanum or cobalt the rhodium loading can be significantly decreased, without sacrificing the hydrogen yield and fuel conversion.

References

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