

Removal of Hydrocarbons and Particulate Matter Using a Vanadia Selective Catalytic Reduction Catalyst: An Experimental and Modeling Study

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ABSTRACT

The use of vanadia selective catalytic reduction (V-SCR) catalysts for NO_x reduction from diesel engine exhaust is well known. These catalysts are also active for hydrocarbon (HC) and particulate matter (PM) oxidation. This dual functionality (oxidation and reduction) of V-SCR catalysts can help certain applications achieve the legislative limits with an improved margin.

In this work, NO_x reduction, HC and CO oxidation over V-SCR were studied independently and simultaneously in microreactor tests. The effect of various parameters (HC speciation, concentration, ANR, and NO₂/NO_x ratio) was investigated and the data was used to develop a kinetic model. Oxidation of CO, C₃H₆, and n-C₁₀H₂₂ is first order in CO/HC, while C₇H₈ oxidation is less than first order in C₇H₈. All these reactions were zero order in O₂. Oxidation activity decreased in order: C₇H₈ > n-C₁₀H₂₂ > C₃H₆ > CO. HC oxidation was inhibited by NH₃. The presence of HCs was found to inhibit NO_x conversion, but only after the HC had started to react. This can be explained by NO_x reduction being inhibited not by the HC itself, but by the CO produced from partial oxidation of the HC.

The V-SCR catalyst was also tested on a diesel engine in the absence of an upstream DOC and DPF to investigate its performance. The results confirm that V-SCR can remove HC and PM effectively: for temperatures above 230°C, V-SCR showed 45-75% HC conversion and 20-60% PM

removal, under the specific engine conditions tested. This data was used to validate the kinetic model.

1. INTRODUCTION

The diesel engine is integral to the transportation, construction and agricultural sectors owing to its power output, reliability and fuel efficiency. However, diesel engines can contribute to air pollution by emitting unburnt hydrocarbons (HC), particulate matter (PM) and nitrogen oxides (NO_x). To address this issue, strict emission standards have been introduced in several countries that minimize these exhaust pollutants.

The use of catalytic diesel exhaust aftertreatment systems is one strategy implemented by engine OEMs to meet the stringent emission standards, while maintaining peak operating efficiency. Typical exhaust aftertreatment systems may be comprised of a diesel oxidation catalyst (DOC) for the oxidation of HCs and carbon monoxide, a catalyzed soot filter to trap and oxidize PM, a selective catalytic reduction (SCR) catalyst or a lean NO_x trap for NO_x reduction and an ammonia slip catalyst to selectively oxidize ammonia to N₂, or combinations thereof [1,2].

The reduction of NO_x over vanadia SCR catalysts with NH₃ to meet emission regulations is well known and has been the subject of extensive reviews [3, 4, 5]. V-SCR catalysts are also active for the oxidation of HC and PM. Previous work has shown that volatile organic compounds (VOCs) [6, 7, 8, 9] and PM [8,10, 11, 12] are oxidized over V-SCR catalysts. The work on VOC oxidation has focused on the removal of

individual VOCs, rather than on the removal of total hydrocarbon (THC). Regarding PM oxidation, it has been shown that V-SCR catalysts are active for the oxidation of not just the volatile fraction of the PM, but also the elemental carbon [11,12]. In this study, the simultaneous oxidation of THC and PM and reduction of NO_X on V-SCR catalysts has been investigated.

The objective of the present study is to investigate the oxidation of HC and PM on V-SCR in the absence and presence of NO_X and NH₃. Bench scale reactor data will be presented showing the effect of temperature, space velocity and feed gas composition on the oxidation of CO and HCs (C₃H₆, C₇H₈, *n*-C₁₀H₂₂). Steady-state and transient (non-road transient cycle (NRTC)) engine testing will also be presented demonstrating the HC, PM and NO_X conversions that are possible in real systems. The reactor data was used to develop a kinetic model showing the interaction between the SCR and oxidation reactions, while the engine data was used for model validation.

