

Global Kinetic Modeling of Lean NO_x Traps

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Abstract

Lean NO_x traps are an important concept for reducing NO_x in lean exhausts from diesel engines and lean burn gasoline engines. A global kinetic model has been developed in this work that can describe the NO_x emissions after the catalyst. The model is based on flow reactor experiments using a model Pt/Rh/BaO/Al₂O₃ catalyst. The objective with the model was to use global kinetics to facilitate rapid simulations and at the same time base the model on physical steps.

A first step in NO_x storage is to oxidize the NO to NO₂, where the latter is stored on the barium to form barium nitrates. Therefore, a global reaction step was initially developed for describing NO oxidation on a Pt/Al₂O₃ catalyst. This model was used when developing the NO_x storage model. The flow reactor experiments used for these simulations were cycling between lean and rich gas composition, using propene as a reducing agent. The experiments were conducted at three temperatures (320, 380 and 440°C) and using two inlet NO concentrations. To describe the mass-transfer in the catalyst a shrinking core model was used. The major path for the storage is in the model the formation of barium nitrates from NO₂ and barium carbonate. In the lean period there is a large storage, but the NO oxidation is quite low. Therefore was it necessary to introduce a second reaction step where barium nitrites were formed initially from NO and barium carbonates. This is consistent with FTIR observations, which have shown that nitrites are first formed, but after prolonged exposures the nitrates are dominating on the catalyst. Reaction steps for the regeneration of the stored NO_x with propene were added. The model was able to describe the NO_x storage in the lean period, the reduction of NO_x in the rich period and the breakthrough of NO_x occurring in the initial part of the rich phase. The model was validated with separate experiments, not included in the model development. In these experiments the oxygen concentration was lowered to 4 %, compared to 8 % that were used in the other experiments. The model was able to adequately predict the results from these experiments, with the lowering of the NO₂ formation and the storage.

A second NO_x storage model was developed for predicting the total NO_x concentration after the lean NO_x trap. The advantage with this model is that it only consists of one reaction for the storage and one reaction for the regeneration. Since this model contains less parameters, it is more rapid to tune in to other NO_x adsorbers with different composition. In addition, experiments where only total NO_x is measured (NO and NO₂ not separated) can be used for fitting parameters in the model. Three experiments were in this case used for fitting the parameters. The model was validated with nine experiments performed at different temperatures and with varying the oxygen and NO concentration. The model was able to predict the experiments well.

Keywords: Emission control, Catalysis, Lean NOx Traps, NOx Storage, Kinetic modeling, Barium, Platinum, Rhodium, NO oxidation, NOx regeneration

1 Introduction

Diesel engines and lean burn gasoline engines have a better fuel economy compared to stoichiometric gasoline engines. However, the three-way catalyst used for removing CO, hydrocarbons and NO_x from stoichiometric gasoline engines is not able to reduce the NO_x in oxygen excess. There are different concepts that are investigated for this purpose, for example hydrocarbon and urea selective catalytic reduction (HC SCR and urea SCR). For these system NO_x is selectively reduced using hydrocarbons or urea. Another concept is the NO_x storage catalysts (Miyoshi et al., 1995; Bögnér et al., 1995; Fridell et al. 1999), where the engine operates mixed lean, that is changing the air-fuel ratios in cycles from oxygen excess (lean) to fuel excess (rich). The NO_x trap contains a storage component, like barium carbonate, and noble metals on a support with high surface area. During the lean periods the NO_x is stored on the catalyst and during the short rich pulses the storage component is regenerated and the NO_x formed are reduced on the noble metal sites to form N₂.

The behavior of NO_x storage catalysts has been simulated using various techniques, global kinetic modeling (Olsson et al., 2004; Hepburn et al., 1996; Hepburn et al., 1998; Koči et al., 2004), detailed kinetic modeling (Olsson et al. 2001, Olsson et al. 2002b), first principle simulations (Broqvist et al., 2002; Broqvist et al. 2004) and thermodynamic calculations (Kobayashi et al., 1997). Hepburn et al., 1996 and 1998 used a shrinking core type of model for describing the mass-transfer in the barium particles in their global kinetic model. Olsson et al. 2004 also applied a shrinking core model in their simulations. In this work a model Pt/Rh/BaO/Al₂O₃ catalyst was used and a mechanism was developed for the storage phase and the regeneration with propene. The model simulates the NO and NO₂ concentration after the catalyst well. The model was validated with additional experiments.

The objective of this work is to further investigate the global mechanism for NO_x storage on lean NO_x traps. A comparison is made between a model that predicts both NO and NO₂ separately and a model that predicts the concentration of total NO_x only.

2 Theory

The results in this paper are a continuation of an earlier work, which is presented in Olsson et al. 2004. In the preceding paper details about the derivation of the global kinetic model for simulating NO and NO₂ from lean NO_x traps as well as rate expressions are presented.

2.1 Lean NO_x trap model for simulating NO and NO₂

The reactions used for simulating the NO and NO₂ concentrations from a lean NO_x trap are summarized in Table 1. The expressions for the rate constants and more details can be found in Olsson et al., 2004.

Table 1. Reactions for LNT model, in which both NO and NO₂ are simulated.

