

Parameter Estimation of a DOC from Engine Rig Experiments with a Discretized Catalyst Washcoat Model

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ABSTRACT

Parameter tuning was performed against data from a full scale engine rig with a Diesel Oxidation Catalysts (DOC). Several different catalyst configurations were used with varying Pt loading, washcoat thickness and volume. To illustrate the interplay between kinetics and mass transport, engine operating points were chosen with a wide variation in variables (inlet conditions) and both transient and stationary operation was used. A catalyst model was developed where the catalyst washcoat was discretized as tanks in series both radially and axially. Three different model configurations were used for parameter tuning, evaluating three different approaches to modeling of internal transport resistance. It was concluded that for a catalyst model with internal transport resistance the best fit could be achieved if some parameters affecting the internal mass transport were tuned in addition to the kinetic parameters. However it was also shown that a model with negligible internal transport resistance still could obtain a good fit since kinetic parameters could compensate for transport limitations. This highlighted the inherent difficulties using kinetic models with high parameter correlation and also showed the importance of using a kinetic model with a structure that is capable of describing exclusively intrinsic kinetics.

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INTRODUCTION

The diesel oxidation catalyst (DOC) is a well established technology to reduce CO and hydrocarbon (HC) emissions from diesel engines that has been in use since the 1990s. Strengthened emission standards have made the importance of the DOC even greater in recent years since it has become an indispensable part in enhancing the performance of diesel particulate filters (DPF) and selective catalytic reduction (SCR) by utilization of oxidation of NO to NO₂. Therefore a correct prediction of the performance of the DOC is very important for the simulation of the entire aftertreatment system.

A vital part of parameter estimation is the formulation of the catalyst model that will be used in the simulations. The model does not only need an accurate description of the reactions taking place in the washcoat but the transport of reacting components from the gas bulk to the washcoat is also of greatest importance. A phenomenon that is very rarely taken into consideration when full scale DOC systems are modeled, but is more common for SCR [1] and Ammonia Slip Catalysts (ASC) [2], is the pore transport resistance. Studies at lab scale have, however, shown that it indeed can be of influence for the conversion of HC [3], CO [3, 4] as well as NO [5].

Large efforts have been made to construct kinetic models for the DOC both of global type [6, 7, 8, 9] and microkinetic type [10, 11, 12]. Kinetic models used for full-scale simulations are in most cases of global type. Since the global kinetic models derived from full-scale simulations generally have been fitted to data in which both transport and reaction rate limited conditions prevail, there is a risk that the resulting kinetic parameters are not purely intrinsic. This means that varying physical properties of the catalyst (such as washcoat thickness, pore size distribution, noble metal loading and other ageing effects) tends to make the kinetic parameters case specific, resulting in the kinetic model only giving reliable predictions for a catalyst close to the one used in the experiments from which the model was derived [13]. A method of retuning parameters to measurement data where catalyst physical properties are efficiently separated from kinetics is therefore desirable. To make such separation possible a model with enough complexity to accurately describe the mass transfer in the washcoat and at the gas-washcoat interface is vital.

In order to evaluate the importance of pore transport resistance or create models that accurately account for it, the effective diffusivities must be known. Effective diffusivities may be calculated from models of varying sophistication which require knowledge of the physical properties of the catalysts [14] and in some cases the detailed pore structure [15, 16]. Still these calculated effective diffusivities can only be regarded as initial estimates, especially considering that they would in the case of hydrocarbons in an exhaust gas, likely be based on a single model species. Alternatively, it is possible to make direct experimental measurements of the effective diffusivity with actual monolith structures by for example chromatographic techniques [17] or in the form of a Wicke Kallenbach diffusion cell [18]. However, these approaches require specialized equipment and again measurements would undoubtedly have to be carried out under conditions that differ somewhat from a true exhaust gas.

The advantage of using an engine-rig is that parameters are estimated directly for their purpose, i.e. full-scale simulations, but the drawback is increased experimental time and the fact that the feed gas composition and resulting experimental space is limited to what is possible for the engine to produce. These engine limitations coupled with the importance of obtaining pertinent experimental data that aids in the distinction between kinetic and transport effects makes a good experimental design very important.

