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, 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.

Keywords

Oxidation catalyst; Spatially resolved reactions; Propylene oxidation; NO_x reduction; Engine emissions

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 hydrocarbons 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 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].

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 emissions.

Both mass spectrometry (MS) and Fourier transform infrared spectroscopy (FTIR) have been used for analysis of 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 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 hr⁻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 hours 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 minutes.

The gas concentration data collected were averaged for every 4 seconds for the CO and propylene conversion data, every 20 seconds for NO₂ and N₂O concentration, and every 100 seconds for the NO concentrations due to increased noise in the 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 of 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 show total NO_x conversion defined as

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

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

2.2 Diffuse Reflectance Infrared 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) 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 more time resolved data set of the light off behavior on the surface, without compromising the integrity of the

measurement by reducing the number of scans, these TPOs were performed with a slower ramp rate than that of the bench reactor testing. A background spectrum was taken at the beginning of the temperature ramp in flowing He, and then the reactant gases were added and the samples were exposed to the feed gas for 1 hour before the temperature ramp was started.

The concentrations used in the DRIFTS experiments were 0 or 3000 ppm CO, 0 or 1000 ppm C₃H₆, 14% O₂, and 1% H₂O in balance He. The absence of CO₂ in the inlet gas is not expected to affect the results. The total flow rate of the inlet stream was maintained at 50 mL/min by MKS mass flow controllers. The water supplied to the DRIFTS was from an absorption/bubbler column with 12 mL/min He flowing.

TPO experiments were also performed with H₂O, O₂, and He only so the spectral data obtained could be subtracted from spectra obtained during the TPOs with CO, C₃H₆, and both CO and C₃H₆. This was done in order to remove the features associated with water during the temperature ramp as well as the background shift due to temperature and any other temperature effects. A pretreatment before the experiments and between each TPO experiment at 500°C with 14% O₂ and 1% H₂O for 30 minutes was used, similar to that of the pretreatment for the bench scale reactor tests.

3. Results and Discussion

3.1 Spatially resolved TPO experiments

3.1.1 Spatially resolved CO and propylene oxidation in the absence of NO_x species

The spatially resolved conversion results for the CO only TPO experiment are shown in Figure 1 a), and the normalized reaction rates for the sequential 0.5 inch segments are shown in Figure 1 b). The plot of normalized reaction rates for the sequential 0.5 inch segments is another way of looking at the conversion plots for the spatially resolved data, and is included to provide a different view of the conversion plots. These data demonstrate that back to front light-off was observed, as has been previously shown when relatively slow ramp rates are used [6,7]. This back-to-front reaction propagation is due to a combination of the exothermic CO oxidation reaction and some oxidation occurring down the length of the channels, which leads to lower CO self-poisoning at the outlet of the sample. With the lowered self-poisoning more CO oxidation occurs as a function of position from the inlet, and thus more heat is generated, such that the outlet of the sample can be at a higher temperature than the inlet (if the ramp rate is slow, as mentioned). This in turn leads to slow solid heat conduction moving upstream and the back-to-front reaction propagation. The data for conversion as a function of temperature for the middle areas of the catalyst, as well as for the measurement done at 0.5 inches, are quite similar. The onset of oxidation at the back of the catalyst is observed at a slightly lower upstream temperature, about 5°C, before the others. These results suggest that the propagation of the reaction front through the catalyst was quite rapid. Previous experiments at a higher space

velocity with only 800 ppm of CO did not show this fast light off behavior, the reaction propagated more slowly over a larger length of catalyst [11]. However, the higher exotherm obtained here resulted in the rapid propagation and the overlapping conversion data through the middle and front of the catalyst. Near the catalyst front, 0.5 inch, 100% conversion was not reached over the temperature range used, likely due to residual CO self-poisoning with the high entering concentrations, as well as mass transport limitations at higher conversions. A similar trend exists in the propylene TPO results, shown in Figure 2 a) and b), where the light-off curves still indicate back to front light off, yet are more spread out for the different capillary positions when compared to the CO data, which indicates different self-inhibition properties for propylene. The peak reaction rate in each 0.5 inch segment (measured from the back of the catalyst) is approximately equal, again showing a slower and progressive reaction front moving from the back to the front of the catalyst. Also note, there was no evidence of intermediate CO formation or any other partial oxidation intermediate during these experiments. While the temperature rise associated with the oxidation of propylene is higher, a maximum catalyst temperature rise of 28°C was measured during the CO TPO experiment, and 57°C for propylene at light-off (adiabatic temperature rise under these conditions calculated to be 30°C and 66°C respectively), this isn't sufficient to overcome the activation barrier as quickly along the length of the catalyst as was for the case of CO. These temperature rise data, taken as the difference between the back of the catalyst and the front of the catalyst, are also plotted in Figure 1 and Figure 2. From these two sets of data, under the conditions tested, nearly all the CO is oxidized by 150°C and propylene is oxidized by 190°C, when these species are oxidized separately.