Reaction	Eq.
$C_3H_6 + 9/2 O_2 \Rightarrow 3CO_2 + 3H_2O$	(1)
$NO + 1/2 O_2 \Leftrightarrow NO_2$	(2)
$NO + 1/9 C_3H_6 \Rightarrow 1/2 N_2 + 1/3 CO_2 + 1/3 H_2O$	(3)
$1/2 BaCO_3 + NO_2 + 1/4 O_2 \Leftrightarrow 1/2 Ba(NO_3)_2 + 1/2 CO_2$	(4)
$1/2 BaCO_3 + NO + 1/4 O_2 \Leftrightarrow 1/2 Ba(NO_2)_2 + 1/2 CO_2$	(5)
$1/2 Ba(NO_3)_2 + 1/6 C_3H_6 \Rightarrow 1/2 BaCO_3 + NO + 1/2 H_2O$	(6)
$1/2 Ba(NO_2)_2 + 1/18 C_3H_6 + 1/3 CO_2 \Rightarrow 1/2 BaCO_3 + NO + 1/6 H_2O$	(7)

2.1.1 Noble metal reactions

Three reactions on the noble sites were used, C₃H₆ oxidation (eq. 1), NO oxidation (eq. 2) and NO reduction with C₃H₆ (eq. 3). NO oxidation was investigated separately, because it is crucial to oxidize NO to NO₂ for the formation of large amounts of nitrates (Fridell et al., 2001). The following reaction rate was used:

$$r_{NOox} = k_{NOox} C_{NO} C_{O_2}^{1/2} - \frac{k_{NOox}}{K_{eq,NOox}} C_{NO_2} \quad (8)$$

The rate for the backward reaction was determined by the thermodynamics.

For propene oxidation (eq. 1) was the classical rate presented by Volz et al. 1973 used, which has been applied in a number of studies (Oh and Cavendish, 1982; Shamim et al., 2000; Koltsakis et al., 1997; Pattas et al. 1994). Subramanian and Varma, 1985, studied the NO reduction with CO and they found a concentration dependence on NO to the power of 0.13. We assumed the same value of the exponent for the reaction between NO and C₃H₆ and the following rate was used:

$$r_{NO-C_3H_6} = \beta_1 k_{NO-C_3H_6} C_{NO}^{0.13} C_{C_3H_6} \quad (9)$$

where β_1 is a function that depends on the stoichiometry of the inlet gas. This function was defined by Montreuil et al., 1992 in their modeling of automotive catalysts, in order to switch smoothly between different kinetics in lean and rich environment. We have chosen to use this concept in our studies in order to prevent NOx regeneration in our model during the lean phase.

2.1.2 NOx storage

In many studies (Miyoshi et al., 1995; Kobayashi et al., 1997; Erkfeldt et al., 2001; Fridell et al., 2000) it has been shown that it is important to form NO₂ for the storage process. Therefore was NO oxidation modeled separately, as described in the previous section. The NO₂ reacts with the barium carbonate and forms barium nitrates (eq. 4). In our work a shrinking core model is used for describing the mass-transport in the barium

particles during NO_x storage. This type of model has been used previously for LNT in studies by Hepurn et al. (1996, 1998). The concept and the derivation of the rates are thoroughly described in Olsson et al. 2004. Briefly, the nitrates start to form at the surface of the barium particle. During the storage process the nitrates form further into the particle. The rate constant decreases when more nitrates are formed since the NO_x needs to penetrate further into the particle. The form of the rate and rate constant that are used is:

$$r_{NO_2-Ba} = k_{NO_2-Ba, f}^{bulk,*} C_{NO_2} C_{O_2}^{1/4} \theta_{BaCO_3} - k_{NO_2-Ba, b}^{bulk,*} C_{CO_2}^{1/2} \theta_{Ba(NO_3)_2} \quad (10)$$

$$k_{NO_2-Ba, f}^{bulk,*} = \frac{k_{NO_2-Ba, f}}{1 + k_{NO_2-Ba, f} \frac{l}{D} \cdot \frac{(R_{tot} - l)}{R_{tot}}} ; k_{NO_2-Ba, b}^{bulk,*} = \frac{k_{NO_2-Ba, b}}{1 + k_{NO_2-Ba, f} \frac{l}{D} \cdot \frac{(R_{tot} - l)}{R_{tot}}} \quad (11)$$

where l is the thickness of the nitrate layer, D the diffusivity and R_{tot} the total radius of the carbonate particle.

However, using NO₂ storage (eq. 4) was not sufficient to describe the experiments, because initially there is a large storage and at the same time the NO oxidation is quite low. Therefore it was necessary to introduce one extra reaction step (eq. 5) where nitrites are formed from NO and barium carbonates. Previous studies have shown that nitrites are formed initially on the surface and when the storage proceeds nitrates are dominating on the surface (Sedlmair et al., 2003; Fridell et al., 2001).

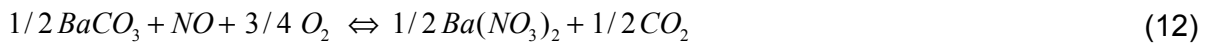
Experimentally, we found that only about 7% of the barium was used in the storage process. We therefore assume that we do not use the whole barium particle, and introduce a core of the particle, which the NO_x cannot access (Olsson et al., 2004).

2.1.3 NO_x regeneration

Two global reactions were used for the regeneration of the stored NO_x with propene, eqs. 6-7. In these reactions NO are formed when barium nitrate and barium nitrite react with propene. The formed NO reacts on the noble metal sites with propene to form N₂ (eq. 3).

