

EFFECT OF PROPYLENE EXPOSURE ON NO OXIDATION OVER DIESEL OXIDATION CATALYSTS

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Summary

The effect of propylene on NO oxidation as a function of temperature and position over a model Pt-Pd/Al₂O₃ diesel oxidation catalyst was investigated. Propylene had an apparent inhibition effect on NO oxidation as a result of the NO₂, as the NO oxidation product, acting as an oxidant in the reaction with propylene. This was verified with experiments that included NO₂, and a resulting significant temperature decrease in the onset of NO₂ reduction when propylene was present. Similar results were observed with m-xylene and dodecane addition as well. The results also demonstrate that NO₂ was consumed preferentially relative to O₂ during hydrocarbon oxidation.

Keywords

Environmental Reaction Engineering, Reaction Path Analysis

Introduction

There is growing interest in more widespread use of lean-burn engines, such as the diesel engine, in passenger vehicles. Using lean-burn engines could lead to decreased fuel consumption and a coincident decrease in CO₂ emissions. For this reason, there has been substantial research directed at diesel and lean-burn gasoline exhaust emissions control catalysts. A common catalyst in many proposed systems is a diesel oxidation catalyst (DOC). DOCs perform a range of functions, including NO, CO and hydrocarbon oxidation. NO₂ is desired for optimum performance in downstream devices. As examples, the 'fast' reaction pathway mechanism in selective catalytic reduction catalysis is based on a 1:1 NO:NO₂ ratio, NO₂ is trapped more readily by NO_x storage/reduction catalysts and soot is burned at a lower temperature with NO₂ as the oxidant, relative to O₂. Furthermore, DOCs can provide heat to the exhaust gas via exothermic reactions between added fuel or fuel-derived hydrocarbons and oxygen, which is used to initiate activity in downstream devices.

While there are DOC models available, validation of the included mechanisms is traditionally accomplished by simply matching the measured species concentrations at the catalyst outlet. A more challenging validation is the accurate prediction of the species concentration profiles along the catalyst length. The overall scope of this project is directed at evaluating DOC global mechanisms based on measured species profiles at the catalyst outlet as well as within the catalyst as a function of axial length, for steady-

state reactor experiments as well as temperature programmed oxidation (TPO) studies. This presentation will show experimentally measured, spatially-resolved distributions of gas-phase species along the axial direction of the catalyst.

MATERIALS AND METHODS

Spatially resolved capillary-inlet mass spectrometry (SpaciMS) was performed using a Hiden Analytical HPR 20 QIC. The mass spectrometer was used to measure the gas-phase species within the monolith-supported catalyst. Spatially resolved measurements were made during TPO experiments and the capillary positions were fixed, as well as at a constant upstream temperature and the capillary pulled to different positions after steady-state had been achieved. Most experiments included a mixture of CO, H₂, C₃H₆, C₁₂H₂₆ and NO. An MKS 2030 FTIR was also used to collect outlet gas concentration data.

A monolith-supported Pt-Pd/Al₂O₃ sample with 8 g/ft³ loading, of 1:2 Pt:Pd, was used in these experiments. The sample was 35 mm in length and 20.4 mm in diameter. The sample was "aged" for 16 hours at 650°C in and air/steam mixture.

RESULTS AND DISCUSSION

A baseline NO TPO experiment was performed and the data are shown in Figure 1. Oxidation conversion was

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measurable at 140°C, reached a maximum of about 33% at 420°C and then decreased, thus showing the typical kinetic limitations at low temperature and thermodynamic limitations at high temperature. The data obtained from TPO experiments containing C₃H₆ in the mixture are also presented in Figure 1. The data clearly show that C₃H₆ resulted in a significant decrease in measured NO conversion to NO₂. With the smallest C₃H₆ addition shown in this figure, NO oxidation was not measured until 210°C, and the maximum conversion reached was 20%. Increasing the C₃H₆ concentration led to further drops in NO conversion, reaching only 7% at 460°C with 1000 ppm added.

