

A simple model for lean NOx adsorber catalysts

C. S. Daw, Kalyana Chakravarthy* and K. E. Lenox
Oak Ridge National Laboratory
Oak Ridge, Tennessee

Abstract

We describe a simple model for simulating the transient behavior of a lean NOx adsorber. The model is based on one-dimensional differential approximations of mass balance equations for nitrogen oxides (NOx) that can be integrated very quickly (i.e., faster than real time). In this paper we focus specifically on the lean (or capture) phase of adsorber operation. During this phase, NOx is removed from the exhaust gas and reversibly reacted with alkali metal oxides in the monolith washcoat to form nitrates. We describe the driving force for the nitration reactions in terms of a pseudo-equilibrium sorption isotherm, which can be experimentally measured. The approach to (pseudo) equilibrium at each axial location is controlled by diffusion across the boundary layer and solid-phase diffusion within the washcoat. Model predictions are compared with experimental data for prototype adsorber materials, and future research directions are discussed.

Introduction

Stringent automotive emission limits in Europe and the U.S. have produced intense interest in NOx reduction technologies for engine exhaust. This is especially true for diesel and lean-burn gasoline engines, for which conventional three way catalysts (TWC) are ineffective. Two promising alternative technologies for lean exhaust are urea-ammonia selective catalytic reduction (SCR) and lean NOx traps (LNT's). The present study focuses on the developing improved dynamic models for LNT's.

Typical LNT's consist of ceramic monoliths containing thousands of parallel channels through which the exhaust gases are directed. Each channel is internally coated with a 'washcoat' containing noble metals (like Pt and Rh) and oxides of alkali/alkaline-earth metals (like Li, K, and Ba) supported on γ -Al₂O₃. During lean operation, NOx is 'stored' in the form of nitrates produced by reversible reactions between the NOx and alkali/alkaline-earths. At regular intervals, a momentary reducing condition is produced inside the monolith by injecting large quantities of reductant (e.g., fuel or gases such as CO and H₂). The reducing conditions cause the nitrates to decompose, whereupon most of the regenerated NOx is reduced to N₂. Some fraction of the released NOx is not reduced, resulting in incomplete global NOx conversion. This latter process is the ultimate source of any residual NOx emissions.

The sorbing function of LNT's makes them significantly different from traditional automotive catalysts, but there are strong similarities between these devices and standard adsorbers used in chemical processing [see for example, Sherwood et al., 1975, Wilke and Hines, 1985, and Perry and Green, 1997]. In particular, standard adsorbers remove gaseous or liquid

species from a gas or liquid stream by reversibly adsorbing or reacting it with a solid phase sorbent. When the sorbent phase becomes saturated, it is regenerated by changing conditions such that the solute is no longer thermodynamically stable in the sorbent phase (i.e., the solute-sorbent equilibrium is shifted to be unfavorable for adsorption). The principal differences between LNT's and standard adsorbers are:

- LNT's must operate under highly transient conditions (due to the demands of driving);
- Noble metal catalysts are required in the washcoat to achieve acceptable rates of storage, release; and regeneration; and
- The ultimate objective during regeneration is to chemically convert released NOx to N₂ instead of just expelling it.

Considering the similarities between LNT's and standard adsorbers, we expect that many of the modeling techniques developed for the latter are likely to be useful for LNT's. For this study, we begin by considering the lean mode (capture phase) of LNT operation.

Specific Objectives

Our primary goal here is to develop and test a transient model for the lean phase (capture mode) operation of an LNT. A principal feature of our approach is the use of a driving force described in terms of a pseudo-equilibrium sorption isotherm, which can be experimentally measured. We test the resulting model predictions with transient LNT data from a laboratory bench-flow reactor.

For the longer term, we also wish to identify the key practical issues in experimentally measuring LNT

* Corresponding author: kalyan@msr.csm.ornl.gov

Associated Web site: <http://www.cleers.org/>

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adsorption isotherms and testing models against transient LNT data. In particular, we are looking for relatively simple laboratory measurements that can be made for candidate LNT materials as they become available and used to compare such materials in consistent ways. Our ultimate objective is to produce predictive models for the full cycle of LNT operation that accurately predict full-scale performance based on such laboratory characterizations.

Modeling Approach

Consistent with traditional adsorber models, our LNT model is based on transient mass balances for total NO_x (NO + NO₂) in the bulk gas and sorbent phases within a single channel. In PDE form, these are

$$\partial C/\partial t + u \partial C/\partial x = K (C_s - C) \quad (1)$$

$$\partial q/\partial t = K(C - C_s) \quad (2)$$

In the equations above, C and C_s represent, respectively, the total NO_x concentration [moles/volume] in the bulk flow and the concentration of gas phase NO_x [moles/volume] in contact with the sorbent. The term q represents the concentration of nitrate in the sorbent [moles/sorbent surface area]. K , x and t are the global mass-transfer coefficient [1/time], axial distance [length], and time, respectively.

Note that the NO and NO₂ balances are combined as total NO_x. This is based on experimental observations that NO oxidation under typical lean conditions in the presence of noble metals is very fast, so that the NO and NO₂ are effectively in equilibrium near the surface. The local equilibrium gas NO_x concentration (C_s) is below the wall boundary layer and is a function of the nitrate loading (q). We use the term pseudo-equilibrium for this function because it lumps together the implied NO/NO₂ equilibrium, the complex interactions of sorbent compounds, and the effects of other gases (e.g., O₂ and CO₂).

Other key assumptions are:

- The overall monolith behavior can be modeled using a ‘typical’ channel, so that only a single channel is actually simulated;
- The rate of approach to equilibrium is dominated by the combined resistance of NO_x diffusion from the bulk gas through the boundary layer and NO_x diffusion through the solid phase to the storage sites;
- Boundary layer diffusion is estimated from standard laminar flow behavior;
- The equilibrium function depends on the specific sorbent, the solid phase temperature, and local concentrations of other gas phase species concentrations (e.g., O₂, CO₂);

- For the lean mode, O₂ and CO₂ are in large excess and remain effectively constant along the length of the channel;
- During the lean mode, the adsorber is isothermal;

If one is given the pseudo-equilibrium function, it is not necessary to understand the surface details of the sorbent itself in order to determine the driving force for additional change at any point in time. This is important because role of the various sorbent components (e.g., noble metals and alkali-alumina complexes) and the various types of nitrate compounds that can form are poorly understood at present. In the approach above, we treat the sorbent as a single phase with averaged properties.

Experimental setup and methods

The bench-flow reactor used for isotherm and transient LNT measurements consists of a 1.9-cm-ID quartz tube enclosed in an electric furnace. The furnace stabilizes the reactor at specified isothermal conditions. Core samples (short sections of monolith), are inserted within the quartz tube and exposed to pre-heated, simulated exhaust gas. The flow rate and composition of the inlet gas is controlled by an array of mass flow controllers, which are programmed and operated using Lab View. The gas pre-heater is controlled by an individual PID control loop. Water is added to the inlet gas by passing the gas through a wetted wick fed with a peristaltic pump. The inlet gas mixture flows through a 7.6-cm-long packed bed of 3mm glass beads to ensure flow uniformity and complete mixing before passing through the core sample.

The reactor exhaust flow is sampled by 2 California Analytical heated chemiluminescent (HCLD) analyzers, one set for total NO_x and the other set for NO. A MIDAC FTIR (Fourier Transform Infrared Spectroscopy) analyzer is also available for more detailed exit gas analyses. The NO_x analyzers have < 1s time response, and measurements are collected using Lab View at 2 Hz.

Inlet gas composition can be automatically cycled rapidly back and forth between lean and rich conditions to simulate LNT operation. For the experiments discussed here, we used a lean gas inlet composition of 12% O₂, 5% CO₂, 5% H₂O, 50-600 ppm NO, with the balance as N₂. During regeneration, the inlet gas composition is switched to replace the O₂ with additional N₂ and 0.2% H₂. Exposure to rich conditions for an extended period of time (e.g., 10 min for the experiments reported here) removes all nitrates from the surface, thus, eliminating any ambiguity about the initial conditions for the next capture cycle.

For estimating the pseudo-equilibrium function, one can measure the total uptake (to near saturation) of core samples exposed to inlet gas with varying concentrations of NO and/or NO₂. Net uptake is determined by

integrating the difference between the inlet and outlet NO_x levels over the interval between the start of exposure and the point where the exit concentration asymptotes. Repeated measurements at different inlet gas concentrations provide points on the pseudo-equilibrium isotherm. As noted before, this uptake will vary as a function of temperature and the concentrations of other gas species, so the measurements must be repeated at each condition of interest for each sorbent material.

We have also measured equilibrium NO_x uptake for washcoat powders for comparison using standard gas chemisorption apparatus. In this case, the samples are exposed to a pure gas (e.g., NO₂) and allowed to reach near saturation in a sealed vessel. By measuring gas pressure change, uptake can be determined. Repeated measurements at different initial gas pressures reveal the isotherm under these conditions. Although, pure gas conditions are different from real exhaust, comparisons with the benchflow reactor measurements can provide helpful insights and gauge the relevance of observations made using powder catalysts to catalysts in washcoat forms. For making this comparison, we have conducted the saturation uptake measurements on the monolith at the 523K, the temperature at which the chemisorption experiments were conducted.

For measuring transient LNT response, 7.6-cm-long core samples are exposed to known transients in inlet NO/NO₂ concentration (e.g., step inputs from zero to some fixed level). The measured NO/NO₂/total NO_x breakthrough curves provide a dynamic signature of the approach to pseudo-equilibrium that can be compared with model predictions. Experiments are performed over a range of temperatures (typically between 473K and 673K) to study the effect of temperature on NO_x capture. The experimental results described here were generated at 573K.

We are currently evaluating a range of sorber materials. For the results here, we used a commercial sorber (trade name SCONO_x) produced by EmeraChem for use in gas turbine applications. This catalyst is based on a Pt/K₂O/γ-Al₂O₃ formulation [Czarnecki et al., 2000] and has a cell density of 200cell per square inch. A powder form of this catalyst (also supplied by Emerachem) is used for the chemisorption experiments. For purposes of thermal stability and extending the operating temperature window, some catalysts [Danan and Balland, 2002; Ohno et al., 2000] contain more than one noble metal and/or more than one sorbent. The SCONO_x catalyst, on the other hand, is a simpler formulation and any characteristics of relevance to modeling (like the isotherm, effect of O₂ etc.) can be uniquely related back to the Pt-K combination.

Results and Discussion

The isotherms generated using the chemisorption measurements on the catalyst powder and the washcoat

saturation capacity measurements are plotted in figures 1 and 2, respectively. Note that the chemisorption measurements (Fig. 1) cover a wider concentration range and have a higher minimum concentration. This minimum limit occurs because of the difficulty in measuring the minute changes in gas pressure resulting from adsorption. Nevertheless, the chemisorption measurements reveal that there are multiple characteristic regions of behavior (indicated by the different slopes) as NO₂ concentration changes. This implies that there are multiple types of nitrate sites being formed, with the sites forming at high NO₂ concentrations being thermodynamically less stable.

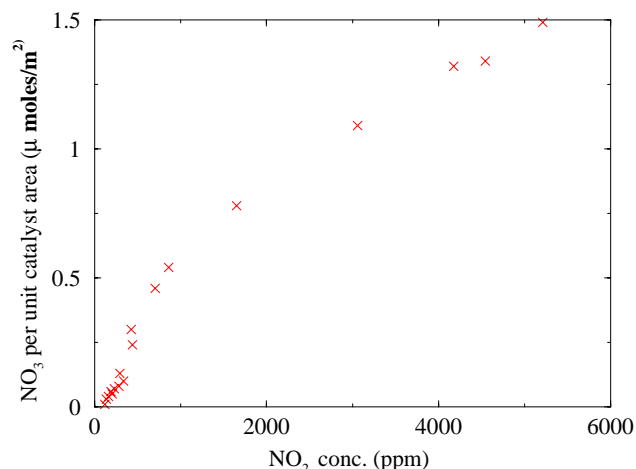


Figure 1: Isotherm from chemisorption experiments using pure NO₂ and SCONO_x sorbent powder.

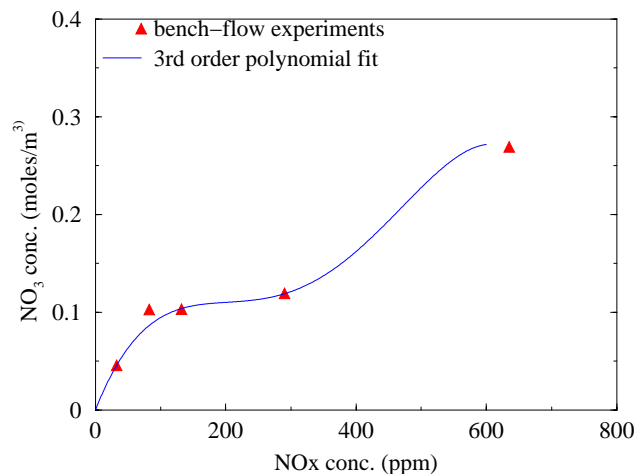


Figure 2: Isotherm generated using NO_x saturation capacity measurements on monolithic SCONO_x sorbent.

Considering only the lower portion of the chemisorption isotherm (which is within the typical NO_x concentration range for engine exhaust), it appears that the behavior can be approximated by a 2-term Freundlich function

$$q = \alpha_1 C_s^{\beta_1} + \alpha_2 C_s^{\beta_2} \quad (3)$$

where α_1 and β_1 and α_2 and β_2 are Freundlich isotherm parameters for two different types of nitrate sites. Freundlich isotherms are commonly observed for heterogeneous sorbents in the standard adsorption literature.

We expect that benchflow saturation isotherms will be more directly useful for modeling because they are measured for actual washcoated monoliths (as opposed to sorbent powders) and because the uptake measurements at concentrations below 100 ppm NOx are more accurate. Also, NOx concentrations in engine exhaust typically fall below 500ppm and frequently below 50 ppm. Note that below 150 ppm, the benchflow measurements reveal another plateau in the isotherm (a significant deviation from Eqn. 3), indicating the formation of yet another type of nitrate site. Considering both sets of isotherm measurements, it appears that the overall behavior is consistent with the so-called type IV pattern seen in traditional adsorbents [Perry and Green, 1997]. For simulation purposes, the functional behavior exhibited in Fig. 2 can be fitted with a third-order polynomial of the form

$$q = aC_s + bC_s^2 + cC_s^3 \quad (4)$$

Once the pseudo-equilibrium function has been determined for a specific set of exhaust conditions, the only remaining information needed to make breakthrough predictions with our model is the effective internal mass-transfer resistance associated with the sorbent. We expect that the general trend should be for this resistance to increase with nitrate loading, since NOx will be penetrating deeper into pores and/or unreacted regions with time. However, in the absence of *a priori* information about the detailed mechanisms and appropriate functional form, we have empirically estimated this term by working backwards from observed breakthrough curves. We did this by first determining the contribution of the laminar boundary layer using standard correlations, and then determining the additional resistance required to produce the observed breakthrough. An example result for the estimated internal mass-transfer resistance is shown in Fig. 3. As expected, the internal resistance (reciprocal of the internal mass-transfer coefficient) rises monotonically with loading, and can be described with a simple polynomial functional such as:

$$1/K_{in} = aq + bq^2 + cq^3 + dq^4 \quad (5)$$

The total mass-transfer rate is determined from the boundary layer mass transfer rate, K_{BL} , which remains fixed and the internal mass transfer rate, K_{in} , which is a monotonic function of q , the nitrate loading. The

resistances from the boundary layer and internal diffusion are assumed to act in series, and K is estimated from

$$K = 1/(1/K_{BL} + 1/K_{in}) \quad (6)$$

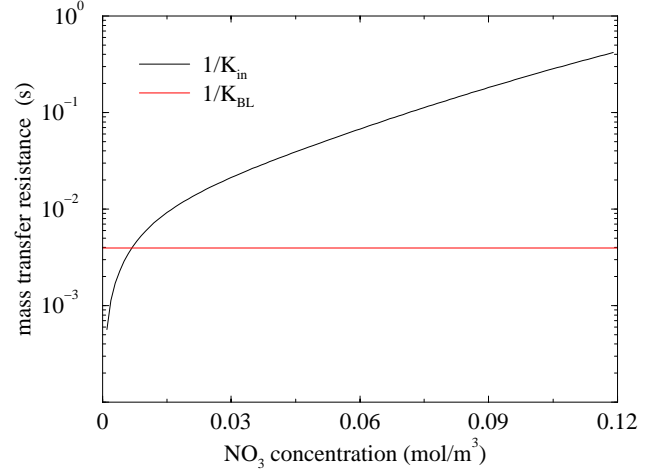


Figure 3: Dependence of internal mass transfer resistance (inverse of the internal mass transfer rate) on nitrate loading. The resistance to mass transfer from the laminar boundary layer is shown in red for comparison.

Using Eqns. 5 and 6, our model can now be used to make predictions for transient LNT breakthrough. Figures 4 and 5 illustrate comparisons between the model and experiments at 573 K for four different inlet NO concentrations (50ppm, 100ppm, 150ppm and 300ppm).

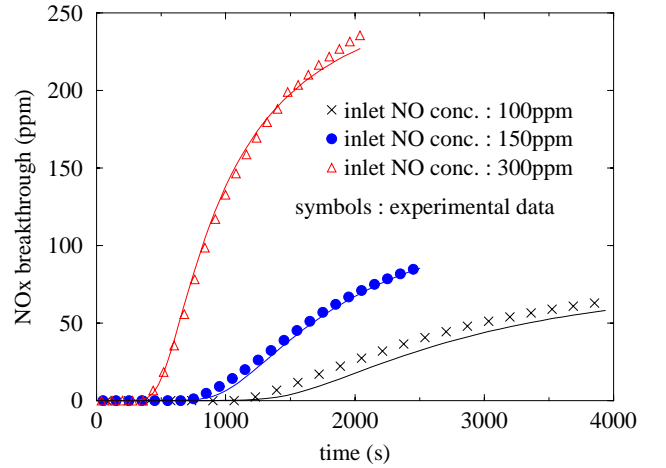


Figure 4: Comparison of predicted and measured NOx breakthrough curves for LNT adsorption transients with inlet NO concentrations of 100ppm, 150ppm and 300ppm

As seen in Fig. 4, the predictions are very close to the experimental results in cases with inlet NO concentrations between 100 and 300ppm. For the case with an inlet NO concentration of 50ppm (Fig. 5), the model predicts a somewhat faster breakthrough compared to the experiments, although the overall shape of the profile is

captured well. Note that when the internal mass-transfer resistance is neglected, the prediction is clearly inaccurate. We expect that some of the discrepancy that still occurs with the compound mass-transfer resistance may be due to inaccuracies in determining the pseudo-equilibrium isotherm. We expect some improvements can be made by increasing the number of experimental data points. Other minor experimental problems with the benchflow apparatus are currently being resolved.

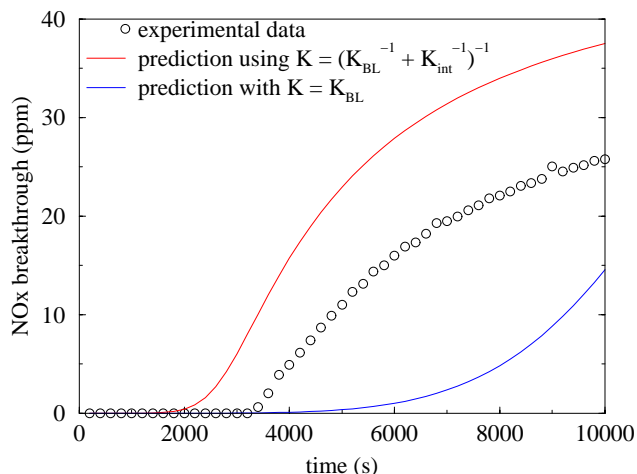


Figure 5: Comparison of predicted and measured NOx breakthrough curves for a NO inlet concentration of 50ppm. Predictions made both with and without and internal mass transfer resistance are shown.

It is important to independently determine the pseudo-equilibrium function and internal mass transport terms to avoid numerical artifacts (i.e., fits of breakthrough data that look accurate, but are physically incorrect). Another way of saying this is that the least-square fitting of LNT breakthrough curves alone, whether with the model proposed here or other models with parameterized kinetic rates, is complicated by the possibility of having non-unique parameter sets that give equally good fits. This is why we have emphasized the need to measure the pseudo-equilibrium function directly.

