

A Three-Parameter Transient 1D Catalyst Model

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ABSTRACT

Interactions between in-cylinder combustion and emission aftertreatment need to be understood for optimizing the overall powertrain system. Numerical investigations can aid this process. For this purpose, simple and numerically fast, but still accurate models are needed for in-cylinder combustion and exhaust aftertreatment. The chemical processes must be represented in sufficient detail to predict engine power, fuel consumption, and tailpipe emission levels of NO_x, soot, CO and unburned hydrocarbons. This paper reports on a new transient one-dimensional catalyst model. This model makes use of a detailed kinetic mechanism to describe the catalytic reactions.

A single-channel or a set of representative channels are used in the presented approach. Each channel is discretized into a number of cells. Each cell is treated as a perfectly stirred reactor (PSR) with a thin film layer for washcoat treatment. Heat and mass transport coefficients are calculated from Nusselt and Sherwood laws. Either detailed or global surface chemistry is applied in the thin film layer. Three global parameters are used to align the detailed chemistry model with a given catalyst topology and composition; one parameter for heat transfer, one for mass transfer and one for overall reaction efficiency. This allows considering detailed surface chemistry, molecular diffusion and heat conductivity while maintaining affordable CPU time. Detailed, usually unknown, specifications of the catalyst material are insignificant for the presented approach.

The models' applicability is demonstrated for a single-channel of a NO_x-storage catalyst (NSC). The detailed

surface chemistry by Koop and Deutschmann is utilized. Good agreement between experimental data and model results is achieved. The investigation of surface site fractions shows, that CO and C₃H₆ from exhaust gases inhibit NO oxidation by the same process; in both cases surface bound CO blocks the sites for NO oxidation. The inhibition effect is mainly determined by the total concentration of carbon atoms contained in CO and HC in the exhaust stream. Oxidation by surface bound oxygen was further found to be the major pathway for HC conversion. The lasting inhibition effect of unburned hydrocarbons on NO oxidation was studied by a transient calculation. In this test a sudden cutoff of unburned hydrocarbons in the exhaust stream was assumed. The response time for NO oxidation was found to be 5.5 seconds. The high response time proves the necessity of using a transient model of sufficient detail to simulate catalytic oxidation during transient engine processes or under cyclic variations.

INTRODUCTION

More stringent emission regulations focus powertrain research and development on exhaust aftertreatment systems. These systems are of increasing complexity and can be understood as a series of chemical reactors. One or more catalytic exhaust converters are the central reactors in the aftertreatment system. The catalyst performance is highly temperature dependent, especially if the temperature is close to the catalyst's light off temperature. Low temperature combustion strategies, lean operation, or hybrid strategies result in low exhaust gas temperatures. This influences the efficiency of the catalyst, and it is necessary to gain an essential understanding of the response of the aftertreatment

system on engine parameters. These parameters also include in-cylinder variations during transient load cycles or cyclic variations. Numerical modeling is a cost effective way to study engine and aftertreatment processes. Thus simple and numerical fast but still accurate models for the aftertreatment system are desired. For this purpose, 1D models are suitable.

Several physical models for catalysts, ranging from very simplistic 1D models to detailed 3D models, have been presented in the literature. A detailed review of 1D models developed until 2004 is discussed in [1]. We emphasize [reference \[2\]](#) for a description of mathematical models (1D, 2D, 3D) before 2008. The state of lean exhaust gas catalysis modeling until 2008 is reported in [reference \[3\]](#).

Global reaction mechanisms are used in most of the 1D catalyst models to describe the gas phase and surface chemistry (e.g. [4, 5, 6, 7]). Active site blocking is modeled through inhibition factors. Individual species oxidation is well described in these models. However, complex interactions between the different exhaust gas components cannot be considered. Furthermore, the range of model validity is dependent on the parameter interval that was used for the global chemistry parameter optimization [8]. Detailed gas phase and surface reaction mechanisms describe, on the other hand, the process on a molecular level. This approach has the potential of predicting the catalyst behavior over wide ranges of external conditions (gas composition, pressure and temperatures). States and processes outside the range of available experimental data can also be studied. The response of the catalyst on fast exhaust gas variations in transient engine cycles is one example for this. Complicated cross-dependencies of emissions can be studied, by examining the reaction flux of surface reactions. The purpose of this work is combining a detailed mechanism for surface chemistry with a CPU efficient 1D model, employing a limited number of user parameters. This model is easy-to-use and capable for detailed studies of the chemical kinetics in catalysts during steady state and transient processes. 1D catalyst models, employing detailed reaction mechanisms, are scarce in literature. Koci et al [9] used a microkinetic model for three-way-catalyst monolith converter. Mladenov et al. recently compared [10] different 1D, 2D and 3D models using detailed surface chemistry [11]. Earlier work combines global reaction mechanisms with species storage models e.g. [12], [13], [14].