2. EXPERIMENTAL

2.1. Samples

All tests were carried out on commercial vanadia based SCR catalysts. Two 10.5 (diameter) × 6in (266.7 × 152.4mm), 400/4.3 (620 000 cells/m², 0.11 mm wall thickness) parts in series were used for both steady-state and transient engine testing. Reactor testing was done on a 1 (diameter) × 3in (25.4 × 76.2mm) core taken from another 400/4.3 part. Samples used for reactor testing were hydrothermally aged for 100 h at 500°C in 10% H₂O, while samples for engine testing were engine aged at 550°C for 150 h. These agings result in catalyst samples with comparable catalytic activity.

2.2. Reactor Testing

Laboratory reactor data were collected using a stainless steel reactor. The flows of reactant gases and diluent (N₂) were controlled by mass flow controllers. Most data were collected at a space velocity of 50 000 h⁻¹, but some experiments were done at 80 000 h⁻¹ to study the effect of space velocity. All tests were run with 5.0% CO₂ and 7.0% H₂O in the gas feed, since these gases are always present in vehicle exhaust. Low concentrations of C₇H₈ (<35ppm) were introduced into the reactor from a cylinder of C₇H₈ in N₂. Higher concentrations of C₇H₈, as well as *n*-C₁₀H₂₂ and H₂O, were introduced using thermostated saturators. Heated lines were used to deliver gas from the reactor exit to the analyzers. O₂ was analyzed using a magnetopneumatic analyzer, THC using a flame ionization detector; other components were analyzed using an FTIR bench.

Analysis of oxygenates that might be produced by partial oxidation of the HCs was not possible. Comparison of HC conversions calculated from the THC analyzer and from the FTIR analysis of the HC reacting suggests that, depending on temperature, conversion of up to 5% C₃H₆ and up to 10% C₇H₈ and C₁₀H₂₂ to oxygenates cannot be excluded. HC conversion was calculated from the THC analyzer measurement.

Steady-state conversions were measured at temperatures between 150 and 500°C. The reactor was held at each temperature for an extended period of time (typically around 15min) to ensure steady-state was reached.

2.3. Engine Bench Testing

Engine testing was done using standard procedures and equipment. Ultra low sulfur diesel fuel was used during all tests. Emissions were measured before and after the SCR. NH₃ was supplied in the form of an aqueous urea solution injected in front of the SCR catalysts using an air-assisted doser. A static mixer was placed after the urea injector to maximize urea mixing and to facilitate decomposition/hydrolysis to NH₃.

2.3.1. Steady-state tests

Steady-state tests were carried out on a Tier 3, 9L, diesel engine. The test cell was equipped with an eddy current dynamometer rated to 1000 hp (746 kW). Exhaust emissions were measured using a Horiba MEXA 7100D Series bench and a MKS 2030-HS Series FTIR. In addition, a heated flame ionization detector was utilized to measure HCs. These analyzers could sample either at the engine out or SCR out positions. SCR catalysts were evaluated on a 7-point steady-state test. For each mode, emissions were first sampled before the catalyst and then after the catalyst, before moving onto the next mode. The tests were carried out on two 10.5 × 6in SCRs in series; no DOC or other catalyst component was present in the system. The SCR inlet temperature and gas hourly space velocity were varied from 200-370°C and 24 000-72 000 h⁻¹ (based on SCR volume), respectively.

Two tests were run, one without urea dosing and the other with urea dosing at ANR=1.0. PM measurements were made before and after the SCR catalyst in the test without urea dosing only. In this test, each mode was run for 15 min, with PM collection during the final 5 min. In the ANR=1.0 test, each mode was held for 30-60 min. PM measurements were not made in this test to avoid any complication with urea byproducts being collected with the PM.

Exhaust particulate matter samples were collected utilizing an AVL 472 SPC Micro Tunnel with a 0.02 sampling ratio for 5 min for each steady-state test point. PM was collected on a 47 mm TX40H120-WW Emfab filter and gravimetrically analyzed following the CFR 40 procedure [13].

the weight of PM at the engine exhaust (SCR inlet) and SCR outlet for each test point.