When comparing these to the results obtained from the TPO with the mixture of CO and propylene, shown in Figure 3 a), it is apparent that both the CO and propylene oxidation reactions are inhibited by the presence of the other reactant, as the onsets of conversion are shifted to substantially higher temperatures, and furthermore, the light-off curves at different capillary positions are more spread out. This is consistent with a mechanism that includes C_3H_6 inhibition of CO oxidation and vice versa [5]. In terms of the propylene, the onset of light off is observed once most of the CO is oxidized. The rapid onset of C_3H_6 oxidation after CO oxidation is caused by the availability of active sites for C_3H_6 adsorption and reaction that were not present at lower temperatures due to the strong adsorption of CO on those sites. The spreading of the light-off curves indicate an additional inhibition interaction, where for example in kinetic studies not only inhibition terms for the individual components, CO and propylene, are present to account for competitive adsorption, but an additional term including the concentration of both CO and propylene is applied when there are high concentrations of the two [5]. This additional inhibition term was related to the low concentration of oxygen on the surface relative to high concentrations of CO and propylene, where the surface is crowded by CO and partial oxidation intermediates.

At the 0.5 inch measurement position, two “steps” in the CO and propylene conversion versus temperature curves were observed, the first occurring around 182-192°C and the second

occurring around 197-207°C. In an experiment done where the full reactor outlet was measured (i.e. not through the capillary, but all flow went through the FTIR analyzer), some formaldehyde byproduct was observed, Figure 3 b), at concentrations too low to detect through the capillary due to the dilution. Formaldehyde is not anticipated to be a reaction intermediate that leads to the inhibiting steps, as it is very easily oxidized on Pt compared to CO [12]; however the involvement of the formaldehyde in the surface chemistry of the intermediates could contribute to the trends observed. The steps and the formaldehyde byproduct suggest the formation and build-up of some surface intermediate causing the observed inhibition, prompting the DRIFTS experiments, which will be discussed below. These steps dissipate along the length of the catalyst; the steps are clearly visible at the 0.5 inch position, appear as slight inflection points at the 1 inch position, and are not apparent in the data obtained at the 1.5 inch and 2 inch positions. This suggests the heat generated from the oxidation reactions occurring upstream, in combination with the lower concentrations of reactants downstream, was sufficient to cause the surface intermediates to completely oxidize or desorb. The measured catalyst temperature rise with CO and propylene reached a maximum of 90°C, approaching the calculated adiabatic temperature rise of 95°C at light-off conversions, and this large exotherm would lead to rapid CO desorption and oxidation, in turn allowing increased propylene adsorption and oxidation, which leads to the formation of surface intermediates and the inhibition of the oxidation of both CO and propylene. In the plot of the temperature rise along the catalyst as a function of inlet temperature in Figure 3 a), there are distinct local maxima in the temperature difference measured, which can be attributed to a reaction starting and then stopping, and are in line with the “steps” in conversion seen. As will be discussed below, with the DRIFTS data, these local maxima are associated with oxidation of surface intermediate species, which are the causes of the observed inhibition effects.

3.1.2 Spatially resolved CO and propylene oxidation, and NO_x reactions

The results of the NO TPO with both NO and NO₂ present in the feed gas are shown in Figure 4. NO oxidation extent builds along the length of the catalyst, plateauing around 180°C, resulting in 88% NO oxidation at the 2 inch position. A back-to-front ignition profile is not observed in this experiment, due to the lack of any significant exotherm due to the low concentration of NO added as well as the smaller heat of reaction.

In comparing the CO oxidation TPO results in the presence and absence of NO_x, Figure 5 a) and Figure 1, the onset of CO oxidation was shifted to higher temperatures in the presence of NO_x. And in comparing the NO oxidation data, Figure 5 b) and Figure 4, the apparent onset of oxidation of NO to NO₂ was also shifted to higher temperature, and the extent of reaction at higher temperatures was decreased. These data demonstrate that CO inhibited NO oxidation as well as NO_x inhibited CO oxidation. The inhibition of CO oxidation is due to competitive adsorption of NO and CO on the active sites [13].

