

# ANALYSIS OF TRAVELING CONCENTRATION AND THERMAL FRONTS IN A LEAN NO<sub>x</sub> TRAP

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## Summary

The propagation of concentration and thermal fronts during the regeneration of a lean NO<sub>x</sub> trap are analyzed. Analytical expressions for the velocity and width of these fronts are obtained, and the predicted values are in agreement with the experimental results reported by Clayton et al.<sup>1</sup>. It is shown that the speed of these fronts depends only on the overall stoichiometry of the reactions, inlet concentrations and the storage capacity, whereas the width depends on the diffusivities in the gas phase and washcoat as well as the kinetics. The lower diffusivity of NH<sub>3</sub> than H<sub>2</sub> is shown to be responsible for the observed wider width of the NH<sub>3</sub> front and earlier appearance of NH<sub>3</sub> in the effluent than H<sub>2</sub>. The concentration front velocities in commercial lean NO<sub>x</sub> traps (LNTs) are estimated to be higher than the thermal front velocities. This feature presents interesting results in commercial size monoliths with the possibility of multiple fronts existing along the length. It is shown that the short monolith reactors used in laboratory bench-scale experiments are not able to capture the thermal front propagation features of a commercial size LNT.

## Keywords

Environmental Reaction Engineering, Multiphase and particulate reactors, Micro-reactors

## Introduction

The strict NO<sub>x</sub> emission standards have resulted in the development of various technologies for NO<sub>x</sub> abatement, including NO<sub>x</sub> storage and reduction (NSR). NSR uses a bifunctional catalyst comprising of noble metals, which are supported on alkaline earth or alkali metals (Ba, K, etc.).

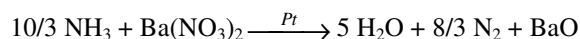
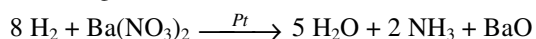
The storage of NO<sub>x</sub> on the LNT catalyst occurs under fuel lean conditions, whereas its reduction occurs under fuel rich conditions. During the lean phase, a storage front of NO<sub>x</sub> propagates along the reactor, which is caused by its uptake on the catalyst and a gradual breakthrough of NO and NO<sub>2</sub> (Bhatia et al.<sup>2</sup>). During the reduction phase, a front comprising the reductant (s) moves along the monolith reactor and exhibits a rather sharp breakthrough at temperatures above 250°C, occurring once most of the stored NO<sub>x</sub> is reduced. In addition, thermal fronts propagate along the monolith length because of the high exothermicity of the reduction reactions.

In the present work, we estimate the width and velocity of the concentration and thermal fronts during the storage and reduction processes in a lean NO<sub>x</sub> trap. The formation of NH<sub>3</sub> during the regeneration of a lean NO<sub>x</sub> trap is analyzed because NH<sub>3</sub> is a desired product in the effluent of a LNT in combined LNT/SCR systems. The velocity of the concentration and thermal fronts are compared and design recommendations are made based on the analysis.

This analysis is also used to explain some of the experimental results reported by Clayton et al.<sup>1</sup>.

## Mathematical model

A one-dimensional two-phase model is used, which consists of species and energy balances in the fluid and solid phases. In addition, the model consists of a species balance for the stored NO<sub>x</sub>, which is based on the following overall reactions:



The balance equations are then written in coordinates which move with the velocity of the concentration or thermal front, i.e.

$$z = x - u_c t \quad (1)$$

where  $x$  is the axial coordinate,  $u_c$  is the velocity of the concentration/thermal front and  $t$  is the time.

## Results and Discussion

The balance equations in the new coordinates are combined and then used to estimate the concentration front velocities for the following special cases:

- (i) fast NH<sub>3</sub> formation and consumption,
- (ii) fast NH<sub>3</sub> formation, but its consumption kinetically limited, and

(iii) NH<sub>3</sub> is the reductant instead of H<sub>2</sub>.

Reaction conditions for case (i) are expected for a high dispersion catalyst at high temperatures (Clayton et al.<sup>3</sup>), whereas the conditions for case (ii) are prevalent at low temperatures (Clayton et al.<sup>1</sup>). The role of NH<sub>3</sub> as a reductant was shown earlier (Clayton et al.<sup>1</sup>) and hence its analysis is considered in the present work. The front velocity for case (i) is given as

$$u_c = \frac{\bar{u}}{1 + \frac{\varepsilon_{wc} \delta_c}{R_\Omega} + \frac{5\delta_c c_{Ba(NO_3)_2}^o}{R_\Omega c_{H_2}^{in}}} \quad (2)$$

The symbols  $\bar{u}$ ,  $\varepsilon_{wc}$ ,  $\delta_c$ ,  $R_\Omega$ ,  $c_{Ba(NO_3)_2}^o$ , and  $c_{H_2}^{in}$  represent the average gas velocity, porosity within the washcoat, thickness of the washcoat, effective transverse length scale, concentration of stored barium nitrates before the onset of regeneration and the inlet concentration of H<sub>2</sub> during the regeneration. The following invariants are derived which relate the gas phase concentrations:

$$c_{H_2,m} + 4c_{NH_3,m} + 5c_{N_2,m} = c_{H_2}^{in} \quad (3)$$

$$c_{H_2,m} - 3c_{N_2,m} + \frac{8}{5}c_{H_2O,m} = c_{H_2}^{in} \quad (4)$$

These relations obviate the need to solve species balances for all of the gaseous species.