2.3.2. Transient tests

NRTC tests [14] were run on a 2007, 9L diesel engine. Five repeat tests were performed. There was a 20 min soak after each of the first two NRTCs; three subsequent tests were run consecutively, without soak. The first NRTC test is termed a “cold” test, the second a “warm” test and the subsequent tests “hot” tests.

Before the first NRTC, the catalyst was preconditioned by running a C100 mode without urea injection for at least 30 min to desorb any stored NH₃; the NH₃ concentration at the SCR outlet was measured during this process to verify all the NH₃ had been removed. The engine was allowed to cool until the SCR bed temperature reached 50°C before running the first test.

Emissions were measured using a Horiba Mexa 7400D Series bench at the engine out and SCR out positions and an MKS 2030-HS FTIR at the SCR out position. The data from the Horiba bench was used to calculate the CO, THC and NO_x conversion across the SCR. FTIR data was used to determine N₂O formation, and NH₃ slip.

PM was measured using a full dilution tunnel. A set of straight pipe NRTCs was run to determine the engine out PM followed by a second set of NRTCs with the SCR catalyst installed, in order to determine the PM reduction across the SCR catalyst. Urea was injected with the SCR catalyst installed. The PM was measured on 47mm TX40H120-WW Emfab filter using a full flow dilution tunnel that utilizes a Horiba particulate sampling system. The filter was conditioned in the cleanroom for 8 h prior to performing the blank weight, following the CFR Section 40 protocol [13]. The filter was put into a filter holder that goes to the Horiba secondary dilution box. The box temperature was controlled to 47°C. Both secondary total sampling flow and the secondary dilution air flow were carefully selected to ensure the filter face temperature was within the 47±0.5°C range. The filter face temperature was also monitored throughout the entire test. After the test, the filter was put back to the cleanroom and was stabilized for 8 hours before taking the final weight.

2.4. Computer Simulation

Computer simulations were carried out using a one-dimensional model for a monolith reactor, which is described in more detail elsewhere [15]. 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 manufacturer's datasheets

with allowance made for the washcoat. The V-SCR kinetics used were based on those from previous models [16,17]. When simulating engine tests, the formation of NH₃ from urea was assumed to be instantaneous.

Kinetic parameter optimization 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 [18,19] were used to describe the kinetics of CO and HC oxidation, while Eley-Rideal rate equations [18,19] were used for the SCR reactions. Apart from C₇H₈ oxidation, the Langmuir-Hinshelwood rate equations used would be mathematically equivalent to Mars-Van Krevelen rate equations [20,21] over much of the conditions used in this work. The exact form of the rate equations was decided on the basis of what best fitted the reactor data, rather than using equations taken from the literature.

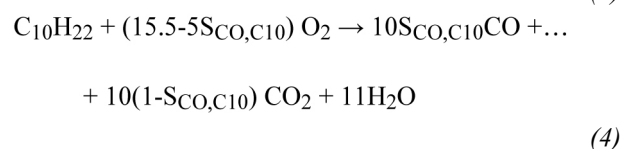
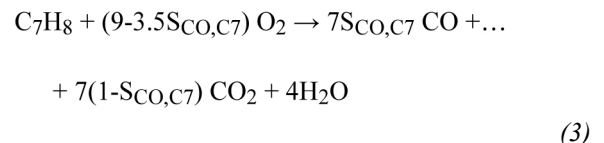
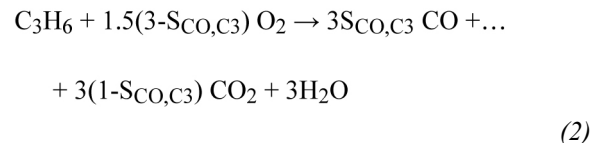
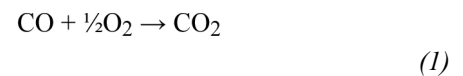
3. RESULTS AND DISCUSSION

3.1. Reactor Data and Model Development

3.1.1. CO and HC oxidation (in the absence of NH₃ and NO_x)

In this section reactor data for CO and HC oxidation in the absence of NH₃ and NO_x (*i.e.* SCR reactions) will be presented. The dependencies of these reactions on reactant concentration will be discussed and the relative activity of different reactants (CO, C₃H₆, C₇H₈, *n*-C₁₀H₂₂) compared. In addition, the development of reaction kinetics for these reactions will be covered.

