C$_3$H$_6$/NO$_x$ Interactions Over a Diesel Oxidation Catalyst: Hydrocarbon Oxidation Reaction Pathways

by

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.
Abstract

C\textsubscript{3}H\textsubscript{6} oxidation over a Pt/Al\textsubscript{2}O\textsubscript{3} catalyst with or without NO\textsubscript{x} present was investigated. In particular, its reaction mechanism was studied using diffuse reflectance infrared spectroscopy (DRIFTS), a reactor system designed for monolith-supported catalysts and a micro-reactor system designed for powder catalysts referred to as CATLAB. These experiments reveal that C\textsubscript{3}H\textsubscript{6} oxidation is inhibited by the presence of NO, NO oxidation is inhibited by the presence of C\textsubscript{3}H\textsubscript{6}, and that adsorbed NO\textsubscript{x} can react with gas phase C\textsubscript{3}H\textsubscript{6}. DRIFTS and CATLAB results confirm the reaction between C\textsubscript{3}H\textsubscript{6} and nitrates, which are formed during NO\textsubscript{x} adsorption, with linear nitrites observed as reaction products. Therefore, a reaction route is proposed for C\textsubscript{3}H\textsubscript{6} oxidation in the presence of NO\textsubscript{x}, namely, nitrates acting as oxidants. Using NO\textsubscript{2} instead of NO, or using a high NO\textsubscript{x}/C\textsubscript{3}H\textsubscript{6} ratio, which is beneficial for nitrate formation, favors this reaction pathway. Data also showed that Pt is required for this reaction, which suggests the nitrates in proximity to the Pt particles are affected/relevant.

Reaction kinetics studies of C\textsubscript{3}H\textsubscript{6} oxidation over Pt/Al\textsubscript{2}O\textsubscript{3} and Pt/SiO\textsubscript{2} catalysts were performed in CATLAB using a temperature-programmed oxidation method with different oxidants: O\textsubscript{2}, NO\textsubscript{2} and nitrates. The reaction kinetics of these possible reactions were compared in order to determine which reaction is more important. NO\textsubscript{x} adsorption does not occur on the SiO\textsubscript{2} surface so the reaction between C\textsubscript{3}H\textsubscript{6} and NO\textsubscript{2} could be isolated and the effect of nitrates could be observed as well when compared to the results from Pt/Al\textsubscript{2}O\textsubscript{3}. The Pt dispersions were determined using H\textsubscript{2} chemisorption and were 1.3 and 1.6% for Pt/Al\textsubscript{2}O\textsubscript{3}.
and Pt/SiO$_2$, respectively. C$_3$H$_6$ oxidation starts at a lower temperature with O$_2$ than with NO$_2$ but the activation energy was lower with NO$_2$. This gives indication that hydrocarbons must be activated first for NO$_2$ to be favored in hydrocarbon oxidation. When the experiment was done with C$_3$H$_6$ and nitrates, the reaction did not occur until NO$_x$ started to desorb from the catalyst at higher temperatures, when nitrates become unstable and decompose. Therefore, O$_2$ was added to the system and the reaction began at even lower temperature than with just C$_3$H$_6$ and O$_2$. This proved that hydrocarbons need to be activated in order for surface nitrates to affect C$_3$H$_6$ oxidation and this reaction also resulted in a lower activation energy than with just C$_3$H$_6$ and O$_2$. Nitrate consumption was also observed as less NO$_x$ desorbed from the catalyst at the later stage of the temperature ramp compared to the amount desorbed when the catalyst was not exposed to C$_3$H$_6$. 
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# Table of Contents

AUTHOR’S DECLARATION........................................................................................................ ii
Abstract ................................................................................................................................... iii
Acknowledgements ................................................................................................................ v
Table of Contents ................................................................................................................ vi
List of Figures ........................................................................................................................ viii
List of Tables ........................................................................................................................ xi
Chapter 1 Introduction ........................................................................................................... 1
Chapter 2 Literature Review ................................................................................................ 6

2.1 Diesel Oxidation Catalyst ............................................................................................... 6

2.1.1 Deactivation ................................................................................................................ 11

2.2 NO Oxidation .................................................................................................................. 12

2.3 Hydrocarbon Oxidation ................................................................................................. 15

2.4 NO\textsubscript{x} and Hydrocarbon Interactions ................................................................ 16

2.5 NO\textsubscript{x} and Hydrocarbon Surface Reactions .................................................... 18

Chapter 3 Experimental Methods ....................................................................................... 20

3.1 Apparatus and Experiment Techniques ....................................................................... 20

3.2 Experimental Procedure .............................................................................................. 24

3.2.1 NO Oxidation Inhibition by HCs over a DOC – Reaction Between Surface Nitrates and HCs ........................................................................................................... 24

3.2.2 Reaction Kinetics of C\textsubscript{3}H\textsubscript{6} Oxidation for Various Reaction Pathways ................. 26

Chapter 4 NO Oxidation Inhibition by HCs over a DOC – Reaction Between Surface Nitrates and HCs* ........................................................................................................ 29

4.1 Results and Discussion ................................................................................................. 29
List of Figures

Figure 1: US transportation greenhouse gas emissions by source in 2006 [6]........................................2
Figure 2: Conversion of pollutants on a diesel oxidation catalyst [11].........................................................5
Figure 3: Schematic of a catalytic converter [16]........................................................................................8
Figure 4: Example of precious metal catalyst (Pt) dispersed on a washcoat (Al₂O₃) adhered on a substrate........................................................................................................................................9
Figure 5: Catalyst deactivation via (a) sintering and (b) poisoning [30].........................................................11
Figure 6: Concentrations of NO and NO₂ during a temperature-programmed oxidation experiment, with 600 ppm NO and 8% O₂ in Argon (Ar) [32]................................................................................13
Figure 7: Example conversion profiles of NO and C₃H₆ during temperature-programmed oxidation over Pt/Al₂O₃ individually (—: NO and —: C₃H₆) and in the presence of one another (--- and ---). Feed gas composition: 250 ppm NO and/or 200 ppm C₃H₆, 6.5% O₂, 5% H₂O and balance N₂........17
Figure 8: Monolith sample with thermocouples attached inside a quartz tube reactor............................21
Figure 9: A sample IR spectrum showing the intensities of different peaks at specific wavenumbers that represent different species formed on the surface.................................................................24
Figure 10: Conversion profiles of C₃H₆ and NO during temperature-programmed oxidation over Pt/Al₂O₃ individually (— and —) and in the presence of one another (--- and ---). Feed gas composition: 200 ppm NO, 1000 ppm C₃H₆, 5% O₂, 5% CO₂, 5% H₂O and balance N₂........30
Figure 11: Concentration of NOₓ released during temperature-programmed desorption over Pt/Al₂O₃ following NO oxidation (—) and then exposure to C₃H₆ (—). Temperature ramp curve shown by ---. Feed gas composition: 500 ppm NO, 50 ppm C₃H₆, 10% O₂ and balance He.................................31
Figure 12: DRIFTS of 1 wt-% Pt/Al₂O₃ at 250°C exposed to NO + O₂ for times 0, 5, 10, 20, 30, 35, 45, 55 and 120 min (black to red). Feed gas composition: 250 ppm NO, 5% O₂ and balance He........32
Figure 13: DRIFTS of 1 wt-% Pt/Al₂O₃ at 250°C exposed to C₃H₆ + O₂ following NO adsorption for times 0, 5, 10, 15, 20, 25, 30, 40 and 60 min (black to red). Feed gas composition: 200 ppm C₃H₆, 5% O₂ and balance He. .......................................................... 33

Figure 14: DRIFTS of 1 wt-% Pt/Al₂O₃ at 250°C exposed to C₃H₆ + O₂ for times 0, 10, 30, 60, 90, 120, 160, 230 and 320 min (black to red). Feed gas composition: 200 ppm C₃H₆, 5% O₂ and balance He. .......................................................... 35

Figure 15: DRIFTS of 1 wt-% at 250°C Pt/Al₂O₃ at 250°C exposed to C₃H₆ + O₂ for 170 minutes after NO adsorption (a) and for 320 minutes on fresh catalyst (b). Feed gas composition: 200 ppm C₃H₆, 5% O₂ and balance He. .......................................................... 36

Figure 16: DRIFTS of 1 wt-% at 250°C Pt/Al₂O₃ at 250°C exposed to NO₂ + O₂ following exposure to C₃H₆ + O₂ for times 0, 10, 30, 60, 90, 120, 160, 230 and 320 min (black to red). Feed gas composition: 250 ppm NO₂, 5% O₂ and balance He. .......................................................... 37

Figure 17: DRIFTS of 1 wt-% Pt/Al₂O₃ at 250°C exposed to: a) NO + C₃H₆ + O₂ for times 0, 10, 30, 60, 90, 110, 150, 200 and 290 min (black to red) and b) NO₂ + C₃H₆ + O₂ for times 0, 10, 30, 60, 90, 110, 150, 200 and 300 min (black to red). Feed gas composition: 250 ppm NO or NO₂, 200 ppm C₃H₆, 5% O₂ and balance He. .......................................................... 39

Figure 18: DRIFTS of 1 wt-% Pt/Al₂O₃ at 250°C exposed to NO + C₃H₆ + O₂ for times 0, 5, 10, 15, 20, 25, 30, 40 and 60 min (black to red). Feed gas composition: 1000 ppm NO, 100 ppm C₃H₆, 5% O₂ and balance He. .......................................................... 40

Figure 19: Sample IR spectra taken from flowing 200 ppm NO and 5% O₂ in He over Pt/SiO₂ catalyst [71]. .................................................................................................................................................. 46

Figure 20: Arrhenius plot of C₃H₆ oxidation over Pt/Al₂O₃ and Pt/SiO₂ performed with two methods: TPO and step ramp with a) O₂ and b) with NO₂ as oxidant. Feed gases: 100 ppm C₃H₆, 6.5% O₂ or 1000 ppm NO₂, 200 ppm Ar and balance He. .................................................................................................................................................. 48
**Figure 21**: Arrhenius plots of C$_3$H$_6$ oxidation over Pt/Al$_2$O$_3$ in the presence of nitrates by TPO. Nitrates made with 500 ppm NO$_2$, 6.5% O$_2$, 200 ppm Ar and balance He (repeated 3 times). TPO gas mixture: 100 ppm C$_3$H$_6$, 6.5% O$_2$, 200 ppm Ar and balance He.......................................................... 52

**Figure 22**: Temperature profiles of NO$_x$ desorption with and without C$_3$H$_6$. Nitrates made with 500 ppm NO$_2$, 6.5% O$_2$, 200 ppm Ar and balance He. TPO gas mixture: 100 ppm C$_3$H$_6$, 6.5% O$_2$, 200 ppm Ar and balance He; 6.5% O$_2$, 200 ppm Ar and balance He. .......................................................... 53

**Figure 23**: DRIFTS of 1 wt-% Pt/Al$_2$O$_3$ exposed to C$_3$H$_6$ + O$_2$ following exposure to NO$_2$ and O$_2$ for times 0, 5, 10, 15, 30, 60, 90, 100 and 130 min (black to red) at (a) 200°C and (b) 150°C. Feed gas composition: 200 ppm C$_3$H$_6$, 5% O$_2$ and balance He.......................................................... 67

**Figure 24**: DRIFTS of γ-Al$_2$O$_3$ at 250°C exposed to NO$_2$ + O$_2$ for times 0, 5, 15, 30, 60, 90 and 110 min (black to red). Feed gas composition: 600 ppm NO, 5% O$_2$ and balance He. ......................... 68

**Figure 25**: DRIFTS of γ-Al$_2$O$_3$ at 250°C exposed to C$_3$H$_6$ + O$_2$ following exposure to NO$_2$ and O$_2$ for times 0, 10, 20, 35 and 70 min (black to red). Feed gas composition: 200 ppm C$_3$H$_6$, 5% O$_2$ and balance He.......................................................... 69

**Figure 26**: TPD of a) NO$_2$ and b) NO from 270 to 515°C after flowing 1000 ppm NO$_2$, 6.5% O$_2$ and balance N$_2$ for 1.5 hours (solid black –), and after 6 pulses (dotted red: – –) and 15 pulses (solid red: –) of 20 ppm C$_3$H$_6$.................................................................................. 71

**Figure 27**: Sample profile of NO$_x$ released during C$_3$H$_6$ pulsing................................................. 72

**Figure 28**: Amount of N$_2$O, NO and NO$_2$ released during each C$_3$H$_6$ pulse for a) 6 pulses and b) 15 pulses. ........................................................................................................ 73
List of Tables

Table I: NO\textsubscript{x} abatement systems and their reactions. ................................................................. 7
Table II: Calculated Pt dispersion (%) of the sample catalysts. ................................................................. 45
Table III: Calculated activation energy for C\textsubscript{3}H\textsubscript{6} oxidation with O\textsubscript{2} and with NO\textsubscript{2} ....................... 50
Table IV: Total amount of NO\textsubscript{x} desorbed during the temperature ramp with C\textsubscript{3}H\textsubscript{6} and O\textsubscript{2} and with O\textsubscript{2}....................................................................................................................... 54
Table V: Total amount of NO, NO\textsubscript{2} and NO\textsubscript{x} released during the TPDs. ................................. 74
Table VI: Arrhenius plot data for C\textsubscript{3}H\textsubscript{6} oxidation with O\textsubscript{2} by TPO over Pt/SiO\textsubscript{2}. ....................... 77
Table VII: Arrhenius plot data for C\textsubscript{3}H\textsubscript{6} oxidation with O\textsubscript{2} by Step Ramp over Pt/SiO\textsubscript{2}................. 77
Table VIII: Arrhenius plot data for C\textsubscript{3}H\textsubscript{6} oxidation with NO\textsubscript{2} by TPO over Pt/SiO\textsubscript{2}. ....................... 78
Table IX: Arrhenius plot data for C\textsubscript{3}H\textsubscript{6} oxidation with NO\textsubscript{2} by Step Ramp over Pt/SiO\textsubscript{2}. ....................... 78
Table X: Arrhenius plot data for C\textsubscript{3}H\textsubscript{6} oxidation with O\textsubscript{2} by TPO over Pt/Al\textsubscript{2}O\textsubscript{3}................................. 79
Table XI: Arrhenius plot data for C\textsubscript{3}H\textsubscript{6} oxidation with O\textsubscript{2} by Step Ramp over Pt/Al\textsubscript{2}O\textsubscript{3}................. 79
Table XII: Arrhenius plot data for C\textsubscript{3}H\textsubscript{6} oxidation with NO\textsubscript{2} by TPO over Pt/Al\textsubscript{2}O\textsubscript{3}................................. 80
Table XIII: Arrhenius plot data for C\textsubscript{3}H\textsubscript{6} oxidation with NO\textsubscript{2} by Step Ramp over Pt/Al\textsubscript{2}O\textsubscript{3}................. 80
Table XIV: Arrhenius plot data for C\textsubscript{3}H\textsubscript{6} oxidation with O\textsubscript{2} and Nitrates by TPO over Pt/Al\textsubscript{2}O\textsubscript{3}...... 81
Table XV: Activation energies of each experiment/oxidation reactions and all the intermediate calculation values. ................................................................................................................................. 85
Table XVI: Average activation energies and variances between experiment repeats. .............................. 87
Chapter 1
Introduction