2.2 Lean NO_x trap model for simulating total NO_x

In order to simplify the model further was the NO oxidation and NO_x storage lumped together to one reaction to predict the total NO_x. The advantage with this model is that only one reaction is needed for the storage and one for the regeneration compared to three reactions for the storage and two for regeneration in the previous model. This makes the model faster to tune in to catalysts with other compositions and it is also possible to tune in the model when NO and NO₂ are not detected separately. In this model all NO_x is treated as NO and the following reaction and rate was used for the storage:



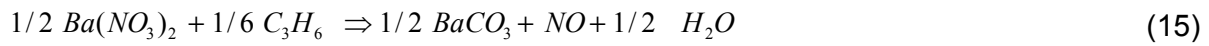
$$r_{NOx-Ba} = k_{NOx-Ba, f}^{bulk,*} C_{NO} C_{O_2}^{1/4} \theta_{BaCO_3} - k_{NOx-Ba, b}^{bulk,*} C_{CO_2}^{1/2} \theta_{Ba(NO_3)_2} \quad (13)$$

where

$$k_{NOx-Ba, f}^{bulk,*} = \frac{k_{NOx-Ba, f}}{1 + k_{NOx-Ba, f} \frac{l}{D} \cdot \frac{(R_{tot} - l)}{R_{tot}}} ; k_{NOx-Ba, b}^{bulk,*} = \frac{k_{NOx-Ba, b}}{1 + k_{NOx-Ba, f} \frac{l}{D} \cdot \frac{(R_{tot} - l)}{R_{tot}}} \quad (14)$$

The rate constant for the backward rate, $k_{NOx-Ba, b}$, was determined by ΔH and ΔS for the reaction. There are unfortunately no data available for surface nitrate formation and therefore was bulk data used for ΔH (-172.2 kJ/mol). There is a discrepancy in the stability of surface nitrates and bulk nitrates and therefore was ΔS fitted to the experiments. Only four parameters were used in the fitting procedure of the storage, the pre-exponential factor and activation energy for the storage process, the diffusivity and ΔS . All other parameters were kept fix from the previous simulation predicting both NO and NO₂.

The regeneration of the stored NOx with propene was described with only one reaction:



$$r_{nitrate-C_3H_6} = \beta_1 k_{nitrate-C_3H_6} C_{C_3H_6} \theta_{Ba(NO_3)_2}^{0.5} \quad (16)$$

where β_1 is a function that depends on the lambda value in the inlet gas feed as described in the previous section. A function of the lambda value has also been used in other simulations of NOx storage and reduction catalysts (Kojima et al., 2001; Kim et al., 2003). The definition for β_1 is, after being adopted for the gases used in our experiments, (Montreuil et al., 1992):

$$\begin{aligned} \beta_1 &= 2500 R_1 + 0.5 \\ R_1 &= 9y_{C_3H_6} - 2 y_{O_2} - y_{NO} \\ \text{if } \beta_1 < 0, \text{ set } \beta_1 &= 0 \\ \text{if } \beta_1 > 1, \text{ set } \beta_1 &= 1 \end{aligned} \quad (17)$$

The regeneration was tuned in by fitting only two parameters, the pre-exponential factor and activation energy for the reaction.

The reaction rates and rate constants for C₃H₆ oxidation and NO-C₃H₆ reaction were kept fixed to the previous NO+NO₂ model.

3 Experimental

One Pt/Al₂O₃ and one Pt/Rh/BaO/Al₂O₃ catalyst were used in this study. The catalysts are monoliths prepared by wet impregnation. Details about the samples are shown in Table 2. The monoliths are 15 mm long and 12 mm in diameter, consisting of 69 channels.

Table 2. Catalysts used in the present study.

Sample	Wash-coat weight (mg)	Pt-content (%)	Rh-content (%)	BaO-content (%)
Pt/Al ₂ O ₃	200	2	0	0
Pt/Rh/BaO/Al ₂ O ₃	200	2	1	20

The activity of the catalysts were measured in a flow reactor system described elsewhere (Olsson et al. 2001). Briefly, it consists of three parts, a gas mixing system, a reactor and analyzers. The gas mixing system consists of several mass flow controllers and the desired gas enters the quartz tube reactor. The monolith is placed in the tube and the temperature in the gas 10 mm in front of the catalyst as well as the temperature in the center of the middle channel is detected. The NO and NO₂ are analyzed with a chemiluminescence detector (Tecan CLD 700 EL ht).

Experiments for investigating the NO oxidation on platinum was performed over the Pt/Al₂O₃ catalyst. In this experiment an inlet feed gas of 600 ppm NO and 8% O₂ was used with a total feed flow rate of 2600ml/min. The temperature was increased from 25 to 500°C.

The NO_x storage activity was examined by transient experiments, switching between lean (240 s) and rich (60s) gas composition. The lean gas consisted of 450 or 900 ppm NO, 4 or 8 % O₂ and 900 ppm C₃H₆ in N₂. The rich gas was produced by turning off the oxygen supply. In total this results in four different cycles (which were repeated) at three temperatures 320, 380 and 440°C. The total feed flow rate was 1500ml/min.

4 Results and discussion

4.1 Kinetic model for lean NO_x traps, simulating NO and NO₂

When the objective with the NO_x storage model is to predict not only the total NO_x but also to separate between NO and NO₂ it is crucial to have a good model for NO oxidation on platinum. It is also shown in many studies that oxidation to NO₂ is the first step in the storage process. NO oxidation has been investigated separately over a Pt/Al₂O₃ catalyst and the results are shown in Figure 1. In this Figure the NO₂ conversion from both the experiment and simulation are shown versus the temperature. In the experiment the catalyst was exposed to 600 ppm NO and 8 % O₂ while increasing the temperature 5°C/min. Also shown in the Figure is the calculated conversion to NO₂ using thermodynamic data. It is shown that at higher temperatures the conversion follows the thermodynamic levels, but at lower temperatures the conversion is kinetically limited. The model, based on the reaction rate described in eq. 8, can simulate the experimental features well.