This paper presents a transient 1D catalyst model using the thin film layer approach. A representative channel model is the base of the approach. However, calculations discussed in the paper consider only single channels. The model formulation and implementation is flexible and various needs in calculation speed and model accuracy can be accomplished. Both global and detailed surface chemistry can be applied, including or excluding gas phase chemistry.

Effectiveness modeling to account for internal diffusion can be selected.

Each catalyst type has a different morphology, geometry and species composition, which greatly affects the conversion efficiencies. The detailed chemical mechanism does not include any information concerning the catalyst's morphology or geometry. Detailed modeling of the washcoat morphology and surface species composition is very rigorous. These models are CPU demanding and extensive user input information is needed. In this work a simplified effectiveness factor model is used, which introduces one user defined parameter for the overall reaction rate effectiveness. This parameter is adjusted for the investigated catalyst by the help of experimental data. The CPU demand of this approach is low.

Heat and mass transfer coefficients are calculated from boundary layer theory. The Sherwood and Nusselt laws considered for this paper assume single first order surface reaction, uniform catalyst coating and smooth tube walls. The usage of these laws is limited for complex chemical systems. Furthermore, corners rounded due to the coating technology affect the transport between surface and bulk gas. The deficiency of the available Sherwood and Nusselt laws is considered in a user defined correction factor.

In this work the 1D modeling approach with detailed chemistry [11] and user parameters for overall effectiveness and heat and mass transport is tested for a steady state flow in a flat-bed catalytic reactor. The chemical processes are analysed and a sensitivity study on model parameters is performed. Finally, the transient model response on sudden changes of the exhaust conditions is investigated and the response time of the catalyst is reported. For this the steady state conditions of the available experiments have been applied successively.

MODEL DESCRIPTION

The catalyst is modeled by a number of representative channels in which gas and surface properties are calculated as functions of axial distance. Heat conduction between the channels is calculated. In this article a single-channel model is used. Thus the heat conduction model has been deactivated for this work, and will not be discussed in detail.

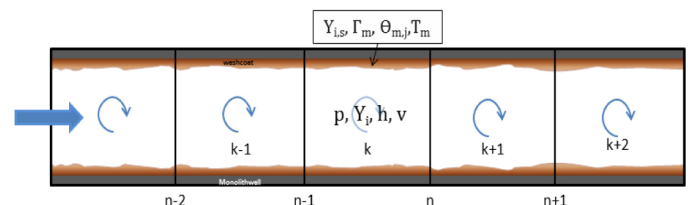


Figure 1. Illustration of channel model

The channel is discretized into a finite number of sections of length Δx (see Figure 1). In each channel section the bulk gas is modeled as a perfectly stirred reactor (PSR). To account for external diffusion the gas close to and inside the wall is modeled as a separate zone, called the *thin film layer*. The thin film layer is illustrated by the dark grey area in Figure 2 below. Heat and mass transfer coefficients are calculated from boundary layer theory. The conservation equations for gas species mass fractions, gas enthalpy, surface temperature, thin film layer gas species mass fractions and surface site fractions are solved in each zone for each time step. The Navier-Stokes equations for pressure and flow velocity are solved over all sections in a separate step.

The model is integrated into the DARS [15] software for chemical reaction calculations.

In the following section the conservation equations are discussed in detail.

