

Lean NO_x Trap Modeling for Vehicle Systems Simulations

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ABSTRACT

A transient, one-dimensional lean NO_x trap (LNT) model is described and implemented for vehicle systems simulations. The model accounts for conservation of chemical species and thermal energy, and includes the effects of O₂ storage and NO_x storage (in the form of nitrites and nitrates). Nitrites and nitrates are formed by diffusion of NO and NO₂, respectively, into sorbent particles, and reaction rates are controlled by chemical kinetics and solid-phase diffusion. The model also accounts for thermal aging and sulfation by means of empirical correlations, which have been derived from laboratory experiments. Example simulation results using the Powertrain Systems Analysis Toolkit (PSAT) are presented.

1. INTRODUCTION

Lean combustion is an attractive option for improving the fuel economy of internal combustion engines. A 3-15% improvement of fuel economy has been reported by using lean combustion in place of stoichiometric combustion [1]. However, one of the major obstacles for lean combustion is the need to reduce NO_x emissions in lean, low temperature exhaust. Recent research shows that using lean NO_x trap (LNT) is a promising strategy for reducing lean NO_x emissions. This strategy was pioneered by Toyota research staff, who found conventional three way catalysts were capable of storing small quantities of NO_x [2, 3]. After several years of research since then, the chemical mechanisms of lean NO_x traps have been identified. To summarize, under lean conditions, part of the NO is oxidized into NO₂ over noble metal sites (such as Platinum, Palladium, and Rhodium), and then NO/NO₂ further reacts with alkali or alkaline earth metals to form nitrite/nitrate species. Under rich conditions, nitrite and nitrate become thermodynamically unstable so that the stored NO_x is released and then

catalytically reduced. Experimental results have confirmed that the NO_x trap could offer high rates of NO_x removal [4, 5].

There remain significant challenges to routine use of LNTs in on-road vehicles. Significant among them are thermal aging and sulfur poisoning, which significantly degrade LNT performance. In addition to models based on comprehensive kinetic mechanisms [6, 7], global [8, 9, 10] and control-oriented models [11,12,13,14] for simulating lean NO_x traps have been developed in various studies. However, application of such models for conventional and hybrid vehicle systems studies have not been reported to date in open literature.

This paper describes a one-dimensional LNT model used to investigate the impacts of LNT operation on conventional and hybrid vehicle NO_x emissions and fuel consumption. In addition to the basic LNT functions, the model accounts for degradation associated with slow aging, sulfation and thermal excursions during desulfation. The model is structured around one-dimensional mass and energy conservation balances over a conventional wash-coated catalytic monolith. For gas phase species balances, flow in the monolith channels is assumed to be plug flow and radial gas phase concentration gradients are neglected. In addition, chemical reactions only occur in the washcoat and mass exchanges between the gas phase and washcoat are assumed to be limited by chemical kinetics and diffusion in the washcoat. This last assumption is based on extensive experimental observations of LNT behavior, and, fortunately, it also helps significantly reduce the computational cost. Within the washcoat, stored NO_x and O₂ are tracked. Energy balances for gas and solid phases are used to compute the temperature profiles of both gas and solid monolith along the length of the catalyst.

The model is implemented in the form of SIMULINK block modules, which have been embedded into the Powertrain

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System Analysis Toolkits (PSAT). PSAT [15] is a state-of-the-art, flexible and forward-looking simulation package that is used to optimize vehicles and their components with regard to fuel consumption and pollutant emissions. With this implementation, it is possible to use the capabilities of PSAT to investigate the impact of LNT performance in full vehicle simulations.

In the following sections we describe the LNT model in more detail and then provide comparisons with experimental results.

2. LNT MODELING APPROACH

Heat and mass balances in the LNT model are implemented as one-dimensional, transient ordinary differential equations (ODEs) that are integrated to simulate the time varying processes in the catalytic monolith. Global kinetic rate expressions for NO_x storage, release, and reduction are combined with numerical approximations of the ODEs to predict the integrated variations in gas composition and temperature between the device entrance and exit. The model tracks the storage of NO_x and oxygen during lean operation. During regeneration, it accounts for the release and reduction of the stored NO_x and oxygen.

The gas species considered in the reactions include NO₂, NO, CO₂, CO, H₂, O₂, and total hydrocarbons. H₂, CO, and hydrocarbons (HC) are all assumed to act as reductants. To minimize the model complexity and maximize the computation speed, all inlet hydrocarbons are assumed to be equivalent to propylene (C₃H₆), and H₂ is assumed to be equivalent to CO. The latter approximation is reasonable since the oxidation rates and heats of oxidation of H₂ and CO are nearly equal. Experiments [16] show that these two reductants are effectively equivalent above 200°C temperature.

2.1. CONSERVATION EQUATIONS

The differential bulk-gas energy balance is:

$$\rho_g c_{p,g} \epsilon \left(\frac{\partial T_g}{\partial t} + u_g \frac{\partial T_g}{\partial z} \right) = h_g G_m (T_s - T_g) \quad (1)$$

where G_m is the surface area per volume of the monolith; h_g is heat transfer coefficient for the fully-developed laminar boundary layer; u_g is:

$$u_g = \frac{\dot{m}_g}{\rho_g \epsilon S} \quad (2)$$

where $\dot{m}_g$ is exhaust gas mass flow rate; S is frontal surface area in the converter.

The gas-phase species conservation equations are of the following form.

$$\rho_g \epsilon \left(\frac{\partial C_i}{\partial t} + u_g \frac{\partial C_i}{\partial z} \right) = \sum_{k=1}^n \alpha_i^k R^k \quad (3)$$

where R^k presents the rate of the k-th chemical reaction, and α_i^k is the stoichiometric coefficient of species i in the k-th chemical reaction. In the current model, effects of mass transfer from exhaust gas to the surface of washcoat have been neglected. This is because NO_x storage/release/Reduction are often kinetically limited and also lean NO_x traps operate at much lower temperatures than three-way catalysts and their operation rarely mass transfer limited.

The differential energy balance in the monolith channel walls is given by:

$$\rho_s c_{p,s} (1 - \epsilon) \frac{\partial T_s}{\partial t} = k_s (1 - \epsilon) \frac{\partial^2 T_s}{\partial z^2} + h_g G_m (T_g - T_s) + \dots + \sum q_{loss} + \sum_{k=1}^n R^k \cdot \Delta H^k \quad (4a)$$

$$\sum q_{loss} = h_{conv} G_a (T_a - T_s) + \epsilon \sigma G_a (T_a^4 - T_s^4) \quad (4b)$$

where G_a is the external heat transfer surface per volume; ΔH^k is the heat generated at the k-step reaction.

A convective heat transfer coefficient, h_{conv} , shown in Eqns. (4c), (4d), (4e) [17] is used to model heat losses due to a combination of free and turbulent forced convections.

$$h_{conv} = Nu_{conv} \frac{k_g}{D} = \sqrt[4]{Nu_{forced}^4 + Nu_{free}^4} \frac{k_g}{D} \quad (4c)$$

$$Nu_{forced} = 0.0371 Re^{4/5} Pr^{1/3} \quad (4d)$$

$$Nu_{free} = \left(0.6 + \frac{0.387 Ra^{1/6}}{\left[1 + (0.559 / Pr)^{9/16} \right]^{8/27}} \right)^2 \quad (4e)$$

where $Ra = \frac{D^3 g (T_s - T_a)}{\nu^2} \frac{1}{T_a} Pr$, and $Re = \frac{u_{veh} L}{\nu}$; Prandtl and Rayleigh numbers are computed at film temperature $T_f = 0.62 T_s + 0.38 T_a$; Re is computed at an average temperature at $T_f = (T_s + T_a)/2$; u_{veh} is vehicle speed.

Mass conservation of nitrate, nitrite, and oxygen in the washcoat require that:

$$\psi_{NOx} \frac{\partial \theta_{nitrate}}{\partial t} = \sum_k \alpha_{nitrate}^k R^k \quad (5a)$$

$$\psi_{NOx} \frac{\partial \theta_{nitrite}}{\partial t} = \sum_k \alpha_{nitrite}^k R^k \quad (5b)$$

$$\psi_{O_2} \frac{\partial \theta_{CeO_2}}{\partial t} = \sum_k \alpha_{CeO_2}^k R^k \quad (5c)$$

where $\theta_{nitrate}$ and $\theta_{nitrite}$ are the coverage fractions of barium nitrate and nitrite, respectively; θ_{CeO_2} is the coverage fraction of CeO_2 ; ψ_{NOx} and ψ_{O_2} are the storage capacities of NO_x and oxygen, respectively.

2.2. CHEMICAL KINETICS AND MASS TRANSFER

Various studies have suggested that internal mass transport, in addition to chemical kinetics, affects the performance of lean NO_x traps [1]. Yet only a couple of models have accounted for the effects of internal mass transfer on reaction rates [1, 8]. Olsson et al. [8] have proposed one such model which used the shrinking-core description for internal diffusion and storage of NO_x within the sorbent particles. A NO_x storage/release/reduction mechanism based on their shrinking core model is used here. It is supplemented by other oxidation and reduction reactions described below. Table 1 lists the entire chemical reactions and their Arrhenius rate parameters.

2.2.1. Oxidation reactions

The oxidation reactions considered here include NO oxidation, CO oxidation, and HC oxidation. Oxidation of NO to NO_2 on noble metal sites is an important reaction step for the NO_x storage mechanism, at least, at low temperatures. This reaction is also reversible and at typical space velocities, it reaches equilibrium across the reactor around 375°C - 400°C. CO oxidation and HC oxidation are modeled as irreversible reactions.

The following rate expressions are used for the three oxidation reactions.

$$R_{NO-O_2} = k_{NO-O_2} C_{NO} C_{O_2}^{0.5} - \frac{k_{NO-O_2}}{K_{eq, NO-O_2}} C_{NO_2} \quad (6)$$

$$R_{CO-O_2} = k_{CO-O_2} C_{CO} C_{O_2} \quad (7)$$

$$R_{C_3H_6-O_2} = k_{C_3H_6-O_2} C_{C_3H_6} C_{O_2} \quad (8)$$

where k_{NO-O_2} , k_{CO-O_2} , and $k_{C_3H_6-O_2}$ are computed from Arrhenius rate parameters, i.e. $k = A \exp(-E/RT)$.

As discussed below, we have used rate parameter values consistent with Olsson et al [8] when possible but we have also adjusted some values for better fits with experimental data. In some instances (indicated by the units) the pre-exponential factors are based on unit noble metal surface area rather than reactor volume, so the pre-exponential factors must be multiplied by the noble metal loading to obtain reaction rates per unit reactor volume.

The quantity $K_{eq, NO-O_2}$ is the equilibrium constant for NO oxidation and can be calculated from the corresponding standard Gibbs free energy change. The latter can be approximated by:

$$\Delta G_{NO-Ba} = -58000 + 76.10T \quad (9)$$

2.2.2. NO_x storage and release/reduction

Experiments indicate the presence of both nitrites and nitrates in the LNT washcoat with nitrate fraction increasing with increasing temperature [1, 8]. In this model we assume these species are formed respectively through reaction of NO and NO_2 respectively (along with O_2) with the sorbent particles. The rate expressions used for nitrate and nitrite formation, respectively, are:

$$R_{NO_2-Ba} = k_{NO_2-Ba,f}^* C_{NO_2} C_{O_2}^{0.25} \theta_{BaCO_3} - k_{NO_2-Ba,b}^* C_{CO_2}^{0.5} \theta_{nitrate} \quad (10)$$

$$R_{NO-Ba} = k_{NO-Ba,f}^* C_{NO} C_{O_2}^{0.25} \theta_{BaCO_3} - k_{NO-Ba,b}^* C_{CO_2}^{0.5} \theta_{nitrite} \quad (11)$$

In the above, the secondary subscripts f and b refer to the forward and backward reactions, respectively.

We also consider the effects of solid-phase diffusion on the NO_x storage rates, which are modeled after that of Olsson et al [8]. When this effect is included, the kinetic rate parameters in above equations are modified to:

$$k_{NO_2-Ba,f}^* = k_{NO_2-Ba,f} \left/ \left(1 + k_{NO_2-Ba,f} \frac{l}{D_f} \frac{r_o}{r_T} \right) \right. \quad (12a)$$

$$k_{NO_2-Ba,b}^* = k_{NO_2-Ba,b} \left/ \left(1 + k_{NO_2-Ba,b} \frac{l}{D_f} \frac{r_o}{r_T} \right) \right. \quad (12b)$$

$$k_{NO-Ba,f}^* = k_{NO-Ba,f} \left/ \left(1 + k_{NO-Ba,f} \frac{l}{D_f} \frac{r_o}{r_T} \right) \right. \quad (13a)$$

$$k_{NO-Ba,b}^* = k_{NO-Ba,b} \left/ \left(1 + k_{NO-Ba,b} \frac{l}{D_f} \frac{r_o}{r_T} \right) \right. \quad (13b)$$

$$l = r_T - \left[r_T^3 - \theta_{nitrate/nitrite} (r_T^3 - r_o^3) \right]^{1/3} \quad (14)$$

$$\frac{r}{r_T} = \left[1 - \theta_{nitrate/nitrite} + \frac{r_o^3}{r_T^3} \theta_{nitrate/nitrite} \right]^{1/3} \quad (15)$$

$$\theta_{nitrate/nitrite} = \theta_{nitrate} + \theta_{nitrite} = \frac{V_{nitrate} + V_{nitrite}}{V_T} = \frac{r_T^3 - r^3}{r_T^3 - r_o^3} \quad (16)$$

where θ_{BaCO_3} is the fraction of barium carbonate; the summation of θ_{BaCO_3} , $\theta_{nitrate}$ and $\theta_{nitrite}$ is equal to one; r_T is the entire radius of barium particle; r_o is the radius of inactive core in barium particle; r is the radius of reaction

front in barium particle, which varies with the progress of NO_x storage and release; D_f (with appropriate units for dimensional consistency of equations (12) & (13) as in [8]) includes the effects of diffusivity in barium particles.

The intra-particle diffusion processes involved in nitration are still not well understood. Since in the Olsson et al [8] model both nitrate and nitrite formation are depicted as being controlled by a single diffusion coefficient, we infer that the rate-limiting diffusing species is probably O_2 . We initially assumed the value of the diffusion coefficient used by Olsson et al [8], but comparisons with experiments indicated that this diffusivity should actually be a function of temperature. Ultimately, we found that the following temperature dependence gives reasonable results:

$$D_f = 1.9399 \times 10^{-5} - 7.222 \times 10^{-8} T_s + 7 \times 10^{-11} T_s^2 \quad (17)$$

The forward rate constants, $k_{NO_2-Ba,f}$ and $k_{NO-Ba,f}$ are determined from Arrhenius parameters, while the rates of the corresponding reverse reactions are determined by the appropriate equilibrium constraints:

$$k_{NO_2-Ba,b} = k_{NO_2-Ba,f} / K_{eq,NO_2-Ba} \quad (18)$$

$$k_{NO-Ba,b} = k_{NO-Ba,f} / K_{eq,NO-Ba} \quad (19)$$

The equilibrium constants K_{eq,NO_2-Ba} and $K_{eq,NO-Ba}$ are estimated from the standard Gibbs free energy changes of the corresponding reactions, which can be estimated from the standard enthalpy and entropy changes for the global reactions given by Olsson et al [8]. The results are:

$$\Delta G_{NO_2-Ba} = -113900 + 95T \quad (20)$$

$$\Delta G_{NO-Ba} = -63750 + 60.41T \quad (21)$$

We also use the rate expression recommended by Olsson and coworkers [8] for the rates of nitrate and nitrite reduction by CO and the C_3H_6 , the HC surrogate:

$$R_{nitrate-CO} = k_{nitrate-CO} C_{CO} \theta_{nitrate}^{0.5} \quad (22)$$

$$R_{\text{nitrite-CO}} = k_{\text{nitrite-CO}} C_{\text{CO}} \theta_{\text{nitrite}}^{0.5} \quad (23)$$

$$R_{\text{nitrate-C}_3\text{H}_6} = k_{\text{nitrate-C}_3\text{H}_6} C_{\text{C}_3\text{H}_6} \theta_{\text{nitrate}}^{0.5} \quad (24)$$

$$R_{\text{nitrite-C}_3\text{H}_6} = k_{\text{nitrite-C}_3\text{H}_6} C_{\text{C}_3\text{H}_6} \theta_{\text{nitrite}}^{0.5} \quad (25)$$

where the reaction order with respect to nitrate or nitrite species is set to 0.5. $k_{\text{nitrate-CO}}$, $k_{\text{nitrite-CO}}$, $k_{\text{nitrate-C}_3\text{H}_6}$ and $k_{\text{nitrite-C}_3\text{H}_6}$ are also computed from appropriate Arrhenius parameters. For storage/release reactions (i.e., reactions not involving noble metal catalytic sites), the tabulated pre-exponential factors, unlike in case of noble metal catalyzed reactions, correspond to reaction rates per unit reactor volume. As noted before, the present model assumes that H₂ and CO behave equivalently.

During LNT regeneration, released NO_x reacts with reductants to produce N₂. Like oxidation reactions, these chemical reaction rates are also proportional to the noble metal surface area. These reaction rates on noble metal surface are expressed by, respectively,

$$R_{\text{NO-CO}} = k_{\text{NO-CO}} C_{\text{NO}}^n C_{\text{CO}} \quad (26)$$

$$R_{\text{NO-C}_3\text{H}_6} = k_{\text{NO-C}_3\text{H}_6} C_{\text{NO}}^n C_{\text{C}_3\text{H}_6} \quad (27)$$

“n” in the above represents reaction order of NO reduction reactions with respect to NO. For NO reduction by CO, a value of 0.13 for “n” was suggested by Subramanian and Varma [18] but their rate expression also was proportional to $O_2^{0.3}$. This expression is clearly invalid during regeneration in LNTs when there is no O₂ present. So, a value of 1.0 was chosen for “n” based on more recent studies [9, 19,20,21,22]. Eqs. (26) - (27) represent reactions catalyzed by noble metal sites and as mentioned previously, the tabulated pre-exponential factors are for unit catalytic surface area.

2.2.3. Oxygen storage and regeneration

In LNTs, oxygen is stored in the washcoat as CeO₂. During the regeneration process, CeO₂ reacts with reductants and is reduced back to Ce₂O₃. The following simple chemical reaction mechanism is used to model the O₂ storage dynamics. The corresponding reaction rates are estimated from:

$$R_{\text{Ce}_2\text{O}_3-\text{O}_2} = k_{\text{Ce}_2\text{O}_3-\text{O}_2} C_{\text{O}_2} \theta_{\text{Ce}_2\text{O}_3} \quad (28)$$

$$R_{\text{CeO}_2-\text{CO}_2} = k_{\text{CeO}_2-\text{CO}_2} C_{\text{CO}_2} \theta_{\text{CeO}_2} \quad (29)$$

$$R_{\text{CeO}_2-\text{C}_3\text{H}_6} = k_{\text{CeO}_2-\text{C}_3\text{H}_6} C_{\text{C}_3\text{H}_6} \theta_{\text{CeO}_2} \quad (30)$$

Where $\theta_{\text{Ce}_2\text{O}_3}$ is the coverage of Ce₂O₃; θ_{CeO_2} is the coverage of CeO₂; and the summation of $\theta_{\text{Ce}_2\text{O}_3}$ and θ_{CeO_2} is equal to one.

Arrhenius rate parameters obtained by calibrating the model using experiments using engine and chassis dynamometer [24, 25] are listed in Table 1. Note that some of the values are unchanged from those reported by Olsson et al [8], and these are indicated in the table. We also point out that the catalysts used in our experiments were based on commercial Umicore and Delphi formulations that are different from each other and are also no longer current, so the listed parameter values are only provided as examples to illustrate general trends. More accurate predictions for specific catalysts clearly should be based on additional data for those catalysts.

<table 1 here>

2.3. NUMERICAL METHOD AND LNT SIMULINK MODULE

In the study, a SIMULINK block code has been developed to account for the one-dimensional representation of exhaust flow through a catalytic monolith and LNT kinetic chemical mechanism, in which all governing equations are discretized along the LNT length and describe by using SIMULINK block module. Briefly, the three subsystems include gas-phase energy equation, solid-phase energy equation, and gas-phase species governing equations describing NO₂, NO, HC, CO, CO₂, and O₂, respectively. The calculation of source terms is based on chemical reaction rates, stoichiometric coefficients or chemical reaction heat. Each subsystem is able to open under the SIMULINK environment. The code has been implanted into PSAT and carried out the simulations with PSAT default solvers and fixed time step.

For the simulations discussed here, the solid wall material properties and gas properties except thermal conductivity and gas-phase density are assumed as constant. The flow in the monolith channels is assumed to be laminar and Nusselt number corresponding to laminar flow through channels is used to compute heat transfer rates. Table 2 lists the values of parameters used in this study.

Table 1. Chemical reaction rate constants.

Rate constant (unit)	A	E (J/mol)	React heat (J/mol)	Chemical reaction
k_{NO-O_2} (mol/m ² -s)	920	39200 ^[8]	---	$NO + 1/2 O_2 \rightleftharpoons NO_2$
k_{CO-O_2} (mol/m ² -s)	7.70e9	90000	2.625e5	$CO + 1/2 O_2 \Rightarrow CO_2 + \Delta H^{CO-O_2}$
$k_{C_3H_6-O_2}$ (mol/m ² -s)	1.70e9	105000 ^[8]	1.926e6	$C_3H_6 + 9/2 O_2 \Rightarrow 3CO_2 + 3H_2O + \Delta H^{C_3H_6-O_2}$
$k_{NO_2-Ba,f}$ (mol/m ³ -s)	6.54e13	82500	---	$1/2 BaCO_3 + NO_2 + 1/4 O_2 \Rightarrow 1/2 Ba(NO_3)_2 + 1/2 CO_2$
$k_{NO_2-Ba,b}$ (mol/m ³ -s)	$k_{NO_2-Ba,f}/K_{eq,NO_2-Ba}$	---	---	$1/2 Ba(NO_3)_2 + 1/2 CO_2 \Rightarrow 1/2 BaCO_3 + NO_2 + 1/4 O_2$
$k_{NO-Ba,f}$ (mol/m ³ -s)	1.644e7	20000	---	$1/2 BaCO_3 + NO + 1/4 O_2 \Rightarrow 1/2 Ba(NO_2)_2 + 1/2 CO_2$
$k_{NO-Ba,b}$ (mol/m ³ -s)	$k_{NO-Ba,f}/K_{eq,NO-Ba}$	---	---	$1/2 BaCO_3 + NO + 1/4 O_2 \Rightarrow 1/2 Ba(NO_2)_2 + 1/2 CO_2$
$k_{nitrate-CO}$ (mol/m ³ -s)	1.82e10	70100	---	$1/2 BaCO_3 + CO_2 + NO \Rightarrow 1/2 Ba(NO_3)_2 + 3/2 CO$
$k_{nitrite-CO}$ (mol/m ³ -s)	1.82e10	70100	---	$1/2 Ba(NO_2)_2 + 1/2 CO \Rightarrow 1/2 BaCO_3 + NO$
$k_{nitrate-C_3H_6}$ (mol/m ³ -s)	2.09e11 ^[8]	100300 ^[8]	---	$1/2 Ba(NO_3)_2 + 1/6 C_3H_6 \Rightarrow 1/2 BaCO_3 + NO + 1/2 H_2O$
$k_{nitrite-C_3H_6}$ (mol/m ³ -s)	3.74e8 ^[8]	60300 ^[8]	---	$1/2 Ba(NO_2)_2 + 1/18 C_3H_6 + 1/3 CO_2 \Rightarrow 1/2 BaCO_3 + NO + 1/6 H_2O$
k_{NO-CO} (mol/m ² -s)	9.76e8	68300	1.800e5	$NO + CO \Rightarrow 1/2 N_2 + CO_2 + \Delta H^{NO-CO}$
$k_{NO-C_3H_6}$ (mol/m ² -s)	15.40e3	60000 ^[8]	2.100e5	$NO + 1/9 C_3H_6 \Rightarrow 1/2 N_2 + 1/3 CO_2 + 1/3 H_2O + \Delta H^{NO-C_3H_6}$
$k_{Ce_2O_3-O_2}$ (mol/m ³ -s)	5.60e10	70000	---	$Ce_2O_3 + 1/2 O_2 \Rightarrow 2CeO_2$
k_{CeO_2-CO} (mol/m ³ -s)	1.61e9	63000	2.625e5	$2CeO_2 + CO \Rightarrow Ce_2O_3 + CO_2 + \Delta H^{CeO_2-CO}$
$k_{CeO_2-C_3H_6}$ (mol/m ³ -s)	5.60e10	71500	2.100e5	$2CeO_2 + 1/9 C_3H_6 \Rightarrow Ce_2O_3 + 1/3 CO_2 + 1/3 H_2O + \Delta H^{CeO_2-C_3H_6}$

Table 2. Constant monolith and gas properties.

Parameter	Value
$Nu_{la \min ar}$	3.6
h_g (W/m ² K)	$Nu_{la \min ar} k_g / d$
k_g (W/mK)	$0.0002269 T_g^{0.832}$
$c_{p,g}$ (J/kgK)	1089
ρ_g (kg/m ³)	$348/T_g$
k_s (W/mK)	1.675
$c_{p,s}$ (J/kgK)	1071
ρ_s (kg/m ³)	3000
Noble metal loading (m ² /m ³)	7.077e4

2.4. LNT REGENERATION STRATEGY

For transient vehicle simulations, it is necessary to define conditions for switching from NO_x capture to regeneration (i.e. fuel-lean to fuel-rich conditions). In the chassis dynamometer experiments discussed below, the lean-rich cycling was implemented strictly on the basis of fixed time intervals for each condition. These experiments also utilized in-pipe injection of reductant into the engine exhaust, so that the engine operation remained unchanged during regeneration.

Our standard approach for more general vehicle simulation cases is to monitor NO_x in the LNT exhaust and modulate the engine fuel-air ratio to trigger regeneration when a critical breakthrough limit is reached. The resulting engine out temperature and emissions transients were predicted by utilizing a transient engine model described elsewhere [23]. In this study we set the critical NO_x level to 10 ppm. We also required that the LNT exhaust temperature be greater than 150°C and the last regeneration have been completed at least 60 s. Regeneration was not allowed to occur until all three criteria were met. When regeneration did occur, it was set for a fixed 3 s period at a fuel-to-air equivalence ratio of 1.13. Fuel in excess of that required for combustion was assumed to decompose into 60% CO, 30% H₂, and 10% HC based on previous experimental observations [4, 5, 24].

3. RESULT AND DISCUSSION

3.1. LNT MODEL PREDICTIONS

Here we compare the LNT model predictions using the above kinetic parameters with previously published data from engine dynamometer and chassis dynamometer experiments [24, 25]. Briefly, the engine dynamometer experiments were made with a Mercedes OM668 4-cylinder, 1.7-liter common-rail diesel engine coupled to a motoring DC dynamometer. The chassis dynamometer experiments, on the other hand,