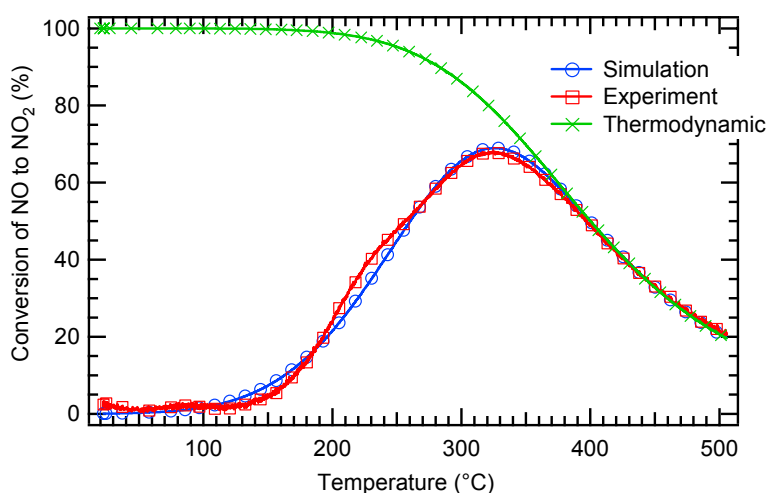


Figure 1. Experimental and simulated NO conversion to NO₂ using a Pt/Al₂O₃ catalyst and 600 ppm NO and 8% O₂ in the inflow. The conversion according to thermodynamic levels is also shown.

The NO oxidation model was used in the NO_x storage model, but since the NO oxidation is lower when barium is present (Olsson and Fridell, 2002a) the rate parameters were fitted again for the Pt/Rh/BaO/Al₂O₃ catalyst. The rate parameters for the storage, regeneration and noble metal reactions (eqs. 1-7) were tuned to six NO_x storage experiments. The lean period of the experiment consisted of 450 ppm NO, 8 % O₂ and 900 ppm C₃H₆ for 240s followed by 60 s rich where the oxygen was turned off. The experiment was repeated with 900 ppm NO and the two experiments were performed at three temperatures 320, 380 and 440°C. The results of the model at 380°C are shown in Figure 2, where the simulations (dashed lines) are shown together with the experimental concentrations (solid lines). The model is able to describe the NO and NO₂ levels, the NO_x storage and NO_x regeneration well. The maximum of the NO_x breakthrough peaks are marked in the figures.

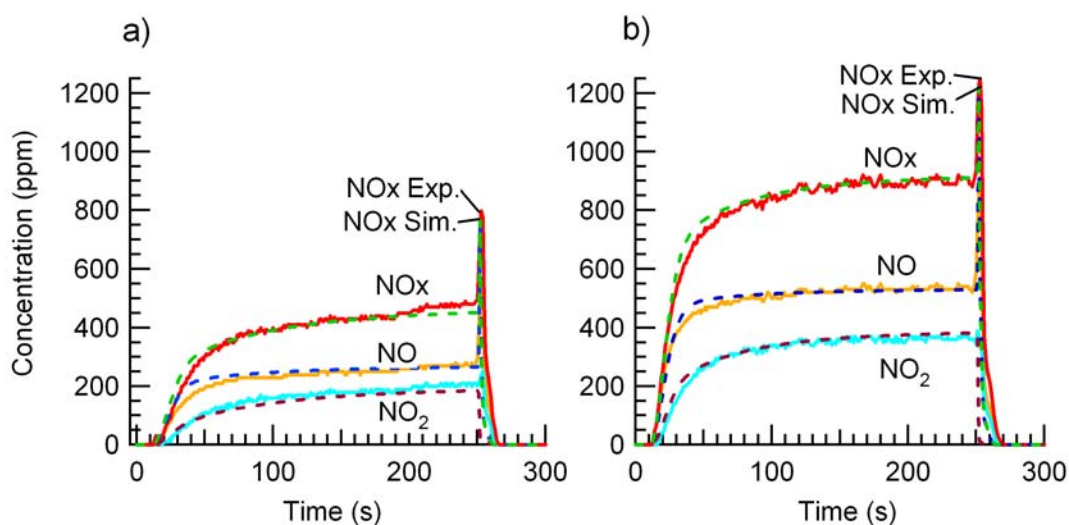


Figure 2. Experimental (solid lines) and simulated (dashed lines) concentrations of NO, NO₂ and NO_x after a Pt/Rh/BaO/Al₂O₃ catalyst during a NO_x storage cycle at 380°C. The inlet feed concentration during lean period was 8 % O₂, 900 ppm C₃H₆ and 450ppm NO (a) or 900 ppm NO (b). The rich period was achieved by turning off the oxygen.

4.1.1 Validation of the model

The model described in the previous section was validated with experiments that were not used in the model development. In these experiments the oxygen level was decreased to 4 % compared to 8 % used previously. Figure 3 shows the results at 380°C for two different NO inlet concentrations, 450ppm (a) and 900ppm (b). In these experiments the lean gas consisted of 4 % O₂, 900 ppm C₃H₆ and 450 or 900 ppm NO. The model is able to predict the experiments well.

