

## Product evolution in the catalytic partial oxidation of ethane over Pt and Rh coated monoliths

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### Introduction

Ethylene is the most important organic commodity chemical, based on world-wide production. Currently, large-scale production of ethylene employs large, heat-integrated process equipment to carry out the homogeneous pyrolysis of ethane. In the early 1990's, the work of Huff *et al.* [1] showed that high selectivities to ethylene could be achieved in short contact times (~10 ms) by catalytic partial oxidation (CPO) with O<sub>2</sub> over Pt. Later work by Bodke [2] demonstrated that, through the use of Pt-Sn catalysts and the co-feeding of H<sub>2</sub>, selectivities as high as 80% with conversions of >70% could be achieved with the same simple reactor configuration.

Contrasting mechanisms have been proposed for the formation of ethylene via CPO. Production at such short contact times suggests a catalytic route to ethylene. Others authors suggest that the catalytic partial oxidation is only relevant to provide heat for homogeneous pyrolysis. Indeed, high yields to ethylene have been demonstrated with different catalysts known to be highly active for combustion [3]. Most of these studies relied on integral data and measurements downstream of the catalyst.

This work compares the product evolution within Pt and Rh coated foam monoliths in order to gain insight into the role of the catalyst in the production of ethylene. Using the spatial sampling technique developed by Horn *et al.* [4], we have collected high resolution temperature and species profiles for a range of feed mixtures, including those with H<sub>2</sub> addition.

### Materials and Methods

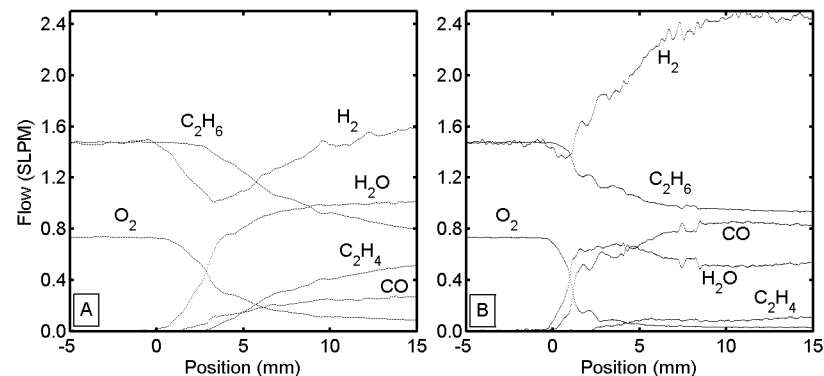
Reactions were carried out with simulated air in an 18 mm I.D. quartz tube containing three 10 x 17 mm 30 PPI alumina monoliths. The middle monolith was impregnated with either Rh or Pt (5 %wt) from aqueous precursors. Prior to impregnation, the monoliths received a ~750  $\mu$ m axial hole to accommodate a 550  $\mu$ m fused silica capillary. To sample gases, a hole was scribed in the side of the capillary allowing a small sample stream to be quickly drawn from the catalyst and sent to a mass spectrometer for analysis. Temperatures were measured by inserting a quartz optical fiber into an un-scribed capillary, which directed radiation to an optical pyrometer. Integral data were sampled 20 mm downstream of the catalytic monolith and sent to a GC.

### Results and Discussion

The spatial profiles measured for C<sub>2</sub>H<sub>6</sub>/O<sub>2</sub> ratios ranging from 1-2 suggest contrasting trends for the two metals. Within the first half of the catalyst, O<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> react quickly and exothermically to partial oxidation products with little or no C<sub>2</sub>H<sub>4</sub> production. At the end of this zone, the temperature reaches a maximum (900°C-1100°C), yielding primarily

H<sub>2</sub>O and CO for Pt and H<sub>2</sub>, CO, and H<sub>2</sub>O for Rh. Following the exothermic zone, C<sub>2</sub>H<sub>4</sub> and trace CH<sub>4</sub> production is observed over Pt, whereas selective reforming of C<sub>2</sub>H<sub>6</sub> with intermediate water yields additional CO and H<sub>2</sub> on Rh.

Although C<sub>2</sub>H<sub>4</sub> production occurs for both metals, the selectivity with Pt is much higher, most likely due to the absence of the endothermic reforming reactions as observed with Rh. The absence of a sharp decrease in surface temperature with Pt suggests that endothermic C<sub>2</sub>H<sub>4</sub> production occurs primarily in the gas phase while net exothermic processes continue on the catalyst surface.



**Figure 1:** Selected species profiles for CPO of ethane at 5 SLPM total flow for C<sub>2</sub>H<sub>6</sub>/O<sub>2</sub>/H<sub>2</sub> = 2/1/2 over (A) Pt and (B) Rh. The catalytic region lies between 0 and 10 mm.

With H<sub>2</sub> addition (figure 1), preferential oxidation of H<sub>2</sub> takes place within the first ~3 mm of the Pt catalyst, leaving C<sub>2</sub>H<sub>6</sub> nearly unconverted in that region. Over Rh, only a small initial consumption of H<sub>2</sub> is observed. In either case, this initial additional heat source allows for greater C<sub>2</sub>H<sub>4</sub> production; however, since the oxidative consumption of C<sub>2</sub>H<sub>6</sub> is reduced over Pt, the increase of selectivity is far more pronounced.

### Significance

Examination of the product evolution of ethane partial oxidation can give new insight to role of the catalysts in these systems and provide a detailed source for validation of theoretical work. On a practical level, spatially resolved measurements can inform catalyst design/selection by revealing the range of operating conditions within a reactor.

### References

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