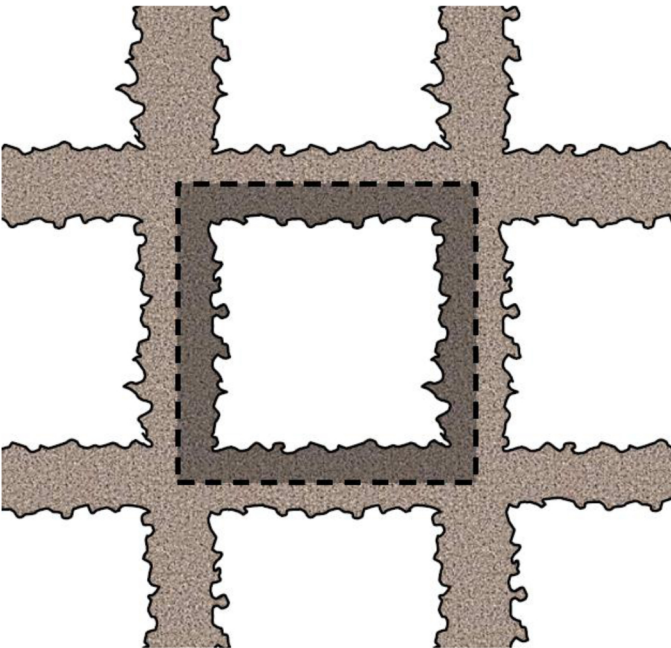


Figure 2. Volume considered in the thin film layer calculations

CONSERVATION EQUATIONS

PSR Equations

The bulk gas in each channel section is modeled by a PSR, assuming constant pressure in the section during the given time step, Δt . Gas phase reactions are accounted for. Species transport between bulk gas and thin film layer is modeled by mass transfer coefficients. The conservation equation for bulk gas species mass fractions is:

$$\begin{aligned} \frac{\partial Y_i}{\partial t} = & \frac{(\rho v)_{in} A}{m_g} (Y_{i,in} - Y_i) + \frac{W_i \omega_{i,g}}{\rho} \\ & - \frac{P \Delta x}{m_g} W_i K_m k_{m,i} (C_{i,g} - C_{i,p}) \\ & + Y_i \frac{P \Delta x}{m_g} \sum_{j=1}^{N_g} W_j K_m k_{m,j} (C_{j,g} - C_{j,p}) \end{aligned} \quad (1)$$

Here Y_i is the mass fraction of species i , m_g is the gas mass in the current channel section, $\omega_{i,g}$ is the species source term for gas phase reactions, K_m is the tunable parameter for overall heat transfer, $k_{m,i}$ is the mass transfer coefficient of species i , $C_{i,g}$ is the concentration of species i in bulk gas, and $C_{i,p}$ is the concentration of species i in the thin film layer. g in the subscript denotes bulk gas, p in the subscript denotes thin film layer zone (pores), and in in the subscript denotes inflow from upstream channel section. All symbols are explained in the Definitions/Abbreviations section.

In the thin film layer gas phase as well as surface reactions are considered. The conservation equation for gas species mass fractions is given by:

$$\begin{aligned} \rho_p \frac{\partial Y_{i,p}}{\partial t} = & \frac{P \Delta x}{V_p} W_i K_m k_{m,i} (C_{i,g} - C_{i,p}) + K_e W_i \omega_{i,p} \\ & + W_i K_e \sum_{m=1}^{N_{surf}} \frac{A_m}{V_p} \omega_{i,m} \\ & - Y_{i,p} \sum_{j=1}^{n_{species}} \left[\frac{P \Delta x}{V_p} K_m k_{m,j} W_j (C_{j,g} - C_{j,p}) + W_j K_e \sum_{m=1}^{N_{surf}} \frac{A_m}{V_p} \omega_{j,m} \right] \end{aligned} \quad (2)$$

V_p is the gas volume of the thin film layer in the current cell, $\omega_{i,p}$ is the species source term for gas phase reactions in the thin film layer, N_{surf} is the number of difference surface materials present in the catalyst (normally 1), A_m the catalytic surface area in current cell, $\omega_{i,p}$ and K_e is the tunable parameter for reaction efficiency. The conservation equation for surface species site fractions is given by:

$$\frac{\partial \theta_{i,n}}{\partial t} = \sigma_{i,n} K_e \frac{\omega_{i,n}}{\Gamma_n} \quad (3)$$

$\theta_{i,n}$ is the site fraction of species i at site n , Γ_n is the site density, $\omega_{i,n}$ the species source term from reactions at site n and $\sigma_{i,n}$ is the site occupancy number of species i at site n .