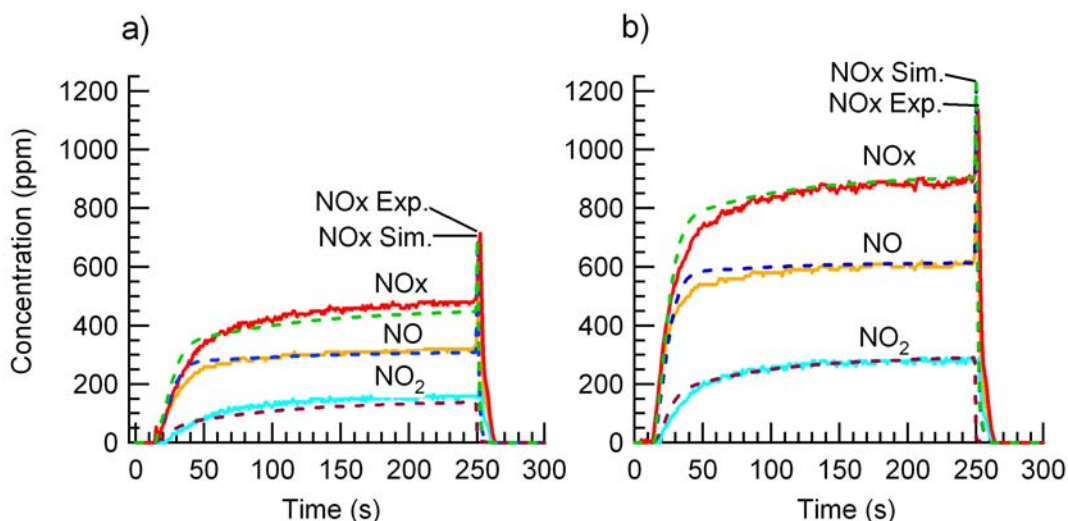


Figure 3. Experimental (solid lines) and simulated (dashed lines) concentrations of NO, NO₂ and NO_x after a Pt/Rh/BaO/Al₂O₃ catalyst during a NO_x storage cycle at 380°C. The inlet feed concentration during lean period was 4 % O₂, 900 ppm C₃H₆ and 450ppm NO (a) or 900 ppm NO (b). The rich period was achieved by turning off the oxygen.

4.2 Kinetic model for lean NO_x traps, simulating total NO_x

The total NO_x model consists of only one reaction for the storage and one for the regeneration. Also one reaction for C₃H₆ oxidation and one for the NO-C₃H₆ reaction is included in the model. Only four parameters were fitted for the storage and two for the regeneration. The other parameters were kept fix from the NO+NO₂ storage model, describe in the previous section. The fitted parameters can be found in Appendix 1. Three experiments at 320, 380 and 440°C were used when tuning in the parameters. In these storage cycles 450ppm NO, 900 ppm C₃H₆ and 8 % O₂ (or 0% O₂ for the rich period) was used. The results are shown in Figure 4, where the total concentration of NO_x is shown from the experiments (solid lines) and simulations (dashed lines) for the three investigated temperatures. The model is able to describe the experimental features of the storage and regeneration well. There is a small discrepancy for the NO_x breakthrough peak when switching to rich conditions at 320°C, but at the higher temperatures the model describes this phenomenon well. The results in Figure 4 also show that the NO_x breakthrough peak increases with temperature, which also the simulation gives.

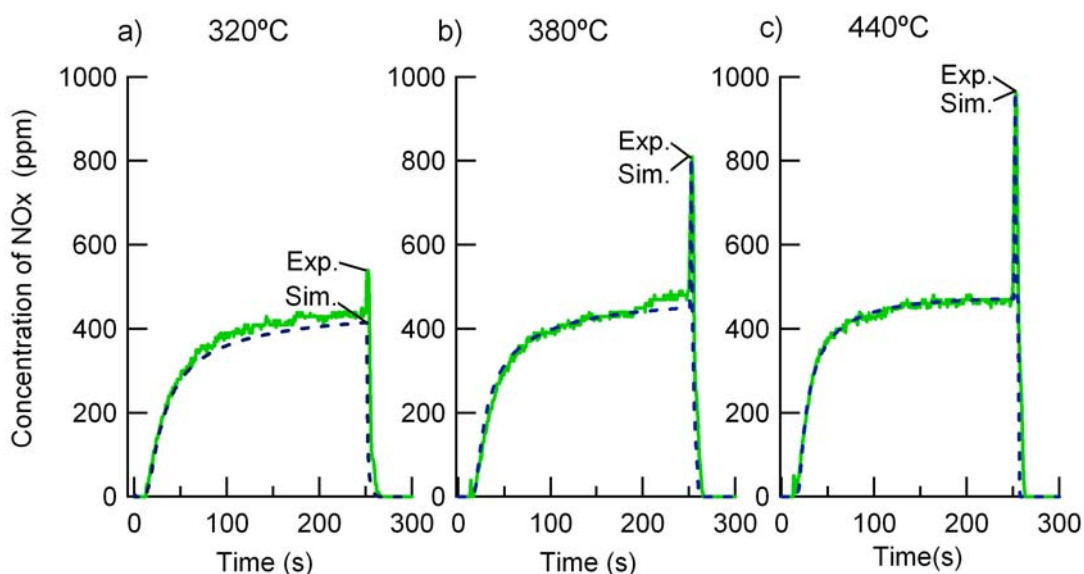


Figure 4. NO_x concentration from experiment (solid lines) and simulation (dashed lines) using a Pt/Rh/BaO/Al₂O₃ catalyst during a NO_x storage cycle. The inlet feed consisted of 8% O₂, 900 ppm C₃H₆ and 450 ppm NO during lean period. The rich period was achieved by turning off the oxygen. The temperature was 320°C (a), 380°C (b) and 440°C (c).