In the current study we present and evaluate an approach where effective diffusivities are fine-tuned in parallel with the estimation of kinetic parameters from experiments with actual exhaust gas generated by an engine. In comparison, two additional models were created where only kinetic parameters were tuned and effective diffusivities remained constant. For one of these models internal transport resistance was neglected. The resulting tuned kinetic models were compared in an effort to investigate the effect of modeling of internal transport resistance. The study also includes Design of

Experiments (DoE) to generate a manageable transient data set that effectively spans the complete operating conditions of the engine and reduces the high correlation between variables that is characteristic for a full scale system. To further enhance the separation of kinetic and transport effects different catalyst configurations with varying Pt loading, washcoat thickness and volume were included in the experimental plan.

EXPERIMENTAL SECTION

All experiments in the present work were performed with a full scale engine rig which also means that the catalysts used were all of dimensions for heavy-duty vehicle aftertreatment systems. The catalysts were of monolith flow-through type with a total diameter of 30.5 cm (12 inch) and a length of 10.2 cm (4 inch). The active material, platinum, was dispersed in a washcoat distributed on the channel walls which means that the reacting species needed to diffuse through the washcoat to react on the active sites. Using an engine as the exhaust source together with full scale catalysts results in challenges for achieving proper design of experiments, catalyst model formulation, and parameter tuning. All of these issues as well as how they were handled in this study are presented in this section.

The Reactor Model

A full scale catalyst monolith, connected to an engine with varying inlet properties displays a highly dynamic behavior. This means that the catalyst outlet conditions will not only be influenced by the current inlet conditions but also those at previous time points. To describe this behavior a transient catalytic reactor model is needed. In this work a uniform radial flow and concentration distribution over the catalyst cross section was assumed which makes it sufficient to model only one channel. The single channel model, closely based on the model presented by Ericson et al. [19], was discretized as tanks in series where the catalyst washcoat was discretized both radially and axially while the gas phase was only discretized axially. This 1D/2D (gas phase/washcoat) structure was chosen since it was considered a good compromise between accuracy and computational speed [20]. A film theory model was used to model the heat and mass transport between gas and washcoat surface. Axial diffusion and radial temperature gradients in the washcoat were neglected.

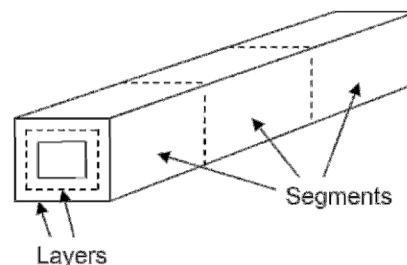


Figure 1. Illustration of the catalyst discretization principle demonstrated by a single channel.

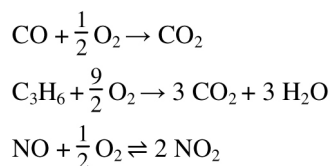


The wide temperature range of vehicle exhaust together with the need to package as much activity into a given volume of the converter as possible to achieve vehicle on-board space-efficiency, leads to transport limitations usually becoming unavoidable at higher temperature. This means that significant gradients in the washcoat are likely to occur which makes the washcoat discretization specifically important for a proper description of the behavior of the system. Full-scale experiments also mean that some additional properties that might be negligible for lab-scale, such as heat losses and heat accumulation in pipes and canning, needed to be included (or taken into account) in the reactor model. A thorough description of the catalyst model is given in the [appendix](#).

Kinetics

The simplest versions of the DOC kinetic models only describe the oxidation reactions of CO, hydrocarbons (HC) and NO. In addition HC is often represented as one molecular species, usually propene [6, 13, 21]. The exhaust composition is far more complex than just one type of hydrocarbon species and there are examples of kinetic models [8, 22] that have been expanded with several types of HC. Other additional reactions that may be added are H₂ oxidation [12, 22] and HC oxidation by NO [7, 23] or by NO₂ [8]. In this work rather than focusing on the required model formulation or level of detail of the kinetic model, it was the method used to estimate kinetic parameters for a given kinetic model that was in focus.