Air pollution has become a serious problem since the late 1960s and much effort has been made by government and industry to better control vehicle emissions. However, this has been offset by the increasing number of cars in the world. The dissatisfaction with the current state of the environment has caused environmental regulations regarding vehicle emissions to be made more rigorous [1]. A main problem is the fossil fuel combustion process in stationary and mobile sources, such as power plants and vehicles, respectively. Internal combustion engines, which are used for vehicles that consume gasoline or diesel fuel depending on the engine. Diesel fuel, which is a mixture of hydrogen and carbon molecules, is derived from crude oil. Unfortunately, it is impossible to have a clean combustion process when fossil fuels are involved. The key pollutants generated in this combustion process are sulfur oxides (SO\textsubscript{x}), particulate matter (PM), which is often referred to as soot, carbon monoxide (CO), unburned hydrocarbons (HC) and nitrogen oxides (NO\textsubscript{x}) [2]. The CO, unburned HC and PM emissions are produced from incomplete combustion while the NO\textsubscript{x} is mostly formed from the reaction of nitrogen (N\textsubscript{2}) and oxygen (O\textsubscript{2}) in the air during combustion [3]. Other sources of HC in diesel exhaust are partially decomposed fuel molecules or recombined intermediate compounds, as well as lubricating oils [4]. Generally, only a low amount of CO remains from diesel combustion because it operates with an excess amount of air, so that oxidation proceeds primarily to CO\textsubscript{2}. NO\textsubscript{x} emissions regulations define two gases, nitric oxide (NO) and nitrogen dioxide (NO\textsubscript{2}). In diesel engine exhaust, NO usually makes up about 70 – 90% of the total NO\textsubscript{x} in the engine exhaust. NO\textsubscript{2} is very reactive and a strong oxidant [2], which is
an important property as it plays a role in the oxidation of HC, CO and soot in catalytic processes in the emission control system.

It has been reported by Environment Canada that passenger vehicles contribute about 21% of NO\textsubscript{x}, 51% of volatile organic compounds (VOC) and 4% of particulate matter smaller than 2.5 micrometers (PM2.5) emissions in Canada [5]. These pollutants negatively affect the environment by leading to photochemical smog formation, acid rain and greenhouse gas effects and are also health threats to humans as well. As shown in Figure 1, light-duty vehicles, which represent passenger cars and light-duty trucks (weighing less than 8500 pounds), contributed about 63% of the greenhouse gas emissions from US transportation sources in 2006.

![Figure 1: US transportation greenhouse gas emissions by source in 2006 [6].](image-url)
Even though significant improvements have been made over the years to the engine, fuel and the exhaust control system [7], vehicles still continue to be a key source of harmful air pollutants.

Due to the negative effects these pollutants have on the environment and the increasing number of cars in the world, emission standards are put in place to help minimize the negative effect. The current emission regulations for internal combustion engines in Canada are governed by Environment Canada and Transport Canada [8]. The general approach for vehicle emission standards in Canada is to harmonize them with the US Environmental Protection Agency (EPA) federal standards as much as possible. The current emissions regulations came into effect under the Canadian Environmental Protection Act (CEPA) in September 1999, which continued its approach of alignment with the US EPA standards. While EPA regulates the federal emission standards in the US, the state of California has its own set of emissions regulations that are generally regarded as the stricter of the two [8]. Other states can make a choice to either follow the federal emissions standards or the California standards.

To keep up with these increasingly stringent restrictions, new technology and improvements to current automotive technology are necessary. One of the major technologies for vehicle pollutant emission removal is the catalytic converter. The purpose of the catalytic converter is to eliminate toxic and smog forming emissions of HC, CO and NOx from the exhaust [9]. The current catalytic converter technology in gasoline-powered vehicles is the three-way catalyst (TWC), while diesel-powered vehicles use a combination of diesel oxidation
catalysts (DOCs), NO\textsubscript{x} abatement systems and particulate filters. Gasoline-powered vehicles are widely available in North America while diesel-powered vehicles are not, although diesel-powered engines are more fuel efficient, reliable, durable and produce significantly less CO and HC emissions. However, since diesel engines produce more torque, they are primarily used for freight movers. Based on these advantages, diesel will continue to have a place in the transportation sector and could continue to become more popular as a source of fuel. For example, since European countries impose a higher fuel tax so it makes sense for diesel powered vehicles to be more widely available due to their better fuel efficiency [10].

Diesel and gasoline combustion engines use different catalytic control systems primarily due to their different operating conditions. Spark-ignited (SI) gasoline engines operate at a stoichiometric air to fuel ratio and TWCs are designed to perform well in this setting, which is relatively O\textsubscript{2} free. On the other hand, since diesel engines operate under lean conditions, which means an excess of air relative to the stoichiometric amount required for fuel combustion, TWCs cannot function efficiently in this condition. Specifically, the excess air creates an O\textsubscript{2}-rich exhaust environment, making NO\textsubscript{x} reduction challenging. A DOC is used to oxidize the HC and CO species to CO\textsubscript{2} and H\textsubscript{2}O as depicted in Figure 2. PAH and SOF are polynuclear aromatic hydrocarbons and soluble organic fractions of PM, respectively, and make up part of the PM composition in the engine exhaust. A very important piece of information about the DOC missing from Figure 2 is the NO oxidation capability of the DOC. Furthermore, the excess air condition results in a lower engine operating temperature relative to a gasoline engine. As will be described below, NO oxidation is kinetically challenging under normal diesel exhaust temperature conditions.
The main focus of this thesis is the investigation of the reactions involving NO\textsubscript{x} and HC species that occur over the DOC. In much of the literature, the focus has been on the separate oxidation of HC and NO oxidation. The limited literature that does exist demonstrates that NO, CO and HC oxidation over a platinum (Pt) supported on alumina (Al\textsubscript{2}O\textsubscript{3}) catalyst, a typical example of a DOC, mutually inhibit one another due to competitive adsorption over the active sites. Also, the reaction between NO\textsubscript{2} and HC/CO occurs where NO\textsubscript{2} oxidizes the HC or CO and reverts back to NO, so NO oxidation is inhibited until HC and CO oxidation is complete [12]. However, another possible route can be proposed where the HC would react with the surface NO\textsubscript{x} species: nitrites and nitrates. This reaction route is suggested because an enhancement in soot oxidation has been linked to surface nitrates/nitrites [13]. This surface reaction route has not been studied extensively thus far; therefore, a qualitative (IR spectroscopy) and quantitative (reaction kinetics) study of this system forms the basis of this thesis.

**Figure 2:** Conversion of pollutants on a diesel oxidation catalyst [11].
Chapter 2
Literature Review

This literature review covers DOC fundamentals and the reactions that occur over the catalyst, and mainly focuses on reactions involving NO_x and unburned HCs in the presence of O_2.

2.1 Diesel Oxidation Catalyst

DOCs are part of the diesel engine exhaust gas aftertreatment system. They commonly consist of precious metals, such as Pt, palladium (Pd) and/or rhodium (Rh) supported on high surface area materials like Al_2O_3. The Pt and Pd components are excellent oxidation catalysts and are used, as mentioned in Chapter 1, to oxidize CO, HC and NO. The DOC is quite effective in the oxidation of CO and HC to CO_2 and H_2O; however, the same cannot be said for NO. Note: when NO is oxidized to NO_2, the net NO_x output is not reduced.

The operating condition of the diesel engine is lean (O_2-rich), which makes reduction of NO_x to N_2 challenging [14]. The lean operating condition also causes the operating and therefore exhaust gas temperature to be lower than those of gasoline engines, which is also why a DOC is used upstream of other catalyst components, because the exotherm generated during CO and HC oxidation can raise the exhaust temperature to the desired range. Since DOCs cannot reduce NO_x emissions, another component, a NO_x abatement system, is required. NO_x abatement systems can include selective catalytic reduction (SCR) catalysts and NO_x
adsorbers (traps) or a combination of the two. The NO$_x$ abatement systems, which are summarized in Table I, actually utilize the higher NO$_2$ output leaving the DOC. The table also includes soot filters, which operate better with higher levels of NO$_2$ to oxidize any trapped soot [15].

Table I: NO$_x$ abatement systems and their reactions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction type</th>
<th>Emissions</th>
</tr>
</thead>
</table>
| Selective catalytic reduction (SCR) | SCR by ammonia/urea:  
4NO + 4NH$_3$ + O$_2$ $\rightarrow$ 4N$_2$ + 6H$_2$O (slow)  
2NO + 2NO$_2$ + 4NH$_3$ $\rightarrow$ 4N$_2$ + 6H$_2$O (fast) | NO$_x$    |
| NO$_x$ adsorbers (traps) | NO$_x$ adsorption - lean exhaust, reduction - rich conditions:  
NO + 0.5O$_2$ $\leftrightarrow$ NO$_2$  
BaO + 2NO$_2$ + 0.5O$_2$ $\rightarrow$ Ba(NO$_3$)$_2$ | NO$_x$, HCs |
| Soot filters           | Oxidation:  
C + 0.5O$_2$ $\rightarrow$ CO (~550°C)  
NO$_2$ + C $\rightarrow$ CO + NO (~300°C)  
CO + 0.5O$_2$ $\rightarrow$ CO$_2$ | PM        |

Since the engine out stream generally has a very high NO to NO$_2$ ratio, a DOC is placed upstream of the NO$_x$ abatement systems for the higher NO$_2$ level needed for them to function more efficiently.

The current diesel oxidation catalyst structure is a ceramic (cordierite) or metal honeycomb monolithic substrate. This is a common structure used for most catalytic converters for vehicle emission control. Figure 3 shows the schematic of a catalytic converter.
Catalyst monoliths are wrapped in a packaging mat and canned into a steel shell. The cordierite honeycomb structure invented by Corning provides thermal and mechanical shock resistance with a high melting point temperature of about 1450°C [3]. Metal supports are also sometimes used, resulting in decreased pressure drop due to thinner walls and also have better thermal conductivity properties [9]. The design flexibility of the honeycomb structure allows optimization of both geometric and physical properties of the substrate, which improve the overall physical strength of the catalytic converter system and make it possible to withstand stress under real applications. However, the cordierite or metal monoliths do not have high surface areas and porosities so it does not make sense to disperse the noble metal catalysts on them directly. Instead, a high surface area material, called the washcoat, is deposited on the substrate, and the metal catalysts are dispersed typically through impregnation. An example is shown in Figure 4.

Figure 3: Schematic of a catalytic converter [16].
Washcoat adhesion to the monolith is a key step in catalyst preparation because in real applications it is subjected to high gas flow rates and significant temperature gradients [3]. As mentioned before, Pt and Al₂O₃ are the common choices for precious metal and washcoat components for DOCs. Other washcoats or support materials are silica (SiO₂), zeolites and different combinations of these choices can be used as well [17]. Each precious metal and support has its own strengths and weaknesses. For example, Rh has better thermal stability than the other metals but it is not economical to use only Rh, while Pt and Pd often prove to be better oxidation catalysts. Zeolites have the ability to adsorb HCs, which could be beneficial for cold start periods since during this period the catalyst temperature is too low to oxidize these species [18]. However, zeolite-based DOCs can be deactivated at high temperatures especially in moist conditions [19] and are also susceptible to chemical deactivation due to fuel impurities [20]. Pd-based catalysts are more economical than Pt-based ones and Pd is also more thermally stable than Pt [21], but it is more susceptible to sulfur poisoning [22]. All these different factors are considered and utilized to optimize and
design the catalyst. Since diesel engines operate at lower temperatures than gasoline engines, DOCs generally require two to three times more precious metal than TWCs to achieve the same level of pollutant removal. Pt is the most common choice since it has the highest oxidation activity at low temperatures [23], a lower relative surface oxygen coverage, with high coverages detrimental by blocking active sites, and is better at oxidizing heavier HCs than other metals [17].

Current commercial catalysts utilize uniform distribution of precious metal loading over the length of the monolith. Recent modeling studies have predicted that zone-coated catalysts (non-uniform distribution) would enhance catalytic converter performance. A study by Kim et al. [24] focused on optimizing a non-uniform distribution of metal catalyst to reduce pollutant emissions. The results showed that by having more catalyst at the front and less at the back, improved light off performance and lowered overall CO, HC and NO emissions could be attained. Other modeling studies show the same prediction that a front-loaded catalyst will reduce the pollutant emissions more effectively [25–26]. However, this distribution can be problematic since it can lead to thermal deactivation and can affect the catalyst inlet more significantly [27], although other studies suggest the back is more affected [28]. Catalyst activity decreases via catalyst agglomeration when subjected to high temperatures.
2.1.1 Deactivation

In catalytic converters, two major types of deactivation occur: physical (sintering) and chemical (poisoning) [29]. Thermal deactivation generally refers to sintering and it is when the surface area decreases due to structural changes. It can occur to both the precious metal and the support [21–22,29]. The main source of poisoning is sulfur, which originates from the fuel or oil, and is oxidized during combustion to $\text{SO}_x$. Other sources of catalyst poisoning originate from fuel impurities and lubricants [9]. Figure 5 illustrates the two deactivation mechanisms: sintering and poisoning.

![Diagram of Catalytic Converter Deactivation](image)

**Figure 5:** Catalyst deactivation via (a) sintering and (b) poisoning [30].
Thermal deactivation can change the Al₂O₃ support morphology. The highest surface area (desired) form is γ-Al₂O₃. During support sintering, the pores become smaller or blocked off, which can effectively trap and seal in precious metal components so that reactants can no longer reach them and the catalytic activity decreases [29]. Sintering can also affect the precious metal itself so that it becomes mobile at higher temperatures and agglomerates with other metal particles. When the particle size increases through agglomeration, it decreases the active area exposed per volume and the catalytic activity.

Poisoning deactivation occurs via undesired chemisorption of species on the active metal or the support. While sintering causes permanent damage to the catalyst, poisoning can be either temporary or permanent. Sulfur poisoning can sometimes be reversible since the sulfur species may desorb above 500°C [17] or irreversible especially when the support morphology is affected.

A more extensive review of the DOC written by Russell and Epling [17] is available in *Catalysis Reviews*.