4.2.1 Validation of the model

The total NO_x model was validated with nine experiments, not included in the fitting procedure, where the inlet concentration of both NO and oxygen was varied. In the experiments used for tuning in the parameters, described in the previous section, the concentration in the inlet feed gas was 450 ppm NO, 8% O₂ and 900 ppm C₃H₆ during the 240 s long lean period. In the rich period the oxygen was turned off for 60 s. In the first set of validation experiments the inlet NO concentration was increased to 900 ppm and the results are shown in Figure 5 for the three temperatures 320, 380 and 440°C. Both the outlet concentration of NO_x from the experiment (solid lines) and the simulation (dashed lines) are shown. The corresponding results when changing the oxygen concentration to 4% while keeping the NO level at 450ppm are shown in Figure 6. In the final validation run both the NO and O₂ concentration were changed to 4% O₂ and 900 ppm NO, respectively. These results are presented in Figure 7. The Figures show that the model are able to predict the experiments, when changing inlet concentrations of NO and O₂, well.

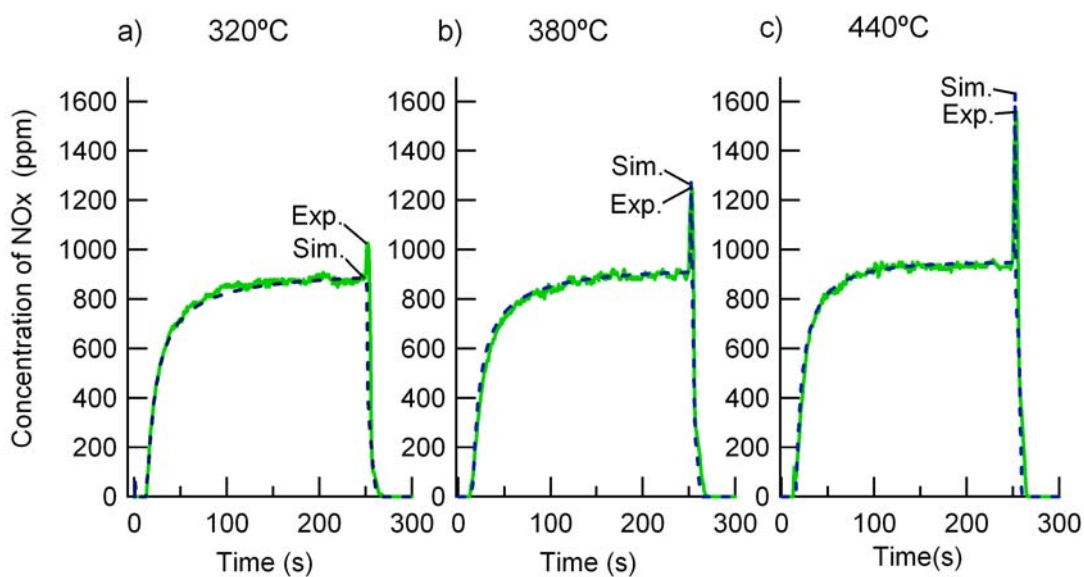


Figure 5. NOx concentration from experiment (solid lines) and simulation (dashed lines) using a Pt/Rh/BaO/Al₂O₃ catalyst during a NOx storage cycle. The inlet feed consisted of 8% O₂, 900 ppm C₃H₆ and 900 ppm NO during lean period. The rich period was achieved by turning off the oxygen. The temperature was 320°C (a), 380°C (b) and 440°C (c).

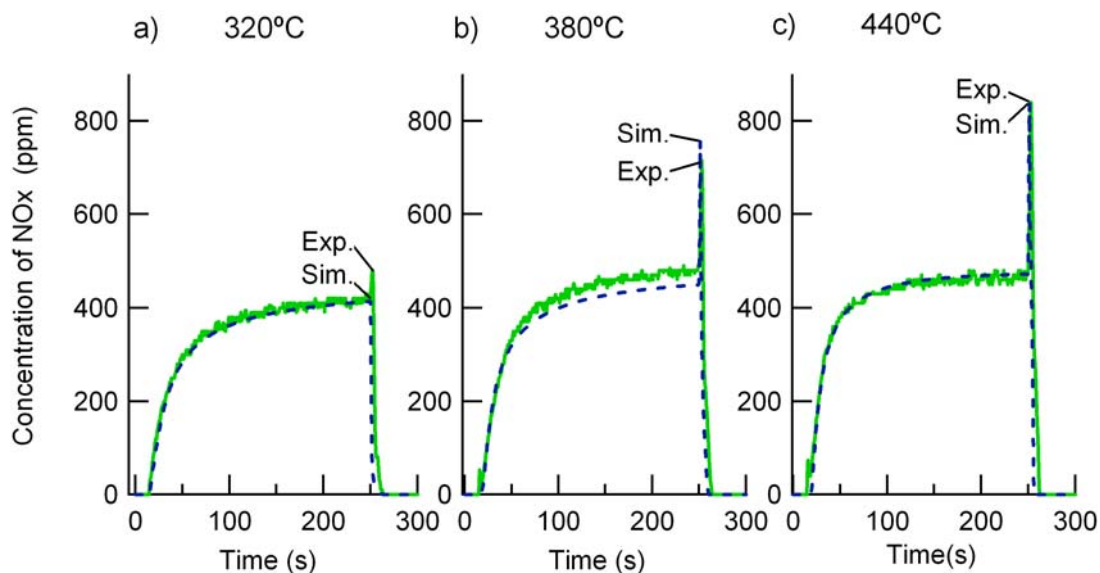


Figure 6. NOx concentration from experiment (solid lines) and simulation (dashed lines) using a Pt/Rh/BaO/Al₂O₃ catalyst during a NOx storage cycle. The inlet feed consisted of 4% O₂, 900 ppm C₃H₆ and 450 ppm NO during lean period. The rich period was achieved by turning off the oxygen. The temperature was 320°C (a), 380°C (b) and 440°C (c).

