

# MICROKINETIC MODELING OF NO<sub>x</sub> STORAGE AND REDUCTION WITH H<sub>2</sub> AS THE REDUCTANT

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## Summary

A microkinetic model is developed that describes the storage and anaerobic reduction of NO<sub>x</sub> on Pt/BaO/Al<sub>2</sub>O<sub>3</sub> monolithic catalysts. The model combines microkinetic descriptions of the storage of NO in O<sub>2</sub> and the regeneration of the stored NO<sub>x</sub> with the assumption that NO<sub>2</sub> is the primary surface species that diffuses between the Pt and Ba phases. The regeneration kinetics builds on an earlier microkinetic model for NO<sub>x</sub> reduction by H<sub>2</sub> in previous studies.<sup>1,2,3</sup> The model predictions capture most of the key trends of experimental results<sup>4</sup>, such as accelerated H<sub>2</sub> breakthrough along the flow direction, evolution of NO at the beginning of the rich phase, among other features. Model predictions and earlier experimental results show that H<sub>2</sub> is an efficient NO<sub>x</sub> reductant and its consumption is feed limited at higher temperature. The supply of H<sub>2</sub> to the Pt surface is a multi-step process consisting of feed in the flow (flow rate and concentration), mass transfer (external and internal) and H<sub>2</sub> dissociative adsorption. NH<sub>3</sub> is formed upstream during NO<sub>x</sub> reduction by H<sub>2</sub> and reacts with downstream NO<sub>x</sub> as a reductant, releasing NO. Gas phase NO can also be oxidized on Pt forming NO<sub>2</sub>, which is then stored on unsaturated BaO sites even during the rich operation.

## Keywords

Environmental reaction engineering; Monolith reactor; Microkinetics; NO<sub>x</sub> reduction; Reactor modeling

## Introduction

NO<sub>x</sub> storage and reduction (NSR) is a promising technique to meet the increasingly stringent NO<sub>x</sub> emission standards. NSR is carried out in the so-called lean NO<sub>x</sub> trap (LNT) which is a catalytic monolith reactors containing a multi-functional catalyst, typically containing a precious metal (Pt) and storage function (BaO) on a high surface area support (Al<sub>2</sub>O<sub>3</sub>).

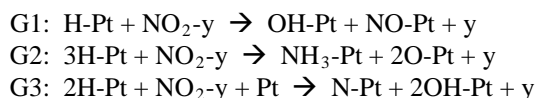
During a practical NSR operation, exhaust NO<sub>x</sub> (NO + NO<sub>2</sub>) in the presence of excess oxygen is stored on BaO in the form of nitrites and nitrates for 30-90s to avoid any significant NO<sub>x</sub> breakthrough. Then the LNT is operated under rich condition to reduce the stored NO<sub>x</sub> and regenerate the NSR catalyst for the use of the next cycle. The presence of O<sub>2</sub> during regeneration can result in significant temperature rise due to exothermic oxidation during the short regeneration.<sup>4</sup> Clayton et al.<sup>4</sup> conducted NSR experiments with an anaerobic regeneration using H<sub>2</sub> as the reductant and the monolith temperature rising was limited to less than 10 °C. The spatial product distributions were also measured using monolith reactors of different lengths. These results are valuable for the current mechanistic-based study.

In the present work, we develop a microkinetic model for stored NO<sub>x</sub> storage and regeneration. Building on

based on a microkinetic model developed in earlier steady-state NO reduction and NO<sub>x</sub> storage studies.<sup>1,2,3</sup> The model is used to simulate NO<sub>x</sub> regeneration by H<sub>2</sub> experiments.<sup>4</sup> Kinetic parameters are estimated to capture the main experimental trends. The calculation results are used to explain some of the most important observations and to speculate on improving the NO<sub>x</sub> trap performance.

## Model

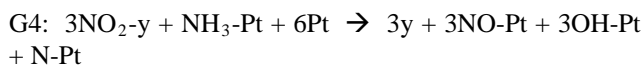
An isothermal, one-dimensional, two-phase reactor model is used to describe the material balances of gas species in the fluid and solid phases and surface species<sup>1,3</sup>. The model considers that isothermal regeneration involves reduction of NO<sub>x</sub> stored in close proximity to Pt. The following reaction groups between H atoms on Pt and NO<sub>x</sub> stored on BaO during regeneration are proposed:



In addition, NH<sub>3</sub> ad molecules on Pt are also considered as an active reductant of stored NO<sub>x</sub> and the following reaction is proposed:

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In the above reactions,  $y$  can be BaO, BaO-O and BaO-NO<sub>3</sub> in the proximity of Pt crystallites<sup>3</sup>. To simplify the analysis, we neglect  $y=\text{BaO}$  for reaction groups G2, G3 and G4. It is also assumed that reactions in the same group with different  $y$  units have the same rate constant.