### 2.2 NO Oxidation

In diesel exhaust, NOₓ is composed of mainly NO. Since NOₓ adsorbers and selective catalytic reduction (SCR) catalysts are more efficient with higher levels of NO₂, a DOC is generally the first catalyst used in a diesel exhaust aftertreatment system to convert NO to NO₂ as well as oxidize the CO and HC species. Pt is an excellent NO oxidation catalyst,
while other precious metals, such as Rh and Pd are not as effective [31]. NO oxidation is an exothermic and equilibrium-limited reaction within the higher temperature range of diesel exhaust: \( \text{NO}(g) + \frac{1}{2} \text{O}_2(g) \leftrightarrow \text{NO}_2(g) \). The NO oxidation reaction is also limited by kinetics at low temperature, at least relative to CO and HC oxidation. For Pt supported on \( \text{Al}_2\text{O}_3 \) (Pt/\( \text{Al}_2\text{O}_3 \)) catalysts, equilibrium is reached in typical exhaust compositions at about 350°C, as reported by Olsson et al [32] as shown in Figure 6.

![Figure 6: Concentrations of NO and NO\(_2\) during a temperature-programmed oxidation experiment, with 600 ppm NO and 8% O\(_2\) in Argon (Ar) [32].](image)

NO oxidation kinetics are affected by Pt loading, dispersion and support material. For NO oxidation, Xue et al. [33] suggested it operates according to the Langmuir-Hinshelwood mechanism, where NO sorbs on the support and migrates to Pt particles, oxidizes to NO\(_2\) and then desorbs. Olsson et al. [34] also found the Langmuir-Hinshelwood model to be most
probable for NO oxidation over Pt/Al₂O₃. NO oxidation kinetics over Pt/Al₂O₃ were also studied by Mulla et al. [35] who found that the reaction is first order in both NO and O₂ and nearly negative first order for NO₂. Westerberg and Fridell [36] observed that nitrites and nitrates readily formed on the surface when the catalyst was exposed to NO oxidation conditions. These surface NOₓ species are thermally stable at temperatures < 300°C. However on a SiO₂ support, which is relatively inert, faster reaction rates are achieved since the formed NO₂ desorbs easily [33]. Surface reactions will be further discussed in section 2.5. Xue et al. also reported an increase in NO oxidation activity with an increase in Pt loading but it was unclear whether the improved performance was directly related to Pt loading.

Several studies have shown that NO oxidation improves with increasing particle size [33,37–38] to a certain point before decreasing. Particle sizes increase with sintering as the Pt particles migrate and agglomerate, leading to a decrease in the exposed active area. So whatever the reason for the positive effect of increasing particle size is, a limit is reached when the active area becomes too small. Denton et al. [37] reported that the activity was still increasing with particle size at a dispersion as low as 2.6%. Olsson and Fridell [38] explained that with small particle sizes (large dispersion), more Pt oxides or more chemisorbed oxygen on the Pt are formed. The product NO₂ from NO oxidation is also a strong oxidant and can also increase the surface oxygen coverage. Parker et al. [39] showed that when Pt was exposed to NO₂, it produced a high coverage of adsorbed oxygen atoms on the Pt surface. As mentioned earlier, surface oxygen coverage can block active sites for oxidation reactions and decrease activity and Pt oxides are less active than metallic Pt. Thus NO oxidation is
inhibited by its own product NO₂. The smaller Pt particles are more easily oxidized and the oxide species are more stable relative to those on larger particles, requiring higher temperatures for the oxygen to desorb and thus lower NO oxidation rates.

### 2.3 Hydrocarbon Oxidation

Diesel engine exhaust contains a complex mixture of unburned HCs, including aromatics, unsaturated (alkenes and alkynes) and saturated (alkanes) HCs. Generally, for experimental studies, propane (C₃H₈) is used for saturated HCs and propylene (C₃H₆) is used for unsaturated HCs [40]. Voltz et al. [41] reported the activation energy of C₃H₆ oxidation over Pt/Al₂O₃ to be 120.97 kJ/mol. However, diesel engine exhaust also contains NOₓ, CO and other pollutants. When all these pollutants are present, they can affect the oxidation of each other over the DOC. When more than one HC is present, they compete for active adsorption sites and the HCs that adsorb most strongly to the active sites are oxidized first. Mittendorfer et al. [42] reported that for aromatics, adsorption to Pt and Pd is dominated by the interaction between the aromatic ring with the surface and they are generally more weakly adsorbed compared to other HCs. Mabilon et al. [43] found most unsaturated HCs adsorb strongly when CO was present and oxidized at below the light off temperature for CO oxidation. They found that acetylene had the strongest inhibition effect of all unsaturated HCs they tested and it determined the light-off temperature of other compounds. They also observed an increase in adsorption strength with molecular size, but other factors play a role based on their findings. For example, Mittendorfer et al. [42] also looked into the adsorption of olefins and compared 1-butene (C₄H₈) and ethylene (C₂H₄). They observed the adsorption of C₄H₈ to be
significantly weaker in terms of adsorption energy, thus showing that it cannot be explained by molecular size only. The interactions also involve the energy associated with the deformation of the molecules and the surface during adsorption [42].

Similar to NO oxidation over Pt/Al$_2$O$_3$, an increase in Pt particle size appears to improve HC oxidation as well. This was seen by Benard et al. [44] and Denton et al. [45], who observed that the Pt-O bond strength is smaller for larger particles, favoring the adsorption of other species and leading to increased total HC oxidation. The same increased activity was seen in an earlier study by Briot et al. [46] in which they studied methane oxidation over Pt/Al$_2$O$_3$.

Grbic et al. [47] tested the oxidation of a binary mixture of HCs, toluene and n-hexane, over Pt/Al$_2$O$_3$ with varying metal dispersions and found that n-hexane could be more strongly bound than toluene to smaller Pt particles and vice versa for larger particles. However, while more n-hexane was adsorbed to the smaller Pt particles than toluene, toluene was still more reactive due to its weaker C–H bonds. This indicates adsorption strength is not the only factor as HC reactivity is also determined by the strength of the C–H bond.

2.4 NO$_x$ and Hydrocarbon Interactions

An important area of study is the interaction of NO$_x$ and HCs on the DOC surface since diesel exhaust contains both pollutants among others. A study by Voltz et al. [41] showed that in a mixture of NO, CO and C$_3$H$_6$, oxidation of each over Pt/Al$_2$O$_3$ was inhibited by the others. This inhibition effect increased with increasing concentrations of each gas. Irani et al.
[12] also observed similar trends in temperature-programmed oxidation experiments over a Pt-Pd/Al₂O₃ sample with NO, C₃H₆ and O₂. Data clearly showed a strong inhibition of NO oxidation in the presence of C₃H₆ and vice versa. The concentration of C₃H₆ was varied from 100 to 1000 ppm and the inhibition effect on NO oxidation increased with C₃H₆ concentration. The inhibition effects are displayed in Figure 7.

![Figure 7](image_url)

**Figure 7**: Example conversion profiles of NO and C₃H₆ during temperature-programmed oxidation over Pt/Al₂O₃ individually (—: NO and —: C₃H₆) and in the presence of one another (--- and ---). Feed gas composition: 250 ppm NO and/or 200 ppm C₃H₆, 6.5% O₂, 5% H₂O and balance N₂.

Although the inhibition of C₃H₆ oxidation by NO is mainly due to competition for adsorption sites, that was not the only reason for NO oxidation inhibition by C₃H₆. While NO oxidation may have been occurring, NO₂ was not observed until most of C₃H₆ was oxidized. This
suggests that NO₂ was being consumed as a reactant, acting as an oxidant for C₃H₆ oxidation. Furthermore, NO₂ was preferentially consumed relative to O₂. Although NO₂ promotes C₃H₆ oxidation, as more NO forms with increasing temperature, the inhibition effect takes over. A similar trend was observed in a study by Al-Harbi et al. [48].

2.5 NOₓ and Hydrocarbon Surface Reactions

As mentioned earlier, NO and NO₂ in the presence of O₂ adsorb quite readily on a Pt/Al₂O₃ catalyst surface, forming nitrites and nitrates, as has been well studied by many researchers [36, 49–51]. Westerberg and Fridell [36] reported that Al₂O₃ was found to be an important storage site for adsorbed NOₓ species at temperatures below 300°C. In a study by Castoldi et al. [15], it was suggested that for some catalyst types, the formation of these surface NOₓ species is one of the most important reasons for enhanced soot oxidation performance. An increase in soot oxidation activity in the presence of NO and O₂ was observed by Pieta et al. [52] as well.

Haneda et al. [53] studied HC oxidation over a Pt/Al₂O₃ catalyst using IR spectroscopy. Using a HC mixture of n-decane and 1-methylnaphthalene, they found carbonate and/or carboxylate species on the surface. It is difficult to accurately assign the corresponding species for HC adsorption as there are many overlapping peaks for HC adsorption in the IR spectra. From their transient analysis, Haneda et al. were able to identify some intermediate species formed, such as acrylates, which were formed first and then consumed as CO₂ formed. It is therefore apparent that Al₂O₃ is also an important site for adsorbed HC species.
Anderson and Rochester [54] studied C₃H₆ oxidation over a Rh/Al₂O₃ catalyst and also observed the formation of carboxylates, carbonates and acrylates on the surface.
Chapter 3
Experimental Methods

To investigate the interaction between NO\textsubscript{x} and HC on a DOC, various experiments were performed. This chapter introduces the different instruments and procedures used in this thesis work.

3.1 Apparatus and Experiment Techniques

A pilot scale plug flow reactor (PFR) was used for experiments with monolith samples of 1 inch diameter and 2 to 3 inches in length that were wrapped in high temperature 3M matting material and inserted into a quartz tube reactor. The purpose of the 3M matting material is to prevent any gas bypass between the quartz tube wall and the wall of the monolith sample.

A Lindberg/Blue Mini-Mite tube furnace was used to heat the reactor. The feed gases were metered with Bronkhorst mass flow controllers before entering the reactor. The tubing leading up to the reactor was heated to above 100°C to prevent H\textsubscript{2}O condensation. All gases were supplied by PraxAir except N\textsubscript{2}, which was generated with a system manufactured by OnSite Gas Systems. Water was added using a Bronkhorst CEM system. Three K-type thermocouples were placed in the upstream, front, and the back of the monolith sample for temperature measurements. Photographs of the pilot reactor with the monolith sample inserted are shown in Figure 8.
Figure 8: Monolith sample with thermocouples attached inside a quartz tube reactor.

The system contains two gas manifolds so that different gas mixtures can be prepared, but only one of these is introduced to the reactor at a time while the other is sent to exhaust ventilation. A LabView program controls the type and amount of gas flowing in each gas manifold and the gas flowing to the reactor. A 4-way actuated switching valve, powered with compressed N\textsubscript{2}, is used to direct the two flows. The LabView program also records the temperature of the various thermocouples in the reactor over time. The outlet gas stream is
analyzed using a MKS 2030 FTIR MultiGas analyzer. The MKS FTIR has calibration files provided by the manufacturer that convert the IR spectra recorded to species concentrations, in either ppm or percent, versus time. Various types of experiments can be performed using this pilot reactor. This includes temperature-programmed oxidation (TPO), where the temperature is ramped at a specified rate to measure its effect on the oxidation reaction or steady state experiments where isothermal inlet conditions are set. Similar to TPO, temperature-programmed desorption (TPD) experiments can be performed to observe what species desorb from the catalyst during a temperature ramp. By using LabView to control the programmed switching function of the two gas manifolds, specific gas mixtures can be “pulsed” into the reactor in this mode; this type of experiment will be referred to as a pulse experiment for the rest of this thesis.

Powder samples were used for the Hiden CATLAB Micro-reactor and the Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) experiments, which were analyzed in a Thermo Nicolet 470 FT-IR Spectrometer equipped with a MCT detector. 1 wt-% Pt/\(\gamma\)-Al\(_2\)O\(_3\) powder (300 m\(^2\)/g) and Al\(_2\)O\(_3\) powder (\(\gamma\)-phase) purchased from Alfa Aesar were used for the powder sample studies. 50 mg of sample catalyst particles (40-60 mesh) were loaded into the quartz-tube CATLAB Micro-reactor. The outlet gas stream was analyzed using a Hiden QIC-20 mass spectrometer (MS-based) or a Pfeiffer Vacuum OmniStar Gas Analysis System (also MS-based) and calibrated with reference gases. This analysis system will be referred to as CATLAB. For CATLAB, small but known amounts of Ar were always introduced as an inert gas, other than the carrier gas, so that any changes due to pressure sensitivity would be corrected by dividing MS measurements of other gas
concentrations by those of the Ar. The gas flow rate in the CATLAB studies was always 95 mL/min. The same types of experimental studies can be performed on the micro-reactor as those previously described for the pilot reactor (TPO, TPD, steady state and pulsing). The MS needs to be calibrated using the raw MS signal and those obtained with reference gases at different concentrations. This is done by flowing a known concentration of a specific gas to the MS and calibrating against the raw signal. TPO experiments reveal inhibition effects and also the oxidation reaction kinetic parameters can be calculated from TPO data. TPD experiments can often be used to quantify how much adsorption occurred on the surface.

For experiments done with the FT-IR Spectrometer, with diffuse reflectance infra-red Fourier transform spectroscopy used, IR spectra can be obtained, and these are used to determine what species are adsorbing/desorbing to/from the catalyst when exposed to the specified gas mixture and temperatures. The sample catalyst was exposed to NO\textsubscript{x} and HC in different sequences or together to characterize the surface interactions. DRIFTS spectra were used for qualitative studies and the data obtained show peaks at certain wavelengths that represent different species. An example DRIFTS spectrum is shown in Figure 9.
Figure 9: A sample IR spectrum showing the intensities of different peaks at specific wavenumbers that represent different species formed on the surface.

The challenge in analyzing DRIFTS data is to correctly identify the species corresponding to each peak through comparison with those available in the literature, i.e. finding literature results that correlate peak position and shape to the surface species present, typically through more fundamental study.

3.2 Experimental Procedure

3.2.1 NO Oxidation Inhibition by HCs over a DOC – Reaction Between Surface Nitrates and HCs

The reaction between NO\textsubscript{x} and C\textsubscript{3}H\textsubscript{6} was also investigated in the pilot reactor system. This was done using a monolith catalyst sample with an Al\textsubscript{2}O\textsubscript{3} loading of 1.59 g/in\textsuperscript{3} and a Pt
loading of 27.5 g/ft$^3$. The catalyst sample was 1 inch in diameter and 3 inches in length. A gas flow rate of 10 L/min was used, which corresponds to a space velocity of 25,000 hr$^{-1}$. C$_3$H$_6$ oxidation and NO oxidation, separately, were evaluated via TPO. Another TPO experiment was performed with both C$_3$H$_6$ and NO present. The temperature was ramped from 80°C to 400°C at a rate of 5°C/min. The feed gas compositions were 200 ppm NO and/or 1000 ppm C$_3$H$_6$, 5% O$_2$, 5% H$_2$O, 5% CO$_2$ with the balance being N$_2$.

