

Development and Validation of a Pt-Pd Diesel Oxidation Catalyst Model

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ABSTRACT

The Diesel Oxidation Catalyst (DOC) is an important technology for the removal of CO and hydrocarbons (HC) from the exhaust of diesel engines, as well as for generating exotherms for active regeneration, and for producing NO₂ used by downstream components.

This paper describes the development of a one-dimensional numerical model for a Pt-Pd DOC for use in designing aftertreatment systems. The model is based on kinetics developed from laboratory microreactor data. The model is a significant advance over previous DOC models we have developed. A much larger experimental matrix was used enabling the kinetics and inhibition effects to be much better defined. The experiments included rich conditions enabling the model to be used in NO_x trap systems, where the exhaust becomes rich during regeneration. Reduction of NO₂ to NO by CO and HC has been included in the model. As well as converting NO₂ entering the DOC, this reaction prevents NO₂ formation while significant levels of CO and HC are present along the catalyst. The conversion of NO to NO₂ is observed to exhibit hysteresis when the temperature is ramped up and then down. This has been explained and successfully modelled in terms of the formation of an oxide layer on the surface of the catalyst, which is inactive for NO oxidation. Including both this effect and NO₂ reduction is important for obtaining a good prediction of the outlet NO₂ concentration, which in turn is crucial for the performance of any downstream model. The model has been successfully validated over both NEDC and FTP75 tests.

Finally, it is demonstrated that this model, developed for an LDD catalyst, is readily adaptable to an HDD catalyst. The HDD version of the model has been extensively validated against engine test data for a range of tests (steady state light-off, transient light-off, HD-FTP, NRTC, WHTC).

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1. INTRODUCTION

The Diesel Oxidation Catalyst (DOC) [1,2] is an important technology for the removal of CO and hydrocarbons (HC) from the exhaust of diesel engines, as well as for generating exotherms for active regeneration, and for producing NO₂ used by downstream components. NO₂ produced by the DOC may be used for oxidising soot trapped on a diesel particulate filter [3,4,5] or may influence the activity of a downstream NH₃ Selective Catalytic Reduction (SCR) catalyst [6] or Lean NO_x Trap (LNT) [7] by changing the NO₂/NO_x ratio. Thus the DOC is a key component of a diesel emissions control system.

When designing an aftertreatment system including a DOC, many factors need to be considered, such as the

catalyst size, substrate type (cell density, wall thickness, material, etc.), Platinum Group Metal (PGM) loading and catalyst positioning relative to the engine. Furthermore, as already mentioned, the DOC will influence the performance of any downstream emissions control components. Thus, individual components cannot be specified in isolation, instead the whole system, consisting of multiple components, needs to be designed as a single unit. Traditionally this has been done by an experimental "trial-and-error" approach, which is both time consuming and costly, particularly as emissions control systems become more complex to meet ever more stringent legislation. By using computer simulations a wide range of design scenarios can be investigated quickly and cost effectively, saving much time and money.

This paper describes the development of a one-dimensional model for a DOC containing both Pt and Pd from laboratory microreactor data and the validation of this model. The basic model has been developed for a Light-Duty Diesel (LDD) formulation and has been validated against the New European Drive Cycle (NEDC) and FTP75. As there was also interest in having a model for Heavy-Duty Diesel (HDD) applications, the basic model has been adapted to work for a HDD formulation. This version of the model has been extensively validated for three different catalyst volumes against a wide range of engine test data, *viz.* steady state and transient light-off tests, World Harmonised Transient Cycle (WHTC), Heavy-Duty FTP transient cycle (HD-FTP) and Non-Road Transient Cycle (NRTC).