Between 80 and 150°C, most of the NO₂ present in the feed gas was reduced to NO, with this apparently a relatively easy reaction since most occurred within the first 0.5 in of the catalyst.

NO₂ reduction to NO over similar catalysts has been regularly observed, and is also responsible for the observed lack of NO oxidation when substantial amounts of CO are still present [14–16]. As the temperature increased there was an intermediate temperature region where most of the NO_x was reduced to N₂. Reduction of NO_x to N₂ and N₂O by CO has been discussed in relation to three-way catalysts for the treatment of gasoline exhaust [17,18], and additionally various hydrocarbons including C₃H₆ have also been found to reduce NO_x to N₂ and N₂O [19,20]. The difference in these experiments is that no N₂O formation was observed with the reduction of NO_x with CO, and this is likely due to the high CO coverage on the surface. Mechanisms reviewed in reference [17] demonstrate that N₂O formation requires adsorbed NO and possibly atomic N on the surface. With such high concentrations of CO, the Pt is likely in a metallic state facilitating relatively rapid NO decomposition and thus there is a lack of available adsorbed NO once reaction onset begins. At 2 in, almost 70% of the NO_x was reduced to N₂ (no N₂O was observed) at about 180°C, which coincided with complete CO consumption. There was a similar trend for the other positions, and at the 0.5 inch position NO_x reduction was maintained at 20% even at high temperatures. As the temperature increased, more and more of the CO was oxidized by O₂, leaving less on the surface available for NO_x or Pt reduction. However, some remained in the upstream portion, since that was the region that was catalyzing the CO oxidation and thus some selectivity for the reduction reaction was still maintained.

The propylene and NO_x conversion results, with no CO in the feed gas, are shown in Figure 6 a), and the NO_x species concentrations are shown in Figure 6 b). During this experiment, reduction of NO₂ to NO was not observed at low temperature, however as the temperature increased there was complete reduction of NO₂ to NO and N₂, and N₂O was also observed. Note, no N₂O was formed in the previous set of results with CO and NO_x. This reduction behavior of NO₂ with propylene, as well as CO, has been previously observed, and the formation of N₂O over Pt/Al₂O₃ catalysts via hydrocarbon selective catalytic reduction (SCR) of NO_x is expected based on previous studies [14,21]. At 208°C, peak N₂O formation was observed and the conversion of NO_x to N₂ was 26%. The NO_x conversion reached a peak at 198°C, 40%, before N₂O formation was noted, and both values were much lower than those with CO as the reductant. However, with propylene, the onset of NO_x conversion actually occurred at a lower temperature and increased with propylene conversion, stabilizing to around 25% at high temperature. In comparing the propylene TPO data in the presence of NO_x to those in the absence, Figure 2, where most of the propylene was oxidized by 190°C, again the presence of NO_x inhibited propylene oxidation, here with a 60°C shift in the light-off curve. This inhibition effect is consistent with previous studies, where competitive adsorption onto active sites was cited as the cause [21]. Peak N₂O formation shifted to lower temperatures further along the length of the catalyst, and it always corresponds to roughly the temperature where 50% of the propylene was oxidized. This is consistent with the idea that incomplete combustion products of propylene are reactive with NO_x species [19,20,22], as these incomplete combustion products, which may include CO and acetate and formate species, would have high surface concentrations right at light-off.

