



Spatially resolving CO and C₃H₆ oxidation reactions in a Pt/Al₂O₃ model oxidation catalyst



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ABSTRACT

Spatially resolved Fourier transform infrared spectroscopy (Spaci-IR) was used to measure gas-phase concentration profiles during CO and C₃H₆ oxidation reactions over a Pt/Al₂O₃ monolith-supported catalyst. The reaction conditions were selected as representative of certain low temperature combustion (LTC) engine exhaust conditions, where in this study higher concentrations of CO and C₃H₆ and lower concentrations of NO_x were used relative to standard engine exhaust. CO and C₃H₆ oxidation and NO_x reduction reactions were examined individually and in combination via temperature programmed oxidation (TPO) experiments. Significant NO_x reduction occurred right at CO and C₃H₆ light off, and NO oxidation only occurred after the oxidation of CO and C₃H₆. C₃H₆ oxidation was not observed until after most of the CO oxidized, as CO was more strongly adsorbed to the active site surface at low temperature. During the TPO of CO and C₃H₆, the conversion versus temperature profiles did not monotonically increase; two inflections were observed where the rate of conversion change as a function of temperature slowed over a small temperature range before again accelerating with temperature. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used in order to characterize intermediates that were present on the surface at the temperatures where these steps were noted. Surface ethylene and formate species were present during the first step, with acetate and formate in the second step. The inhibition steps were therefore attributed to the partial oxidation of propylene to ethylene, and then the subsequent partial oxidation of ethylene to acetate.

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1. Introduction

Concerns over global warming, climate change and vehicle exhaust impacts on human health have led to the implementation of regulations on vehicle emissions by agencies such as the Environmental Protection Agency (EPA). These policies have acted as a driving force in optimizing engine operation as well as catalytic after-treatment systems, in order to reduce harmful emissions. New low temperature combustion (LTC) engines have been developed with improved fuel economy, but it is still necessary to understand how their exhaust conditions will affect the performance of catalytic after-treatment systems, which have been optimized for different exhaust conditions.

LTC technologies include Premixed Charge Compression Ignition (PCCI) and Reactivity Controlled Compression Ignition (RCCI) as two examples. Oak Ridge National Laboratory, in a comparison of conventional, PCCI and RCCI combustion [1], have shown that RCCI combustion produced much larger concentrations of CO and hydro-

carbons than either the conventional or PCCI combustion, and the engine out temperature was also lower. The PCCI emissions showed similar hydrocarbon concentrations to conventional combustion and slightly higher CO concentrations, while RCCI showed CO concentrations four times greater and hydrocarbon concentrations ten times greater than conventional combustion. In terms of the NO_x concentrations, both the PCCI and RCCI engines produced lower emissions than conventional combustion; with PCCI combustion having about a 33% reduction in NO_x and RCCI about 93% reduction compared to the conventional combustion emissions. The diesel oxidation catalyst (DOC) is a standard after-treatment component and is meant to oxidize the CO and hydrocarbons present in the engine exhaust. However, with the lower exhaust temperature, higher DOC space velocity, and higher hydrocarbon levels, the Oak Ridge National Laboratory data also show that the hydrocarbon emissions from the RCCI combustion exhaust after a DOC were high compared to conventional and PCCI exhaust. They showed that compared to conventional combustion, where the lower CO and HC levels allow the DOC to operate at full conversion by 190 °C under their test conditions, the high concentrations of CO and HC in RCCI engine exhaust moved 100% conversion over the DOC to 300 °C [2].

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For LTC engines, with their potentially higher levels of engine out CO and hydrocarbons and lower exhaust temperatures [3], DOCs need to be evaluated and optimized for these conditions. Typically, studies that included the oxidation of CO and hydrocarbon mixtures over DOCs have used lower total concentrations of CO and hydrocarbons; or in situations with high CO concentrations (on the order of 1 vol%) very low hydrocarbon concentrations were used (100 ppm) [4,5]. On the other hand, where comparable hydrocarbon concentrations were tested, the CO concentrations were nearly an order of magnitude lower than RCCI emissions [6]. Since CO strongly inhibits hydrocarbon oxidation and vice versa, it is important to consider situations where both concentration levels are high in order to select appropriate DOCs to treat LTC engine emissions.

Both mass spectrometry (MS) and Fourier transform infrared spectroscopy (FTIR) have been used to analyze gas-phase concentrations along diesel oxidation catalysts, as well as other after-treatment catalysts [6–10]. Regardless of the analyzer used, the concept of these experiments remains the same. A small capillary is inserted into one of the channels of the monolith such that some of the flow in the channel travels through the capillary and into a gas analyzer, thereby allowing the study of axial concentration profiles of gas species along the length of the catalyst as that capillary is moved along the channel. In this study, Spaci-FTIR was used to monitor NO, CO and C₃H₆ oxidation along a Pt/Al₂O₃ catalyst. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was also used to characterize the surface of the catalyst during reaction.

2. Materials and methods

2.1. Catalyst information and reactor testing

The catalyst used in this study was provided by Johnson Matthey. The catalyst is a Pt/ γ -Al₂O₃ monolith catalyst, with a platinum loading of 50 g/ft³, an Al₂O₃ loading of 1.59 g/in³, and a cell density of 325 channels/in². A monolithic core with a cross section of 132 channels and cut to a length of 2 inches was used in the bench scale reactor experiments. The catalyst was wrapped in insulation and placed in a quartz tube reactor placed inside a Lindberg temperature controlled furnace. Four thermocouples were inserted to monitor the upstream gas temperature, the catalyst front and back temperatures at the radial center, and the catalyst front at the wall. Small glass tubes, with an ID of 2.5 mm and OD of 3 mm, were placed upstream of the sample to ensure good mixing of the inlet flow and avoid a fully developed flow pattern.