While the model we previously developed for a Pt-based DOC worked well [8,9], we wanted to include a number of new features / improvements in this model. Firstly, a much larger experimental matrix was used than before to enable the kinetics, particularly inhibition effects, to be better defined. Secondly, the DOC may be used in front of an LNT and so subject to rich conditions during LNT regeneration. Therefore, the experimental matrix included rich conditions and reactions occurring under rich conditions, *e.g.* steam reforming, were included in the model. Thirdly, as already mentioned, the prediction of outlet NO₂ is crucial for the performance of any downstream component, so the description of NO₂ formation and destruction was improved. Prediction of outlet NO₂ is also of interest as there are limits on either the increase in NO₂ across the emissions system [10,11,12] or the outlet NO₂/NO_x ratio [13] for retrofit systems in some areas. It has been reported that NO₂ is reduced to NO by CO and HC [14], which can have a large impact on outlet NO₂ at temperatures below that required for HC light-off. It has also been reported that the catalysts activity for NO oxidation can change with time on stream due to the formation of an oxide layer on the surface of the catalyst, which is inactive for NO oxidation [15,16]. This oxide layer is formed by oxidation by NO₂ and can be removed by reduction with NO. Both of these effects have been included in the model to improve the NO₂ prediction. Fourthly, CH₄ was included in the model to enable the prediction of Non-Methane Hydrocarbon (NMHC). The prediction of outlet CH₄ is also of interest in its own right as CH₄ is a greenhouse gas with a global warming potential 72 times that of CO₂ over a 20 year period [17]. The new additions / improvements made in this DOC model can be summarised as:

- Large data set used for better defined kinetics
- Include data / reactions for rich conditions
- Include NO₂ reduction reactions
- More detailed NO oxidation kinetics
- Prediction of tailpipe CH₄ and NMHC

The rest of this paper is laid out as follows. In the first section (section 3.1), the development of the model for an LDD DOC formulation from microreactor data will be described. In this section the reaction scheme will be discussed as will insights into the chemistry occurring over the DOC gained in the course of this work. The next section (3.2) describes the validation of this model against vehicle data for LDD legislative cycles. The final section (3.3) describes the adaptation and validation of the model for an HDD formulation.

2. EXPERIMENTAL

2.1. SAMPLES

Model development and LDD vehicle testing were carried out using a commercial LDD DOC with a PGM loading of 120 g ft⁻³ and a Pt:Pd ratio by weight of 2:1, which had been hydrothermally aged for 10h at 780°C. The catalyst was on a 4.66 (diameter) × 3.60 in (118.4×91.4 mm), 400/4.3 (620 000 cells/m², 0.11 mm wall thickness), cordierite substrate. This catalyst was smaller than would normally be fitted on the vehicle used to collect LDD validation data to ensure near constant CO and HC slip throughout the NEDC and FTP75; modelling this data is a better test for the model than data for a larger part that would show zero slip through much of the test. Exactly the same sample was used for LDD vehicle testing and microreactor testing, *i.e.* the part was first tested on the vehicle before taking cores from it for microreactor testing. This ensures that the catalyst used for microreactor testing was in the same state as a catalyst on a vehicle; a new sample was used for each microreactor test.

HDD testing was carried out on a commercial Pt-Pd DOC with a typical EUVI / US10 formulation with a corresponding PGM loading. Parts with three different lengths, *viz.* 3.0, 4.5 and 6.0 in (76.2, 114.3, 152.4 mm), were used. These were 12 in (304.8 mm) in diameter, all had the same washcoat and PGM loading and were coated on 400/6 (620 000 cells/m², 0.15 mm wall thickness), cordierite substrates. The parts were used in a fresh state.

2.2. MICROREACTOR TESTING

Laboratory microreactor data was collected for developing reaction kinetics. To minimise the influence of heat and mass transfer on the measured conversions, and hence to measure as close to intrinsic kinetics as possible, tests were done using a packed bed obtained by grinding and sieving cores taken from a monolith sample to give tiny catalyst pellets of well-defined size. The sample (0.8 g) was placed in a stainless steel reactor. The flows of reactant gases and diluent (N₂) were controlled by mass flow controllers. The total gas flow was 2.0 L min⁻¹. All tests were run with 4.5% CO₂ and 4.5% H₂O in the gas feed, since these gases are always present in vehicle exhaust. The flow of liquid H₂O into the reactor was controlled by a peristaltic pump. Liquid HCs could be introduced into the gas feed using a

thermostated saturator. The reactor was heated in an oven. Experiments were typically run with a temperature ramp of $5^{\circ}\text{C min}^{-1}$. Gas from the reactor exit was led to analysers by heated lines. Separate analyser units were used to measure the concentration of CO (infra-red), CO_2 (infra-red), NO and NO_x (chemiluminescence), total hydrocarbon (THC, flame ionisation) and O_2 (electrochemical cell). Gas Chromatography (GC) was used in some tests for H_2 analysis and for analysis of individual HCs when the feed contained more than one HC. An FTIR bench was used in some tests for N_2O analysis. Around 75 microreactor tests were used for developing the model. A brief survey of the engine out emissions for current passenger cars, including some equipped with an LNT, over the NEDC and FTP75 was carried out to ensure the microreactor experiments covered the full range of concentrations likely to be encountered in real applications.

2.3. ENGINE / VEHICLE TESTING

2.3.1. LDD Vehicle Testing

LDD testing was carried out on a chassis dynamometer using a 1.5L, EU4 passenger car with a common rail fuel system and EGR. NEDC and FTP75 tests were run according to standard procedures. In each case, a number of repeat tests were done to ensure the data was representative. Emissions were measured simultaneously before and after the DOC. NO_x and NO emissions at the DOC inlet were measured using separate chemiluminescence analysers; NO_2 was determined by difference. At the tailpipe, total NO_x was measured by another chemiluminescence analyser, while NO and NO_2 were determined by an FTIR bench. The tailpipe NO and NO_2 concentration values used in this work were calculated from the total tailpipe NO_x (measured by chemiluminescence) and the $\text{NO}/(\text{NO} + \text{NO}_2)$ and $\text{NO}_2/(\text{NO} + \text{NO}_2)$ ratios obtained from the FTIR. Other gas analysis was performed using standard analysers and methods. The temperature of the exhaust gas before and after the catalyst was measured using 1.5 mm diameter thermocouples placed 25 mm in front or behind of the catalyst with the tips in line with the centre of the catalyst.

2.3.2. HDD Engine Testing

HDD testing was carried out on an engine dynamometer using a 13L, inline 6 cylinder, EUVI / US10 type engine with EGR. The temperature of the exhaust gas before and after the catalyst was measured using 3 mm diameter thermocouples placed 75 mm in front or behind of the catalyst with the tips in line with the centre of the catalyst. Each catalyst was conditioned on the engine (C100, 30 min) before testing. The following tests were run in sequence: steady state light-off, transient light-off, warm WHTC, warm HD-FTP, warm NRTC. Light-off tests were run at constant engine speed (A-speed); the temperature was increased by increasing the

engine load. With the steady state light-off tests the catalyst inlet temperature was increased in steps, with each temperature being held for 14 min. With the transient light-off test the inlet temperature was increased continuously with a temperature ramp of approximately $20^{\circ}\text{C min}^{-1}$ between 150 and 300°C , falling to approximately $1.2^{\circ}\text{C min}^{-1}$ above 370°C ; the ramp was practically linear between 150 and 300°C . With the legislative tests (WHTC, HD-FTP and NRTC), each test was actually run twice with a 10 min soak between tests; only the second test was used. This was done to ensure repeatable and stable temperature profiles and emissions levels. The whole procedure was run several times for each DOC; test to test variability was found to be low.

2.4. SIMULATIONS

Computer simulations of engine / vehicle tests were carried out using a one-dimensional model for a monolith reactor, which has been described in more detail elsewhere [18]. The model treats the gas and solid (monolith) phases separately with heat and mass transfer between the gas and solid being described by correlations. The physical properties of the catalyst (channel dimensions, thermal conductivity, heat capacity, etc.) were based on values given in substrate manufacture's datasheets with allowance made for the washcoat. A similar model was used for modelling the microreactor data and developing kinetics, except that the heat and mass transfer correlations were replaced by ones appropriate for a packed bed reactor. Kinetic parameter optimisation was carried out either automatically, using either a simplex or genetic algorithm method, or by a manual ("trial and error") approach. Langmuir Hinshelwood type rate equations [19] were used to describe the kinetics of each reaction. The exact form of the rate equations was decided on the basis of what best fitted the data, rather than using equations taken from the literature.

3. RESULTS AND DISCUSSION

3.1. MODEL DEVELOPMENT

In this section the development of reaction kinetics from microreactor data will be discussed. In the first section (3.1.1) the reaction scheme will be presented. While this was largely determined from the microreactor data, it was decided to discuss this before the data by way of introduction to the reactor data. Next the development of kinetics will be presented. The strategy was to first develop kinetics for individual reactions occurring in isolation, *e.g.* NO oxidation, CO oxidation, etc. Once rate equations describing the concentration and temperature dependency of these reactions in isolation had been developed, data with more complicated gas mixtures was considered to enable terms describing inhibition effects to be added to the rate equations. Thus, the development of kinetics has been divided into two sections; the first discussing reactions occurring in isolation (section

Table 1. Reactions included in the DOC model

Reaction	Equation
CO oxidation	$\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$ (1)
Oxidation of HC or oxygenate	$\text{C}_x\text{H}_y\text{O}_z + (x+y/4-z/2)\text{O}_2 \rightarrow x\text{CO}_2 + (y/2)\text{H}_2\text{O}$ (2)
Steam reforming	$\text{C}_x\text{H}_y + (x-n_{\text{WGS}})\text{H}_2\text{O} + n_{\text{WGS}}\text{CO}_2 \rightarrow (x+n_{\text{WGS}})\text{CO} + (x+y/2-n_{\text{WGS}})\text{H}_2$ (3)
HC SCR	$(1-S_{\text{N}_2\text{O}}/2)\text{C}_3\text{H}_6 + 9\text{NO} \rightarrow 3(1-S_{\text{N}_2\text{O}}/2)\text{CO}_2 + 3(1-S_{\text{N}_2\text{O}}/2)\text{H}_2\text{O} + 4\frac{1}{2} S_{\text{N}_2\text{O}} \text{N}_2\text{O} + 4\frac{1}{2}(1-S_{\text{N}_2\text{O}})\text{N}_2$ (4)
H ₂ oxidation	$\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$ (5)
NO oxidation	$\text{NO} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{NO}_2$ (6)
NO ₂ reduction by CO	$\text{CO} + \text{NO}_2 \rightarrow \text{CO}_2 + \text{NO}$ (7)
NO ₂ reduction by HC	$\text{C}_x\text{H}_y + (2x+y/2)\text{NO}_2 \rightarrow x\text{CO}_2 + (y/2)\text{H}_2\text{O} + (2x+y/2)\text{NO}$ (8)
Extra reaction added to fit vehicle data	$\text{NO}_2 \rightarrow \frac{1}{2}\text{N}_2 + \text{O}_2$ (9)

3.1.2) and the second describing inhibition and other effects occurring with more complex gas mixtures (section 3.1.3).

3.1.1. Reaction Scheme

The reactions included in the model are listed in Table 1. Oxidation of CO and of HCs and oxygenates (Eq. 1 and 2) are obviously included in the model. Steam reforming of HC (Eq. 3) was included as it is a reaction that can occur during the rich conditions of an LNT regeneration. CO and H₂ produced by this reaction are important for regeneration of any downstream LNT and thus correct prediction of this is important for the performance of a downstream LNT model. It was found that the amount of CO formed by this reaction was greater than the amount of HC consumed on a C₁ basis. This could be explained by some inter-conversion of CO and H₂ occurring presumably via the reverse Water Gas Shift (WGS) reaction. However, this seems unlikely as this catalyst was not found to be active for WGS (section 3.1.2.2). This will be discussed further in section 3.1.2.3. Nether the less, for simplicity, this reaction has been written as a reaction with stoichiometry equivalent to a combination of steam reforming and reverse WGS with a constant (n_{WGS}) to describe the amount of apparent reverse WGS occurring.

The next reaction (Eq. 4) is HC SCR, *i.e.* reduction of NO by HC. As NO may be reduced to N₂ or N₂O [20], this reaction includes the term $S_{\text{N}_2\text{O}}$ to describe the selectivity to N₂O. This reaction has been written with C₃H₆ as the HC as it was the only one of the HCs tested to show measurable activity for NO reduction; no significant activity was observed with C₇H₈ or n-C₁₀H₂₂.

Oxidation of H₂ (Eq. 5) was included primarily as a good prediction of outlet H₂ is important for any downstream LNT model.

For obtaining a good prediction of NO₂, the model includes not only oxidation of NO to NO₂ (Eq. 6), but also the reduction of NO₂ to NO by both CO and HC (Eq. 7 and 8, respectively). These NO₂ reduction reactions have been shown to have an important effect on DOC out NO₂ [14]. NO oxidation is reversible and the rate equation includes a description of thermodynamic equilibrium, as normal.

The final reaction (Eq. 9) was not observed in the microreactor data, but was required to give a good prediction with the vehicle data. This will be discussed in more detail in the section on LDD validation (section 3.2).