The kinetic model used in this study is of Langmuir-Hinshelwood type and was originally suggested in the classical work by Voltz et al [6] and later modified by Oh and Cavendish [21]. The model, which has been widely and frequently used in DOC modeling over the years, only includes three reactions of which one is an equilibrium reaction:



The reaction rates were calculated according to [equation 1, 2, 3, 4, 5](#).

$$r_1 = \frac{k_1 y_{\text{CO}} y_{\text{O}_2}}{G(y_i, T_s)} \quad (1)$$

$$r_2 = \frac{k_2 y_{\text{C}_3\text{H}_6} y_{\text{O}_2}}{G(y_i, T_s)} \quad (2)$$

$$r_3 = \frac{k_3 y_{\text{NO}} y_{\text{O}_2}}{G(y_i, T_s)} \left(1 - \frac{K'}{K_p}\right) \quad (3)$$

$$K' = \frac{y_{\text{NO}_2}}{y_{\text{NO}} y_{\text{O}_2}^{1/2}} \quad (4)$$

$$G(y_i, T_s) = T_s \left(1 + K_4 y_{\text{CO}} + K_5 y_{\text{C}_3\text{H}_6}\right)^2 (1 + K_6 y_{\text{CO}}^2 y_{\text{C}_3\text{H}_6}^2) (1 + K_7 y_{\text{NO}}^{0.7}) \quad (5)$$

Where K_j is the reaction rate coefficient for the inhibition terms in the denominator G and K_p is the equilibrium constant for NO oxidation. At thermodynamic equilibrium, K_p will be equal to K' and reaction rate r_3 will be equal to zero. Both reaction rate coefficients k_j and K_j were described by Arrhenius expressions:

$$k_j = A_j e^{-\frac{E_{A,j}}{RT_s}} \quad (6)$$

The start values for estimation of kinetic parameters were taken from [13] where results from several studies [24, 25, 26, 27, 28, 29, 30] were compiled. The initial values for kinetic parameter estimation used in this study are shown in [table 6](#).

The kinetic parameters in [equations 1, 2, 3, 4, 5](#) are in some cases highly correlated and since the initial parameter values in [table 6](#) were taken from different studies, the fit of the model to experimental data was expected to be poor before any parameter tuning was performed. However, the parameters were successfully used as a starting point for parameter tuning of a DOC against engine rig data in [13] which was also the intended application in the present work.

Adjustable Parameters

To tune the model to the measurement data a number of parameters in scaled and centered forms [31] can be adjusted. These parameters can be divided into kinetic parameters, mass transfer parameters and heat transfer parameters. In the current section some extra attention will be given to the mass transfer parameters and some of the kinetic parameters, all the adjustable parameters are however described in detail in the [appendix](#).

Kinetic Parameters

Three types of kinetic parameters are adjusted; pre-exponential factors, activation energies and activity scaling factors. The former two are described in the [appendix](#).

It has been shown that the catalyst active surface area could be used as a single parameter in a global model [32]. In addition to the pre-exponential factors and the activation energies, an activity scaling factor has therefore also been selected as an adjustable kinetic parameter. The activity scaling factor is simply a scale factor for all reaction rates on a certain site on a certain catalyst (parameters were tuned to several different catalysts simultaneously) with the purpose of

accounting for different properties of catalyst samples, such as metal dispersion. This means that the catalyst active surface area (A_m) was tuned for each catalyst sample since only one single site is used in the kinetic model.

Mass Transfer Parameters

The species used in the kinetic model are O_2 , NO, NO_2 , CO, and HC which means that these also are the species whose mass transport is significant for the behavior of the model. In the current study the effective diffusivity was initially calculated as a function of the f_D factor, the gas diffusivity and the Knudsen diffusivity according to [equation A13](#) in the appendix. This expression is only an estimate of the transport resistance in the complex porous body that is a catalyst washcoat. Firstly the f_D factor itself should account for both the tortuosity and the porosity by just one constant which makes it difficult to estimate. Secondly the structure of the pores may contain cracks and other discrepancies which would make the resistances in parallel suggested by the model (denominator of $1/D_{i,k} + 1/DK_{i,k}$ in [equation A13](#)) far from reality. Tuning the effective diffusivities was therefore evaluated as a method of tuning the transport resistance with the aim of reducing the correlation between mass transport and kinetic parameters.

The species were divided into two groups, where the first group contained O_2 , NO, NO_2 , and CO and the second group contained HC. In the first group all species are well defined with similar diffusivities and could be expected to have similar mass transport properties in the washcoat with presumably the same bias from their true values. To reduce the number of parameters to tune the same scale factor was used for all species in this group. The second group contained HC which was represented as C_3H_6 but in reality it is a wide range of hydrocarbons with different mass transport properties. The scale factor for the second group was in other words expected to be influenced both by the hydrocarbon composition and the washcoat structure while the scale factor for the first group mainly accounted for only washcoat structure. The equations for adjusting the mass transfer parameters can be found in the [appendix](#).

