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## Transient Modeling of NO<sub>x</sub> Reduction in Automobile Exhausts

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### Abstract

Regulations on automotive emissions are becoming increasingly stringent owing to the toxicity of gases like NO<sub>x</sub>, CO and unburned hydrocarbons. This brings the need for catalytic converters that convert the nitrogen oxides, CO and hydrocarbons to less harmful components. Steady state pseudo-homogeneous models for packed bed reactors have been developed earlier, taking into account the catalytic reduction of NO in the presence of CO. However, these models do not capture the transient behaviour of the reactor in real time systems. This project aims at developing a suitable transient model that is not computationally expensive but at the same time satisfactorily explains the behaviour of the converter at various operating conditions. The effect of the various operating parameters on the exit concentrations has also been studied. The major advantage of this system is that it takes into account the formation of N<sub>2</sub>O as an undesirable by-product, during the reduction of NO. It also captures the selectivity of N<sub>2</sub> formation under various conditions, and is expected to be useful in predicting start-up emissions of the vehicle.

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### 1. Introduction

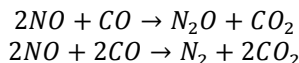
Gases from automobile exhausts have always been a major source of pollution. Outlet streams from the engines consist of varied compositions of nitrogen oxides, carbon monoxide and unburned hydrocarbons, all of which are extremely harmful to the atmosphere. As a measure to reduce the release of toxic gases from automobiles, government imposes regulations to reduce the toxicity of these emissions. In order to achieve future emission standards in different countries, conversions very close 100% have to be achieved under warmed up conditions. This brings the need for catalytic converters that convert the nitrogen oxides to the less harmful N<sub>2</sub> and the CO and hydrocarbons to carbon dioxide and water. Conversion and selectivity in these reactors need to be optimum in order to meet the regulations.

Here, we aim to develop a satisfactory transient model incorporating the complex global kinetic expressions of the reduction of NO with CO (which are the major components of engine exhaust, aside from the hydrocarbons). The model is validated, and will serve as the basis for future developments of accurate transient predictions of catalytic converter performance.

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## 2. Mathematical Model

A 1-D pseudo-homogeneous model is taken into consideration in this paper. In order to model the catalytic converter, we make use of the kinetics of the reduction of NO in the presence of CO. Based on the micro-kinetic model developed earlier for the reduction of NO [1], reduced order rate expressions were arrived at in earlier work [2], according to which the following two global reactions are expected to occur:



The importance of the undesirable side product  $N_2O$  is considered explicitly in this kinetic model, and this is expected to be of particular importance for Pt catalyst based devices [1,2].

With typical simplifying assumptions considered, the mass and energy balance equations for the Packed Bed catalytic reactor can be represented as

$$\begin{aligned} \frac{\partial y_k}{\partial t} &= -u \frac{\partial y_k}{\partial z} - M \sum_{i=1}^n (-r_A)_V \\ \frac{\partial T}{\partial z} + \frac{\partial T}{\partial t} &= \frac{1}{\rho u_m \bar{c}_p} \sum_{i=1}^n (-r_A)_V (-\Delta H_R) \end{aligned}$$

where the notations are the same as in standard reaction engineering textbooks.

**Table 1.** Model parameters for simulation of NO reduction

<b>Reactor design parameters:</b>	
Length (m)	0.014
Diameter (m)	0.004
Catalyst Surface area (m <sup>2</sup> )	0.0827
Catalyst active site density (mol/m <sup>2</sup> )	0.207 x 10 <sup>-4</sup>
<b>Operating conditions:</b>	
Temperature range (K)	623 – 823
Pressure (atm)	1
Inlet composition of NO (ppm)	3000
Inlet composition of CO (ppm)	3400
Inlet volumetric flow rate (m <sup>3</sup> /min)	100 x 10 <sup>-6</sup>