Assuming negligible washcoat diffusional limitations, an expression for the width of the H<sub>2</sub> front is obtained for case (i) and is given as

$$w_{H_2} = \frac{4\bar{u}R_\Omega^2}{D_{H_2,m} Sh_{H_1,\infty}} \ln(100) \quad (5)$$

The symbols  $w_{H_2}$ ,  $D_{H_2,m}$ , and  $Sh_{H_1,\infty}$  represent the width of the H<sub>2</sub> front, gas-phase diffusivity of H<sub>2</sub> and the asymptotic Sherwood number, respectively. If NH<sub>3</sub> is the reductant (case (iii)), the width of the NH<sub>3</sub> front is given as

$$w_{NH_3} = \frac{4\bar{u}R_\Omega^2}{D_{NH_3,m} Sh_{H_1,\infty}} \ln(100) \quad (6)$$

Eqns. (5) and (6) suggest that the width of the concentration front is inversely proportional to the gas-phase diffusivities. Since the gas-phase diffusivity of NH<sub>3</sub> is ca. three times lower than that of H<sub>2</sub>, the width of NH<sub>3</sub> front is ca. three times higher than that of H<sub>2</sub>. This explains the earlier appearance of NH<sub>3</sub> in the effluent than H<sub>2</sub>. However, this is complicated by the adsorption of NH<sub>3</sub>, especially at lower temperatures.

Calculations were performed with H<sub>2</sub> as the reductant and the diffusivity of NH<sub>3</sub> was artificially decreased to one-fifth of its original value. The H<sub>2</sub> and NH<sub>3</sub> breakthrough curves for the original values of diffusivity and those with the reduced NH<sub>3</sub> diffusivity are shown in Fig. 1. It is observed that decreasing the NH<sub>3</sub> diffusivity results in increasing the time delay between the appearance of NH<sub>3</sub> and H<sub>2</sub>, with NH<sub>3</sub> appearance in the effluent earlier than H<sub>2</sub>. Also, the width of the NH<sub>3</sub> front is higher than the

original value. Calculations were performed in which the diffusivity of NH<sub>3</sub> is artificially increased to higher than H<sub>2</sub>. It was observed that H<sub>2</sub> appeared earlier in the effluent than NH<sub>3</sub>. Hence, it is concluded that the lower diffusivity of NH<sub>3</sub> as compared to H<sub>2</sub> is responsible for the earlier appearance of NH<sub>3</sub> in the effluent than H<sub>2</sub>.

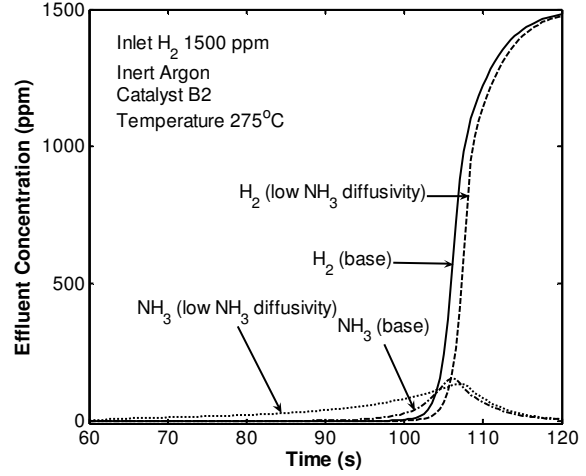


Fig. 1. Comparison of H<sub>2</sub> and NH<sub>3</sub> breakthrough profiles for two different diffusivities of NH<sub>3</sub> (Base: H<sub>2</sub> diffusivity=2.05 cm<sup>2</sup>/s and NH<sub>3</sub> diffusivity=0.69 cm<sup>2</sup>/s; Low NH<sub>3</sub> diffusivity=0.69/5=0.14 cm<sup>2</sup>/s)

The heat Peclet number is given as

$$Pe_h = \frac{\bar{u}L\rho_f C_{pf} R_\Omega}{k_w \delta_w} \quad (7)$$

In Eq. (7),  $L$  represents the length of the monolith. In bench-scale laboratory experiments, the velocities are chosen such that the residence time ( $= L/\bar{u}$ ) has the same order of magnitude as in a real vehicle exhaust. Since the length and the velocity are proportionately decreased, the heat Peclet number (Eqn. 7) is very different from the real monolith. Hence, the propagation of thermal fronts is not effectively captured in a bench-scale experiment.

In the full-length article, the width and speed of thermal and concentration fronts will be estimated under non-isothermal conditions. The effect of diffusional limitations, adsorption/desorption of NH<sub>3</sub> and the interactions between concentration and thermal fronts will be analyzed.

## References

- (1) Clayton R.D.; Harold M.P.; Balakotaiah V. NO<sub>x</sub> storage and reduction with H<sub>2</sub> on Pt/BaO/Al<sub>2</sub>O<sub>3</sub> monolith: Spatio-temporal resolution of product distribution. *Applied Catalysis B: Environmental* **2008**, 84, 616.
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