Experimental Set-up

Engine Rig

A Euro IV calibrated heavy duty diesel engine with disabled exhaust gas recirculation (EGR) was used as the exhaust source and Swedish MK1 diesel, a commercial low-sulfur (approximately 5 ppm S) diesel, was used as fuel. The engine was equipped with a dynamometer control system enabling independent control of load and speed. A change in operating point for the engine could be implemented very fast, although the dynamics of the engine rig itself were much slower due to the large thermal mass.

Catalysts

To further widen the experimental range, four different catalyst configurations with different noble metal loading, lengths, and washcoat thicknesses were used. All catalysts, shown in [table 1](#), were Pt on alumina model catalysts provided by Johnson Matthey.

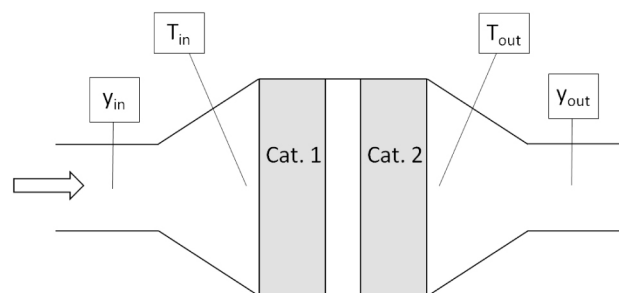
[Table 1](#). Catalyst configuration used for parameter estimation (a-d). Catalyst configuration c consists of two catalysts in series. The Pt-loading is shown in both mass % of washcoat and g/ft^3 total catalyst volume.

<u>Config- uration</u>	<u>Pt- loading</u> [mass % washcoat]	<u>Pt-loading</u> [g/ft^3 mon- olith]	<u>Length</u> [cm]	<u>Washcoat thickness</u> [mm]
a	0.30	15	10.2	0.110
b	0.59	30	10.2	0.110
c	0.30	15	2x10.2	0.110
d	0.59	15	10.2	0.055

All configurations have a 30.5 cm diameter (12 inch), 62 channels/cm² (400 cpsi) cell density and a wall thickness of 0.152 mm and the substrate material used was cordierite. The catalysts were thermally aged for one hour at 600°C.

Measurements

The temperature and composition measurements were made according to [figure 2](#) where the downstream catalyst position (Cat. 2) is left empty for all configurations except configuration c (see [table 1](#)).



[Figure 2](#). Illustration of temperature and gas composition measurement

The temperatures were measured with 3 mm thermocouples positioned at the center of the pipe and close to the catalysts. The inlet gas composition was measured just before the pipe expansion and the outlet gas composition was measured directly downstream the pipe contraction. Separate analyzer units were used to measure the concentration of CO (infra-red), CO_2 (infra-red), NO and NO_x (chemiluminescence), total hydrocarbon (flame ionization) and O_2 (electrochemical cell). The NO_2 composition was determined by the NO_x and NO difference. Although measurements of total hydrocarbon were made, results here will be reported as equivalent concentrations of the selected model hydrocarbon compound propene (C_3H_6). The total mass flow into the catalyst is

calculated from the sum of the air mass flow and the fuel flow to the engine. The air mass flow was measured using a thermal mass flow meter and the fuel flow is measured using a continuous fuel meter

Since the flow resistance will depend on the catalyst length an orifice was used to maintain constant engine out back pressure independent of the catalyst configuration. This was done to ensure that a certain engine load and speed would generate the same exhaust composition and flow for all configurations. The pressure in the catalyst was near atmospheric which was assumed when concentration calculations were performed with the ideal gas law.

Parameter Estimation Method

As mentioned in the introduction the available exhaust composition, flow and temperature is limited by the operating points of the engine. It also takes several minutes for the catalyst inlet conditions to reach stability when switching between operating points, which means that experimental time will be a factor when deciding the number of different operating points when the full transient behavior is of interest. An important part of the current work is to investigate what experiments are suitable for parameter tuning and therefore both transient and steady-state data is desirable. Since the number of catalyst configurations was large (table 1) and some replicates also were necessary only 8 different operating points were selected according to table 2. The variables in the table have the following approximate spans; NO_x 100-1600 ppm, HC 50-200 ppm, CO 0-200 ppm, O_2 5-20 %, temperature 200-500°C and flow 5-40 kg/s. The operating points were selected manually but were later confirmed to be a close to D-optimal selection with a model based design analysis of the engine map in temperature, concentrations and flow. Figure 3 shows an example of how the operating points span over the engine map for the case of temperature.