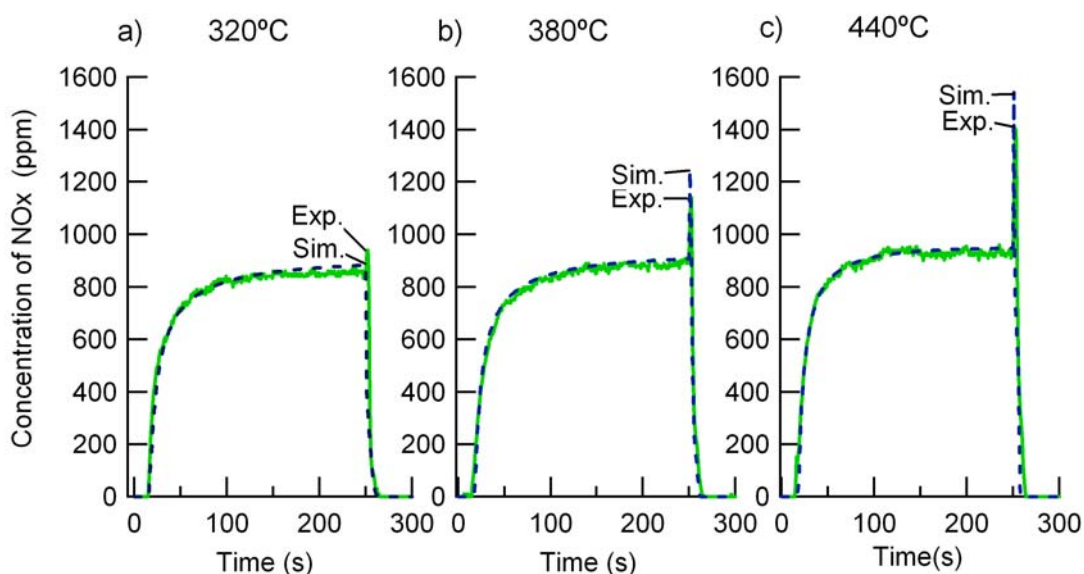


Figure 7. NO_x concentration from experiment (solid lines) and simulation (dashed lines) using a Pt/Rh/BaO/Al₂O₃ catalyst during a NO_x storage cycle. The inlet feed consisted of 4% O₂, 900 ppm C₃H₆ and 900 ppm NO during lean period. The rich period was achieved by turning off the oxygen. The temperature was 320°C (a), 380°C (b) and 440°C (c).

5 Concluding Remarks

Two models for lean NO_x traps are presented in this work. In the first model both NO and NO₂ can be predicted and in the second model only NO_x is predicted. The mass transfer in the barium particles were described by a shrinking core model, where the rate constant for storage decreases when the amount of stored NO_x increases, due to the longer transportation path for the NO_x. NO_x storage cycles were used for fitting the parameters and validating the models. The experiments were performed at three temperatures (320, 380 and 440°C) and the inlet feed gas consisted of NO, O₂ and C₃H₆ during the lean period and during the rich period of only NO and C₃H₆.

In the first model (NO+NO₂) the NO is oxidized on the noble metal sites and the formed NO₂ is stored on the barium carbonate to form barium nitrates. It was necessary to introduce one additional reaction step where barium nitrite was formed from NO and barium carbonate. This was done in order to describe the high storage in the initial part of the storage process at the same time as a quite low NO₂ production. This is also consistent with in situ FTIR, where nitrites are formed initially and after longer exposures nitrates are dominating on the catalyst. In the experiments the stored NO_x was regenerated with propene and two reactions were added for the decomposition of the barium nitrate and barium nitrite in the presence of propene. The parameters were fitted using NO_x storage cycles at three temperatures (320, 380 and 440°C) and using two different concentrations of NO in the inlet gas. The model was also validated with experiments using a lower oxygen concentration and the model was able to predict the experiments well.

The second model contains only one reaction for the storage and one for the regeneration and this model can be used for simulating the concentration of NO_x after the catalyst, but not separate the NO and NO₂. The parameters for the reactions on noble metals were kept fixed to the values obtained in the first model (NO+NO₂). Storage and

regeneration cycles at 320, 380 and 440°C were used to tune in the new parameters. The model was validated with nine experiments where the NO and O₂ concentration as well as temperature was varied. The model could predict the storage and regeneration period well.

Both models have advantages and the choice of model depend on the objective with the simulations. The first model can simulate both the NO and NO₂ concentration and this model can be used when it is important to predict the NO₂ content as well as total NO_x. The second model can only predict the total NO_x, but on the other hand contains less reaction steps. This makes this model easier to tune in to catalysts with other compositions. In addition, the model can also be tuned in to experiments where only total NO_x is measured.

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7 References

Broqvist, P., Panas, I., Fridell, E., Persson H., "NO_x storage on BaO(100) surface from first principles: a two channel scenario", *J. Phys. Chem. B*, 106, 2002, 137-145.

Broqvist, P., Grönback H., Fridell E., Panas, I., "Characterization of NO_x species adsorbed on BaO: Experiment and theory", *J. Phys. Chem. B*, 108 (11), 2004, 3523-3530.

Bögner, W., Krämer, M., Kruttsch, B., Pischinger, S., Voigtländer, D., Wenninger, G., Wirbeleit, F., Brogan, M. S., Brisley, R. J., and Webster, D. E., "Removal of nitrogen oxides from the exhaust of a lean-tune gasoline engine", *Appl. Catal. B*, 7, 1995, 153-171.

Erkfeldt, S., Jobson, E., Larsson, M., "The effect of carbon monoxide and hydrocarbons on NO_x storage at low temperatures", *Topics in Catalysis* 16/17, 2001, 127-131.