The reactivity between C$_3$H$_6$ and stored nitrites/nitrates was also investigated using CATLAB on a 1 wt-% Pt/$\gamma$-Al$_2$O$_3$ powder. The outlet gas stream was measured by a Hiden QIC-20 mass spectrometer. For experiments done on CATLAB, the sample was cleaned by heating in 10% O$_2$, 0.1% Ar in a He balance for 90 minutes at 500°C. After cooling down to 250°C, 500 ppm NO, 10% O$_2$, 0.1% Ar in a He balance were introduced for 2 hours to store NO$_x$ species on the catalyst. Then, temperature-programmed desorption (TPD) was performed from 250°C to 500°C at a heating rate of 10°C/min. The same experiment was also performed except that the catalyst was exposed to 50 ppm C$_3$H$_6$ for 3h after NO$_x$ adsorption. Therefore, the amount of NO$_x$ remaining on the surface before and after C$_3$H$_6$ exposure could be quantitatively analyzed.

For DRIFTS experiments, the catalyst was pretreated with 40 mL/min of He at 500°C for 30 minutes, followed by 5% O$_2$ in He for 30 minutes and then 5% H$_2$ in He for another 30 minutes. For each spectrum, 45 scans were collected at a resolution of 4 cm$^{-1}$. The spectra were recorded in the 650 to 4000 cm$^{-1}$ range. Bronkhorst mass flow controllers were used to set the feed gas concentrations and flow rates. A total gas flow rate of 40 mL/min was used.
for all the experiments. Different sequences of C<sub>3</sub>H<sub>6</sub> and NO exposure were evaluated. To characterize the interaction between gas-phase C<sub>3</sub>H<sub>6</sub> and surface nitrates, first, 250 ppm NO, 5% O<sub>2</sub> and balance He were first introduced at 250°C for 120 minutes in order to form surface nitrites/nitrates; afterwards, 200 ppm C<sub>3</sub>H<sub>6</sub>, 5% O<sub>2</sub> and balance He were introduced to investigate the reaction between C<sub>3</sub>H<sub>6</sub> and nitrates. By replacing NO with NO<sub>2</sub>, a similar experiment was performed as well. Experiments were also performed where the catalyst was exposed to C<sub>3</sub>H<sub>6</sub> and O<sub>2</sub> first followed by NO<sub>x</sub> and where NO<sub>x</sub> and C<sub>3</sub>H<sub>6</sub> were introduced together were also done.

3.2.2 Reaction Kinetics of C<sub>3</sub>H<sub>6</sub> Oxidation for Various Reaction Pathways

The different pathways of C<sub>3</sub>H<sub>6</sub> oxidation were investigated in the CATLAB by analyzing the outlet gas with a Pfeiffer Vacuum OmniStar Gas Analysis System. C<sub>3</sub>H<sub>6</sub> oxidation via O<sub>2</sub>, NO<sub>2</sub> and nitrates were studied over 1 wt-% Pt/Al<sub>2</sub>O<sub>3</sub> and 1 wt-% Pt/SiO<sub>2</sub> powder samples. The Pt/SiO<sub>2</sub> catalyst sample used was made in the laboratory. In order to more directly compare the two catalysts a similar Pt dispersion was desired. H<sub>2</sub> chemisorption was performed on both catalysts to determine the Pt dispersion. Chemisorption experiments were done in CATLAB at a flow rate of 50 mL/min. For Pt/SiO<sub>2</sub>, the catalyst was heated to 450°C in 5% H<sub>2</sub> in He for 30 minutes and cooled down to 40°C in pure He. 100 μL of 5% H<sub>2</sub> in He were pulsed into the 50 mL/min of He flow every 30 seconds over a total of 26 cycles. For Pt/Al<sub>2</sub>O<sub>3</sub>, the catalyst was heated to 500°C in 5% H<sub>2</sub> in He for 30 minutes and then the same procedure as above was used. The Pt/Al<sub>2</sub>O<sub>3</sub> sample was then thermally aged at 650°C in 5% H<sub>2</sub> in He for 2 hours and then exposed to 6.5% O<sub>2</sub> in He for 15 minutes followed by exposure
to 5% H₄ in He for another 15 minutes. These 15 minute exposures were repeated twice (total duration at 650°C was 3 hours). The sample was then cooled down to 40°C in He followed by H₂ chemisorption over 17 pulse cycles. Pt dispersions of Pt/SiO₂, Pt/Al₂O₃ and aged Pt/Al₂O₃ catalyst samples were 1.6, 23.1 and 1.3%, respectively.

Following the chemisorption tests, the reactivities of C₃H₆ with O₂ and then with NO₂ were investigated with CATLAB. TPO experiments were performed on the Pt/SiO₂ sample and the aged Pt/Al₂O₃ sample using 100 ppm C₃H₆, 6.5% O₂ and balance He as the feed gas at a flow rate of 95 mL/min. The temperature was ramped from 70°C to 300°C at a rate of 5°C/min. With the same feed gas composition, a similar experiment was done but in steps, where the temperature was held at a specific level until steady state was reached (constant conversion). Overall, the temperature was varied from 70 to 150°C, generally in 5°C intervals. This will be referred to as the steady state ramp for this thesis. Step intervals of 5°C were used because it was difficult to accurately measure the change in C₃H₆ concentration for anything less than a 5°C change. The TPO and steady state ramp experiments were repeated with 1000 ppm NO₂ instead of 6.5% O₂. Prior to each of these experiments, the catalyst was pre-treated to 450°C for Pt/SiO₂ and 500°C for Pt/Al₂O₃ in He and then switched in exposure to 6.5% O₂ and 5% H₂ in He 10 times in 1 minute intervals. Each experiment was repeated at least once for reproducibility.

Lastly, to characterize the reactivity between nitrates and C₃H₆, the Pt/Al₂O₃ sample (fresh 1 wt-% standard) was tested under the assumption that no nitrates can form on SiO₂ (which was proven, details follow). The same pre-treatment, switching between 6.5% O₂ and 5% H₂
in He at 500°C, was done prior to this experiment. Following the pre-treatment, the sample was cooled down to 275°C and then 1000 ppm NO₂, 6.5% O₂ and balance He was flown over the catalyst for 2 hours. After 2 hours, the sample was cooled in 6.5% O₂ in He for 15 minutes and then cooled to 70°C in pure He. 100 ppm C₃H₆ in He was then added and the temperature was ramped to 350°C at 1°C/min. This experiment was also repeated with 100 ppm C₃H₆ and 6.5% O₂ in He, with pure He and with 6.5% O₂ in He for the temperature ramp.
Chapter 4
NO Oxidation Inhibition by HCs over a DOC – Reaction Between Surface Nitrates and HCs*


4.1 Results and Discussion

As reported in the literature, NO oxidation inhibits C₃H₆ oxidation while the product NO₂ acts as an oxidant for C₃H₆ oxidation. However, when NO₂ reacts with C₃H₆, it produces NO, which leads to C₃H₆ oxidation inhibition. In the case of soot oxidation, NO₂ is a strong oxidant. For some catalyst types, the formation of nitrites/nitrates on the surface is proposed to be one of the most important reasons for enhanced soot oxidation performance [13]. Since adsorbed nitrites and nitrates have also been observed on Pt/Al₂O₃ catalysts with exposure to NO/NO₂ [36,49–51], these may account for some of the HC oxidation activity. In order to determine whether HCs can be oxidized by surface NOₓ species, DRIFTS was used to characterize surface species that formed or were consumed before, during and after different sequences of NOₓ and C₃H₆ exposures. The reaction between NOₓ and C₃H₆ was also investigated in a pilot reactor system and CATLAB.

4.1.1 Pilot Reactor

C₃H₆ oxidation in the presence and absence of NO, and NO oxidation in the absence and presence of C₃H₆ were evaluated via TPO to yield the results displayed in Figure 10. C₃H₆ oxidation was negatively affected in the presence of NO in the feed stream as expected, with
the light-off temperature increased by around 60°C due to competitive adsorption of NO and C₃H₆ for Pt sites [12,41].

Figure 10: Conversion profiles of C₃H₆ and NO during temperature-programmed oxidation over Pt/Al₂O₃ individually (—— and ——) and in the presence of one another (--- and ----). Feed gas composition: 200 ppm NO, 1000 ppm C₃H₆, 5% O₂, 5% CO₂, 5% H₂O and balance N₂.

When the temperature was below 200°C, NO oxidation to NO₂ was negatively affected by the presence of C₃H₆, with NO₂ observed only once most of the C₃H₆ was oxidized, as any NO₂ formed can be consumed by C₃H₆ [12]. However, between 200 and 250°C, there was a slight improvement in NO conversion to NO₂ observed in the presence of C₃H₆ before being inhibited again between 250 and 320°C.
4.1.2 CATLAB and DRIFTS

As an initial demonstration of adsorbed nitrites/nitrates acting as reactants, TPD of NO\textsubscript{x} from a Pt/Al\textsubscript{2}O\textsubscript{3} powder surface first exposed to NO + O\textsubscript{2} was run and then compared with a TPD run where the sample was exposed to C\textsubscript{3}H\textsubscript{6} after the NO + O\textsubscript{2} exposure in the CATLAB micro-reactor. The results are shown in Figure 11.

![Figure 11: Concentration of NO\textsubscript{x} released during temperature-programmed desorption over Pt/Al\textsubscript{2}O\textsubscript{3} following NO oxidation (—) and then exposure to C\textsubscript{3}H\textsubscript{6} (—). Temperature ramp curve shown by ---. Feed gas composition: 500 ppm NO, 50 ppm C\textsubscript{3}H\textsubscript{6}, 10% O\textsubscript{2} and balance He.](image)

Approximately 50.4% of the NO\textsubscript{x} was left on the surface after C\textsubscript{3}H\textsubscript{6} exposure, indicating that reaction can indeed occur between C\textsubscript{3}H\textsubscript{6} and surface nitrates.
The DRIFTS spectra showing evidence of NO adsorption at 250°C over 1 wt-% Pt/γ-Al₂O₃ as a function of time are shown in Figure 12.

![Figure 12: DRIFTS of 1 wt-% Pt/Al₂O₃ at 250°C exposed to NO + O₂ for times 0, 5, 10, 20, 30, 35, 45, 55 and 120 min (black to red). Feed gas composition: 250 ppm NO, 5% O₂ and balance He.](image)

Most of the peaks in the range from 1200 to 1800 cm⁻¹ can be assigned to nitrates formed on the alumina surface. Specifically, overlapping bands in the 1500–1650 cm⁻¹ and 1200–1350 cm⁻¹ region can be attributed to monodentate, bidentate and bridged nitrates [36,49–51]. Within the first 5 minutes, bridging nitrite bands appear at 1233 and 1310 cm⁻¹ and a low coverage nitrate band appeared at 1550 cm⁻¹ along with a small shoulder at 1615 cm⁻¹. With the Pt/Al₂O₃ catalyst, nitrites are readily oxidized to form nitrates, which began to appear, at 1303 cm⁻¹, in the spectrum within 15 minutes of exposure. The peak intensities increased
with time until saturation was reached after about 75 minutes of exposure. The final peaks at 1585 and 1303 cm\(^{-1}\) are most likely monodentate nitrates with the 1615 cm\(^{-1}\) shoulder attributed to bidentate nitrates. Assigning each of these peaks to a specific type of nitrate is difficult due to the overlap and is not the specific focus of this paper, and so they will simply be considered as nitrites or nitrates, with emphasis being on what happens to these in the presence of C\(_3\)H\(_6\) and O\(_2\). The exact same peaks excluding formation of nitrites were observed in spectra obtained using NO\(_2\) as the feed NO\(_x\) source.

Following NO\(_x\) adsorption, the catalyst was exposed to C\(_3\)H\(_6\) and O\(_2\) and the resulting DRIFTS spectra as a function of time are shown in Figure 13.

![Figure 13: DRIFTS of 1 wt-% Pt/Al\(_2\)O\(_3\) at 250°C exposed to C\(_3\)H\(_6\) + O\(_2\) following NO adsorption for times 0, 5, 10, 15, 20, 35, 60, 95 and 170 min (black to red). Feed gas composition: 200 ppm C\(_3\)H\(_6\), 5% O\(_2\) and balance He.](image-url)
With extended \( \text{C}_3\text{H}_6 \) exposure, the nitrate bands, such as that at 1303 cm\(^{-1}\), decreased substantially. The bands around 1580 cm\(^{-1}\) decreased as well, but not as significantly as carboxylate species were formed simultaneously during \( \text{C}_3\text{H}_6 \) oxidation, and have bands at 1580 cm\(^{-1}\) (OCO symmetric stretching) that overlap with the nitrate features. At the same time, other bands at 1330 cm\(^{-1}\) (OCO asymmetric stretching) and 1400 cm\(^{-1}\) (C-H bending) indicate the formation of formate species [55–60]. It is worth noting that a peak at 1463 cm\(^{-1}\) was also observed. This peak can be attributed to the formation of either linear nitrites [59,61] resulting from the reduction of nitrates by \( \text{C}_3\text{H}_6 \) exposure or acetate and acrylate species [61–64] resulting from \( \text{C}_3\text{H}_6 \) oxidation. This feature will be discussed in detail below.

The group of peaks at 1642, 1650, 1658, 1665 and 1672 cm\(^{-1}\), on the shoulder of the 1580 cm\(^{-1}\) band, are associated with carboxylate groups (C=O stretch) [56,65]. The intensities of the newly formed bands increased until saturation was reached after around 130 minutes.

For comparison, \( \text{C}_3\text{H}_6 \) adsorption over a clean surface, without pre-adsorption of NO\(_x\), was also evaluated and the results are shown in Figure 14.
Figure 14: DRIFTS of 1 wt-% Pt/Al₂O₃ at 250°C exposed to C₃H₆ + O₂ for times 0, 10, 30, 60, 90, 120, 160, 230 and 320 min (black to red). Feed gas composition: 200 ppm C₃H₆, 5% O₂ and balance He.

The intensities of the adsorption bands were much lower than when NOₓ is present and the major bands at 1332, 1395 and 1665 cm⁻¹ can be attributed to formate formation. All three of these peaks appeared at the same time and the intensities increased very slowly until reaching saturation after around 290 minutes.
**Figure 15:** DRIFTS of 1 wt-% at 250°C Pt/Al₂O₃ at 250°C exposed to C₃H₆ + O₂ for 170 minutes after NO adsorption (a) and for 320 minutes on fresh catalyst (b). Feed gas composition: 200 ppm C₃H₆, 5% O₂ and balance He.