## Results and Discussion

Typical model predicted transient effluent concentrations of H<sub>2</sub>, NO, N<sub>2</sub>O and NH<sub>3</sub> as a function of reactor length are shown in Fig. 1. Initial model predictions capture the following important trends observed in the experiments<sup>4</sup> during the rich period: 1) the unreacted NO forms a sharp peak (so-called “NO<sub>x</sub> puff”) upon the introduction of reductant; 2) the generation of N<sub>2</sub>O occurs in the early stage of the rich period and its concentration decreases with regeneration time; 3) the breakthrough of H<sub>2</sub> is not a step change but a gradual process; 4) the NH<sub>3</sub> effluent concentration has a time delay with increasing reactor length which is attributed to its reaction with NO<sub>x</sub> stored downstream. Unlike the experiments, the model predicts an earlier appearance of NH<sub>3</sub> than H<sub>2</sub>; this premature breakthrough is a sensitive function of the role of NH<sub>3</sub> as a reductant.

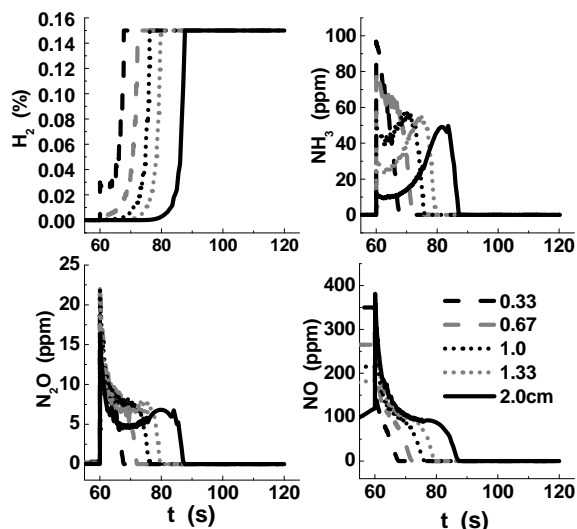


Fig.1 Model predicted H<sub>2</sub>, NH<sub>3</sub>, N<sub>2</sub>O and NO concentrations as a function of time and reactor length during the regeneration period at cyclic steady-state. Lean: 500 ppm NO, 5% O<sub>2</sub>, 60s; rich: 0.15% H<sub>2</sub> (free of oxygen and NO<sub>x</sub>), 60s. Temperature: 340°C. Pressure: 1 atm. Average velocity: 4m/s. Inert carrier gas.

The model also captures the experimentally observed feature of accelerated H<sub>2</sub> breakthrough along the flow direction<sup>4</sup>. The four shorter reactors are equally spaced by 0.33cm and can be seen as a series of monolith blocks with the same length. The breakthrough intervals between two adjacent blocks are calculated to be 4.5, 3.9 and 3.6s, respectively, decreasing along the flow direction. The calculation results showed that the barium surface is

saturated with Ba(NO<sub>3</sub>)<sub>2</sub> up to a reactor length of 1.0cm, including the first three blocks. This indicates that another NO<sub>x</sub> consuming process occurs before the arrival of H<sub>2</sub> front, which is confirmed by the instantaneous drop of Ba(NO<sub>3</sub>)<sub>2</sub> coverage for all reactor lengths right after the switch to H<sub>2</sub> feed. As mentioned, the NO<sub>x</sub> stream stored downstream is consumed by NH<sub>3</sub> formed in the front part of the reactor.

The above discussions confirm the existence of a “feed- limited” state of H<sub>2</sub> breakthrough as described by Clayton et al.<sup>4</sup>. Downstream H<sub>2</sub> breakthrough is accelerated from the front to the end as a combined result of NO<sub>x</sub> reduction by NH<sub>3</sub> and NO<sub>x</sub> storage that decreases with length. In addition to the feed concentration and flow rate, mass transfer (external and internal) and dissociative adsorption of H<sub>2</sub> have effects on the hydrogen supply to Pt surface. The simulations show that significant mass transfer limitation exists in this system and neglecting mass transfer limitation results in a later and sharper H<sub>2</sub> breakthrough. On the other hand, H<sub>2</sub> adsorption has only secondary effects. These results show that the overall H<sub>2</sub> supply to Pt surface is a multi-step process, resulting in gradual breakthrough profile.

An interesting experimental observation is the “NO<sub>x</sub> puff” in the effluent that occurs right after the introduction of reductant. In this case of anaerobic regeneration, the temperature rise due to reaction heat is negligible. Thus, the NO<sub>x</sub> release cannot be explained by thermally-induced nitrate decomposition and subsequent NO desorption from Pt. Rather, it is caused by the complex coupling between reaction of spilled over NO<sub>2</sub> and H atoms on Pt, which generates adsorbed NO. The NO-Pt may desorb, dissociate, or combine with N-Pt, forming N<sub>2</sub>O, or H-Pt, forming NH<sub>3</sub>. Finally, H<sub>2</sub> is such an efficient reductant that all of the stored NO<sub>x</sub> is converted before its complete breakthrough.

In the full-length article, the model development and the simulation results will be presented and discussed in more detail.

## References

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