# Microkinetic Model Development of NOx Storage and Reduction over Pt/BaO/Al$_2$O$_3$ Catalysts using Temporal Analysis of Products

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## Introduction

NOx Storage and Reduction (NSR) is an emerging technology for NOx emission abatement for lean burn and diesel engines. The NOx removal process involves two stages on a bifunctional catalyst in the lean NOx trap (LNT). The first stage involves storage of NOx on an alkali earth component (Ba, Ca) mediated by precious metal (Pt, Rh). The second stage involves injecting a rich pulse of shorter exposure to reduce the stored NOx. In this study we employ Temporal Analysis of Products (TAP) experiments and microkinetic mechanistic modeling to further the understanding of NSR. TAP experiments are carried out isothermally in the Knudsen transport regime thereby avoiding complicating thermal and mass limitations encountered in atmospheric pressure studies. Transient TAP experiments are carried out on a series of Pt/BaO/Al$_2$O$_3$ catalysts having a range of Pt loadings and dispersions. A systematic method is developed that involves a kinetic parameter estimation scheme imbedded in a TAP model.

## Materials and Methods

A series of model Pt/Al$_2$O$_3$ and Pt/Ba/ Al$_2$O$_3$ catalysts provided by BASF Catalysts LLC for the study had Pt loadings between 0 and ca. 4 wt.% with the BaO loading fixed at 16 wt.%. The TAP studies involve feeding pulses of reactant to model Pt/Al$_2$O$_3$ catalyst at ~10$^{-8}$ torr pressure and temperature range of 150 $^O$C - 400 $^O$C. Two kinds of experiments are performed on TAP, the Storage/Adsorption experiment, in which NO is pulsed with spacing time ($\tau_s$) and Pump-Probe experiment in which NO/H$_2$ are pulsed with a prescribed delay time ($\tau_d$) and spacing time ($\tau_s$). The product gas emerging from the catalyst bed is analyzed by a Quadrapole Mass Spectrometer (QMS) in a separate chamber maintained at ~10$^{-8}$ torr. The QMS monitors effluents N$_2$, NO, NH$_3$, N$_2$O, H$_2$ and H$_2$O. The feed intensities are suitably chosen to ensure Knudsen regime. Post-reaction TPD is performed (T$_c$) to quantify the adsorbed species. TAP modeling is carried out by solving the transient reaction and Knudsen diffusion equations. Selected kinetic parameters are estimated through the simulation of a series of transient experiments intended to isolate key kinetic features.

## Results and Discussion

During NO storage/adsorption experiments on Pt and Pt/BaO catalysts, NO decomposes forming N$_2$ as the dominant product. Oxygen adatoms accumulate on the Pt, leading to a decrease in the decomposition rate and breakthrough of NO. Secondary product N$_2$O achieves a maximum at the NO breakthrough. At lower temperatures adsorbed NO strongly inhibits the reaction. The NO decomposition rate decreases as the temperature is decreased with negligible reaction at 150$^o$C.

To get an insight into the reduction chemistry of NO by H$_2$, NO and H$_2$ were pulsed alternately (pump-probe experiments). The temperature (T$_c$), NO/H$_2$ ratio, and delay time

between NO and H$_2$ pulses ($\tau_d$) affect the selectivity to N$_2$, NH$_3$ and N$_2$O. NH$_3$ selectivity increases with decreasing T$_c$, NO/H$_2$, and $\tau_d$. In pump-probe experiments in excess H$_2$ (NO/H$_2$ < 2), NH$_3$ is the major product at 150 °C whereas N$_2$ is the major product at 350 °C. N$_2$O is the major product during NO/H$_2$ pump-probe at 150 $^o$C in excess NO; conditions for which NO decomposition does not occur.

**Table 1. Proposed mechanism for NO + H$_2$ on Pt.**

| | | |
|---|---|---|
| | **NO Decomposition:** | |
| 1 | NO + Pt | ↔ NO–Pt |
| 2 | NO–Pt + