



# Effect of hydrocarbon species on no oxidation over diesel oxidation catalysts

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## ABSTRACT

The effect of propylene concentration on NO oxidation as a function of temperature and position over a model Pt-Pd/Al<sub>2</sub>O<sub>3</sub> diesel oxidation catalyst was investigated. Propylene had an apparent inhibition effect on NO oxidation. This apparent inhibition is a result of NO<sub>2</sub>, as the NO oxidation product, acting as an oxidant in the reaction with propylene. This was verified with experiments that included NO<sub>2</sub>, and a resulting significant temperature decrease in the onset of NO<sub>2</sub> reduction when propylene was present. Furthermore, increasing amounts of propylene further decreased the NO<sub>2</sub> reduction temperature. Similar results were observed with m-xylene and dodecane addition as well. The results also demonstrate that NO<sub>2</sub> was consumed preferentially relative to O<sub>2</sub> during hydrocarbon oxidation. With low inlet levels of O<sub>2</sub>, the addition of NO<sub>2</sub> apparently inhibited propylene oxidation after the onset of NO<sub>2</sub> reduction. This subsequent inhibition was due to the NO formed, demonstrating that propylene results in reduced NO<sub>2</sub> outlet levels while NO inhibits propylene oxidation.

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## 1. Introduction

With the recently fluctuating fuel prices and focus on fuel efficiency and emissions, there has been an increasing interest in lean-burn engines for passenger vehicles. Lean-burn engines are more fuel efficient than today's standard stoichiometric-burn gasoline vehicles. This increased fuel efficiency also results in lower CO<sub>2</sub> emissions. The challenge is reducing the other emissions, specifically NO<sub>x</sub>, hydrocarbons and CO, and particulate matter in the case of diesel engines. Therefore, there has been increasing research in the area of lean-burn exhaust emissions catalysts.

A common catalyst in many proposed lean-burn and diesel exhaust gas aftertreatment systems is a diesel oxidation catalyst (DOC). Most DOCs are composed of ceramic cordierite or metal monolith supports coated with a high surface area, alumina- or zeolite-based washcoat containing highly dispersed noble metals such as Pt, Pd or a Pt/Pd blend. Compared to Pd, Pt-based DOCs are regarded as more active for oxidation reactions [1]. However, sintering of monometallic Pt DOCs is quicker in an oxygen-rich atmosphere compared to Pt/Pd formulations [2,3], and therefore Pt/Pd catalysts are also studied. It has been speculated that the reason for this improvement is that at temperatures between 300 and 700 °C the alloy undergoes oxidation to produce less mobile

particles on the catalyst surface. This prevents particle growth and maintains the original highly dispersed active site surface area [2].

DOCs perform a range of functions in an integrated emission control system, including oxidation of exhaust hydrocarbons and CO. They also oxidize NO to NO<sub>2</sub>, which is important for efficient performance of various downstream catalysts, such as NO<sub>x</sub> storage/reduction (NSR) catalysts, selective catalytic reduction (SCR) catalysts and diesel particulate filters (DPFs). An NSR catalyst selectively stores NO<sub>x</sub> during lean-phase operation and reduces this stored NO<sub>x</sub> through a short, reductant-enriched (rich) phase. Several studies have proposed that NO<sub>2</sub> is a precursor for, or intermediate in, the trapping process [4–8] and overall, the presence of NO<sub>2</sub> enhances the performance of the NSR catalyst through improved NO<sub>x</sub> storage [9–15]. SCR catalysts selectively reduce equi-molar concentrations of NO and NO<sub>2</sub> to N<sub>2</sub> in the presence of NH<sub>3</sub> at a faster rate than if only NO was available [16]. This observed enhancement in performance with NO<sub>2</sub> is the reason why most NSR and SCR catalyst systems have a DOC installed upstream. DPFs require temperatures of about 500–600 °C to oxidize diesel particulate matter, or soot, with O<sub>2</sub>. However, NO<sub>2</sub> oxidizes soot at temperatures close to 350 °C [17] and thus, most soot filters also have DOCs upstream to facilitate lower temperature soot oxidation.