For the spatial resolution set-up, a fused silica capillary with an ID of 320 μ m and OD of 430 μ m was inserted into a channel in the center of the catalyst. The axial location of the capillary was changed by pulling or pushing the capillary through a graphite ferrule seal at the reactor outlet, similar to experiments done by Luo et al. [8]. The outlet of the capillary was connected to a stream of N₂ (390 mL/min) to carry the gas mixture to the gas analyzer. The gas analyzer used was an MKS MultiGas 2030 FTIR, with a 200 cm³ cell. The gas hourly space velocity (GHSV) of each experiment was 55,000 h⁻¹, with a total flow rate of 12.2 L/min. An estimated 92 mL/min of gas flowed through each channel. The flow through the capillary was maintained at 20 mL/min, using a needle valve placed downstream of the reactor to provide a pressure in the reactor slightly above ambient (about 1.15 bar). The flow through the capillary was found to not vary with the capillary position along the length of the catalyst.

There are studies that have evaluated the extent of the intrusiveness of this technique with regards to the flow patterns and rates and reactions taking place in the channel of the monolith [9,10]. In this study we recognize that the capillary carrying the flow from

the channel, in our case taking about a quarter of the flow in the channel, may impact the reaction, however we believe the technique still provides valuable qualitative information regarding key trends in the reaction profiles along the length of the catalyst.

All the gases except for the balance N₂ were supplied by Praxair, and the balance N₂ was supplied via an On-Site N₂ generator. A Bronkhorst CEM system was used to introduce water to the gas stream. The gas flows were controlled with various Bronkhorst mass flow controllers, and the gases used were CO, C₃H₆, NO, NO₂, and CO₂. All the upstream and downstream lines were heated above 100 °C at all times in order to prevent water condensation.

Temperature programmed oxidation (TPO) experiments were performed with different CO, C₃H₆ and NO concentrations: 0 or 3000 ppm CO, 0 or 1000 ppm C₃H₆, 0 or 50 ppm NO, 0 or 30 ppm NO₂, 14% O₂, 5% H₂O, 5% CO₂ and a N₂ balance. These levels were chosen based on data provided by Oak Ridge National Laboratory, obtained via measurements of the exhaust from a Reactivity Controlled Combustion Ignition (RCCI) engine. Temperature ramps from inlet gas temperatures of 80 °C to 300 °C at a ramp rate of about 7.3 °C/min were used. The inlet gas stream was also heated by a preheater that was ramped in temperature during the TPO in order to keep the temperature gradient under non-reacting conditions along the catalyst length below 3 °C. This was tested and verified with only N₂ flowing. The sample was aged at 700 °C in 14% O₂ and 5% H₂O for 5 h prior to testing, and a few TPO experiments with CO and propylene in the gas mixture were done to ensure catalyst stability and repeatability. In between each TPO experiment a pretreatment in the aging gas mixture was done at 500 °C for 30 min.

The gas concentration data collected were averaged for every 4 s for the CO and propylene conversion data, every 20 s for NO₂ and N₂O concentration, and every 100 s for the NO concentrations due to increased noise in the low NO, N₂O and NO₂ signals after the dilution with the N₂ carrier stream. All the conversion data are plotted as a function of the gas inlet temperature, measured from the thermocouple placed 1 cm in front of the catalyst in the middle of the reactor tube. The catalyst exotherm data plotted is the difference between the temperature of the back of the catalyst and the temperature of the inlet gases. Adiabatic temperature rises were calculated assuming the ideal gas law applies. Plots for the experiments in the following sections have total NO_x conversion defined as

$$X_{\text{NO}_x} = \frac{\left[(C_{\text{NO}} + C_{\text{NO}_2} + 2 \times C_{\text{N}_2\text{O}})_{\text{inlet}} - (C_{\text{NO}} + C_{\text{NO}_2} + 2 \times C_{\text{N}_2\text{O}})_{\text{outlet}} \right]}{(C_{\text{NO}} + C_{\text{NO}_2} + 2 \times C_{\text{N}_2\text{O}})_{\text{inlet}}} \times 100\%;$$

in other words describing the amount of inlet NO_x that is converted to nitrogen.

2.2. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments

In order to identify adsorbed species and surface reaction intermediates during reaction, in situ DRIFTS experiments were performed using a Nicolet 6700 spectrometer equipped with a MCT detector and a high temperature reaction chamber (Harrick Scientific Praying Mantis) equipped with ZnSe windows. The catalyst was scraped off the cordierite and pressed to a pellet of 60 mg. The DRIFTS spectra were collected in the 4000–650 cm⁻¹ wavenumber range, accumulating 64 or 128 scans at 4 cm⁻¹ resolution. Nicolet OMNIC software was used to process the absorbance data into Kubelka–Munk (KM) format.

TPO experiments were performed on the sample with a gas stream temperature ramp from 84 to 210 °C at 4.2 °C/min, collecting 128 scans or 66 to 175 °C with a ramp rate of 1.7 °C/min collecting 64 scans for further temperature resolution. In order to obtain a

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