An example of this problem is illustrated in Fig. 6, where we have plotted experimental data against a model prediction for which the mass-transfer has been held fixed at the boundary-layer value, and the isotherm has been assumed to follow the two-term Freundlich form in Eqn. 3. Least-square fitting was done using just the Freundlich parameters. As can be seen, the predicted NOx breakthrough curve is very close to the experimental curve for the case with 300ppm inlet NO, but we know from independent saturation experiments that the fitted isotherm is incorrect. We also find that this fitted isotherm, unlike the measured one, incorrectly predicts the breakthrough when used to simulate experiments with other inlet NO concentrations. The apparently good result is actually an artifact resulting from the fact that non-

unique set of pseudo-equilibrium and mass transfer characteristics can result in the same NOx breakthrough curve.

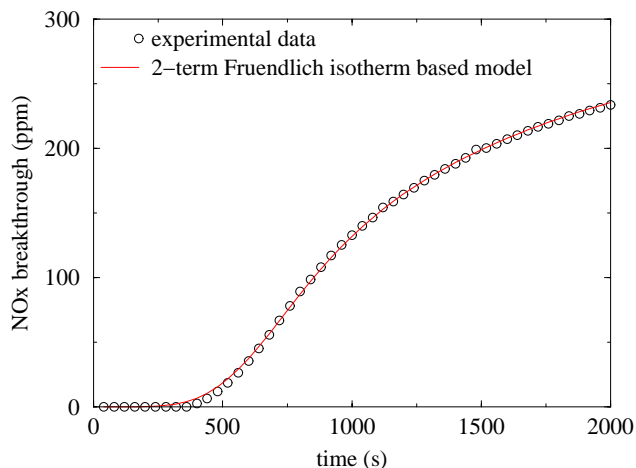


Figure 6: prediction of NOx breakthrough profile using a fixed mass transfer rate and a 2-term Freundlich isotherm

Another reason that determination of the correct isotherm is important is that it affects the predicted saturation profile along the reactor axis. Since the axial nitrate profile is an initial condition for simulating regeneration, errors in the adsorption behavior become compounded in the full cycle.

Conclusions

The pseudo-equilibrium model appears to be a feasible approach for constructing fast, simple models of the lean-phase operation of LNT adsorbers, provided that accurate methods for determining saturation uptake at different gas phase conditions is available. Benchflow saturation measurements with monolith cores appear to be able to provide the required uptake data, although some experimental details of the procedure need to be refined. Such experimental measurements can be made without any *a priori* knowledge of sorbent composition, making this approach readily adaptable for screening proprietary candidate LNT materials in the laboratory.

Additional experimental measurements are needed to confirm the applicability of the key model assumptions; including:

- the assumption that local gas concentrations of NO and NO₂ at the sorbent surface are effectively in equilibrium with the surface nitrates;
- the assumption that boundary-layer and solid-phase diffusion are the dominant NOx transport resistances; and
- the assumption that solid-phase diffusion resistance increases with nitrate loading.

The use of a pseudo-equilibrium isotherm circumvents the need for more complex NOx storage mechanisms [e.g., Lietti et al., 2001; Olsson et al., 2001],

which inevitably require more detailed knowledge of the sorbent surface, additional kinetic parameters, and increased numerical complexity. For comparison, the transient breakthrough simulations discussed here run at least an order of magnitude faster than the corresponding kinetics simulations using the Olsson et al parameters for LNT adsorption. Thus we believe the pseudo-equilibrium approach is especially suited for rapid characterization of materials and model based control of LNT devices [see for example, Asik et al., 1999; Ketfi-Cherif et al., 2000, Larsson et al., 1999].

Future work

The experimental procedure to obtain pseudo-equilibrium isotherms is currently being refined. Dependence of the isotherms on various parameters like temperature and exhaust gas composition (especially O₂, CO₂, and water.) needs to be carefully studied in order to account for realistic engine transients. The functional dependencies of the isotherm may shed additional light on the chemical and physical steps underlying adsorption and assist in developing explicit reaction kinetic models. The nature and distribution of the different types of nitrate sites is likely to play a critical role in optimizing the sorbent regeneration process.

Direct measurement of internal mass transfer should have high priority. The mass-transfer resistance also needs to be directly connected to the actual mechanisms by which NO_x is transported to reaction sites, especially those not directly exposed on the surface. Identifying the role of noble metals (e.g., as possible transport conduits) will also be critical.

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