Fridell, E., Skoglundh, M., Westerberg, B., Johansson, S., and Smedler, G., "NO_x storage in barium-containing catalysts", *J. Catal.* 183, 1999, 196-209.

Fridell, E., Persson, H., Westerberg, B., Olsson, L., and Skoglundh, M., "The mechanism for NO_x storage", *Catal. Lett.* 66, 2000, 71-74.

Fridell, E., Persson, H., Olsson L., Westerberg, B., Amberntsson, A., and Skoglundh, M., "Model studies of NO_x storage and sulphur deactivation of NO_x storage catalysts", *Topics in Catalysis* 16/17, 2001 133-137.

Hepburn, J. S., Thanasiu, E., Dobson, D. A., and Watkins, W.L., "Experimental and modelling investigations of NO_x trap performances", *SAE Paper* 962051, 1996.

Hepburn, J. S., Kenney, T., McKenzie, J., Thanasiu, E. and Dearth, M., "Engine and aftertreatment modeling for gasoline direct injection", *SAE Paper* 982596, 1998.

Kim, Y-W, Sun, J., Kolmanovsky, I. and Koncsol, J., "A phenomenological control oriented lean NO_x trap model", *SAE Paper* 2003-01-1164, 2003.

Kobayashi, T., Yamada, T., and Kayano, K., "Study of NO_x trap reaction by thermodynamic calculation" *SAE Paper* 970745, 1997.

Koči, P., Marek, M., Kubiček, M., Maunula, T. and Härkönen, M., "Modelling of catalytic monolith converters with low- and high temperature NO_x storage compounds and differentiated washcoat", *Chem. Eng. Journal*, 97 (2-3), 2004, 131-139.

Kojima, S., Baba, N., Matsunaga, S., Senda, K. and Itoh, T., "Modeling and numerical analysis of NO_x storage-reduction catalysts –On the two effects of rich-spike duration", SAE Paper 2001-01-1297, 2001.

Koltsakis, G.C., Konstantinidis, P.A. and Stamatelos, A.M., "Development and application range of mathematical models for 3-way catalytic converters", Appl. Catal. B, 12, 1997, 161-191.

Miyoshi, N., Matsumoto, S., Katoh, K., Tanaka, T., Harada, J., Takahashi, N., Yokota, K., Sugiura, M., and Kasahara, K., "Development of new concept three-way catalyst for automotive lean-burn engines" SAE Paper 950809, 1995.

Montreuil, C.N., Williams, S.C. and Adamczyk, A.A., "Modeling current generation catalytic converters: Laboratory experiments and kinetic parameter optimization –Steady state kinetics", SAE Paper 920096, 1992.

Oh, S.H. and Cavendish, J.C., "Transients of monolithic catalytic converters: Response to step changes in feedstream temperature as related to controlling automobile emissions", Ind. Eng. Chem. Prod. Res. Dev., 21, 1982, 29-37.

Olsson, L., Persson, H., Fridell, E., Skoglundh M., and Andersson, B., "A kinetic study of NO oxidation and NO_x storage on Pt/Al₂O₃ and Pt/BaO/Al₂O₃", J. Phys. Chem. B 105, 2001, 6895-6906.

Olsson, L. and Fridell E., "The influence of Pt oxide formation and Pt dispersion on the reactions NO₂ <-> NO+1/2 O₂ over Pt/Al₂O₃ and Pt/BaO/Al₂O₃", J. of Catal. 210 (2), 2002a, 340-353.

Olsson, L., Fridell, E., Skoglundh. M. and Andersson, B., "Mean Field Modelling of NO_x Storage on Pt/BaO/Al₂O₃", Catal. Today 73, 2002b, 263-270.

Olsson, L., Blint, R.J. and Fridell, E., 2004.

Pattas, K.N., Stamatelos, A.M., Pistikopoulos, P.K., Koltsakis, G.C., Konstantinidis, P.A., Volpi, E., and Leveroni, E., "Transient modelling of 3-way catalytic converters", SAE Paper 940934, 1994.

Shamim, T., Shen, H. and Sengupta, S., "Comparison of chemical kinetic mechanisms in simulating the emission characteristics of catalytic converters", SAE Paper 2000-01-1953, 2000.

Sedlmair, Ch., Seshan, K., Jentys, A. and Lercher, J.A., "Elementary steps of NO_x adsorption and surface reaction on a commercial storage-reduction catalyst", J. Catal. 214, 2003, 308-316.

Subramanian, B., and Varma, A., "Reaction kinetics on a commercial three-way catalyst: the CO-NO-O₂-H₂O system", Ind. Eng. Chem. Prod. Res. Dev., 24, 1985, 512-516.

Voltz, S.E., Morgan, C.R., Liederman, D., Jacob, S.M., "Kinetic study of carbon monoxide and propylene oxidation on platinum catalysis", Ind. Eng. Chem. Prod. Res. Dev. 12, 1973, 294-301.

Appendix 1

The kinetic parameters used for the total NO_x model are given in Table 3 below. Only parameters that differ from the LNT model simulating NO and NO₂ (Olsson et al. 2004) are given.

Table 3. Kinetic parameters for LNT model for simulating total NO_x.

Parameter	Description	Pre-exponential factor	Activation energy (kJ/mol)	Parameter value
$k_{\text{NOx-Ba}}$	Rate constant, storage	$2.14 \cdot 10^7$	76.1	-
$k_{\text{nitrate-C3H6}}$	Rate constant, regeneration	$1.67 \cdot 10^8$	97.1	-
D	Diffusivity (m ² /s)	-	-	$6.70 \cdot 10^{-10}$
$\Delta S_{\text{Ba(NO3)2}}$	Entropy (fitted) (kJ/mol)	-	-	-187.4