The CO and HC oxidation reactions included in the model are listed below:



All of the HCs tested (C₃H₆, C₇H₈, *n*-C₁₀H₂₂) were found to exhibit partial oxidation, *i.e.* a mixture of CO and CO₂.

formed, rather than total oxidation, *i.e.* with only CO_2 being formed. Thus, the rate equations for HC oxidation (Eq. 2, 3, 4) contain a term for the selectivity of these reactions to CO, $S_{\text{CO,CX}}$. Note that CO formed from these reactions (Eq. 2, 3, 4) can oxidize further to CO_2 by Eq. 1. Thus the observed selectivity to CO at the reactor exit will decrease with increasing contact time if O_2 is available and will likely be smaller than $S_{\text{CO,CX}}$; $S_{\text{CO,CX}}$ should be regarded as the selectivity to CO at zero contact time.

The conversion of CO as a function of inlet temperature for three different inlet gas compositions is shown in Fig. 1. Analysis of the data shows that changing the gas composition has no obvious effect on the conversion, suggesting that the reaction is first order in CO and zero order in O_2 over the range of concentrations investigated. This is consistent with a mechanism in which CO reacts directly from the gas phase with oxygen on the catalyst surface. It is likely that this surface oxygen is actually lattice oxygen from the vanadia [20, 21, 22]. Reaction of lattice oxide results in the oxide being reduced; the fact that the reaction is zero order in O_2 suggests that reoxidation of the vanadia is rapid [21].

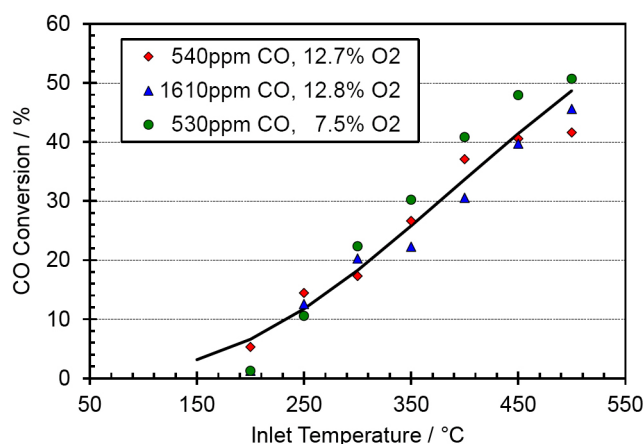


Figure 1. CO oxidation: Comparison of measured (points) and simulated (line) CO conversion as a function of inlet temperature for reactor tests with various inlet concentrations. The same simulated line applies for all concentrations. 5.0% CO_2 and 7.0% H_2O was present in all tests. 50 k h^{-1} space velocity.

A comparison of the measured conversion (points) with that predicted by the model (line) can be seen in Fig. 1. The measured data for the three gas compositions can be represented by a single simulated line, further indicating that the reaction is first order in CO and zero order in O_2 .

Data for C_3H_6 oxidation at two space velocities (50 and 80 k h^{-1}) is shown in Fig. 2. This is shown in two parts, with total C_3H_6 conversion (*i.e.* to both CO and CO_2) in the top pane and C_3H_6 conversion to CO in the lower pane. The

conversion of HC to CO was calculated as the outlet CO concentration divided by the inlet HC concentration on a C_1 basis. When data measured at the same space velocity is compared, it is clear that both total conversion and conversion to CO is unaffected by both the C_3H_6 and O_2 concentrations, *i.e.* C_3H_6 oxidation is first order in C_3H_6 and zero order in O_2 . As expected, both total C_3H_6 conversion and conversion of C_3H_6 to CO decrease with increasing space velocity.

It is worth comparing the CO and C_3H_6 oxidation data (Fig. 1, 2). The most obvious difference is that the CO data shows much more scatter than the C_3H_6 data. It seems that the rate of CO oxidation is less stable than that of C_3H_6 oxidation.