Table 2. Engine operation points and levels of variables, Med=medium.

Number	Description				
	NO_x	HC + CO	O_2	Temp.	Flow
1	Low	High	High	Low	Low
2	Low	High	High	Low	Med
3	High	Med	Med	Med	Low
4	Med	Low	Med	Med	High
5	High	Low	Low	High	Med
6	Med	Low	Med	Med	High
7	High	Low	Low	High	Med
8	Med	Low	Low	High	High

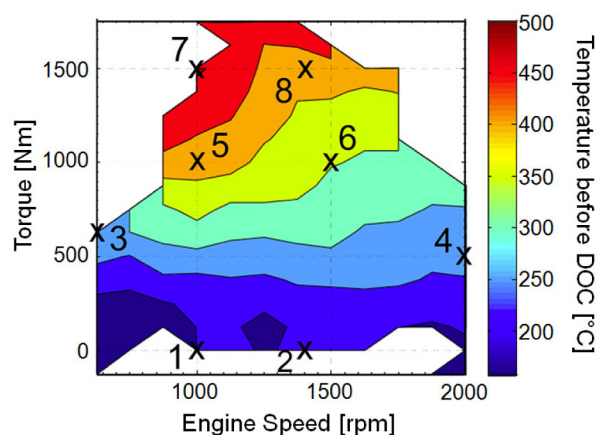


Figure 3. Temperature engine map and selected operating points

The operating points were selected to make as large steps as possible in the different variables including concentrations of NO , NO_2 , HC, CO and O_2 as well as temperature and flow rate with the purpose of making the experimental space as large as possible. Some of the variables, such as concentrations of NO and NO_2 and concentrations of HC and CO, are closely correlated and it is difficult to create transients where they are changed independently. This is also the case for O_2 and temperature, i.e. an operation point with low temperature will have high oxygen concentration and an operation point with high temperature will have low oxygen concentration. This means that some of the input variables cannot be varied independently. A good experimental plan (such as D-optimal design) will however ensure that the variables are varied as independently as possible.

The operation points were run in the order 1, 7, 2, 8, 3, 4, 5, 6 for all catalyst configurations to make as large changes as possible in as many variables as possible. For some of the configurations several additional sequences were also run. To achieve steady state conditions all points were run for 15 minutes each. With very good reproducibility for all catalyst configurations, one of each of the transients 1 to 7, 2 to 8, 3 to 4, and 5 to 6 were selected for every catalyst, thereby reducing the used experimental data to two hours per catalyst configuration.

When starting simulations with the catalyst model the only known conditions were those of the inlet and outlet flow. This meant that initial properties such as concentrations and temperature inside the catalyst needed to be assumed which resulted in the first seconds of every simulation being unreliable. To avoid parameters being tuned against unreliable simulation results the first 120 s of every transient was removed from the calculation of the residual.

Several different optimization methods can be used to minimize the simulated residuals and the most common method is probably the gradient search method which was also the method used in this study. The method is very efficient for linear systems but can also be applied for non-linear systems such as catalyst models. For a non-linear system the residual function is first linearized for all parameters and then a step in

the parameter space is made in the direction of the steepest descent. This process is repeated until the change in residual is below a certain tolerance. For a thorough description of this method see for example [33]. The parameter tuning was not only complicated by the non-linearity of the system but also by the high correlation of the estimated parameters. The scope of this study did, however, not include a method for parameter sensitivity analysis or calculation of confidence intervals.

The gradient search method of choice in this work was the trust-region-reflective method [34]. This is the standard method for over determined non-linear least square problems in Matlab, the software used in this project. This method is implemented in the Matlab function lsqnonlin.

The heat production from the reactions taking place in the DOC was small compared to the convective heat transport due to gas flow and heat losses to the environment. This means that the kinetic parameters and the mass transport parameters will have only a small influence on the outlet temperature and thus the heat transfer parameters can be estimated separately.

