Partial Oxidation of Methane over staged Pd-Rh Catalyst: Temperature and concentration profiles by SpaciPro

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Introduction

Hydrogen production by catalytic partial oxidation (CPOX) of hydrocarbon fuels represents a process, in which catalytic and gas-phase reactions as well as mass and heat transfer occur simultaneously. To gain a deeper understanding of the process, in-situ sampling techniques are employed [1-4]. In these investigations, the separation of the reaction sequence in a channel of a catalytic monolith into an oxy-reforming and a reforming zone has been shown. In the oxy-reforming zone, total oxidation and steam reforming are the predominant reactions. In the reforming zone, steam reforming is the prevalent reaction. Based on these observations, a two-stage catalyst is used, with a slice of Pd for the oxy-reforming zone and a slice of Rh in the reforming zone. Pd is a known total oxidation catalyst [5], which is expected to increase the share of total oxidation in the oxy-reforming zone. In this work, spatially-resolved concentration and temperature profiles are detected in one channel of the investigated catalyst with the SpaciPro Technique, a capillary-based sampling technique using several analytical devices (FTIR, MS, GC), an extension of the well-known SpaciMS technique [1], now combined with CFD simulations. Single slices of Pd and Rh are investigated for CPOX of methane under similar conditions as the two-stage catalyst to reveal the influence of the different catalytically active materials.

Materials and Methods

For the experiments, honeycomb monoliths (600 channels per square inch (cpsi), Ø 19 mm) coated with either Rh/Al_2O_3 or Pd/Al_2O_3 were used. For the single-slice catalysts, a length of L=10 mm was chosen, for the two-stage catalyst, a Pd stage (L = 2 mm) was followed by a Rh stage (L = 8 mm). For all investigated catalytic systems, heat shields (uncoated monoliths, 600 cpsi, Ø = 19 mm, L = 10 mm) were placed up- and downstream of the catalyst. The CPOX of methane was studied at a molar C/O ratio of 1.0 for all investigated catalysts. To collect concentration profiles, a capillary (outer diameter = 170 µm) is inserted into a channel and a constant gas sample is withdrawn. An axial resolution of 0.25 mm is possible with this method. Analysis of the gas composition takes place in an FT-IR and MS. For the temperature profiles, two different methods are employed. The gas-phase temperature is collected with a thermocouple; the surface temperature with an optical fiber, connected to a pyrometer.

Results and Discussion

Figure 1 shows the concentration profiles of the reactants and products for CPOX of CH_4 at C/O = 1.0 over the two-stage catalyst. Oxygen consumption is complete after z = 1.25 mm. Thus, no more oxygen is available for the Rh stage. Methane consumption occurs in the Pd stage as well as in the Rh stage. The mole fraction of CH_4 still decreases after all oxygen has been consumed (z > 1.25 mm) due to steam reforming. This conclusion is also confirmed by the mole fraction of H_2O, which shows a peak at z = 1.25 mm, followed by a decrease. In the Pd stage, hydrogen is not formed, as long as oxygen is still detected. The formation of hydrogen occurs only after all oxygen has been consumed. This behavior differs from data shown before in CPOX of CH_4 over Pd [6], where a direct route of syngas formation, i.e. simultaneous formation of H_2O, CO_2, H_2 and CO, is seen. However, with the in-situ measurements shown here, an indirect route to syngas seems more likely, in which H_2O and CO_2 are formed, followed by reforming reactions which lead to syngas formation. CFD simulations support this conclusion.

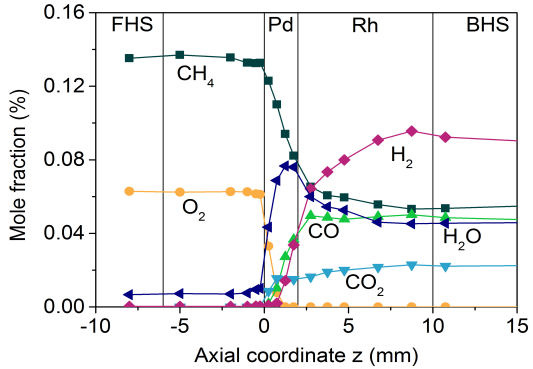

Figure 1. Mole fractions of reactants and products as a function of the axial coordinate for CPOX of CH_4 over Pd-Rh catalyst at C/O = 1.0. Position of staged catalyst and heat shields (FHS – Front Heat Shield, BHS – Back Heat Shield) are depicted as vertical lines.

Significance

Combinations of different catalytically active materials can be attractive to influence the reaction sequence during CPOX. Using the example of a staged Pd-Rh catalyst, axial profiles have been collected and compared to single-stage Rh and Pd catalysts. The comparison reveals a significant influence of the used catalyst on the mole fractions in the gas phase along the channel of the catalyst and gives an insight into the different mechanisms of CPOX on Rh and Pd.

References

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