In Figure 15, the spectra collected after C₃H₆ oxidation (Fig. 14) in the absence of NOₓ and after NOₓ exposure followed by C₃H₆ oxidation (Fig. 13) are overlaid. This comparison demonstrates that the bands at about 1580 and 1463 cm⁻¹ are directly related to the reaction between surface nitrates and C₃H₆ since they do not appear in the absence of NOₓ.

When the catalyst was first exposed to C₃H₆ and O₂ in the absence of NOₓ but then exposed to NO₂, the spectra shown in Figure 16 are obtained.
Figure 16: DRIFTS of 1 wt-% at 250°C Pt/Al₂O₃ at 250°C exposed to NO₂ + O₂ following exposure to C₃H₆ + O₂ for times 0, 10, 30, 60, 90, 120, 160, 230 and 320 min (black to red). Feed gas composition: 250 ppm NO₂, 5% O₂ and balance He.

The intensity of the band at 1665 cm⁻¹, due to C=O stretching, decreased slightly with time and shifted to 1677 cm⁻¹ with two small shoulders at 1631 and 1641 cm⁻¹ (carboxylate) becoming evident. Similarly, the bands at 1400 and 1332 cm⁻¹, assigned to formate species, also showed little change. The nitrate peak at 1303 cm⁻¹, previously attributed to monodentate nitrate species, appeared but its associated peak at 1585 cm⁻¹ observed above did not, instead a band at 1554 cm⁻¹ formed. This lower wavenumber band has been attributed to low coverage of either bidentate or monodentate nitrates [36]. Compared to NO₂ adsorption over, or interaction with, the clean Pt/Al₂O₃ surface, the rate of NO₂ adsorption over the C₃H₆ pre-adsorbed surface was significantly slower. This is evident by comparing the intensities between figures as well as noting that the low coverage 1554 cm⁻¹ nitrate peak
remained after nearly 100 minutes of NO\textsubscript{x} exposure compared to the same low coverage nitrate peak shifting to 1585 cm\textsuperscript{-1} within 20 minutes of NO\textsubscript{x} exposure on the fresh catalyst. The peak intensities reached a saturation point after around 75 minutes, and the end result is that there were barely any nitrates formed when directly compared to the case when NO\textsubscript{x} adsorbs on the fresh catalyst.

Recently, it was reported by Henry et al. [66] that adsorbed C\textsubscript{3}H\textsubscript{6} can promote low temperature NO oxidation. They proposed that HC adsorbed on the surface can act as an oxygen sink to keep the Pt surface in a less oxidized state, which is beneficial for NO oxidation to NO\textsubscript{2}. The DRIFTS results here indicate that less nitrates form on a surface with pre-adsorbed HC. Nitrates are also strong oxidants and since less nitrates formed, this could in turn lead to less extensive Pt surface oxidation. This might help explain the observed promotion of NO oxidation by stored HC noted in the previous research as well as the observed enhancement noted between 200 and 240\degree C in Figure 10.

Finally, the clean catalyst was exposed to NO + C\textsubscript{3}H\textsubscript{6} or NO\textsubscript{2} + C\textsubscript{3}H\textsubscript{6} simultaneously in the presence of oxygen, to yield spectra shown in Figures 17a and 17b, respectively.
Figure 17: DRIFTS of 1 wt-% Pt/Al2O3 at 250°C exposed to: a) NO + C3H6 + O2 for times 0, 10, 30, 60, 90, 110, 150, 200 and 290 min (black to red) and b) NO2 + C3H6 + O2 for times 0, 10, 30, 60, 90, 110, 150, 200 and 300 min (black to red). Feed gas composition: 250 ppm NO or NO2, 200 ppm C3H6, 5% O2 and balance He.

For NO and C3H6 co-addition, almost the same spectra were obtained as under C3H6-only conditions, with the bands at 1332, 1390–1400 and 1665 cm⁻¹ attributed to the formation of
formate species. For NO\textsubscript{2} and C\textsubscript{3}H\textsubscript{6}, the spectra were essentially the same but with a minor peak at 1470 cm\textsuperscript{-1} also evident, which is relatively close to the 1463 cm\textsuperscript{-1} peak observed in Figure 13. Nitrate formation was not observed in these two sets of spectra. The reason is that the concentration of C\textsubscript{3}H\textsubscript{6} (200 ppm) was relatively high, based on stoichiometry, which requires a high ratio of NO\textsubscript{x} to C\textsubscript{3}H\textsubscript{6} for the formation of nitrates and the reaction between nitrates and C\textsubscript{3}H\textsubscript{6}, compared to NO\textsubscript{x} (250 ppm) in the feed. The experiment was therefore repeated with 1000 ppm NO and 100 ppm C\textsubscript{3}H\textsubscript{6} and the resulting DRIFTS spectra are shown in Figure 18.

**Figure 18:** DRIFTS of 1 wt-% Pt/Al\textsubscript{2}O\textsubscript{3} at 250°C exposed to NO + C\textsubscript{3}H\textsubscript{6} + O\textsubscript{2} for times 0, 5, 10, 15, 20, 25, 30, 40 and 60 min (black to red). Feed gas composition: 1000 ppm NO, 100 ppm C\textsubscript{3}H\textsubscript{6}, 5% O\textsubscript{2} and balance He.
These spectra are very similar to those with C₃H₆ exposure on the surface with pre-adsorbed nitrates. With the higher NO concentration in the feed, the nitrate bands at 1585 and 1303 cm⁻¹ formed. As observed in the last few time points in the spectra shown in Figure 18, the 1303 cm⁻¹ nitrate band decreased slightly, which indicates continued nitrate consumption, leading to the formation of the band at 1463 cm⁻¹. Such evidence of consumption was not observed for the nitrates in the 1585 cm⁻¹ region because it overlaps with the carboxylate species bands formed in this same region. Overall, the higher concentration of NO in the feed allowed net nitrate formation on the surface. Nitrates can still react with C₃H₆, but are observed when NOₓ is added in excess amounts relative to C₃H₆.

The band at 1463 cm⁻¹ appeared when the catalyst was exposed first to NOₓ and then to C₃H₆ after. This is directly related to the reaction between gas-phase C₃H₆ and stored nitrates. In the case of 250 ppm NO and 200 ppm C₃H₆ in the feed stream together, C₃H₆ was mainly oxidized mainly by O₂ and not by nitrates due to the excess amount of C₃H₆ relative to NO, and the 1463 cm⁻¹ band was absent. In the case of NO₂ and C₃H₆ in the feed together, the formation of nitrates was relatively easier and faster. Thus, a portion of the C₃H₆ could be oxidized by nitrates in addition to O₂, which lead to the appearance of a small peak at 1470 cm⁻¹ was observed, which is attributed to a low coverage nitrite peak. These results indicate that the surface nitrates may have been reduced to nitrite species by C₃H₆, with it most likely a linear nitrite, which has an IR band assignment at 1465 cm⁻¹ [59,61]. However, a COO⁻ symmetric stretching vibration of adsorbed acetate ions [62–64] and acrylate species [61] has a similar band assignment so cannot be completely dismissed. The results of this study show surface nitrates do indeed react with C₃H₆, with the likely formation of linear nitrites.
Therefore, nitrates acting as the oxidant for $\text{C}_3\text{H}_6$ oxidation is a possible reaction pathway. The evidence, and possible relevance, strongly depends on the NO$_x$ source (NO vs. NO$_2$) and inlet NO/$\text{C}_3\text{H}_6$ ratios. Using NO$_2$ instead of NO, or with a high NO$_x$/$\text{C}_3\text{H}_6$ ratio, some of the $\text{C}_3\text{H}_6$ can be oxidized via this nitrate as an oxidant route.
5.1 Results and Discussion

In Chapter 4, it was discovered that surface NO\textsubscript{x} species were shown to oxidize C\textsubscript{3}H\textsubscript{6}. However, which of the possible reactions, oxidation with O\textsubscript{2}, NO\textsubscript{2} or nitrates, is more critical or relevant is not clear. Therefore, in this chapter, the kinetics of C\textsubscript{3}H\textsubscript{6} oxidation via O\textsubscript{2}, NO\textsubscript{2} and nitrates are compared. Since nitrates are readily formed by exposure of Pt/Al\textsubscript{2}O\textsubscript{3} to NO\textsubscript{2}, a different support had to be used to investigate C\textsubscript{3}H\textsubscript{6} oxidation with only NO\textsubscript{2} as the oxidant (i.e. to avoid nitrates oxidizing the C\textsubscript{3}H\textsubscript{6}). Consequently, Pt/SiO\textsubscript{2} was used because SiO\textsubscript{2} is known to be relatively inert [33] and therefore should not adsorb any NO\textsubscript{x} on its surface, allowing the isolation of the oxidizing nitrates or NO\textsubscript{2}. NO\textsubscript{x} adsorption over Pt/SiO\textsubscript{2} was evaluated with DRIFTS to confirm, and no surface NO\textsubscript{x} species were formed as expected.

5.1.1 Determination of Pt Dispersion by H\textsubscript{2} Chemisorption

H\textsubscript{2} and CO chemisorption are commonly used to determine the precious metal dispersion and surface area in supported metal catalysts [67]. Under certain conditions, precious metals will chemisorb these gases stoichiometrically while the support will not. Typically the catalyst is heated and then reduced by H\textsubscript{2} prior to chemisorption. Past studies have shown that hydrogen adsorption on Pt is commonly used [67–70] so H\textsubscript{2} was chosen as the gas for chemisorption to determine the Pt dispersions. The pulse chemisorption method first reported by Gruber [69]
uses multiple pulses of adsorbate (H$_2$) of known volume, which are injected into a flow of inert gas and passed over the catalyst. H$_2$ adsorbs irreversibly onto Pt sites with each pulse until all the sites become saturated. Several fully eluted pulses are recorded at the end of the experiment and any partly adsorbed pulses are calibrated against the full pulses at the end to determine how much H$_2$ was chemisorbed on the metal. For H$_2$ chemisorption on Pt, a stoichiometric relation of two Pt sites for one molecule of H$_2$ is used [67, 69–70]. Each H$_2$ pulse is measured with a MS, with the data resulting in a “peak” of H$_2$. An example is shown in Figure 19.

![Figure 19: A sketch of H$_2$ chemisorption peaks collected by MS over time.](image)

The area of each peak was calculated using the peak analyzer tool in Origin Pro 8. Pt dispersion (%) is calculated using equation (1).
Pt Dispersion (%)= \left( \frac{A_S}{N_S} \right) \cdot \left( \frac{N_A}{A_A} \right) \cdot \left( \frac{V_{H2}}{V_{STP}} \right) \cdot \left( \frac{m_{cat}}{m_{Pt}} \cdot \beta_{Pt} \right) \cdot 100\% \quad (1)

In this equation, \( A_S \) is the total area of the saturated peaks, \( N_S \) is the number of the saturated peaks, \( A_A \) is the total area of the adsorbed peaks, \( N_A \) is the number of adsorbed peaks, \( V_{H2} \) is the volume of \( \text{H}_2 \) pulsed into the reactor flow, \( V_{STP} \) is the standard volume of 22.4 L/mol, \( \beta_{Pt:H2} \) is the 2:1 stoichiometric ratio of Pt sites to \( \text{H}_2 \), \( m_{cat} \) is the mass of the sample catalyst in the reactor, \( \beta_{Pt} \) is the Pt loading (%) and \( M_{Pt} \) is the atomic weight of Pt. The dispersion values of the two catalyst samples are listed in Table II. Sample calculations are included in Appendix B.

**Table II:** Calculated Pt dispersion (%) of the sample catalysts.

<table>
<thead>
<tr>
<th>Catalyst Type</th>
<th>Pt Dispersion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/SiO2</td>
<td>1.6</td>
</tr>
<tr>
<td>Standard Pt/Al₂O₃</td>
<td>23.1</td>
</tr>
<tr>
<td>Aged Pt/Al₂O₃</td>
<td>1.3</td>
</tr>
</tbody>
</table>

The Pt/SiO₂ sample had a much lower Pt dispersion of 1.6% than the Pt/Al₂O₃ catalyst. Although not required for the kinetic analysis, it would be better if these dispersions were similar. \( \text{H}_2 \) chemisorption on the standard Pt/Al₂O₃ showed a higher dispersion, 23.1%. Therefore, it was thermally aged at 650°C for two hours to sinter the particles and reduce the dispersion. After aging, the dispersion was reduced to 1.3%, which is relatively close to the Pt dispersion on Pt/SiO₂ sample.
The idea behind oxidizing C\textsubscript{3}H\textsubscript{6} on two different supports was to determine the effect of nitrates on the oxidation reaction. As mentioned earlier, SiO\textsubscript{2} supports do not adsorb any NO\textsubscript{x} on the surface, which was confirmed with the DRIFTS data obtained by Pieta [71] and displayed in Figure 19.

\textbf{Figure 19:} Sample IR spectra taken from flowing 200 ppm NO and 5% O\textsubscript{2} in He over Pt/SiO\textsubscript{2} catalyst [71].

At an inlet gas composition of 200 ppm NO and 5% O\textsubscript{2}, only weak bands were observed, at about noise level. Also, following the NO\textsubscript{x} adsorption experiments, the catalyst was heated and no NO\textsubscript{x} desorption was observed.
5.1.2 Temperature Dependence of C\textsubscript{3}H\textsubscript{6} Oxidation with O\textsubscript{2} and with NO\textsubscript{2}

The temperature dependence of C\textsubscript{3}H\textsubscript{6} oxidation with O\textsubscript{2} or NO\textsubscript{2} as the oxidant over the Pt/Al\textsubscript{2}O\textsubscript{3} and Pt/SiO\textsubscript{2} catalysts was evaluated using TPO and a step ramp experiment. Concentration profiles as a function of temperature and/or time of C\textsubscript{3}H\textsubscript{6} in the presence of O\textsubscript{2} and of NO\textsubscript{2} were obtained using CATLAB. The Arrhenius equation, \( k = Ae^{-E/RT} \), where \( k \) is the specific reaction rate, \( A \) is the pre-exponential factor or frequency factor, \( E \) is the activation energy (J/mol), \( R \) is the gas constant (8.314 J mol\textsuperscript{-1}K\textsuperscript{-1}) and \( T \) is the absolute temperature (K), can be used to determine activation energies. By taking the natural log of the equation, the equation becomes, \( \ln k = \ln A - \frac{E}{R}(1/T) \), which is used to derive the temperature dependence of a reaction [72]. The slope of the line (\(-E/R\)) of \( \ln k \) versus \( 1/T \) can be used to calculate the apparent \( E \). Morooka and Ozaki [73] showed that the reaction rate is proportional to the observed conversion (\( X \)); therefore, the slope calculated using the line of \( \ln X \) vs \( 1/T \) is equivalent to the line of \( \ln k \) vs \( 1/T \). This was validated with the collected experimental data. The temperature range that resulted in low C\textsubscript{3}H\textsubscript{6} conversion (<15%) was used to calculate the apparent \( E \) for the C\textsubscript{3}H\textsubscript{6} oxidation reaction, in order to apply the principles of a differential reactor [73–74]. By using the low conversion region, the reaction is kinetically limited, thereby avoiding mass transfer limitations. Also, this reduces the effect of the exotherm [17] so that the temperature used for the calculations reflects the actual temperature of the system. The Arrhenius plots for C\textsubscript{3}H\textsubscript{6} oxidation with O\textsubscript{2} and with NO\textsubscript{2} are shown in Figure 20.
Figure 20: Arrhenius plot of C₃H₆ oxidation over Pt/Al₂O₃ and Pt/SiO₂ performed with two methods: TPO and step ramp with a) O₂ and b) with NO₂ as oxidant. Feed gases: 100 ppm C₃H₆, 6.5% O₂ or 1000 ppm NO₂, 200 ppm Ar and balance He.