The influence from the temperature on the reaction rates is however substantial which means that a good estimation of the heat transfer parameters is an important foundation for tuning the kinetic and mass transport parameters. The heat transfer parameters were therefore estimated before the other parameters and since temperature will not be affected by other parameter values they were not re-tuned later on. When the heat transfer parameters were calculated the only residual used was outlet temperature.

When parameter tuning of the kinetic and mass transport parameters was performed the simulated outlet concentrations of NO, NO₂, HC and CO were compared to measurement data to form the model residuals. To avoid having the residuals from the higher concentration components dominate the parameter tuning, all residuals for a certain component were weighted by their average outlet concentration. This meant that the residuals of NO_x were decreased in relation to the residuals of HC and CO.

To verify the significance of estimating effective diffusivity and including internal transport resistance in the models, parameter estimations were performed according to three different modes summarized in [table 3](#).

Table 3. Short description of the modes of Parameter Estimation

Nr	Modes of Parameter Estimation	Number of parameters	Discretization	
			Seg-ments	Lay-ers
1	Negligible internal mass transfer resistance	17	10	8*
2	Discretized washcoat and fixed effective diffusivity	17	10	8
3	Discretized washcoat and tuned effective diffusivity	19	10	8

*Since concentration gradients in the washcoat were expected to be absent, two layers would have sufficed for this case, however eight layers were used for computational consistency

Mode 1 represents a case where the effective diffusivities were set to very high values (1000 times initial estimates) which, in effect, makes it a case with negligible internal transport resistance. Mode 2 and Mode 3 differ only by the fact that the latter has enabled estimation of the effective diffusivity whereas the former has not. For Mode 2 the effective diffusivities were fixed at the initially estimated values (see [equation A22](#) in appendix). Mode 3 uses one effective diffusivity scaling factor for small molecules and one for large molecules where all components except HC are considered small.

RESULTS AND DISCUSSION

Heat Transfer Parameter Tuning

The heat transfer parameters thermal mass (s_{heat}), environmental temperature (T_{∞}), and lumped heat transfer coefficient (α_{tot}) were tuned before any additional parameter tuning was performed. The final values of the temperature parameters are shown in [table 4](#).

Table 4. Results of heat transfer parameter tuning

Parameter	Value
s_{heat}	4.7 kJ/K
T_{∞}	112.2 °C
α_{tot}	5.0 J/K,s

Note that these parameters are lumped to account for several different phenomena and therefore are difficult to interpret physically. The results for one of the catalyst configurations are shown in [figure 9](#).

The simulated temperature shows a good fit both during the fast transient changes in inlet temperature and the slower approach to steady states. The largest errors occur during high exhaust flow at high temperature (2700-3600 s) where the model under-predicts the heat loss and during low flow at low temperature (3600-4500 s) where the model over-predicts the heat loss. The maximum temperature deviation was 20 °C with the root mean square average being 3.6 °C. With only three parameters to tune, a perfect fit can however not be expected for all time points and thus the tuned temperature parameters were deemed good enough for continued parameter tuning of the kinetic and mass transport parameters considering the level of detail of the single channel model used. If the heat transfer parameters would not be included in the model the simulated outlet temperature would be close to the inlet temperature since the heats of reactions will have a minor effect on the temperature.

If only the measured temperatures in [figure 9](#) are studied, it is evident that the temperatures of all engine operating points were not stabilized even after 15 minutes (most apparently point 3 at 1800-2700 s). The temperature is however the only variable in [table 2](#) for which this was the case.

Catalyst Parameter Tuning

The final results of the tuning of the kinetic parameters for the different parameter estimation modes are summarized in [table 6](#). Since catalyst configuration c (see [table 1](#)) consists of the catalyst in configuration a in series with another identical catalyst, the same activity scaling factor is assumed for both configuration a and c.

For Mode 3 an effective diffusivity scaling (see [equation A22](#)) for small components (NO , NO_2 , CO and O_2) and large components (HC) were also tuned where the final tuning gave a value 7.71 times the initial estimate for the effective diffusivity for small components and a value 2.11 times the initial estimate for the effective diffusivity for large components. The correlation between the activity scaling factors and pre-exponential factors in the numerator of the rate expressions (A_{1-3}) were linear. Equal changes in either the activity scaling factor or pre-exponential factor gave identical changes in the reaction rate. This was the case since the kinetic model only uses one type of reaction site.

The activity scaling factor was only intended to serve as a handle to tune differences in properties of the catalysts, such as metal dispersion, and should only be interpreted as a relative difference and not an absolute value for activity scaling. During the parameter tuning an upper limit of 1% for the activity scaling factors was therefore applied in order to facilitate the comparison between the three modes.

In general it can be expected that a high noble metal loading should correspond to a low dispersion and thereby also a lower activity scaling factor. It is therefore surprising that none of the modes have the highest activity scaling factor for the lowest loading, i.e. 0.30 wt% Pt loading (act_a and act_c). Both Mode 1 and 3 have the highest activity scaling factor for configuration d where the washcoat is thinner than for the other configurations and has a high loading of 0.59 wt% Pt. Whereas, Mode 3 has the highest activity scaling factor for catalyst configuration b where the loading is also 0.59 wt% Pt. It should however be mentioned that the differences between the activity scaling factors are rather small.

The complexity of the kinetic model and the catalyst model complicates a thorough analysis of every single parameter value but some general remarks can be made. The original parameters over-predicted the conversion for all components and gave a very poor fit in general. The tuned parameters have therefore been changed in a direction where the reaction rates in general are slower. This is not always obvious when examining the parameter values since a large pre-exponential factor in the numerator (A_{1-3}) may be compensated by a large pre-exponential factor in the denominator (A_{4-7}) and differences in activation energies ($E_{A,j}$) will make different pre-exponential factors significant at different temperatures. Mode 2 and 3 both show reduced pre-exponential factors in the numerator for all reactions which leads to reduced reaction rates. Mode 1 on the other hand has increased pre-exponential factors in the

numerator for both reaction 1 and 3 (CO and NO oxidation). This, together with the fact that Mode 1 has negligible internal mass transfer resistance, would lead to a significantly increased reaction rate compared to the start values if it was not for the simultaneous increase of A_7 with about 3 orders of magnitude. A high value for the pre-exponential factor A_7 will decrease all reaction rates since it is a part of the common denominator G (see [equation 5](#)) for all reaction rate expressions. The assumed physical interpretation of $K_7 y_{\text{NO}}^{0.7}$, where A_7 is included, is the inhibiting effect of adsorbed NO on the surface. Since all NO is never consumed due to thermodynamic limitations, this factor will always influence the reaction rates of Mode 1 and generally cause them to be slower than for the start parameter values. This trend can also to a lesser extent be observed for Mode 3 but for Mode 2 the influence of the pre-exponential factor A_7 is small.

If the other pre-exponential factors and activation energies used in the common denominator G are studied, it becomes clear that A_6 and $E_{A,6}$ are insignificant for the simulation results. The highest value of the factor $1 + K_6 y_{\text{CO}} + K_5 y_{\text{HC}}^2$ for all modes and simulated time points is 1.1 and more than 99.9% of the values are below 1.01. In the data used to formulate the original kinetic model proposed by Voltz et al. [6], the molar fractions of HC and CO were considerably higher than those measured in the current study. It is therefore possible that the inhibition by HC-CO interaction is no longer an issue for a modern engine exhaust and this inhibition term could be omitted from the kinetic model. However, the factor $1 + K_4 y_{\text{CO}} + K_5 y_{\text{HC}}$ has a mean of 5.47 and a maximum of 99.75 and is significant for all modes.

Under equal conditions the reaction rates of Mode 2 were significantly larger than the reaction rates of Mode 1 showing that the kinetic parameters in Mode 2 needed to compensate for internal transport resistance.

The scaling of the effective diffusivity performed in Mode 3 resulted in a reduction in the internal transport resistance for all species. If the parameter values are studied, it can be seen that for Mode 3 they are in most cases between the values for Mode 1 and Mode 2. This is of course not unexpected, since the effective diffusivities of Mode 3 have values between the effective diffusivities of Mode 1 and Mode 2.

If the trends in the pre-exponential factors were fairly clear the relations between activation energies were more complicated. The differences between the modes were relatively small and usually close to the initial value which could indicate that the activation energies are not as case specific as the pre-exponential factors. If the activation energy (or heat of adsorption) $E_{A,7}$ is studied it should be noted that the sign is positive and opposite to the other activation energies in the denominator. This means that the inhibition by NO will increase with temperature and that this factor will result in a reduction of the reaction rate with temperature. In other words, it is the same kind of phenomena that transport resistance would cause and could explain the success of