3.1.2. Kinetics of Individual Reactions

3.1.2.1. NO Oxidation

The first reaction considered is NO oxidation and its reverse reaction, NO₂ decomposition (Eq. 6). A larger number of experiments was used to develop the kinetics than used in previous models by this group. As a result it was found that the simple NO oxidation kinetics used previously were not adequate to describe all the data. Thus, in this section results for two kinetic models will be presented; a simple model which predicts some, but not all of the data, and a more advanced model that is capable of describing all of the available data.

Figure 1 shows measured reactor outlet NO₂/NO_x ratio as a function of inlet temperature for a series of inlet

concentrations together with predictions from a simple model for NO oxidation / NO₂ decomposition. Before discussing the model prediction, it is useful to first look at the measured data to understand how the conversion / rate of reaction depend on the inlet concentrations. This gives an insight into how the rate equation should look and into what is happening on the surface of the catalyst. Considering just the measured data when only NO and O₂ are fed, it can be seen that increasing the NO concentration at constant O₂ concentration decreases the conversion of NO to NO₂, indicating that NO oxidation is inhibited by NO and possibly NO₂. Note that in experiments where there is no NO₂ in the feed, the outlet NO₂/NO_x ratio is equal to the conversion of NO to NO₂ (assuming no NO_x reduction). Increasing O₂ concentration at constant NO concentration increases the NO conversion, indicating that NO oxidation has a positive order with respect to O₂. Similar observations have been previously made [16,21]. All of this suggests a situation on the catalyst surface where NO adsorbs more strongly than O₂ resulting in NO (and perhaps NO₂) being the dominant species on the surface.

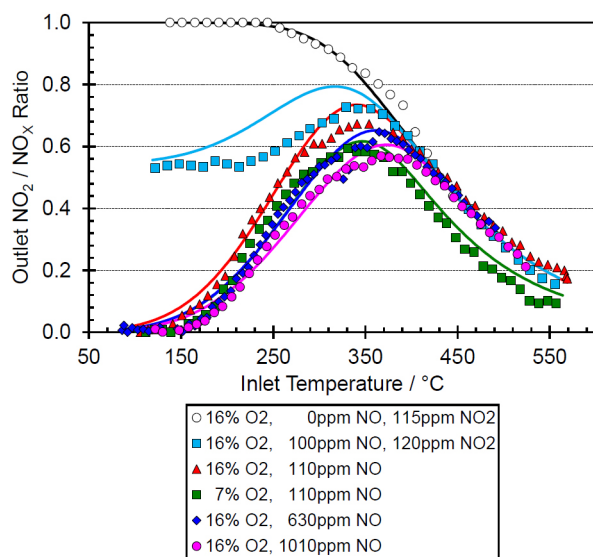


Figure 1. Simple model for NO oxidation: Comparison of measured (points) and simulated (lines) reactor outlet NO₂/NO_x ratio as a function of inlet temperature for microreactor tests with various inlet concentrations. 4.5% CO₂ and 4.5% H₂O was present in all tests.

Figure 1 also compares the experimental data with the prediction from a simple model similar to those used previously [8,21,22]. This model gives a good prediction when the feed consists of either NO+O₂ or NO₂+O₂, but over predicts NO oxidation when both NO and NO₂ are fed together with O₂. This suggests that NO₂ is suppressing NO oxidation to a greater extent than predicted by the simple model. Attempts were made to improve the prediction by increasing the inhibition of NO₂ on NO oxidation, but it was

not found possible to improve the fit to the NO+NO₂+O₂ experiment without making the fit to the other data unacceptably bad. A further failing of these simple kinetics was found when an experiment was run in which the temperature was ramped up and then down (Fig. 2). NO oxidation was found to exhibit hysteresis with this catalyst, with the NO conversion being higher on ramp down than ramp up; no hysteresis was predicted by the simple model (Fig. 2). This hysteresis was not due to the heat generated by the reaction leading to multiple steady states as the adiabatic temperature rise calculated for this feed composition was only 0.3°C. In all cases, the prediction above 390°C, where the outlet NO₂/NO_x ratio is determined by thermodynamics is good, as it should be.

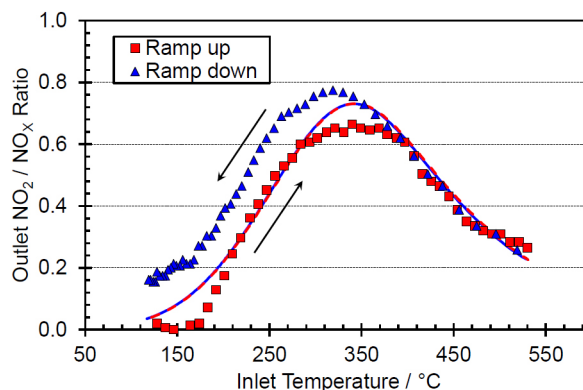


Figure 2. Simple model for NO oxidation: Comparison of measured (points) and simulated (lines) reactor outlet NO₂/NO_x ratio in an experiment where the temperature was ramped up and down. Feed: 4.5% CO₂, 4.5% H₂O, 155 ppm NO, 16% O₂. 5°C min⁻¹ ramp (except at the end of the ramp down).

Hysteresis in NO oxidation over a supported Pt catalyst was previously reported by Hauptmann *et al.* [23], although, rather intriguingly, their hysteresis was the other way round, *i.e.* they found lower activity for NO oxidation on ramp down. They attributed the hysteresis to the formation of an oxide layer on the surface of the catalyst, which was inert for NO oxidation. This oxide layer is formed by oxidation of the catalyst surface by NO₂ and is removed by reduction with NO. Possible reasons for the hysteresis in this work and that by Hauptmann *et al.* being the other way round are that Hauptmann *et al.* used a reductive pre-treatment before each experiment, which would tend to put the catalyst in a reduced (maximum activity) state at the start of the experiment (*i.e.* a state from which activity can only decrease), while here the catalyst was tested on a vehicle before microreactor testing (and so at some intermediate activity state) and that this study is on a Pt-Pd DOC while Hauptmann *et al.* used a Pt catalyst.

This deactivation of NO oxidation over Pt catalysts by the formation of an inert oxide layer has been suggested by other workers. For example, Olsson and Fridell [15] found that activity for both NO oxidation to NO₂ and for NO₂

decomposition decreased with time on stream. Evidence that this deactivation was due to the formation of a Pt oxide layer was obtained by X-ray Photoelectron Spectroscopy (XPS). Després *et al.* [16] found that pre-treating a Pt catalyst with NO₂ resulted in deactivation of the catalyst for NO oxidation. In contrast, pre-treatment with O₂ did not cause deactivation. Activity could be restored by either a thermal treatment in air at 650°C or by reduction at 250°C. They also found evidence for the formation of Pt oxide using XPS.

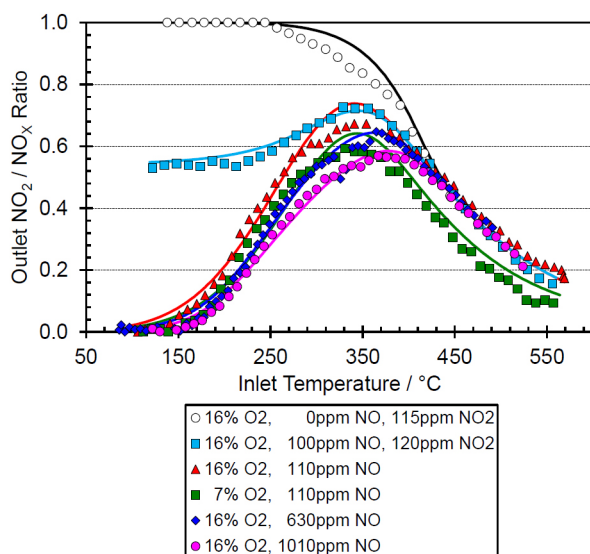


Figure 3. Advanced model for NO oxidation including “oxide effect”: Comparison of measured (points) and simulated (lines) reactor outlet NO₂/NO_x ratio as a function of inlet temperature for microreactor tests with various inlet concentrations. 4.5% CO₂ and 4.5% H₂O was present in all tests.

Given the poor performance of the simple NO oxidation kinetics and the experimental evidence for deactivation of NO oxidation activity by the formation of an inert oxide layer (hereafter referred to as the “oxide effect”), improved NO oxidation kinetics were developed including this phenomena. Modelling the data with this new model gave a much improved prediction (Fig. 3, 4). The new model gives a good prediction for the experiment with a NO+NO₂+O₂ feed, while still giving a comparable (good) fit to the simple model for data with a NO+O₂ feed (Fig. 3). The prediction of NO₂ decomposition with the experiment with a NO₂+O₂ feed is, however, slightly worse, but still acceptable. The hysteresis is now also well predicted by the model (Fig. 4). One remaining issue with the prediction is that the outlet NO₂/NO_x ratio is generally over predicted around the maxima in the NO₂/NO_x curve (at around 350°C). This is a problem with both the simple kinetics and those incorporating the “oxide effect”. A possible explanation for this is that the samples tested contain some soot as the parts were vehicle tested before being used for microreactor testing (certainly the front faces of the parts

were visibly blackened after vehicle testing) and that this soot reacts with NO₂ resulting in some lowering in the measured NO₂ concentration in this temperature region. For comparison, the model of Hauptmann *et al.* model [23] tends to slightly over predict NO conversion around the maxima on ramp up, but under predicts slightly around the maxima on ramp down.

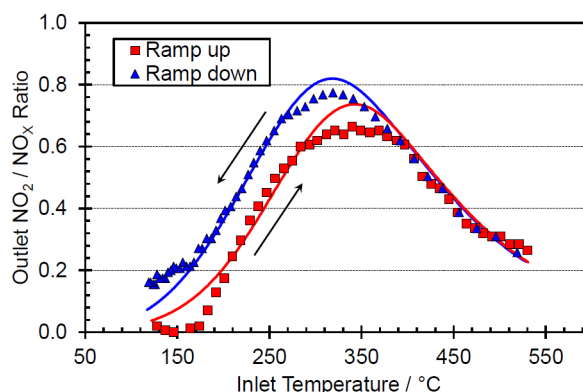


Figure 4. Advanced model for NO oxidation including “oxide effect”: Comparison of measured (points) and simulated (lines) reactor outlet NO₂/NO_x ratio in an experiment where the temperature was ramped up and down. Feed: 4.5% CO₂, 4.5% H₂O, 155 ppm NO, 16% O₂. 5°C min⁻¹ ramp (except at the end of the ramp down).

3.1.2.2. CO Oxidation

Microreactor CO light-off curves for a number of different inlet compositions, together with model predictions for this data, are shown in Fig. 5. Inspection of the measured data (points on the figure) reveal that increasing the inlet O₂ concentration at constant inlet CO concentration shifts the light-off curve to lower temperature, indicating that CO oxidation on this catalyst has a positive order with respect to O₂. Conversely, increasing the CO concentration at constant O₂ concentration shifts the light-off to higher temperature, indicating that CO oxidation is negative order in CO, *i.e.* CO oxidation is inhibited by CO. These conclusions are in agreement with the literature on CO oxidation over both supported [21,24,25] and unsupported [25] PGM catalysts. This suggests a situation on the catalyst surface where CO adsorbs strongly and hence is the dominant species on the catalyst surface, while the surface coverage of oxygen is low / negligible. This figure contains one rich experiment (35000 ppm CO, 1% O₂), typical of an LNT regeneration. Note that once all the O₂ is consumed, no further increase in CO conversion occurs up to 480°C (not shown in the figure) indicating that this catalyst is not active for WGS.

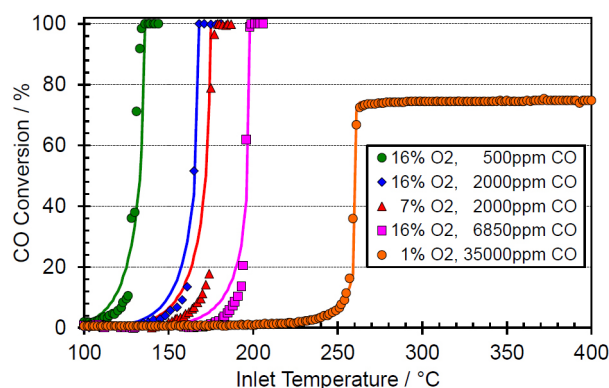


Figure 5. CO oxidation: Comparison of measured (points) and simulated (lines) CO conversion as a function of inlet temperature for microreactor tests with various inlet concentrations. 4.5% CO₂ and 4.5% H₂O was present in all tests.

oxidation kinetics discussed in the previous section which tended to over predict conversion at low conversions.

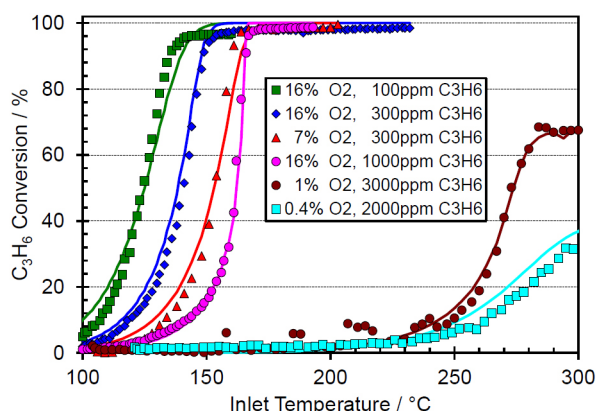
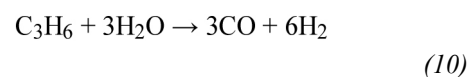


Figure 6. C₃H₆ oxidation: Comparison of measured (points) and simulated (lines) C₃H₆ conversion as a function of inlet temperature for microreactor tests with various inlet concentrations. 4.5% CO₂ and 4.5% H₂O was present in all tests.

Figure 7 shows measured data and model fit for a rich C₃H₆ experiment in more detail. As the temperature is increased, C₃H₆ oxidation causes the C₃H₆ conversion to increase until a plateau is reached at 40% conversion when all the O₂ is consumed. As the temperature is further increased, initially the conversion remains constant before starting to rise again due to reaction by steam reforming, which produces CO and H₂. All of this is well predicted by the model. Initially, it was assumed that steam reforming would produce three CO molecules per C₃H₆ molecule reacted according to:



However, the measured outlet CO/H₂ ratio was considerably higher than the 0.5 predicted by this equation. One explanation for this is that some inter-conversion of CO and H₂ was occurring presumably via the reverse WGS reaction. However, this seems unlikely as the catalyst was not found to be active for WGS (section 3.1.2.2). A more plausible explanation could be that some partial oxidation of C₃H₆ to CO and H₂O is occurring in competition to total oxidation (Eq. 2) at low O₂ concentrations in addition to steam reforming (Eq. 10) resulting in CO and H₂ being formed in the ratio observed. For simplicity, this has been modelled as a single reaction with a stoichiometry equivalent to a combination of steam reforming and reverse WGS (Eq. 3); the reaction has been written with a constant (n_{WGS}) to describe the amount of apparent reverse WGS occurring.

The kinetics developed from this data give a good prediction of the effect of inlet concentration and temperature on CO conversion (Fig. 5). However, except for the rich experiment, there is a tendency to over predict CO conversion when the conversion is below 20%. The authors speculate that this may indicate some change in the surface of the catalyst occurs at the start of the light-off, perhaps similar to the “oxide effect” described in the previous section for NO oxidation, which results in the catalyst becoming more active once light-off is underway. The current kinetics then only describe the more active state of the catalyst that exists once around 20% CO conversion is exceeded. More advanced kinetics may be able to give a good prediction of CO conversion through the whole curve. However, as this discrepancy only affects a small part of the light-off curve, the current kinetics were deemed adequate for this model.

3.1.2.3. Oxidation of Unsaturated HCs

C₃H₆ conversion versus temperature for six different inlet compositions (four lean, two rich), together with model predictions for this data, are shown in Fig. 6. Increasing C₃H₆ concentration at constant O₂ concentration shifts the light-off curve to higher temperature, indicating that C₃H₆ oxidation is inhibited by C₃H₆, while increasing O₂ concentration at constant C₃H₆ concentration shifts the curve to lower temperature, indicating the reaction is positive order in O₂. This is in agreement with the literature for C₃H₆ oxidation on both supported [24,25] and unsupported [25] Pt and Pd catalysts. This suggests a situation on the catalyst surface where C₃H₆ adsorbs strongly (by virtue of its double bond) and hence is the dominant species on the catalyst surface, while the surface coverage of oxygen is low / negligible. The C₃H₆ oxidation kinetics developed from this data give a good fit to the measured data. Note that the prediction is good through the whole light-off curve. This differs from the CO