The conversion data and NO_x concentration profiles obtained when using the full mixture (CO , C_3H_6 and NO_x) are shown in Figure 7 a) and Figure 7 b) respectively. Nearly all of the NO_2 is reduced at low temperatures at the front of the catalyst, as was the case with just CO and NO_x , Figure 5 b), demonstrating that propylene does not inhibit this reduction reaction. One of the inhibition steps observed during the CO and propylene TPO, without NO_x present, in Figure 3 a), was again evident but under these conditions was present throughout the length of the catalyst, shifting slightly to lower temperatures along the catalyst length and over a smaller temperature range. This indicates that NO_x is reacting with a surface species that was responsible for the second inhibition step in the absence of NO_x . Previous work has shown that surface nitrates react with propylene to form surface carboxylic species [23]; specifically it was found that acetate intermediates react with nitrates [22]. Therefore, likely propylene adsorbed and oxidized partially to acetate (evidence to be shown below), which then was immediately oxidized by nitrates on the surface, leading to only one observable inhibition step since the acetate intermediate was no longer stable or long lived on the surface. Formation of N_2O was again observed in the temperature range where some but not all of the propylene was oxidized. The peak in N_2O production seems to correspond to a temperature where most of the propylene is oxidized. The formation of N_2O in the presence of propylene has been related to a shift in the ratio of adsorbed propylene and surface NO_x , where the less surface NO_x leads to an incomplete reduction of nitrates to N_2O [21]. As shown in Figure 7 a), the NO_x conversion data look more similar to the case of the C_3H_6 and NO_x TPO than that of the CO and NO_x TPO, suggesting that the propylene adsorbed on the surface inhibits the surface CO from acting as an NO reductant in this temperature range, while the CO still acts as an NO_2 reductant to NO at the lower temperatures. These trends can be related to surface overages. At the beginning of each of the CO and NO_x and the CO , C_3H_6 and NO_x TPOs, the CO is able to reduce all the NO_2 to NO because CO or NO is preferentially adsorbed on the surface relative to propylene. In the presence of both CO and propylene, once the CO lights off, the surface would then become covered with propylene and intermediates of propylene, which would effectively block the active sites and stop the reduction of NO by CO . For ease of comparison, Table 1 lists the T_{50} 's for all the experiments performed.

3.2 DRIFTS TPO Experiments

The inflection, or step, in conversion as a function of temperature, where the rate of conversion change slows, during a propylene oxidation light-off experiment has previously been observed experimentally under conditions more relevant to conventional diesel exhaust, i.e. with lower CO and propylene concentrations and higher NO concentrations [24]. As observed in the data shown in Figure 3 and Figure 7, these steps occurred in both CO and propylene light-off curves, with and without NO_x . To better understand this inhibition effect, the interaction between CO and propylene was characterized using DRIFTS. DRIFTS TPOs were conducted with similar experimental conditions to those of the bench scale reactor tests. The differences between these experiments was that the water concentration was lower, only 1% by volume instead of 5%, there was no CO_2 in the feed gas for these tests, and the ramp rates used were

slower. These changes are not expected to influence the nature of the surface intermediates observed, and if anything should exaggerate them. Due to inherent differences in the DRIFTS cell and bench scale reactor, particularly the space velocity; the temperatures at which the CO and C₃H₆ light off were expected, and were observed, to be much lower in the DRIFTS data compared to the bench scale reactor.

3.2.1 CO TPO

Representative DRIFTS spectra obtained during the CO TPO experiment are shown in Figure 8. There was a shift from high coverage at low temperature of linearly bound CO, 2090 cm⁻¹, to bridged CO at low coverages and high temperatures, 1800 and 1730 cm⁻¹, consistent with previous observations [25]. Bands at 1455, 1330, and 1540 cm⁻¹ increased with temperature over the course of the TPO, and these have been assigned to absorbed carbonate species, either in the monodentate or bidentate adsorption mode[25]. A band at 1650 cm⁻¹ also increased slightly over the span of the temperature ramp, and this is attributed to the bending of water adsorbed on Pt [25]. Bands at 1300 and 1500 cm⁻¹ are assigned to surface carboxyl groups [25]. Over the course of the temperature ramp a large broad peak between 1200-1260 cm⁻¹ developed, and can be attributed to -COH and other species with more hydrogen content [26–28]. From these results, and the observed depletion of the -OH feature at 3740 cm⁻¹, it is inferred that some CO adsorbed and reacted with the Lewis acid sites on the alumina support to form surface formate species [29]. νCH features at 2962 cm⁻¹ increased over the temperature ramp, further substantiating the formation of surface formate species on the alumina [30,31]. Other peaks related to the formate species can be observed at 1332, 1370, 1395 and 1665 cm⁻¹ [21,23,32,33]. There is also evidence of bands at lower temperatures, 2185-2190 cm⁻¹, corresponding to CO on alumina's Lewis acid sites, as well as H-bonded CO on hydroxyl sites on the alumina at 2160 cm⁻¹ [34].

3.2.2 C₃H₆ TPO

The formation of formates on Pt/Al₂O₃ during propylene oxidation has been reported in the literature, with bands associated with said formates at 1332, 1370, 1395 and 1665 cm⁻¹, all of which were observed during the propylene TPO, Figure 9 a). Peaks that have been associated with an acetate species at 1457 cm⁻¹, and carboxylate species at 1580, 1642 and 1672 cm⁻¹ [21,23,32,33] are also evident. Again the feature at 2962 cm⁻¹ was observed (Figure 9 b)), and this time was present over the entire temperature range. The initial spectrum before the temperature ramp shows a broad peak in the range of 1680-1560 cm⁻¹, which increased with temperature and has been attributed to π-bonded ethylene on Pt/SBA-15 catalysts [35]. This seems reasonable as the adsorption of propylene on Pt could be activated to form formate and ethylene intermediates, substantiated by the observed ethylene and formate peaks at the beginning of the ramp and their increase as the temperature increased.

3.2.3 CO and C₃H₆ TPO

The IR spectral features observed during CO and propylene (co-added) oxidation are largely the same as those noted during the oxidation of the single components. As with CO oxidation, the peaks for linearly- and bridge-bound CO are observed. If the CO peak height is

plotted as a function of temperature for both the CO TPO and the CO/C₃H₆ TPO, shown in Figure 10 a), a step in the surface concentration of CO is present when C₃H₆ was part of the mixture, similar to the step in the conversion vs temperature data obtained during the TPO in the bench reactor, and is absent when C₃H₆ was not part of the mixture. There is also a region at higher temperatures, after this step where the surface CO rate loss appears to slow, which may correspond to the second inhibition step observed in the bench reactor data.

The peak for linearly bound CO shifted from 2090 to 2073 cm⁻¹ in the presence of propylene as temperature increased, shown in Figure 11. Part of this shift is solely due to temperature, when only CO is oxidized the shift with temperature is 2090 to 2082 cm⁻¹, with literature suggesting this is the CO moving from terrace sites to edge or kink sites, or represents an electron transfer due to another adsorbed species [25,36]. The larger CO peak shift in the presence of propylene suggests that the electron transfer is from an intermediate of propylene oxidation; a similar peak shift was noted during co-adsorption of ethylene and CO, due to the π -ethylene species [35–37]. Since ethylene and propylene can both form this π -species on the surface, it is not immediately clear whether the adsorbed species here is propylene or ethylene. There was an increased amount of formate formed in the presence of propylene which would suggest a scission of the propylene into ethylene and formate species. At the beginning of the temperature ramp, the CO was linearly bound, however as the temperature increased this peak shifted and the peaks for π -bonded propylene or ethylene and formate species began to emerge, suggesting that as some CO was oxidized at the beginning of the temperature ramp, propylene was able to adsorb on the active sites and either co-adsorbed with CO, or went through an activated adsorption to form ethylene and formate. A subtraction of the spectra of the CO TPO at 106°C from the spectra of the CO/C₃H₆ TPO at 110°C yields the results shown in Figure 12. The only unique peaks observed are at 1454 cm⁻¹ and 2966 cm⁻¹, which are attributed to either π -ethylene or π -propylene [36], as well as the presence of a larger amount of formate, a band shift in the CO-related adsorbed species, and a small peak at 1666 cm⁻¹ which has also been attributed to π -ethylene [35]. As mentioned earlier, the increased amount of formate, as well as the emission of formaldehyde during the bench reactor tests, Figure 3 b), suggest that the scission of propylene to ethylene and formates is taking place in one activated adsorption step. These data demonstrate that the adsorbed ethylene is a surface intermediate species during the co-oxidation of CO and propylene and was observed on the surface in the same temperature range as the first inhibition step during the bench reactor experiments. In terms of the second step, if the carboxylate peaks are plotted as a function of temperature, Figure 10 b), the only increase in peak height observed, compared to the case without propylene, is *after* the surface CO step and still in the region where the CO was present on the surface. Therefore, as the reaction proceeds, the carboxylate peaks increase with temperature, indicating that either the adsorbed propylene or the ethylene can partially oxidize to form the acetate and formate species, which covers the active sites and leads to the second inhibition step. The absence of a second step in the presence of NO_x is related to consumption of the acetate species, i.e. the second inhibition step. This is based on the formation of more significant formate species on a Pt/Al₂O₃ surface in the presence

of surface nitrates [21], and in the data shown in Figure 10 b) this coincides with the higher temperature step, which is therefore associated with the acetate species.