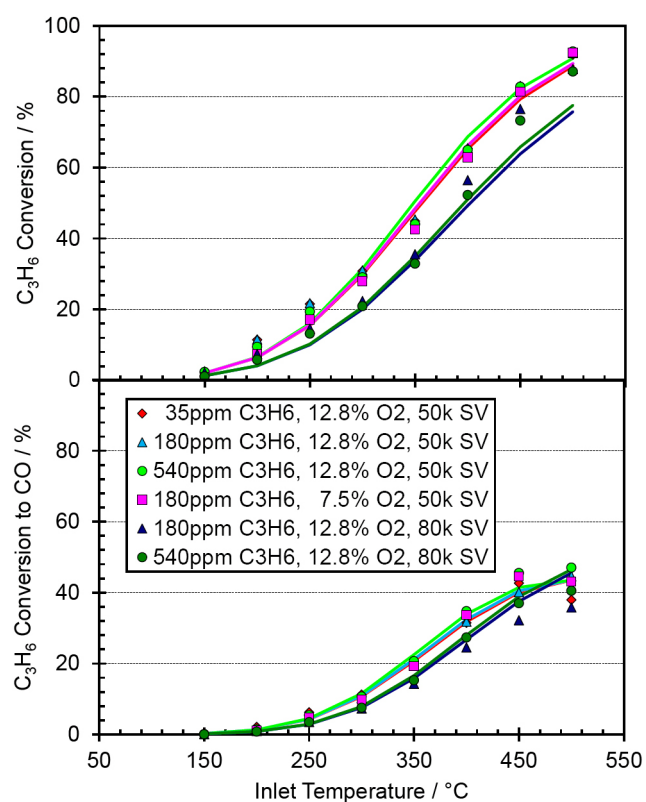


Figure 2. C_3H_6 oxidation: Comparison of measured (points) and simulated (lines) total C_3H_6 conversion (top) and C_3H_6 conversion to CO (bottom) as a function of inlet temperature for reactor tests with various inlet concentrations and for two space velocities (50 and 80 k h^{-1}). 5.0% CO_2 and 7.0% H_2O was present in all tests.

The other difference is that the catalyst is much more active for C_3H_6 oxidation than for CO oxidation, *e.g.* at 500°C , 90% C_3H_6 conversion is achieved, while the CO conversion is less than 50% at the same temperature. This differs from Platinum Group Metal (PGM) based catalysts, where activity for CO and C_3H_6 oxidation is more comparable [23]. The relatively low activity of vanadia for CO oxidation is presumably why

C_3H_6 is only partially oxidized, even though excess O_2 is present. Another potential explanation of this limit in activity could be the ready availability of lattice oxygen from the vanadia species: more oxygen is required to convert a molecule of C_3H_6 to CO_2 , and even more to convert a molecule of $C_{10}H_{22}$, thus availability of oxygen from the lattice makes it difficult to get to complete HC oxidation, leading to CO production. Both CO and C_3H_6 exhibit the same kinetics, *i.e.* first order in reductant (CO or C_3H_6) and zero order in O_2 .

When modeling the oxidation of C_3H_6 (and other HCs) it was found that the selectivity to CO before any further oxidation of CO occurs, $S_{CO,Cx}$, could be described by a sigmoidal function of the form:

$$S_{CO,Cx} = 1/(1 + \exp(-A(T_S - T_m))) \quad (5)$$

where T_S is the catalyst temperature in K and A and T_m are constants; T_m is the temperature at which $S_{CO,Cx}=0.5$. $S_{CO,Cx}$ was found to increase with temperature.

Figure 2 also shows the model prediction of C_3H_6 oxidation. Kinetic parameters were optimized using the $50k\ h^{-1}$ space velocity data only; the $80k\ h^{-1}$ data was used to verify the ability of the model to predict the effect of flow rate. Generally, the model predictions are good, but the model does under predict total conversion and over predict conversion to CO at 450 and $500^\circ C$ for the $80k\ h^{-1}$ data. This discrepancy may be due to experimental error or because something different is happening on the catalyst at these high temperatures, which is not captured by the model. However, the overall model prediction for both the total C_3H_6 conversion and the conversion to CO are satisfactory.