A conversion range of 8 to 15% was used for the TPO experiments, while 4 to 15% was used for the step ramp experiments. Results revealed that these conversion ranges corresponded to temperature ranges for C₃H₆ oxidation with NO₂ for Pt/Al₂O₃ and Pt/SiO₂ to be from 105 to
120°C and 120 to 150°C, respectively. With O₂, for both catalysts, the temperatures were in the 85 to 100°C range. C₃H₆ oxidation with NO₂ began at a higher temperature (~92°C for Pt/Al₂O₃ and ~90°C for Pt/SiO₂) than with O₂ (~77°C for both catalysts), which was not expected as the reported evidence suggests that NO₂ is a stronger oxidant than O₂. For example, soot oxidation occurs at lower temperatures with NO₂ than O₂ [75]. While NO₂ is a stronger oxidant, C₃H₆ or HC molecules may not interact the same way with NO₂ as soot does, NO₂ adsorbs directly to the soot surface, whereas in this process, the NO₂ adsorbs on the catalyst, on which HCs also adsorb.

The activation energy of the proposed oxidation reactions can be determined by first checking the linearity of the Arrhenius plot. The coefficients of determination (R²) for all plots were at least 0.95 and the slope of each line was used to calculate the activation energy by multiplying the slope with R (8.314 J mol⁻¹K⁻¹). Each experiment was repeated at least once for reproducibility and the values were averaged. The errors of each slope (confidence interval) were also calculated at a 95% confidence level. Sample calculations are shown in Appendix B. Calculated activation energies with their 95% confidence interval are listed in Table III.
Table III: Calculated activation energy for C3H6 oxidation with O2 and with NO2.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Method</th>
<th>E (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C3H6 + O2</td>
</tr>
<tr>
<td>Pt/Al2O3</td>
<td>TPO</td>
<td>143.9 ± 17.0</td>
</tr>
<tr>
<td>Pt/SiO2</td>
<td>TPO</td>
<td>112.6 ± 15.7</td>
</tr>
<tr>
<td>Pt/Al2O3</td>
<td>Step Ramp</td>
<td>131.2 ± 13.5</td>
</tr>
<tr>
<td>Pt/SiO2</td>
<td>Step Ramp</td>
<td>137.8 ± 15.8</td>
</tr>
</tbody>
</table>

The results show the E obtained from two methods: TPO and step ramp, are relatively close in all cases. Statistical evidence also confirmed this to be true with a t-test [76] at a 95% confidence level. This t-test performed for all oxidation reactions on both catalysts consistently showed that there were no significant differences between the TPO and step ramp method. If only the averages of the TPO and step ramp between C3H6 oxidation with O2 and NO2 over Pt/Al2O3 were considered, it does appear that with NO2 as the oxidant, the activation energy is less than with O2 (O2 to NO2 – TPO: 144 to 120 kJ/mol and Step Ramp: 131 to 111 kJ/mol). However, considering the errors, it is more difficult to distinguish between the calculated activation energies for Pt/Al2O3. On the other hand, for Pt/SiO2, when comparing the activation energies of C3H6 oxidized by NO2 and by O2, a significant difference exists. The activation energy with NO2 is significantly lower than with O2. It is important to note that a significant difference is clearly observed when comparing the oxidants over Pt/SiO2 and the only difference between Pt/Al2O3 and Pt/SiO2 is that no surface NOx species are formed over the SiO2 support. Results show that less energy is required for C3H6 oxidation with NO2 as the oxidant in the absence of nitrates; therefore, this suggests...
that nitrates influence the kinetics of \( C_3H_6 \) oxidation with \( NO_x \) in the gas phase for a Pt/Al\(_2\)O\(_3\) catalyst, which would be the case in real applications with actual exhaust gas.

### 5.1.3 Temperature Dependence of \( C_3H_6 \) Oxidation with Nitrates

To further investigate the effect of nitrates on \( C_3H_6 \) oxidation, the standard Pt/Al\(_2\)O\(_3\) catalyst in powder form was first saturated with nitrates by exposing it to a stream of \( NO_2 \) and \( O_2 \) at 275\(^\circ\)C in the CATLAB. \( NO_2 \) was turned off and then cooled down and then the temperature was ramped in the presence of \( C_3H_6 \) to determine whether the nitrates can oxidize \( C_3H_6 \). \( C_3H_6 \) began to oxidize at about 190\(^\circ\)C, which is much higher than with \( O_2 \) or \( NO_2 \); however, during a repeat of this experiment in the absence of \( C_3H_6 \), \( NO_x \) began to desorb at this temperature as well. The desorbed \( NO_x \) gave \( C_3H_6 \) a source of oxidant, which then resulted in the start of \( C_3H_6 \) oxidation. Without any oxidant in the gas phase, activation of \( C_3H_6 \) or HC molecule does not occur even with nitrates on the surface, prior to nitrate decomposition, and with nitrate decomposition the formed \( NO_2 \) can act as the oxidant. A similar effect was also observed by Irani et al. [12] where addition of HCs significantly decreased the \( NO_2 \) reduction temperature but to different extents depending on the HC that was correlated to the activation of HCs. It appears, based on these results, that in order for the nitrates to have an effect, \( C_3H_6 \) first has to be activated. Therefore, the experiment was repeated with \( C_3H_6 \) and \( O_2 \) instead of just \( C_3H_6 \).

In the presence of nitrates, \( C_3H_6 \) and \( O_2 \), \( C_3H_6 \) oxidation began at around 63\(^\circ\)C, which was lower than the previous starting temperatures involving just \( O_2 \) or \( NO_2 \). Arrhenius plots from
8 to 15% conversion, which corresponded to a temperature range of 77 to 84°C, are displayed in Figure 21.

![Figure 21](image_url)

**Figure 21:** Arrhenius plots of C₃H₆ oxidation over Pt/Al₂O₃ in the presence of nitrates by TPO. Nitrates made with 500 ppm NO₂, 6.5% O₂, 200 ppm Ar and balance He (repeated 3 times). TPO gas mixture: 100 ppm C₃H₆, 6.5% O₂, 200 ppm Ar and balance He.

A consistent set of data was obtained from 4 separate experiments with all R² values greater than 0.97. Sample calculations are included in Appendix B. With O₂ and nitrates present, C₃H₆ oxidation starts earlier than with just O₂ or NO₂. This gives further indication that C₃H₆ must to be activated in order for the nitrates to have an effect. It was also confirmed that the nitrates were present even after C₃H₆ was completely oxidized as NOₓ desorption was observed at higher temperatures. C₃H₆ oxidation reached completion at about 100°C and NOₓ began to desorb at about 190°C. The activation energy calculated from the Arrhenius
The equation is approximately 100 kJ/mol. The activation energy of C\textsubscript{3}H\textsubscript{6} oxidation with O\textsubscript{2} and nitrates is lower than that of the oxidation reactions with O\textsubscript{2} or NO\textsubscript{2}. With the surface covered with nitrates, C\textsubscript{3}H\textsubscript{6} oxidation occurs at a lower temperature and has a lower energy barrier as well. Just to confirm that NO\textsubscript{x} desorption was not occurring on its own before C\textsubscript{3}H\textsubscript{6} oxidation was complete, the temperature ramp portion of the experiment was repeated without C\textsubscript{3}H\textsubscript{6} (only O\textsubscript{2}). The temperature profiles of NO\textsubscript{x} desorption with and without C\textsubscript{3}H\textsubscript{6} are displayed in Figure 22.

![Temperature profiles of NO\textsubscript{x} desorption with and without C\textsubscript{3}H\textsubscript{6}](image)

**Figure 22:** Temperature profiles of NO\textsubscript{x} desorption with and without C\textsubscript{3}H\textsubscript{6}. Nitrates made with 500 ppm NO\textsubscript{2}, 6.5% O\textsubscript{2}, 200 ppm Ar and balance He. TPO gas mixture ◆: 100 ppm C\textsubscript{3}H\textsubscript{6}, 6.5% O\textsubscript{2}, 200 ppm Ar and balance He; ◇: 6.5% O\textsubscript{2}, 200 ppm Ar and balance He.

The results show that NO\textsubscript{x} began to desorb at a higher temperature in the absence of C\textsubscript{3}H\textsubscript{6}. Previous research indicates that barium nitrates are more stable when O\textsubscript{2} is present, and this
apparently extrapolates to nitrates on the Al₂O₃ surface [77–78]. This was not the case when C₃H₆ was also present, NOₓ began desorbing at the same temperature as it did during a TPD without any O₂ and C₃H₆. In the presence of C₃H₆, it is also apparent that less NOₓ desorbed during the temperature ramp, based on Figure 22. To quantify the consumption of nitrates by C₃H₆ oxidation, the integrated areas of the NOₓ desorption peaks are tabulated in Table IV.

**Table IV**: Total amount of NOₓ desorbed during the temperature ramp with C₃H₆ and O₂ and with O₂.

<table>
<thead>
<tr>
<th>Inlet gases</th>
<th>Desorbed NOₓ (ppm*s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 ppm C₃H₆, 6.5% O₂, 200 ppm Ar, balance He</td>
<td>74068.3</td>
</tr>
<tr>
<td>6.5% O₂, 200 ppm Ar, balance He</td>
<td>81159.3</td>
</tr>
</tbody>
</table>

The amount of NOₓ desorbed decreased by about 9% with C₃H₆ oxidation. This is consistent with the theory of nitrates being reduced by C₃H₆ as was noted in Chapter 4. When exposed to C₃H₆ and O₂ during the temperature ramp, less NOₓ desorbed from the catalyst surface as some of it was consumed during C₃H₆ oxidation.

The results of this study showed that nitrates do indeed play a role in C₃H₆ oxidation, causing the reaction to occur at lower temperatures, and with a lower activation energy based on the obtained reaction kinetics data. It also added further evidence that HCs must be activated in order for NOₓ to have any effect on HC oxidation.
Chapter 6
Conclusions

Diesel oxidation catalysts are a critical component of diesel exhaust aftertreatment systems. DOCs readily oxidize CO and HC species but also oxidize NO to NO₂. Oxidizing NO to NO₂ does not reduce the total NOₓ level; however, higher NO₂ concentrations improve NOₓ storage on downstream NOₓ traps, improve the low temperature efficiency of SCR catalysts, and lower the soot oxidation temperatures on particulate filters [17]. DOCs commonly consist of precious metals, such as Pt, for their oxidation ability and a high surface area support, such as Al₂O₃ to disperse the metal. A pilot reactor, CATLAB and DRIFTS were used to investigate the interaction between surface NOₓ species and HCs.

TPO experiments on a Pt/Al₂O₃ monolith catalyst in a pilot reactor system showed definite low temperature inhibition of NO oxidation by C₃H₆ and vice versa. C₃H₆ oxidation is inhibited by competitive active site adsorption while NO oxidation inhibition is explained by active site adsorption inhibition as well as the product NO₂ being consumed as an oxidant for C₃H₆ oxidation. On CATLAB, NOₓ TPD experiments were performed with a powder Pt/Al₂O₃ catalyst. When the adsorbed NOₓ was exposed to C₃H₆ prior to the TPD, around 50% of the adsorbed NOₓ was consumed which confirmed that C₃H₆ can react with the surface NOₓ species. Using DRIFTS, it was determined that exposing Pt/Al₂O₃ to NOₓ led to formation of surface nitrates. When the surface nitrates were exposed to C₃H₆ and O₂, the nitrates were consumed and a new species formed, which could be identified as either linear nitrites from the nitrates being reduced by subsequent C₃H₆ exposure or HC intermediates.
from C$_3$H$_6$ oxidation. Additional experiments with different sequences of gas exposure show that the new species formed on the surface were most likely nitrites. The results indicate that surface nitrates can indeed act as an oxidant for C$_3$H$_6$ oxidation and in order for clear evidence of this reaction to occur, a high inlet NO$_x$ to C$_3$H$_6$ ratio is required, or it was also readily evident with NO$_2$ as the NO$_x$ source.

With evidence suggesting that surface NO$_x$ species can oxidize C$_3$H$_6$, it added to the possible sources of oxidant for C$_3$H$_6$ oxidation, O$_2$ and NO$_2$. Reaction kinetics studies were done for the three possible oxidants in C$_3$H$_6$ oxidation over Pt/Al$_2$O$_3$ and Pt/SiO$_2$ in CATLAB. Since nitrates are readily formed on Pt/Al$_2$O$_3$ catalysts with NO$_2$, a Pt/SiO$_2$ catalyst, which is known to be inert toward nitrate formation, was used to isolate the reaction between C$_3$H$_6$ and NO$_2$. Pt dispersions of the Pt/Al$_2$O$_3$ and Pt/SiO$_2$ samples, determined by H$_2$ chemisorption, were 1.3 and 1.6%, respectively.