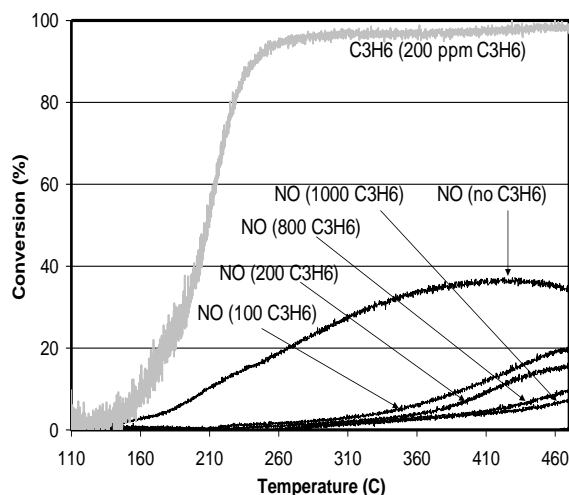


Figure 1: NO and C₃H₆ oxidation conversion as a function of temperature and C₃H₆ concentration. The feed stream contained 200 ppm NO, 10% O₂, 5% H₂O and either 0, 100, 200, 800 or 1000 ppm C₃H₆, and a balance of N₂.

The C₃H₆ and NO oxidation conversions were also spatially resolved. As with the outlet concentration data presented in Figure 1, the presence of C₃H₆ suppressed the maximum NO oxidation conversion. Furthermore, NO oxidation was primarily observed after C₃H₆ light-off, confirming severe NO oxidation inhibition in the presence of C₃H₆. Although at the intermediate higher temperatures C₃H₆ oxidation had lit off and primarily occurred in the front half of catalyst, the small amounts still being oxidized in the back half did suppress NO oxidation, in line with the data shown in Figure 1, where small amounts still had a significant inhibiting effect.

These results in conjunction with experiments containing NO₂ in the inlet feed, and those previously published [1,2], demonstrate that NO oxidation does indeed occur, but that the product NO₂ is then consumed in oxidizing the hydrocarbon. This leads to an apparent NO oxidation inhibition. An example of supporting data is presented in Figure 2. Approximately 200 ppm NO₂ was included in the inlet gas composition. With no hydrocarbon, NO₂ reduction, via reaction to establish thermodynamic equilibrium, begins to occur at around 300°C. At 420°C, 50% conversion is observed. However,

when C₃H₆ was added, NO₂ reduction began at a significantly lower temperature, ~190°C, with 50% conversion attained at 223°C. Similar trends were noted when testing with dodecane and m-xylene, but with reduction onset at higher temperatures than that noted with C₃H₆, but much lower than that in the absence of hydrocarbons. These results therefore show that it is activation of the hydrocarbon that is limiting, and once its activation on the surface begins NO₂ is consumed in the oxidation reaction.

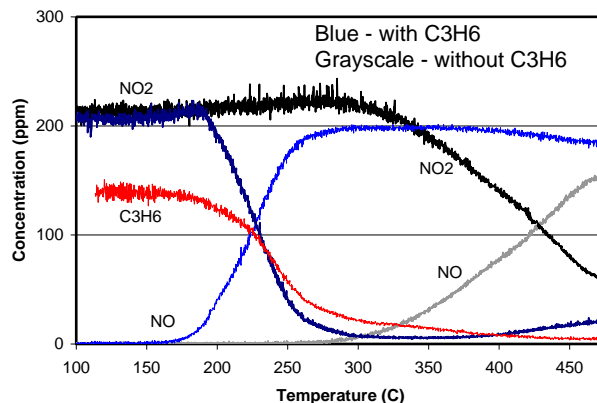


Figure 2: NO, NO₂ and C₃H₆ concentrations as a function of temperature. The feed stream contained 200 ppm NO₂, 10% O₂, 5% H₂O, 120 ppm C₃H₆, and a balance of N₂.

References

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- (2) Katare, S.R.; Patterson, J.E.; Laing, P.M. Aged DOC Is a Net Consumer of NO₂: Analyses of Vehicle, Engine-Dynamometer and Reactor Data. *SAE Technical Paper Series* 2007-01-3984.