Evaluation of a zoned Rh-Pt catalyst for hydrogen generation from diesel fuel via autothermal reforming

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Introduction

Onboard reforming technologies are considered feasible short-term alternatives to supply fuel cells with hydrogen. Autothermal reforming (ATR) has received a lot of attention lately as one of the most promising methods for generating hydrogen from diesel fuel. ATR, which uses air and water vapor as reactants, has several benefits for the use in onboard reforming. This is due to its high thermal efficiency and dynamics during transient operation as well as its lower system complexity. Several studies have shown that the exothermic partial oxidation (PO) initiates ATR [1]. This is due to the faster kinetics of the PO. Heat generated from PO is consumed by the sequential endothermic steam reforming (SR), where most of the hydrogen is generated. Despite this known fact, no studies have been made developing a catalyst that considers the thermodynamic behavior of the ATR process. A zoned catalyst could be an interesting solution for ATR of diesel. The concept of the zoned catalyst is to coat a cordierite monolith with two different layers of washcoat of certain length in the axial direction. The first layer is for handling the PO while the second layer deals with the SR. Tailored zoned ATR catalyst could improve onboard reforming for the use of fuel cells by providing higher H_2 productivity, and H_2 and CO_2 selectivity.

The objective of this study was to design and evaluate a zoned catalyst for ATR of diesel. Screening tests were carried out at laboratory scale at first to find promising catalysts that could be used for the construction of the zoned catalyst. This zoned catalyst was then used for full scale testing on a reformer designed to generate hydrogen for a 1–5kW$_e$ polymer electrolyte fuel cell (PEFC). All evaluations were done by analyzing the temperature profiles and product gas composition.

Materials and Methods

Previous work in our laboratory has shown that Rh-CeO_2-La_2O_3, with 1 wt% Rh, on alumina is very active for ATR of transportation fuels such as diesel, gasoline and E85 [2]. A recent study by Kaila et al. [3] has shown that bimetallic Rh-Pt is also very selective for ATR of diesel. For the screening test, four catalysts were prepared using the incipient wetness technique (IW) and deposited on 400 cpsi cordierite monoliths (d=1.78 cm, l=3.05 cm). All catalysts were made using pretreated alumina (calcined in air 1000 ºC/ 1h) as support material. Three of the catalysts were uniformly coated while the fourth catalyst, the zoned catalyst, constituted two different layers of washcoat. All catalysts were calcined in air at 800 ºC/3h. Table 1 exhibits the catalyst candidates for the screening study showing materials wt% in washcoat in parenthesis. All experiments for the screening tests were executed at reactor inlet temperature 650 ºC and operating conditions P=1.44 kWe, H_2O/C=2.5, O_2/C=0.49 (λ=0.33), GHSV=17700 h^{-1}. A standard diesel fuel (6 ppm S, C/H=6.43) were used as fuel and tested in a vertically mounted stainless steel tubular reactor with ID= 2.37 cm. The product gases were evaluated using FTIR and TCD. For the full scale test the zoned catalyst (#4) was prepared using IW and deposited on a 400 cpsi cordierite monolith (d=8.03 cm, l=7.62 cm). Experiments are currently being carried out using commercial diesel as fuel at operating conditions P=5 kWe, H_2O/C=2.5, O_2/C=0.49 (λ=0.33), GHSV=10800 h^{-1}. The product gases are being evaluated using FTIR and GC.

Table 1 Catalyst candidates for the screening study

Catalyst number (#)	1	2	3	4
Coating type	Uniform	Uniform	Uniform	Zoned
Active metal (wt%)	Rh(1)Pt(1)	Rh(3)	Rh(3)	Rh(1)Pt(1) - Rh(3)
Promoters (wt%)	Ce(10)La(5)	Ce(10)La(5)	Ce(10)La(10)	Ce(10)La(10)
Coating degree (vol %)	100	100	100	30:70
Surface area (m^2/g)	88	89	80	-
Pore volume (cm^3/g)	0.60	0.58	0.43	-

Results and Discussion

Figure 1 shows the calculated and gas product results (vol%) for catalyst #3 and #4. The primary 30 vol % Rh-Pt layer in the zoned catalyst has a significant positive effect, compared to the uniformly coated catalyst, resulting in a 20 % increase of the hydrogen selectivity and ~5 vol % more hydrogen content in the product gas. Both catalysts reached almost full conversion (~99%). The lower CO_2 selectivity for the zoned catalyst suggests that further optimization of the diesel reforming is needed. Experiments will be performed, where the coated length of the primary waschcoat layer of the zoned catalyst is to be varied. The full scale test results of the zoned catalyst are currently being evaluated.

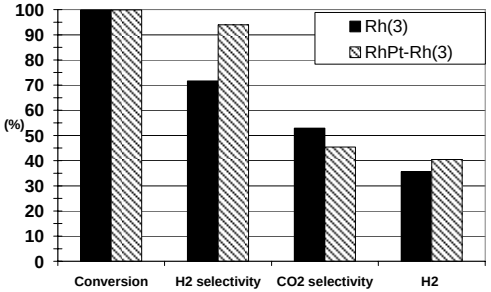

Figure 1. Screening study test results for catalyst #3 and #4.

Significance

Our results indicate possibilities for the developed zoned catalyst to be used in onboard vehicle fuel processing systems for energy efficient hydrogen production from diesel.

References

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