NO oxidation to NO<sub>2</sub>, however, is limited by kinetics at lower temperatures and by thermodynamics at higher temperatures. NO/NO<sub>2</sub> equilibrium limitations are typically observed above 350 °C in NO oxidation tests [18]. Mulla et al. have studied NO oxidation kinetics over Pt/Al<sub>2</sub>O<sub>3</sub> and NSR catalysts [19,20]. Their studies have demonstrated that the rate is approximately first order each in NO

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and O<sub>2</sub>, but has an approximate negative first order dependency on NO<sub>2</sub>. This product inhibition imposes significant constraint on conversions. NO oxidation inhibition by NO<sub>2</sub> has also been observed over a Pt/SiO<sub>2</sub> catalyst [21]. The inhibition effect has been attributed to the high sticking coefficient of NO<sub>2</sub> on Pt [22,23], preventing other species from gaining access to the surface. Various studies have found that the activity of the catalyst for NO oxidation depends on the size of the Pt particle, where NO oxidation is better with larger particle size. This has been observed with Pt supported on Al<sub>2</sub>O<sub>3</sub> [24–28], SiO<sub>2</sub> [25,26,28] and TiO<sub>2</sub> [29], and suggests that some amount of thermal aging may actually improve NO oxidation performance.

Diesel exhaust contains many pollutants, including unburned hydrocarbons, CO, NO<sub>x</sub> and particulates, all of which are regulated. Depending on their relative affinity towards active catalyst sites, different hydrocarbons show different reactivities [30]. There have been studies which evaluated oxidation of mixtures of volatile organic compounds over Pt-based monolithic catalysts [31,32], however, most studies have evaluated individual hydrocarbons. Of interest for actual application is the study of competitive oxidation reactions over a DOC to understand the influence of various species on the reaction rates of the others. As an example, in H<sub>2</sub>/CO oxidation, the addition of H<sub>2</sub> to a gas mixture containing CO causes a reduction in the light-off temperature of CO. It has been reported that H<sub>2</sub> enhances desorption of CO from Pt [33].

Another area that has not gained much attention is the effect of various hydrocarbons on NO oxidation and vice versa. One study [34] has reported that increasing the amount of either CO, NO or propylene lowers the oxidation conversions of both CO and propylene. However, the CO and propylene inhibition effect decreased with temperature while that of NO increased with temperature. Katare et al. [35] found a significant delay in NO oxidation light-off and a lower amount of NO<sub>2</sub> produced over a DOC, in the presence of hydrocarbons and CO, which they attributed to the competition between CO, hydrocarbons and NO for NO oxidation sites. In a subsequent study [36], the effect of hydrocarbons and CO on NO oxidation over a commercial DOC was investigated and the authors showed that with aged DOCs, reductants can facilitate the complete reduction of product NO<sub>2</sub> back to NO. They concluded that only once all the reductants were consumed, did the NO oxidize back to NO<sub>2</sub>. These findings indicated that for aged DOCs, as long as hydrocarbons and CO are present in the exhaust, NO<sub>2</sub> can be consumed by the DOC, thus hindering the performance of the downstream devices. NO<sub>2</sub> reduction, and therefore the observed NO oxidation conversion, is also affected by the presence of CO, individually and together with propylene [4]. Over an NSR catalyst, CO reduced NO<sub>2</sub> to NO at temperatures > 100 °C, thus decreasing the amount of NO<sub>x</sub> stored on the surface. However, when propylene was present along with CO at low temperature, NO<sub>2</sub> reduction was actually inhibited, thus improving NO<sub>x</sub> storage.

In this study, NO and hydrocarbon oxidation experiments were run. These experiments were performed with different gas mixtures to evaluate the effects of hydrocarbons on NO oxidation and NO on hydrocarbon oxidation. To better understand the mechanism behind the observed hydrocarbon effects on NO oxidation, experiments were also run with NO<sub>2</sub>.

## 2. Experimental

A monolith-supported Pt-Pd/Al<sub>2</sub>O<sub>3</sub> sample with 8 g/ft<sup>3</sup> loading, of 1:2 Pt:Pd, was used in these experiments. The sample was 35 mm in length and 20.4 mm in diameter. The sample was “aged” for 16 h at 650 °C in an air/steam mixture. The reactor consisted of a horizontal quartz tube placed inside a temperature-controlled furnace. The catalyst was wrapped with high-temperature 3 M

Interam matting material to cover the gap between the catalyst and the reactor wall to ensure that no gas slipped around the sample. K-type thermocouples were used to measure temperatures at the inlet face of the catalyst, the outlet face of the catalyst and ~5 cm upstream of the sample.