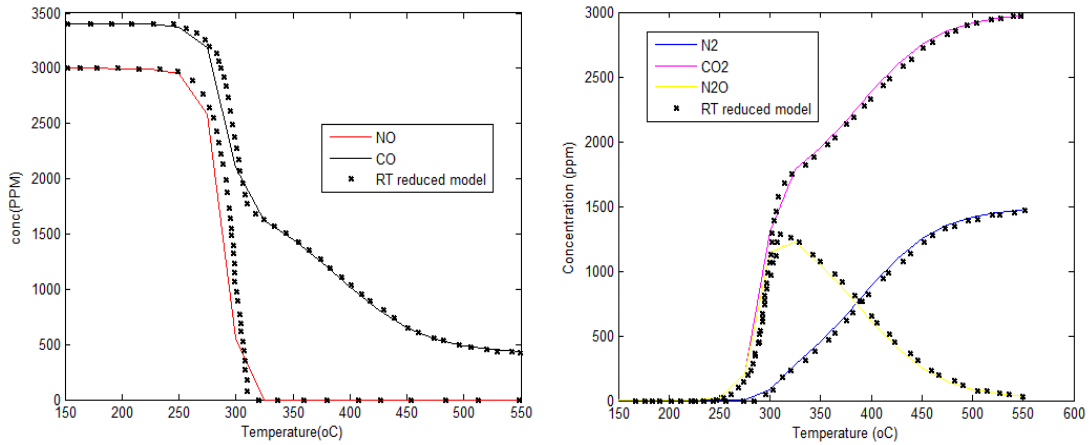
To solve the partial differential equations thus obtained we have used MATLAB. The numerical technique used is called the method of lines in which the space variable was discretized. The first step was to set up the equations with the corresponding reactor parameters. The gas phase domain of the channel was partitioned into discrete elements with grid space distance  $\Delta z$ . Subsequently, at the time step  $t$ , the concentrations of each species in the gas phase for each node  $i+1$  was computed using the conditions known for the node  $i$  at time step  $t$ .

Hence we get a system of ordinary differential equations of the form

$$\frac{dy_k}{dt} = -u \frac{y_{ki} - y_{ki-1}}{\Delta z} - M \sum_{i=1}^n (-r_A)_V$$

## 3. Results and Discussion

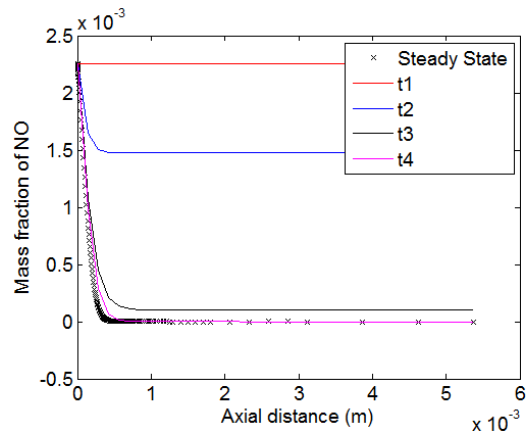
The steady state modelling of the above mentioned system gave the following plots with respect to temperature [2].



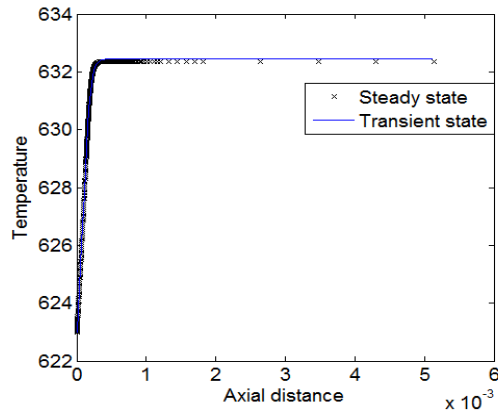
**Figure 1.** Variation of concentration of various species with reactor temperature, from earlier work [2]. Experimental results [3] are shown in symbols, while the results of PBR simulations using the global kinetic model [2] are shown in lines.

It can be seen that the results are in agreement with experimentally obtained results. It is important to note that the model accounts for the production of  $N_2O$ . Up to  $T = 350^\circ C$ , the formation of  $N_2O$  is favoured, whereas at higher temperatures, the formation of  $N_2$  is predominant.

On developing the transient state model, we first validated the results by comparing the composition of the gas mixture at different points in the reactor at large times with that obtained at steady state. Figure 2 shows a plot of mass fraction of NO against axial distance at different times bench-marked with the corresponding steady state results. It can be noted that at the largest time  $t_4$ , the system has reached steady state and the mass fraction of NO is the same as that found in the steady state system. In this case  $t_4 = 0.5$  s.