In summary, the first step observed in the bench reactor data appears to be caused by propylene adsorbing to the surface and forming ethylene and formate, then as the temperature increases an activation barrier to partially oxidize the ethylene to acetate is overcome to reach the second step where the acetate species and adsorbed CO coexist on the surface causing the second inhibition step.

4. Conclusions

During the oxidation of CO and C₃H₆, as well as reactions involving NO_x, CO poisons the catalyst and acts as a strong inhibitor for the oxidation of both NO and C₃H₆. Furthermore, the NO_x reduction capability at the high concentrations of CO used was significant; NO₂ was consistently reduced to NO at low temperatures in the presence of CO, and at CO light-off, 70% of the NO_x was reduced to N₂. The reduction ability of the propylene was less significant, as not all of the NO₂ was reduced to NO at low temperature, and only about 40% NO_x conversion to N₂ was observed at light-off, where some N₂O was also observed. In the presence of both CO and C₃H₆, low temperature NO₂ reduction again occurred, due to the high CO or NO coverage at low temperature, relative to propylene, thus resulting in a similar trend as the experiment with CO and no propylene. However, low NO_x conversion and N₂O formation at light-off was attained, as was the case with C₃H₆ as the reductant. At CO light-off, the propylene adsorbs to the active sites and thus the NO_x reduction trends then follow those observed when just propylene was added.

In the absence of NO_x, there were two inflections in the CO conversion versus temperature results when propylene was part of the feed mixture, indicating inhibition “steps”. DRIFTS results show that ethylene and formaldehyde intermediates formed during the first step, and then acetates in the second step. These partial oxidation products of propylene, in the presence of high CO surface coverages, were able to inhibit the light-off of each species, resulting in the observed inhibition. In the case of CO, C₃H₆ and NO_x all reacting at once, only one of the inhibition effects was observed. This indicates that one of these intermediates was consumed in NO_x reduction, while the other intermediate was not as easily oxidized by surface NO_x species. This is likely due to reaction between partially oxidized intermediate acetate species with surface nitrates leading to the formation of formate, while the ethylene species does not easily react with the surface nitrates and remains an inhibiting species.

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Figure and Table Captions

Figure 1: CO conversion as a function of upstream gas temperature at four positions along the catalyst length during a TPO with a ramp rate of 7.3°C/min. Feed gas composition: 3000 ppm CO, 14% O₂, 5% CO₂, 5% H₂O, balance N₂. b) Reaction rate per 0.5 inch segment of catalyst.

Figure 2: Propylene conversion as a function of upstream gas temperature at four positions along the catalyst length during a TPO with a ramp rate of 7.3°C/min. Feed gas composition: 1000 ppm C₃H₆, 14% O₂, 5% CO₂, 5% H₂O, balance N₂. b) Reaction rate per 0.5 inch segment of catalyst.

Figure 3: a) CO and propylene conversion as a function of upstream gas temperature at four positions along the catalyst length. b) CO and propylene conversion at the reactor outlet, and formaldehyde formation. Feed gas composition: 3000 ppm CO, 1000 ppm C₃H₆, 14% O₂, 5% CO₂, 5% H₂O, balance N₂.

Figure 4: NO_x concentrations as a function of catalyst position and upstream gas temperature. Feed gas composition: 50 ppm NO, 30 ppm NO₂, 14% O₂, 5% CO₂, 5% H₂O, balance N₂.

Figure 5: a) CO and NO_x conversion at different catalyst positions as a function of upstream gas temperature. b) NO_x species concentration profiles at different catalyst positions as a function of upstream gas temperature. Feed gas composition: 3000 ppm CO, 50 ppm NO, 30 ppm NO₂, 14% O₂, 5% CO₂, 5% H₂O, balance N₂.

Figure 6: a) Propylene and NO_x conversion at different catalyst positions as a function of upstream gas temperature. b) NO_x species concentration profiles at different catalyst positions as a function of upstream gas temperature. Feed gas composition: 1000 ppm C₃H₆, 50 ppm NO, 30 ppm NO₂, 14% O₂, 5% CO₂, 5% H₂O, balance N₂.

Figure 7: a) CO, Propylene and NO_x conversion at different catalyst positions as a function of upstream gas temperature. b) NO_x species concentration profiles at different catalyst positions as a function of upstream gas temperature. Feed gas composition: 3000 ppm CO, 1000 ppm C₃H₆, 50 ppm NO, 30 ppm NO₂, 14% O₂, 5% CO₂, 5% H₂O, balance N₂.

Figure 8: DRIFTS spectra obtained during the CO TPO; ramp rate of 4.15°C/min a) 1100-2500cm⁻¹ wavenumber region, b) 2500-3900cm⁻¹ wavenumber region.

Figure 9: DRIFTS spectra obtained during the C₃H₆ TPO; ramp rate of 4.15°C/min a) 1100-2500cm⁻¹ wavenumber region, b) 2500-3900cm⁻¹ wavenumber region.

Figure 10: CO peak height as function of temperature during the DRIFTS TPO experiments. Feed gas composition: 3000 ppm CO and 1000 ppm C₃H₆, 3000 ppm CO in 14% O₂, 1% H₂O, balance N₂, ramp rate of 1.7 °C/min, a) CO peak only, taken only as 2090cm⁻¹. b) Dashed line 1457cm⁻¹ vsRCOO⁻, solid line 1575cm⁻¹ vsCOO⁻.

Figure 11: DRIFTS CO peak shift during CO and C₃H₆ TPO.

Figure 12: Residual spectrum after the subtraction of the CO DRIFTS spectrum obtained at 106°C from the spectrum obtained during the CO + C₃H₆ TPO obtained at 111°C.

Table 1: T50s for different reaction conditions

Figures

Figure 1: a) CO conversion as a function of upstream gas temperature at four positions along the catalyst length during a TPO with a ramp rate of $7.3^{\circ}\text{C}/\text{min}$. Feed gas composition: 3000 ppm CO, 14% O_2 , 5% CO_2 , 5% H_2O , balance N_2 . b) Reaction rate per 0.5 inch segment of catalyst.

Figure 2: Propylene conversion as a function of upstream gas temperature at four positions along the catalyst length during a TPO with a ramp rate of 7.3°C/min. Feed gas composition: 1000 ppm C₃H₆, 14% O₂, 5% CO₂, 5% H₂O, balance N₂. b) Reaction rate per 0.5 inch segment of catalyst.

Figure 3: a) CO and propylene conversion as a function of upstream gas temperature at four positions along the catalyst length. b) CO and propylene conversion at the reactor outlet, and formaldehyde formation. Feed gas composition: 3000 ppm CO, 1000 ppm C₃H₆, 14% O₂, 5% CO₂, 5% H₂O, balance N₂.

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Figure 9: DRIFTS spectra obtained during the C_3H_6 TPO; ramp rate of $4.15^\circ\text{C}/\text{min}$ a) $1100\text{-}2500\text{cm}^{-1}$ wavenumber region, b) $2500\text{-}3900\text{cm}^{-1}$ wavenumber region.

Figure 10: CO peak height as function of temperature during the DRIFTS TPO experiments. Feed gas composition: ◆ 3000 ppm CO and 1000 ppm C₃H₆, ▲ 3000 ppm CO in 14% O₂, 1% H₂O, balance N₂, ramp rate of 1.7 °C/min, a) CO peak only, taken only as 2090cm⁻¹. b) Dashed line 1457cm⁻¹ ν_sRCOO⁻, solid line 1575cm⁻¹ ν_{as}COO⁻.

Figure 11: DRIFTS CO peak shift during CO and C₃H₆ TPO.

Figure 12: Residual spectrum after the subtraction of the CO DRIFTS spectrum obtained at 106°C from the spectrum obtained during the CO + C₃H₆ TPO obtained at 111°C.

Tables

Table 1: T₅₀s for different reaction conditions.

	CO Oxidation	C ₃ H ₆ Oxidation	CO + C ₃ H ₆ Oxidation		CO + NO _x	C ₃ H ₆ + NO _x	CO + C ₃ H ₆ + NO _x	
Position	T ₅₀	T ₅₀	T ₅₀ CO	T ₅₀ C ₃ H ₆	T ₅₀	T ₅₀	T ₅₀ CO	T ₅₀ C ₃ H ₆
0.5 inch	145.9	174.2	180.8	196.5	178.2	246.7	230.5	233.6
1 inch	144.5	163.2	164.1	176.4	163.2	213.8	211.1	224.5
1.5 inch	144.5	153.9	154.3	165.0	161.0	206.5	167.8	212.4
2 inch	138.8	148.1	146.4	151.7	159.4	201.7	--	--

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