C$_3$H$_6$ oxidation with O$_2$ and NO$_2$ were performed with two different methods: TPO and step ramp on CATLAB for both Pt/Al$_2$O$_3$ and Pt/SiO$_2$. Statistical analysis showed there was no significant difference between the activation energies calculated from the two methods. C$_3$H$_6$ oxidation began earlier with O$_2$ than with NO$_2$ but the activation energy was lower for the reaction between C$_3$H$_6$ and NO$_2$ for Pt/SiO$_2$. These results suggest that HCs need to be activated first for NO$_2$ to be favored in HC oxidation. On Pt/Al$_2$O$_3$, the activation energies between C$_3$H$_6$ oxidation with O$_2$ and NO$_2$ were not significantly different, which suggests that nitrates have an effect on the kinetics of C$_3$H$_6$ oxidation. When the experiment was conducted with nitrates and C$_3$H$_6$ present, the reaction did not occur until NO$_x$ began to
desorb from the catalyst. The stored NO\textsubscript{x} desorbed at higher temperatures as it became thermally unstable and began to react with C\textsubscript{3}H\textsubscript{6}, which gave further evidence that C\textsubscript{3}H\textsubscript{6} needs to be activated in order for NO\textsubscript{x} to have any effect, whether it be surface nitrates or gas phase NO\textsubscript{2}. Therefore, C\textsubscript{3}H\textsubscript{6} and O\textsubscript{2} were exposed to the nitrates during the temperature ramp and C\textsubscript{3}H\textsubscript{6} oxidation began earlier than with O\textsubscript{2} by itself. It not only proved that nitrates affect C\textsubscript{3}H\textsubscript{6} oxidation once it becomes activated, but also results in a lower activation energy than C\textsubscript{3}H\textsubscript{6} oxidation with O\textsubscript{2} (without nitrates). Also, nitrate consumption was observed during C\textsubscript{3}H\textsubscript{6} oxidation as less NO\textsubscript{x} desorbed from the catalyst than when the temperature was ramped in just O\textsubscript{2} (no C\textsubscript{3}H\textsubscript{6} exposure), which was consistent with the DRIFTS results showing nitrate consumption during C\textsubscript{3}H\textsubscript{6} oxidation.
Chapter 7
Recommendations

Based on the results obtained, further experiments can be envisioned to validate the findings at different scales, as well as to more accurately determine some of the values calculated. These are:

- Add more thermocouples inside the monolith sample to more accurately determine the temperature distribution within the catalyst to observe the exotherm effect of HC oxidation.
- Repeat experiments with Pd catalysts or Pt-Pd catalysts to compare the results to the results from this thesis, which only evaluated a Pt/Al₂O₃ catalyst - there is a lack of literature data available for Pd catalysts.
- Formulate a Pt/SiO₂ monolith catalyst to perform the experiments from Chapter 5 on a pilot reactor to compare the data obtained from CATLAB.
- Install a USB – Ethernet adaptor to connect the OMNISTAR to the computer controlling CATLAB reactor. It can help as both devices could be remotely controlled away from the laboratory. The current setup has the MS connected to a different computer as all the Ethernet ports are used up on the CATLAB computer.
- Kinetics study done in Chapter 5 could be repeated involving other gases such as CO and/or NO to simulate actual exhaust.
- The outlet of the DRIFTS should be connected to the MS to measure outlet gases while simultaneously observing what is occurring on the catalyst surface.
References


   http://www.dieselnet.com/tech/emi_gas.php


   http://www.dieselnet.com/tech/diesel_emiform.php


   http://www.dieselnet.com/tech/engine_control.php

   http://www.dieselnet.com/standards


[71] I.S. Pieta “CeO₂, Pt/CeO₂, SiO₂ and Pt/SiO₂ DRIFTS Results and Discussion” unpublished.

63


Appendix A
Addendum to Chapter 4

Additional experiments were performed to support the discussion presented in Chapter 4 “NO Oxidation Inhibition by HCs over a DOC – Reaction Between Surface Nitrates and HCs”. In Chapter 4, a Pt/Al₂O₃ sample was evaluated at one temperature, 250°C. In this Appendix, the reaction over Al₂O₃ and over Pt/Al₂O₃ at other temperatures was investigated. Also, the reaction was performed in a pilot reactor system as well.

A.1 Experimental Methods

Using the same 1 wt-% Pt/γ-Al₂O₃ powder sample, the temperature effect on the reaction between surface nitrates and C₃H₆ was investigated using DRIFTS. The same equipment setup and pretreatment method as previously described in Chapter 3.2.1 were used. To characterize the interaction between gas-phase C₃H₆ and surface nitrates, 600 ppm NO₂, 5% O₂ and balance He were first introduced at 250°C in order to form surface nitrites/nitrates. Once the nitrate peaks reached a saturation point, NO₂ was turned off and then the temperature was lowered to 200°C in one experiment and 150°C in another experiment in just 5% O₂ in He. The nitrates on the Pt/Al₂O₃ catalyst are thermally stable when formed at temperatures below 300°C [31,36]. 200 ppm C₃H₆, 5% O₂ and balance He were introduced to investigate the reaction between C₃H₆ and nitrates at different temperatures. The same experiment was performed at 250°C for pure Al₂O₃ sample as well.
For the pilot reactor study, a monolith sample of 1 in diameter and 2 in length with an Al₂O₃ loading of 1.59 g/in³ and a Pt loading of 20 g/ft³ was used. TPD experiments were performed to quantify the reaction between stored NOₓ species and HC. 1000 ppm NO₂, 6.5% O₂ and balance N₂ were introduced at 270°C for 1.5 hours, then NO₂ and O₂ were turned off and the temperature was ramped to 515°C at 10°C/min. This experiment was then repeated twice more, with 10 second pulses of 20 ppm C₃H₆ for 2 minutes (6 total pulses) and for 5 minutes (15 total pulses) prior to the temperature ramp. The pulses were performed with a 4-way actuated switching valve to alternate the gas manifolds between 100% N₂ and 20 ppm C₃H₆ in N₂.

A.2 Results and Discussion

A.2.1 DRIFTS

Nitrates were formed at 250°C by exposing Pt/Al₂O₃ to 1000 ppm and 6.5% O₂ in He on Pt/Al₂O₃ and after reaching a saturation point (prior to C₃H₆ addition), the temperature was lowered to 200 and 150°C, in two separate experiments, in O₂ and He, and the nitrates remained stable as expected [36,79]. 200 ppm C₃H₆, 5% O₂ and balance He were introduced and the resulting IR spectra are shown in Figure 23.
Figure 23: DRIFTS of 1 wt-% Pt/Al₂O₃ exposed to C₃H₆ + O₂ following exposure to NO₂ and O₂ for times 0, 5, 10, 15, 30, 60, 90, 100 and 130 min (black to red) at (a) 200°C and (b) 150°C. Feed gas composition: 200 ppm C₃H₆, 5% O₂ and balance He.

The same features and trends were observed as those at 250°C with the only difference being at 250°C (Chapter 4, Figure 13), the nitrate peak at 1303 cm⁻¹ was almost completely reduced, over 80% of its original intensity, but at lower temperatures (Figure 23), the nitrate
peak was still visible at the end of the experiment as it had decreased by around 70% and 30% at 200°C and 150°C, respectively. The same reactions were occurring but simply not as fast at lower temperature.

The reactivity between nitrates and C₃H₆ on an Al₂O₃ sample was also studied. While nitrates form on the Al₂O₃ surface when exposed to NO and O₂, this does not occur without Pt. Only a very small amount of nitrites may form and NOₓ storage is also known to be difficult on Al₂O₃ alone; however, exposure to NO₂ and O₂ does lead to the formation of nitrates on Al₂O₃ (no Pt) [36]. The DRIFTS results obtained after exposing the Al₂O₃ sample to NO₂ and O₂ for 110 minutes are displayed in Figure 24.

![Figure 24: DRIFTS of γ-Al₂O₃ at 250°C exposed to NO₂ + O₂ for times 0, 5, 15, 30, 60, 90 and 110 min (black to red). Feed gas composition: 600 ppm NO, 5% O₂ and balance He.](image-url)
The same nitrate peaks observed on the Pt/Al₂O₃ sample were observed here at 1303 and 1585 cm⁻¹. The nitrate peak in the 1500 – 1700 cm⁻¹ region was more defined, with peaks at 1585 and 1610 cm⁻¹, representing monodentate and bidentate nitrates, respectively [36,79]. Also, a distinct peak at 1393 cm⁻¹, which was not present in data obtained from the Pt/Al₂O₃ sample, was identified as bulk nitrate on Al₂O₃ (Al(NO₃)⁺) [36]. After the nitrates were formed, the flow of NO₂ was turned off and C₃H₆ was introduced; results are displayed in Figure 25.

![Figure 25: DRIFTS of γ-Al₂O₃ at 250°C exposed to C₃H₆ + O₂ following exposure to NO₂ and O₂ for times 0, 10, 20, 35 and 70 min (black to red). Feed gas composition: 200 ppm C₃H₆, 5% O₂ and balance He.](image)

After 70 minutes, the nitrate peak at 1303 cm⁻¹ slightly decreased (around 10%); however, no significant reaction occurred, as was the case with the Pt/Al₂O₃ sample where the nitrates
were reduced to nitrites. The reaction was either extremely slow, but most likely does not occur without Pt present.

**A.2.2 Pilot Reactor**

To further validate the theory of nitrates being reduced by C\textsubscript{3}H\textsubscript{6}, TPD experiments on the monolith-supported catalyst in the pilot reactor were performed. First, nitrates were formed at 275°C, similar to the DRIFTS experiment. After the flow of NO\textsubscript{2} and O\textsubscript{2} were turned off, the temperature was ramped to 515°C with only N\textsubscript{2} flowing for TPD. The experiment was repeated including a C\textsubscript{3}H\textsubscript{6} pulse step prior to the temperature ramp (6 and 15 pulses of 20 ppm C\textsubscript{3}H\textsubscript{6}). TPD results are shown in Figure 26.
Based on Figure 26, less NO₂ and more NO were released during the TPD when the nitrates were exposed to C₃H₆. No N₂O was released during the TPD. However, peaks of N₂O, NO
and NO₂ were observed during each C₃H₆ pulse. A sample profile of the NOₓ released during C₃H₆ pulsing is shown in Figure 27.

![Sample profile of NOₓ released during C₃H₆ pulsing.](image)

**Figure 27**: Sample profile of NOₓ released during C₃H₆ pulsing.

The profiles of NO, NO₂ and N₂O in Figure 27 during C₃H₆ pulses indicate that C₃H₆ was reacting with the stored NOₓ. N₂O is generally formed as a by-product when NOₓ and HCs react over Pt/Al₂O₃ [80] and there is reported evidence suggesting that the N₂O production mechanism involves adsorbed NO species and surface HC species [23]. The integrated areas of the N₂O, NO and NO₂ released during each C₃H₆ pulse are displayed in Figure 28.
Figure 28: Amount of N₂O, NO and NO₂ released during each C₃H₆ pulse for a) 6 pulses and b) 15 pulses.

With an increasing number of C₃H₆ pulses, more NOₓ was of course released. Of the total NOₓ released, about 1.5% and 2.2% is formed as N₂O during C₃H₆ pulsing. The amount of N₂O and NO released increased while the amount of NO₂ released decreased with each C₃H₆ pulse. With an increasing C₃H₆ to NOₓ ratio, more NO₂ can be reduced to NO, which
explains why the amount of NO released increased with each pulse, since with each pulse there is less surface NO\textsubscript{x} species remaining. The amount of NO released with each pulse leveled off after around 7 pulses while N\textsubscript{2}O continued to increase. This again is due to an increasing C\textsubscript{3}H\textsubscript{6} to surface NO\textsubscript{x} ratio. The ratios of the total amount of NO to NO\textsubscript{2} released were 0.43 and 0.45 for 6 and 15 pulses, respectively.

During the TPD, more NO and less NO\textsubscript{2} was released when the C\textsubscript{3}H\textsubscript{6} pulsing step was performed beforehand, as shown in Figure 26. The degree of reduction depended on how much C\textsubscript{3}H\textsubscript{6} was exposed to the surface NO\textsubscript{x}. To quantify the degree of reduction, the integrated area of the NO and NO\textsubscript{2} peaks of the TPD are tabulated in Table V.

**Table V**: Total amount of NO, NO\textsubscript{2} and NO\textsubscript{x} released during the TPDs.

<table>
<thead>
<tr>
<th>TPD Type</th>
<th>NO (ppm*s)</th>
<th>NO\textsubscript{2} (ppm*s)</th>
<th>Total NO\textsubscript{x} (ppm*s)</th>
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</thead>
<tbody>
<tr>
<td>No Pulse</td>
<td>20273.93</td>
<td>76702.00</td>
<td>96975.93</td>
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<tr>
<td>6 Pulses</td>
<td>28484.88</td>
<td>52837.82</td>
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<td>15 pulses</td>
<td>31349.00</td>
<td>46731.12</td>
<td>78080.12</td>
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Around 79.1% of the released NO\textsubscript{x} during the TPD without any exposure to C\textsubscript{3}H\textsubscript{6} was released as NO\textsubscript{2} while 65.0% and 59.9% were released as NO\textsubscript{2} with 6 and 15 ten-second pulses of 20 ppm C\textsubscript{3}H\textsubscript{6}, respectively. Also, it is important to note that the total amounts of NO\textsubscript{x} released were not the same in experiments with and without C\textsubscript{3}H\textsubscript{6} pulses even though the same amount of NO\textsubscript{x} should have been stored on the catalyst, which indicates that the
nitrates were reduced not just to nitrites, with NO$_x$ release during TPD, but some were even further reduced to N$_2$ and N$_2$O.

**A.3 Conclusions**

DRIFTS experiments showed that nitrates get reduced to nitrites at lower temperatures and that Pt is required for this reaction to occur. TPD experiments validated that nitrates on the Pt/Al$_2$O$_3$ catalyst surface were reduced as more NO was released during the TPD than NO$_2$ when exposed to C$_3$H$_6$, and that some were even further reduced to N$_2$ as well.
Appendix B
Sample Calculations and Additional Data

B.1 Sample calculation for Pt dispersion (%)

- Pt/SiO$_2$

Pt Dispersion (%) =$\left(\frac{A_S}{N_S} \cdot \frac{A_A}{N_A}\right) \cdot \left(\frac{V_{H_2}}{V_{STP}}\right) \cdot \left(\frac{\upsilon_{Pt:H_2}}{m_{cat} \cdot \omega_{Pt}}\right) \cdot M_{Pt} \cdot 100\%$

Areas of the peaks of the pulses were calculated using OriginPro 7.0.

Pt Dispersion (%) =

$$\left(\frac{4.07711 \times 10^{-5}}{24} \cdot \frac{3.1179 \times 10^{-6}}{4.07711 \times 10^{-5}}\right) \cdot \left(\frac{5 \times 10^{-6}\text{L}}{22.4\text{L/mol}}\right) \cdot \left(\frac{2}{0.045 \text{ g Cat} \times 1\% \text{ Pt}}\right) \cdot 195.1 \frac{\text{g}}{\text{mol}} \cdot 100\%$$

= 1.6%
B.2 Additional Data – Reaction Kinetics

B.2.1 Pt/SiO$_2$

**Table VI:** Arrhenius plot data for C$_3$H$_6$ oxidation with O$_2$ by TPO over Pt/SiO$_2$.

<table>
<thead>
<tr>
<th>Experiment 1</th>
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<th>Repeat 2</th>
<th>Repeat 3</th>
</tr>
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<td>Ln X</td>
<td>1/T (K$^{-1}$)</td>
<td>Ln X</td>
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**Table VII:** Arrhenius plot data for C$_3$H$_6$ oxidation with O$_2$ by Step Ramp over Pt/SiO$_2$.