It is notable in Fig. 2 that the predicted conversion for a given temperature and space velocity increases slightly with increasing C_3H_6 conversion, despite the rate equation being first order in C_3H_6 . This is due to the heat generated by the reactions. This was verified by setting the heat of C_3H_6 oxidation in the model to zero, which resulted in the same simulated conversions for all compositions.

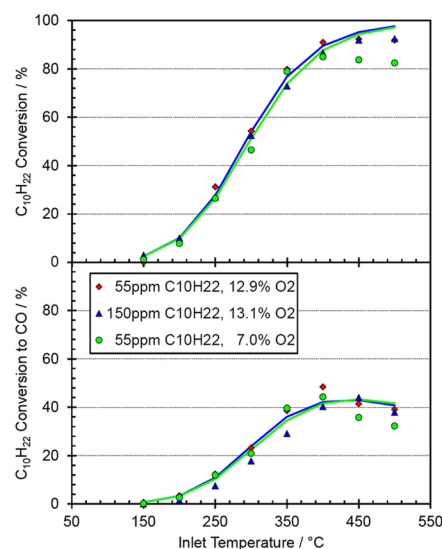


Figure 3. n - $C_{10}H_{22}$ oxidation: Comparison of measured (points) and simulated (lines) total $C_{10}H_{22}$ conversion (top) and $C_{10}H_{22}$ conversion to CO (bottom) as a function of inlet temperature for reactor tests with various inlet concentrations. Note that the simulated lines for 55ppm $C_{10}H_{22}$ lie on top of each other. 5.0% CO_2 and 7.0% H_2O was present in all tests. $50k\ h^{-1}$ space velocity.

Measured and simulated n - $C_{10}H_{22}$ conversions are compared in Fig. 3. As with C_3H_6 , the conversion is not significantly affected by the inlet concentrations, indicating that $C_{10}H_{22}$ oxidation is first order in the HC and zero order in O_2 . The model generally gives very good prediction to the data, with the only discrepancy being over prediction of the conversion at $450^\circ C$ for the 7% O_2 data and at $500^\circ C$ for all concentrations. This requires further investigation and is outside the scope of this work.

C_7H_8 oxidation (Fig. 4) exhibits slightly different behavior to CO, C_3H_6 and $C_{10}H_{22}$ (Fig. 1, 2, 3, respectively) in that the conversion decreases slightly with increasing C_7H_8 concentration instead of being unchanged, indicating that C_7H_8 oxidation is less than first order in C_7H_8 ; closer analysis of the data reveals that the reaction is between zero and first order in C_7H_8 . The different behavior seen with C_7H_8 is not due to higher C_7H_8 concentrations being used compared to the other HCs; the maximum CO and HC concentrations used are much the same on a C_1 basis for all species (approx. 1600 ppm C_1). This order of reaction suggests that C_7H_8 adsorbs on the surface, perhaps by virtue of the delocalized electron cloud of the aromatic ring. The observed order of reaction is not believed to be due to coking as the conversion at each temperature was generally observed to be constant over the period of measurement (approx. 15min). C_7H_8 oxidation, however, like

oxidation, is unaffected by the O_2 concentration, indicating that the reaction is zero order in O_2 . The model generally gives an excellent prediction of the measured data (Fig. 4).

A comparison of the conversion of CO and all three HCs at approximately the same reductant concentration on a C_1 basis is shown in Fig. 5. It is clear that these species exhibit a wide range of activity with the activity decreasing in the order:

$$C_7H_8 > n-C_{10}H_{22} > C_3H_6 > CO$$

It is intriguing that this order is nearly opposite of that observed with a Pt or Pt-Pd based DOC for reactants oxidizing in isolation (*i.e.* without inhibition by species not involved in the reaction) at comparable concentrations, *viz.* $CO \approx C_3H_6 > C_7H_8 > n-C_{10}H_{22}$ [15,23]. In this sense, vanadia and PGM based catalysts could be regarded as complementary; the species slipped most by one catalyst are most easily removed by the other. Thus a PGM containing NH_3 slip catalyst could not only control NH_3 slip, but also CO and HC slipping from the SCR.