In the conservation equation for bulk gas energy, heat transport by convection and molecular transport are taken into account. The conservation equation for bulk gas specific enthalpy is given by:

$$\begin{aligned} \frac{\partial h_g}{\partial t} = & -K_h h_T \frac{P\Delta x}{m_g} (T_g - T_w) + \frac{(\rho v)_{in} A}{m_g} (h_{in} - h_g) \\ & + \frac{P\Delta x}{m_g} \sum_{j=1}^{N_g} W_j K_m k_{m,j} (C_{j,g} - C_{j,p}) (h_g - h_{j,g \leftrightarrow p}) \end{aligned} \quad (4)$$

Here h_g is the bulk gas specific enthalpy, h_T the convective heat transfer coefficient between bulk gas and surface, T_g the bulk gas temperature, T_w the thin film layer temperature, h_{in} is the specific enthalpy of gas from upstream section and $h_{j,g \leftrightarrow p}$ the specific enthalpy of species j transported between bulk gas and thin film layer. If the species is transported from bulk gas, the bulk gas enthalpy is used, if it is transported to bulk gas, the thin film layer enthalpy is used.

The temperature in the thin film layer, T_w , is assumed to be homogeneous, for substrate as well as for gas. Constant pressure is assumed in the thin film layer gas. With these assumptions, the conservation equation for the surface temperature is given by:

$$\begin{aligned} (\rho_s V_s c_{p,s} + \rho_p V_p c_{p,p}) \frac{\partial T_w}{\partial t} = & V_s \frac{\partial}{\partial x} \left(k_s \frac{\partial T_w}{\partial x} \right) + K_h h_T P \Delta x (T_g - T_w) \\ & - \sum_{j=1}^{N_{g,p}} W_j P \Delta x K_m k_{m,j} (C_{j,g} - C_{j,p}) (h_{j,p} - h_{j,g \leftrightarrow p}) \\ & - \sum_{j=1}^{N_{g,p}} W_j \left[h_{j,p} V_p K_e \omega_{j,p} + h_{j,p} K_e \sum_{m=1}^{N_m} A_m \omega_{j,m} \right] \\ & - K_e \sum_{m=1}^{N_m} \sum_{j=1}^{N_{s,m}} h_{j,m} W_j A_m \omega_{j,m} \end{aligned} \quad (5)$$

Here V_s is the volume of solid wall material (washcoat and substrate) in current cell, $c_{p,s}$ is the specific heat capacity for

the solid material, $c_{p,p}$ is the specific heat capacity at constant pressure for the gas and K_h is the tunable parameter for heat transfer. Heat conduction along the channel, heat convection/diffusion to the bulk gas, molecular heat transport as well as heat released by reactions are taken into account in this expression.

Heat and Mass Transfer Coefficients

The heat and mass transfer coefficients, h_T and $k_{m,i}$, used in the conservation equations, are calculated from the Nusselt and Sherwood numbers, Nu and Sh_i , according to boundary layer theory (see e.g. [16]):

$$h_T = Nu \frac{k_g}{d_h} \quad (6)$$

$$k_{m,i} = Sh_i \frac{D_i}{d_h} \quad (7)$$

Here k_g is the thermal conductivity of the gas, D_i is the binary diffusion coefficient of species i and d_h is the hydraulic diameter of the channel.

In this work, correlations for Sherwood and Nusselt numbers derived for simultaneously developing velocity, concentration and thermal boundary layer flow and single first order surface reaction, presented by Ramanathan et al [17], are used:

$$Sh_i(x) = \begin{cases} \frac{0.35 \left(\left(\frac{d_h}{4} \right)^2 v \right)^{\frac{1}{2}}}{Sc_i^{\frac{1}{6}} \left(\frac{d_h}{4} \right)^{\frac{1}{2}} x D_i}, & 0 < x < \frac{\left(\frac{d_h}{4} \right)^2 v}{D_i} \frac{1}{Sc_i^{\frac{1}{3}}} \left(\frac{1.4}{Sh_{T,\infty}} \right)^2 \\ Sh_{T,\infty}, & x \geq \frac{\left(\frac{d_h}{4} \right)^2 v}{D_i} \frac{1}{Sc_i^{\frac{1}{3}}} \left(\frac{1.4}{Sh_{T,\infty}} \right)^2 \end{cases} \quad (8)$$

$$Nu(x) = \begin{cases} \frac{0.35 \left(\left(\frac{d_h}{4} \right)^2 v \right)^{\frac{1}{2}}}{Pr^{\frac{1}{6}} \left(\frac{d_h}{4} \right)^{\frac{1}{2}} x D_T}, & 0 < x < \frac{\left(\frac{d_h}{4} \right)^2 v}{D_T} \frac{1}{Pr^{\frac{1}{3}}} \left(\frac{1.4}{Nu_{T,\infty}} \right)^2 \\ Nu_{T,\infty}, & x \geq \frac{\left(\frac{d_h}{4} \right)^2 v}{D_T} \frac{1}{Pr^{\frac{1}{3}}} \left(\frac{1.4}{Nu_{T,\infty}} \right)^2 \end{cases} \quad (9)$$

D_i is the species diffusion coefficient for species i , D_T is the thermal diffusion coefficient and v is the fluid velocity along the channel. $Sh_{T,\infty}$ and $Nu_{T,\infty}$ are the asymptotic Sherwood and Nusselt numbers for constant flux boundary condition. Values of $Sh_{T,\infty}$ and $Nu_{T,\infty}$ for different channel geometries were taken from Santos and Costa [18]. Washcoat diffusion is

neglected. In this work the value for circular channels, 3.656, is used.

The Schmidt number of species i , Sc_i , is given by:

$$Sc_i = \frac{\mu_i}{\rho D_i} \quad (10)$$

Here μ_i is the dynamic viscosity and D_i the diffusion coefficient of species i .

The Prandtl number, Pr , is given by:

$$Pr = \frac{c_p \mu}{k_g} \quad (11)$$

Here c_p is the heat capacity at constant pressure, μ the dynamic viscosity and k_g the thermal conductivity of the gas.

Effectiveness Factor

To account for reaction-diffusion of NO in the washcoat the effectiveness factor approach, used previously by e.g. Koop and Deutschmann [11], is invoked. See Mladenov et al [10] for a detailed description of the model. This approach is possible when considering single species consumption with a rate proportional to the species concentration. The species should also be representative for the behavior of the whole system. With the assumption of a constant diffusion coefficient for the representative species throughout the washcoat, and washcoat thickness large enough to obtain a zero concentration gradient at the deepest point of the washcoat, an analytical expression for the effective reaction rate can be derived. This analytical expression is used to calculate a multiplication factor for all species participating in surface reactions:

$$\dot{s}_{eff,i} = \eta \dot{s}_i \quad (12)$$

The effectiveness factor, η , is given by

$$\eta = \frac{\tanh\left(\sqrt{\frac{\gamma k_{eff}}{D_{eff}}} t_w\right)}{\sqrt{\frac{\gamma k_{eff}}{D_{eff}}} t_w} \quad (13)$$

Here D_{eff} is the diffusivity of the representative species, t_w is the washcoat thickness, and γ is the active surface area per washcoat volume

$$\gamma = \frac{A_m}{V_p} \quad (14)$$

k_{ieff} is the overall reaction rate of the representative species (NO in this study):

$$k_{ieff} = \frac{\omega_{ieff}}{W_{ieff} c_{ieff}} \quad (15)$$

Flow Equations

To limit CPU time the flow is assumed to be in steady state. This gives the following conservation equations:

Continuity equation (conservation of mass):

$$\frac{\partial(\rho v)}{\partial x} = -\frac{A_{w,g}}{m_g} \sum_{i=1}^{N_g} W_i k_{m,i} (C_{i,g} - C_{i,p}) \quad (16)$$

Momentum equation:

$$\frac{\partial(\rho v^2)}{\partial x} + \frac{\partial p}{\partial x} = -\frac{f_F}{2} (\rho v) |v| \frac{P}{A} \quad (17)$$

A is the cross-sectional channel area. With the assumptions of laminar and fully developed flow, the friction factor, f_F , is given by:

$$f_F = \frac{16}{Re} = \frac{16\mu}{\rho v d_h} \quad (18)$$

RESULTS AND DISCUSSION

The model is applied to experiments with a flat-bed reactor published elsewhere ([11], [19]). The catalyst is equipped with lateral outlets, giving the possibility to measure and study gas concentration profiles along the length of the catalyst. The experimental setup, measurements and catalyst used is thoroughly described in Ref. [11] and [19]. Next follows a brief description of the setup.

The experiments are carried out under isothermal and steady state conditions in a flat-bed reactor manufactured by Delphi catalyst. The catalyst used is a platinum γ -alumina washcoat carried by a monolithic honeycomb structure (10319) ([19], [11]). See Table 1 for reactor specifications. The space velocity of the gas is 40000 h⁻¹. A realistic model exhaust gas for Diesel engine emissions under fuel lean and fuel rich conditions was used. The gas compositions used are given in Table 2. The model gas includes CO, CO₂, O₂, H₂O, NO, NO₂, H₂ and C₃H₆. C₃H₆ is used as model species for

unburned hydrocarbons, simulating reactive unburned hydrocarbons such as olefins or aromatic hydrocarbons.

The calculations are run transient until steady state is reached. The detailed surface reaction mechanism published by Koop and Deutschmann [11] is used for the calculations. This mechanism includes detailed reaction steps for nitrogen oxide conversion, decomposition of hydrocarbons by hydrogen abstraction, oxidation of hydrocarbons by surface bound oxygen, oxidation of carbon monoxide to carbon dioxide and formation of water from hydroxyl adsorption. The model comprises 73 reactions among 22 surface and 11 gas phase species. All reactions are elementary except for oxidation of C_3H_4 by surface bound oxygen, since the reaction paths of this process are unknown.

Gas phase reactions are deactivated since the reactivity is very low at the studied temperatures. The model parameters for overall efficiency and mass transfer are adjusted to the current system. The cases with 0% and 0,08% CO are left out during parameter adjustment. The parameter for overall efficiency can be used as tuning parameter since the morphology of the surface is not known nor considered in the model. The parameter for mass transfer can be used as tuning parameter since the underlying assumptions of the Sherwood number calculation (laminar flow, single first order surface reaction, uniform catalyst coating and very thin washcoat) are not fully valid. The final values, given in [Table 3](#), are used for all cases.

The calculations are compared with the experimental results and studied kinetically. A parameter study is carried out for sensitive cases. A transient case is further created from the lean phase; the calculation starts with 90 ppm propene present in the exhaust stream, and is then suddenly cut off. The consequent effect on NO conversion is studied. The studies are described in detail in the following sections.

Table 1. Specifications of the flat bed reactor

Slice length	40 mm
Slice width	30 mm
Slice height	One channel width
Total length	0.2 m
Channel diameter	1.0 mm
Channel density	400psi
Wall thickness	0.1524 mm
Washcoat	Pt/Al ₂ O ₃
Platinum dispersion	16 %
BET surface area	49 m ² /g
Median pore diameter	10 nm
Washcoat porosity	40 %

Table 2. Model gas compositions. All measures are by volume.

Species	Lean	Rich
NO	~200 ppm	~200 ppm
C ₃ H ₆	60 ppm / varying	60 ppm
CO	varying / 0.04 %	2.1 %
O ₂	12 %	0.9 %
CO ₂	7 %	7 %
H ₂ O	10 %	10 %
H ₂	-	varying
N ₂	dilution	dilution

Table 3. Model parameters and settings

Mass transfer factor, K_m	0.3
Overall reaction efficiency, K_e	0.2
Cell length, Δx	1 mm
Gas pressure	1 atm
Gas temperature	250 °C, 350 °C, 450 °C
Space velocity	40000 h ⁻¹
Inlet velocity	8 m/s (250 °C) 9.5 m/s (350 °C) 11.1 m/s (450 °C)
Void fraction	0.4
Washcoat thickness	0.1 mm
Effectiveness factor species	NO
Catalytic surface area per geometric surface area, $A_m/A_{w,G}$	25

SIMULATION OF EXPERIMENTS UNDER STEADY STATE CONDITIONS

Fuel Lean Phase

CO and C₃H₆ inhibition during fuel lean conditions is studied. Results for propene inhibition are shown in [Figure 3](#). Good agreement with experiments is achieved. For 250 °C the inhibition effect of propene is caught by the model. For 350 °C and 450 °C, the model predicts no inhibition effect at all, contrary to the experiments. The NO oxidation by the entrance of the channel is slightly overrated. Overall conversion efficiency is accurately predicted.

In [Figure 4](#) the site fractions for all major species ($\theta_{i,max} > 10^{-3}$) are shown for 250 °C. Surface bound CO is found to be the major inhibiting species. The occurrence of CO(s) is significantly increased when C₃H₆ is present in the exhaust stream. As a consequence, the number of active sites for NO and oxygen adsorption is decreased. The number of surface bound oxygen atoms is decreased by about 2%, giving a