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Table VIII: Arrhenius plot data for C\textsubscript{3}H\textsubscript{6} oxidation with NO\textsubscript{2} by TPO over Pt/SiO\textsubscript{2}.

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Table IX: Arrhenius plot data for C\textsubscript{3}H\textsubscript{6} oxidation with NO\textsubscript{2} by Step Ramp over Pt/SiO\textsubscript{2}.

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### B.2.2 Pt/Al₂O₃

**Table X:** Arrhenius plot data for C₃H₆ oxidation with O₂ by TPO over Pt/Al₂O₃.

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**Table XI:** Arrhenius plot data for C₃H₆ oxidation with O₂ by Step Ramp over Pt/Al₂O₃.

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</table>
Table XII: Arrhenius plot data for C$_3$H$_6$ oxidation with NO$_2$ by TPO over Pt/Al$_2$O$_3$.

<table>
<thead>
<tr>
<th>Experiment 1</th>
<th>Repeat 1</th>
<th>Repeat 2</th>
<th>Repeat 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1/T$ (K$^{-1}$)</td>
<td>Ln X</td>
<td>$1/T$ (K$^{-1}$)</td>
<td>Ln X</td>
</tr>
<tr>
<td>0.002619</td>
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Table XIII: Arrhenius plot data for C$_3$H$_6$ oxidation with NO$_2$ by Step Ramp over Pt/Al$_2$O$_3$.

<table>
<thead>
<tr>
<th>Experiment 1</th>
<th>Repeat 1</th>
<th>Repeat 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1/T$ (K$^{-1}$)</td>
<td>Ln X</td>
<td>$1/T$ (K$^{-1}$)</td>
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0.002574 2.43
Table XIV: Arrhenius plot data for C₃H₆ oxidation with O₂ and Nitrates by TPO over Pt/Al₂O₃.

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<thead>
<tr>
<th>Experiment 1</th>
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<th>Repeat 2</th>
<th>Repeat 3</th>
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</thead>
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<td>I/T (K⁻¹)</td>
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</table>
B.3 Sample Calculations – Activation Energy, Errors and t-test

B.3.1 Activation Energy and Error Calculations

Using the data set of C₃H₆ oxidation with O₂ by TPO over Pt/SiO₂ in Table VI, sample calculations of activation energy and the error of the slope are shown.

The linear set of data can be fitted with the following equation: \( \ln X = A₀ + A₁ \cdot 1/T \)

A model with 2 parameters (p): slope and intercept; \( A₁ \) and \( A₀ \), respectively.

And from the Arrhenius equation, the slope represents – \( E/R \).

The repeated experiment data is combined into one data set as they are the same experiment done independently. This way the error can be just calculated from the error of the slope.

In matrix form the 1/T and lnX data set transforms to the following:

<table>
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<tr>
<th>1/T</th>
<th>Ln X</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.002729</td>
<td>2.115484</td>
</tr>
<tr>
<td>0.002721</td>
<td>2.229184</td>
</tr>
<tr>
<td>0.002717</td>
<td>2.295103</td>
</tr>
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<td>0.002713</td>
<td>2.329219</td>
</tr>
<tr>
<td>0.002709</td>
<td>2.34557</td>
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<tr>
<td>0.002702</td>
<td>2.486772</td>
</tr>
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<td>2.56912</td>
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<td>0.002691</td>
<td>2.62341</td>
</tr>
<tr>
<td>0.002688</td>
<td>2.666611</td>
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<td>2.562207</td>
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</tr>
<tr>
<td>0.002697</td>
<td>2.609194</td>
</tr>
<tr>
<td>0.002693</td>
<td>2.581541</td>
</tr>
<tr>
<td>0.002689</td>
<td>2.655565</td>
</tr>
</tbody>
</table>
General Linear Regression formulas are shown below:

Parameter matrix: \([A] = (X'X)^{-1} (X'Y)\) outputs \(A_0\) and \(A_1\)

Sum of squares error: \(SSE = Y'Y - A'(X'Y)\)

Sum of squares regression: \(SSR = A'(X'Y) - n\text{avg}^2\)

Sum of squares Total: \(SST = Y'Y - n\text{avg}^2\)

Sample Variance: \(s^2 = \frac{SSE}{(n - p)}\)

\(R^2 = \frac{SSR}{SST}\)

Confidence interval (CI): \(A_i \pm t_{\alpha/2, n-p} \cdot \sqrt{\frac{s^2(X'X)^{-1}_{i+1,i+1}}{}}\)

\[
[X'] = \begin{bmatrix} 1 & 0.002729 \\ 1 & 0.002721 \\ 1 & 0.002717 \\ 1 & 0.002713 \\ 1 & 0.002709 \\ 1 & 0.002702 \\ 1 & 0.002695 \\ 1 & 0.002691 \\ 1 & 0.002688 \\ 1 & 0.002733 \\ 1 & 0.002729 \\ 1 & 0.002717 \\ 1 & 0.002713 \\ 1 & 0.002709 \\ 1 & 0.002705 \\ 1 & 0.002701 \\ 1 & 0.002697 \\ 1 & 0.002693 \\ 1 & 0.002689 \end{bmatrix} \quad [Y] = \begin{bmatrix} 2.115484 \\ 2.229184 \\ 2.295103 \\ 2.329219 \\ 2.34557 \\ 2.486772 \\ 2.56912 \\ 2.62341 \\ 2.666611 \\ 2.089547 \\ 2.12122 \\ 2.243153 \\ 2.391564 \\ 2.502966 \\ 2.562207 \\ 2.564913 \\ 2.609194 \\ 2.581541 \\ 2.655565 \end{bmatrix}
\]

\(n = 19, p = 2\)
\[ [X'Y] = [45.98234, 0.124469]; [A] = [39.08288, -13539.1]; [Y'Y] = [111.9664]; A'[X'Y] = [111.9308] \]

\[ Y_{\text{avg}} = 2.420123 \]

\[ A_1 = -13539.1 \text{ is the slope} \]

Therefore, \( E = -13539.1 \text{ K} \cdot \frac{8.314 \text{ J}}{\text{mol K}} \cdot \frac{1}{1000 \frac{\text{J}}{\text{kJ}}} = 112.564 \frac{\text{kJ}}{\text{mol}} \)

\[ \text{SSE} = 111.9664 - 111.9308 = 0.035636 \]

\[ \text{SSR} = 111.9308 - 19(2.420123)^2 = 0.647812 \]

\[ \text{SST} = 0.035636 + 0.647812 = 0.683447934 \]

\[ R^2 = \frac{\text{SSR}}{\text{SST}} = \frac{0.647812}{0.683447934} = 0.947859 \]

\[ s^2 = \frac{\text{SSE}}{n - p} = \frac{0.035636}{19 - 2} = 0.002096 \]

\[ [X'X]^{-1}_{22} = 282963221 \]

Confidence interval: \( A_i \pm t_{\alpha, n-p} \cdot \sqrt{s^2(X'X)^{-1}_{i+1,i+1}} \)

At 95% Confidence level (\( \alpha = 0.05 \)):

\[ t_{\alpha, n-p} = t_{0.025, 19-2} = 2.458051 \]

\[ A_1 \pm 2.458051 \cdot \sqrt{(0.002096)(282963221)} = -13539.1 \pm 1893.103 \]

Therefore, \( E = 112.564 \pm 15.73926 \text{ kJ/mol} \)

Same method of calculation is used for the rest of the experiments and they are listed in Table XV.
**Table XV:** Activation energies of each experiment/oxidation reactions and all the intermediate calculation values.

<table>
<thead>
<tr>
<th>Experiment Type / Catalyst</th>
<th>n</th>
<th>s²</th>
<th>(X'X)_2^{-1}</th>
<th>t_a</th>
<th>A_1</th>
<th>R²</th>
<th>CI</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃H₆ + O₂ TPO Pt/SiO₂</td>
<td>19</td>
<td>0.00210</td>
<td>2.83E+08</td>
<td>2.46</td>
<td>-13539.1</td>
<td>0.9479</td>
<td>1893.1</td>
<td>112.56 ± 15.74</td>
</tr>
<tr>
<td>C₃H₆ + O₂ TPO Pt/Al₂O₃</td>
<td>22</td>
<td>0.00275</td>
<td>2.60E+08</td>
<td>2.42</td>
<td>-17310.9</td>
<td>0.9545</td>
<td>2048.8</td>
<td>143.92 ± 17.03</td>
</tr>
<tr>
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<td>8</td>
<td>0.00572</td>
<td>7.19E+07</td>
<td>2.97</td>
<td>-16577.6</td>
<td>0.9911</td>
<td>1904.4</td>
<td>137.83 ± 15.83</td>
</tr>
<tr>
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<td>14</td>
<td>0.00561</td>
<td>7.14E+07</td>
<td>2.56</td>
<td>-15782.3</td>
<td>0.9811</td>
<td>1620.3</td>
<td>131.21 ± 13.47</td>
</tr>
<tr>
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<td>60</td>
<td>0.00231</td>
<td>1.16E+07</td>
<td>2.30</td>
<td>-9972.5</td>
<td>0.9853</td>
<td>376.8</td>
<td>82.91 ± 3.13</td>
</tr>
<tr>
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<td>50</td>
<td>0.00240</td>
<td>8.44E+07</td>
<td>2.31</td>
<td>-14444.1</td>
<td>0.9555</td>
<td>1040.6</td>
<td>120.09 ± 8.65</td>
</tr>
<tr>
<td>C₃H₆ + NO₂ Step Ramp Pt/SiO₂</td>
<td>9</td>
<td>0.00195</td>
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<td>-10303.7</td>
<td>0.9946</td>
<td>813.9</td>
<td>85.67 ± 6.77</td>
</tr>
<tr>
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<td>-13336.9</td>
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<td>1351.5</td>
<td>110.88 ± 11.24</td>
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<tr>
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<td>-12046.2</td>
<td>0.9765</td>
<td>784.5</td>
<td>100.15 ± 6.52</td>
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</table>

The activation energies of individual repeated experiments were also calculated and averaged and the variances between the repeated experiments were calculated with the following equation.

\[
s^2 = \left(\frac{1}{n-1}\right) \cdot \left\{ \sum_{i=1}^{n} E_i^2 - n \left(\sum_{i=1}^{n} E_i\right)^2 \right\}
\]
Sample calculations using Pt/SiO$_2$ C$_3$H$_6$ + O$_2$ Step Ramp:

\[ n = 2 \]

\[ E_{\text{average}} = \frac{132.99 + 142.45}{2} = 137.72 \text{ kJ/mol} \]

\[
\begin{align*}
    s^2 &= \left(\frac{1}{2 - 1}\right) \cdot \left\{ \sum_{k=1}^{n} (17686.14 + 20292.75) - 2 \left( \sum_{k=1}^{n} (132.99 + 142.45) \right)^2 \right\} \\
    E_{\text{average}} &= 137.72 \\
    s^2 &= 44.78
\end{align*}
\]

Same method of calculation is used for the rest of the experiments and they are listed in Table XVI.
Table XVI: Average activation energies and variances between experiment repeats.

<table>
<thead>
<tr>
<th>Experiment Type / Catalyst</th>
<th>Expt #</th>
<th>E</th>
<th>$s^2$</th>
<th>Eavg</th>
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<tr>
<td>$\text{C}_3\text{H}_6 + \text{O}_2$ TPO Pt/SiO$_2$</td>
<td>Expt 1</td>
<td>119.94</td>
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<td>Repeat 1</td>
<td>114.36</td>
<td>91.20</td>
<td>119.69</td>
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<td></td>
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<td>Expt 1</td>
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<td>160.20</td>
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<td>Repeat 2</td>
<td>131.29</td>
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<tr>
<td></td>
<td>Repeat 3</td>
<td>134.53</td>
<td></td>
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</tr>
<tr>
<td>$\text{C}_3\text{H}_6 + \text{O}_2$ Step Ramp Pt/SiO$_2$</td>
<td>Expt 1</td>
<td>132.99</td>
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<td>Repeat 1</td>
<td>142.45</td>
<td>44.78</td>
<td>137.72</td>
</tr>
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<td>145.00</td>
<td>550.81</td>
<td>142.28</td>
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<tr>
<td>$\text{C}_3\text{H}_6 + \text{NO}_2$ TPO Pt/SiO$_2$</td>
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<td>Repeat 1</td>
<td>74.99</td>
<td>47.46</td>
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<td>Repeat 3</td>
<td>101.27</td>
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B.3.2 t-test calculations

To compare the activation energies calculated for $\text{C}_3\text{H}_6$ oxidation with different oxidants and between TPO and step ramp method, t-test at 95% confidence level was used.

A sample calculation is shown for $\text{O}_2$ vs $\text{NO}_2$ on Pt/SiO$_2$. 

87
\[
s^2 = \left( \frac{1}{n-1} \right) \cdot \left\{ \sum_{k=1}^{n} E_i^2 - n \left( \sum_{k=1}^{n} E_i \right)^2 \right\}
\]

\[
s_{O_2}^2 = \left( \frac{1}{2-1} \right) \cdot \left\{ (132.99^2 + 142.45^2) - 2 \left( \frac{132.99 + 142.45}{2} \right)^2 \right\} = 44.78
\]

\[
s_{NO_2}^2 = \left( \frac{1}{2-1} \right) \cdot \left\{ (88.52^2 + 76.17^2) - 2 \left( \frac{88.52 + 76.17}{2} \right)^2 \right\} = 76.25
\]

H\_0: E\_O\_2 - E\_NO\_2 = 0

H\_1: E\_O\_2 - E\_NO\_2 \neq 0

\[
s_{\text{pooled}}^2 = \frac{(2 - 1) \cdot 44.78 + (2 - 1) \cdot 76.25}{2 + 2 - 2} = 60.51
\]

\[
T_{\text{obs}} = \frac{E_{O_2} - E_{NO_2} - 0}{\sqrt{s_{\text{pooled}}^2 \cdot \left( \frac{1}{n_1} + \frac{1}{n_2} \right)}} = \frac{137.72 - 82.34 - 0}{\sqrt{60.51 \cdot \left( \frac{1}{2} + \frac{1}{2} \right)}} = 7.119
\]

\[
t_{\text{critical}} = t_{0.05,4+3-2} = 6.205347
\]

\[
t_{\text{critical}} < T_{\text{obs}}
\]

Therefore, it can be said with 95% confidence that the activation energies calculated between O\_2 and NO\_2 are significantly different for the experiment done on Pt/SiO\_2.

Same calculation method was used to determine whether the calculated activation energies are different between oxidants, supports, and methods (TPO vs Step Ramp). When T\_obs is less than t\_critical, then there is a significant difference between the two being compared.
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