The feed stream during the experiments contained different concentrations of gases including NO, NO<sub>2</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>8</sub>H<sub>10</sub> and C<sub>12</sub>H<sub>26</sub>. Oxygen and H<sub>2</sub>O were included in all experiments, with N<sub>2</sub> as the balance gas. The gas flow rate used was 19.06 L/min (equivalent to a space velocity of 100,000 h<sup>-1</sup>). In comparing experiments with and without CO<sub>2</sub>; no influence on the oxidation reaction rates was observed and hence CO<sub>2</sub> was not included in the feed stream in order to simplify mass spectrometer data analysis. Gases and gas mixtures were supplied by Praxair and were metered via calibrated Bronkhorst mass flow controllers. The mixture of gases excluding carbon-containing molecules and some N<sub>2</sub> was sent through a high-capacity furnace, achieving the target test temperature prior to entering the tube furnace holding the sample. This minimized any artificial axial and radial temperature gradients during experiments. Dodecane or m-xylene (laboratory grade supplied by Fisher Scientific) was injected into the quartz tube reactor using a Bronkhorst High-Tech series E-7000 Controlled Evaporator Mixer (CEM) system and part of the total N<sub>2</sub> flow as the carrier gas; it was not input upstream of the high-capacity furnace. When propylene was used, it was also introduced with the small amount of carrier N<sub>2</sub> directly into the tube reactor. This avoided any reactions between the carbon-containing species and O<sub>2</sub> on the hot, upstream steel tubing. Dodecane injection began at a catalyst temperature of about 120 °C. The gases exiting the reactor were maintained at >120 °C to avoid condensation.

For all experiments, the exiting gas compositions were measured using a MKS MultiGas 2030 FT-IR analyzer at approximately a 2 Hz collection rate. CO, CO<sub>2</sub>, NO, NO<sub>2</sub>, N<sub>2</sub>O, NH<sub>3</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>8</sub>H<sub>10</sub>, C<sub>12</sub>H<sub>26</sub> and H<sub>2</sub>O concentrations were measured. Preliminary tests verified accuracy of the concentrations of the NO, NO<sub>2</sub>, N<sub>2</sub>O and C<sub>3</sub>H<sub>6</sub> to <±2 ppm. In this work, both temperature programmed oxidation (TPO) as well as spatial resolution experiments at a steady-state inlet temperature (further described below) were performed. During each TPO experiment, the catalyst temperature was ramped at a rate of approximately 7.5 °C/min. Initially, tests with no reactant gases were performed and demonstrated that there was a maximum of 4 °C difference between the front and back of the sample during the temperature ramps. In the data shown below, the x-axis temperature is that of the upstream thermocouple, thereby avoiding complications from exotherm-generated heat on or in the sample. Dodecane cracking upstream of the catalyst was observed just above 300 °C via the mass spectrometer during preliminary temperature ramps and hence the results for the temperature ramps that included C<sub>12</sub>H<sub>26</sub> are shown only to these temperatures.

Spatially resolved capillary-inlet mass spectrometry (SpaciMS) [37,38] was also used to characterize the reactions. During these experiments, a fixed inlet temperature was established and then a silica capillary, I.D. = 0.3 mm and O.D. = 0.43 mm, placed within one of the radially central channels was pulled to different positions within the catalyst channel to measure the gas species concentrations as a function of catalyst length. This was then repeated at a different temperature. The capillary was connected to a Hiden Analytical HPR 20 QIC mass spectrometer. Outside of the reactor, the capillary was heated along its entire length to avoid condensation. The gases measured by the mass spectrometer were; H<sub>2</sub>O, NO, NO<sub>2</sub>, O<sub>2</sub>, C<sub>3</sub>H<sub>6</sub> and CO<sub>2</sub>. In the figures below, the conversions of NO, NO<sub>2</sub> and C<sub>3</sub>H<sub>6</sub> are plotted. The MKS 2030 FT-IR was also used to verify calibration accuracy of the data measured by the mass spectrometer.

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