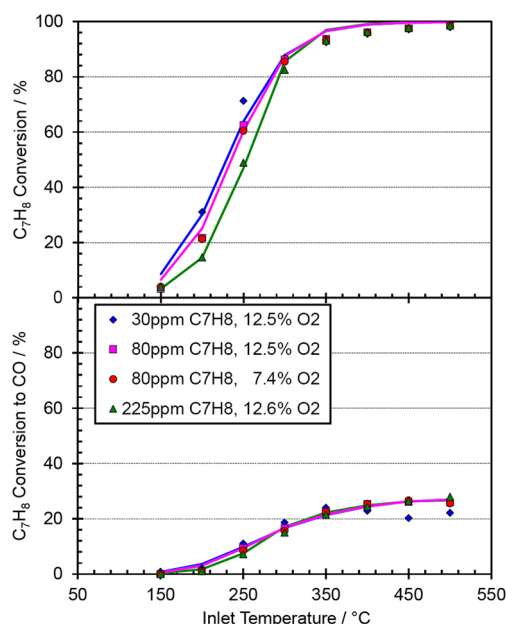


Figure 4. C_7H_8 oxidation: Comparison of measured (points) and simulated (lines) total C_7H_8 conversion (top) and C_7H_8 conversion to CO (bottom) as a function of inlet temperature for reactor tests with various inlet concentrations. Note that the simulated lines for 80ppm C_7H_8 lie on top of each other. 5.0% CO_2 and 7.0% H_2O was present in all tests. $50k\ h^{-1}$ space velocity.

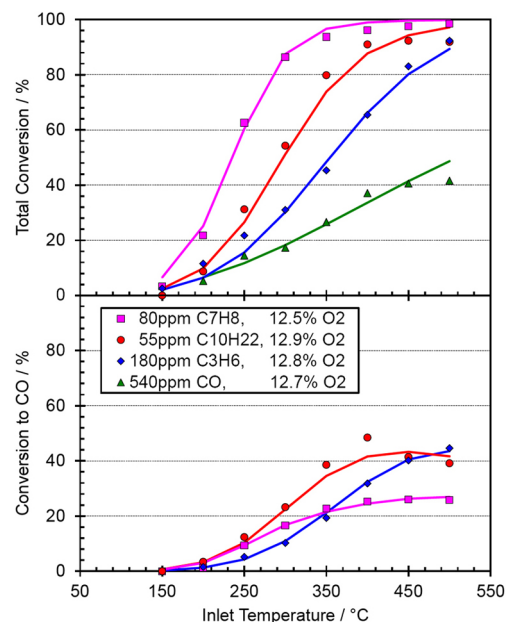


Figure 5. Comparison of CO and HC oxidation activities. All data is for approx. 540ppm C_1 . Points are measured, lines simulated. Total conversion (top) and conversion to CO (bottom). 5.0% CO_2 and 7.0% H_2O was present in all tests. $50k\ h^{-1}$ space velocity.

The selectivity of HC oxidation to CO formation also depends on the HC (Fig. 5, bottom). C_7H_8 has the lowest selectivity to CO; while it exhibits the highest total conversion at all temperatures it produces the least amount of CO of all the HCs per number of carbon atoms reacting.

The other feature of note in Fig. 5 is the way the HC to CO conversion curves for C_7H_8 and $C_{10}H_{22}$ flatten and even start to decrease with increasing inlet temperature as the total HC conversion approaches 100%. This is due to CO formed from HC oxidation being further oxidized to CO_2 (Eq. 1); if the CO oxidation reaction is turned off, the model predicts the conversion of HC to CO to continue to rise with increasing temperature. The curve for C_3H_6 conversion to CO does not flatten to the same extent as the other two curves, since the total C_3H_6 conversion barely approaches 100%.

3.1.2. The interaction between HC oxidation and SCR

In the previous section, oxidation of CO and HC was studied in the absence of SCR reactivity, *i.e.* in experiments without NH_3 and NO_x in the feed gas. In this section the impact of SCR on HC oxidation and *vice versa* will be studied.

The reaction scheme for the SCR part of the model used is given below:

