

Effects of Thermal Degradation on the Ignition Properties of Propylene Oxidation

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Introduction

The typical support for an exhaust emissions catalyst, for both stationary power sources and vehicles, is the honeycomb monolith. These are integral devices, and gradients in reactant and product concentrations exist and evolve along the surface during operation. As a result, gradients in temperature exist as well, and due to these different concentrations and temperatures, the rates/kinetics of the reactions occurring on the surface are not uniform along the direction of flow. Significant temperature differences can exist between regions along the monolith, possibly resulting in non-uniform thermal degradation along the catalyst.

The ability to accurately predict the reactivity within a monolith-supported catalyst, as well as the effect of a number of variables on its performance, has been the scope of many modeling efforts over the years, but experiments designed to measure and provide complimentary data to verify the simulation efforts are lacking. The conventional method for spatially resolving temperature is through an array of thermocouples located at different positions along the axis of the reactor [1,2]. For better spatial resolution, and via a non-intrusive method, IR thermography has been used to observe variations in temperature over catalysts [2]. For gas-phase concentration measurements, Oak Ridge National Laboratory has been developing a method to measure transient gas-phase concentration profiles, referred to as spatially resolved capillary-inlet mass spectrometry (SpaciMS) [3,4].

In this work, IR thermography and SpaciMS have been combined to provide detail of the temperature and gas species concentrations profiles during propylene oxidation over a Pt/Al₂O₃ monolith-supported catalyst before and after thermal aging.

Materials and Methods

SpaciMS was used to measure the gas-phase species within a 3" long, model, monolith-supported Pt/Al₂O₃ catalyst and IR thermography was used to measure the surface temperatures. The measurements were made during temperature ramps with the capillary positions fixed. 0.45% C₃H₆ and 6.5% O₂ were mixed with a balance of N₂. This was done with both a fresh sample and one aged at 675°C in air.

Results and Discussion

The IR thermography and gas concentration data clearly demonstrated where reaction was occurring in the monolith, and changes in the reaction profile as a function of time and temperature. Under the conditions tested, and as expected, back-to-front oxidation light-off was observed. Changes in the temperature and concentration profiles before and after thermal degradation were compared and show that after thermal degradation the ignition front moved

toward the inlet significantly more slowly relative to the non-thermally degraded sample. The two techniques proved complimentary in application. A complete data set was obtained with one experiment using IR thermography, while obtaining the spatial profile of the gas species measurements required multiple experiments. The IR thermography data, however, were confounded by conductive and convective heat transfer, but were decoupled from the reaction heat after confirming a relationship between the reaction position and temperature profiles using the SpaciMS gas species data.

An example of the spatially resolved temperature data, with one concentration data set overlaid, is shown in Figure 1. The temperature at 1.5" from the inlet peaked at a temperature difference value of 70°C, and lined-up exactly with the point at which the propylene concentration dropped to zero. The data indicate that at each position, no reaction took place after the temperature rise peaked and started decreasing.

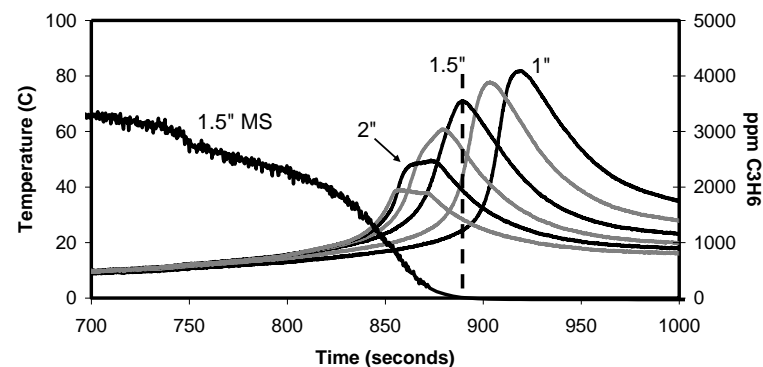


Figure 1. Temperature rise associated with the oxidation reaction as a function of time and catalyst position. Concentration data at one position is also overlaid.

Significance

In developing catalyst or reactor models, typically only outlet concentration and temperatures can be verified. Spatially resolving these two parameters can further validate the accuracy of catalytic reactor models. Furthermore, these data form the basis for tailored catalyst design, where the gradients in activity observed guide preparation of catalysts with gradients in active site distributions, to maximize performance per volume or active site amount as well as minimize degradation.

References

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