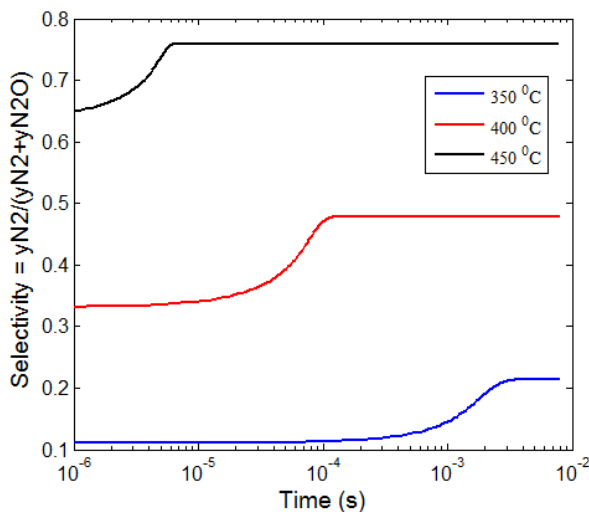
**Figure 2** Variation of mass fraction along reactor length under isothermal conditions where  $t_1 < t_2 < t_3 < t_4$  in comparison with steady state system. Steady state conditions are shown in symbols and results from transient state simulations are shown in lines. At large times ( $t_4$ ), the system reaches steady state.



**Figure 3** Variation of temperature along reactor length at large times under non-isothermal conditions in comparison with steady state system. Steady state conditions are shown in symbols and results from transient state simulations are shown in lines. The inlet temperature for the plot shown is  $\sim 623K$  ( $350^\circ C$ )

We then extended the model to observe the behaviour of the system under non-isothermal conditions as well. In the steady state system, the temperature was found to increase along the reactor length. The exit temperature increased with an increase in inlet temperature. The transient model was observed to show similar behaviour in the non isothermal case. Figure 3 shows a plot of temperature along reactor length at a large time bench-marked against steady state results. Overall, as the reactions are not highly exothermic, the rise in temperature when the non-isothermal case is considered is not very high.

The major advantage of using the reduced order rate expressions for the NO-CO system was that it captures the selectivity of  $N_2$  over  $N_2O$  as a function of temperature. Hence, we checked if the transient model also captures this behaviour of the system by calculating the selectivity of the  $N_2$  and plotting it against reaction time for different temperatures, as shown in Figure 4.



**Figure 4.** Variation of selectivity =  $\frac{y(N_2)}{y(N_2)+y(N_2O)}$  with time at three different temperatures. The system reaches steady state by  $t = 0.008$  s. It can be seen that the selectivity is poor at lower temperatures as established in the steady state results [2].

#### 4. Conclusions

We have successfully demonstrated a non-isothermal, transient packed bed catalytic reactor model incorporating complex global kinetics for the reduction of NO in the presence of CO. The model uses validated kinetics and is computationally cheap and handy. At large times, the model behaves as in steady state and satisfactorily agrees with previously obtained results. All the reactant and product species give meaningful conversions. Also, the temperature sensitivity established in steady state was shown in the transient model as well. The variation in the selectivity to  $N_2$  with reactor temperature was observed from the model predictions. At lower temperatures, and start-up conditions (small times), the selectivity to  $N_2$  was found to be very poor, as expected. The challenge of these start-up emissions and the importance of catalyst light-off are clearly demonstrated by these results.

#### 5. References

- [1] Mantri, Dinesh, and Preeti Aghalayam. "Detailed surface reaction mechanism for reduction of NO by CO." *Catalysis today* 119.1 (2007): 88-93.
- [2] Ravikeerthi, T., et al. "Microkinetic model for NO-CO reaction: Model reduction." *International Journal of Chemical Kinetics* 44.9 (2012): 577-585.
- [3] Chambers, Dean C., Dennis E. Angove, and Noel W. Cant. "The Formation and Hydrolysis of Isocyanic Acid during the Reaction of NO, CO, and H<sub>2</sub> Mixtures on Supported Platinum, Palladium, and Rhodium." *Journal of Catalysis* 204.1 (2001): 11-22.