

## Catalytic Partial Oxidation of Methane: Sulfur & High Space Velocity

Anders Bitsch-Larsen, N. J. Degenstein, L. D. Schmidt\*

Dept. of Chemical Engineering & Materials Science, University of Minnesota, Minneapolis,  
MN 55455 (U.S.A)

\*schmi001@umn.edu

### Introduction

Catalytic partial oxidation (CPO) of hydrocarbons over precious metal catalysts can be obtained at millisecond contact times with high selectivities to syngas or olefins from a variety of feedstocks [1]. This provides an alternative to the traditional technologies, which are difficult to scale down economically. Since CPO is a relative new technology, investigations of the effect of impurities such as sulfur on catalyst performance has not been investigated even for methane. The millisecond contact times inherent in the reactor makes it difficult to obtain data on the reaction pathway due to high temperature and concentration gradients in the catalyst foam monoliths used as support. In order to obtain an understanding of the reaction pathway it is necessary to sample inside the catalyst without perturbing the system.

### Materials and methods

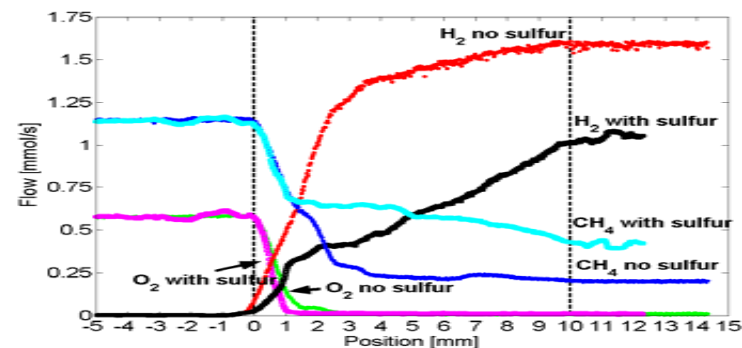
Precious metal catalysts were prepared by the incipient wetness technique with  $\alpha$ - $\text{Al}_2\text{O}_3$  as support. In order to investigate the reaction pathways a newly developed technique that allows for sampling inside the catalyst was employed [2,3]. By drilling a small hole ( $\sim 0.75\text{mm}$ ) axially through the monolith it is possible to insert a fused silica capillary (diameter  $\sim 0.65\text{mm}$ ). Sampling through this capillary it is possible to obtain both species profiles and measure temperatures by using a fiber optic pyrometer and a thermocouple. The positioning of the capillary is electronically controlled by a linear actuator. This allows the sampling resolution to be on the order of the pore size of the foam support,  $\sim 200\mu\text{m}$  (although the resolution of the linear actuator is much better).

Partial oxidation of methane was performed around syngas producing conditions  $\text{CH}_4/\text{O}_2 \sim 2$  at a GHSV of  $135,000\text{h}^{-1}$ , with and without sulfur addition to observe how sulfur addition affects catalyst performance. Sulfur, in the form of  $\text{CH}_3\text{S}$ , was added to the feed stream at 14–28 ppm. This effect of sulfur is reversible since the absence of sulfur allows the catalyst to regain its activity.

### Results and Discussion

The profiles without  $\text{CH}_3\text{SH}$  show a short zone of 1–2 mm where all the oxygen and part of the methane are consumed. In this exothermic zone  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$  and  $\text{CO}_2$  are all produced. This is followed by an endothermic steam reforming (SR) zone where  $\text{CH}_4$  and  $\text{H}_2\text{O}$  are consumed to produce more  $\text{CO}$  and  $\text{H}_2$ .

Figure 1 shows the effect of addition of  $\text{CH}_3\text{SH}$  which results in a severe temperature increase. This is due to a much lower catalytic activity for the SR reaction, however the oxidation length remains essentially unchanged. The reduction in SR reduces the  $\text{CH}_4$  conversion and the yield of  $\text{H}_2$ .



**Figure 1** Species profile comparing the effect of sulfur for Rh-Ce catalyst on  $\alpha$ -alumina foam. GHSV  $135,000\text{h}^{-1}$ . Feed  $\text{CH}_4/\text{O}_2=2$ .

### Significance

The presented work is significant because for the first time the effect of sulfur on CPO of methane has been investigated. The evolution of species and temperature has been examined with very high resolution thus yielding new insight to the poisoning effect of sulfur.

### References

1. Goetsch D., Schmidt, L. D., *Science* 271, 1560 (1996).
2. Horn, R., Williams, K. A., Degenstein N. J., Schmidt, L. D., *J. Catal.* 242, 92 (2006).
3. Horn, R., Degenstein, N. J., Williams, K. A., Schmidt, L. D., *Catal. Lett.* 110, 169 (2006)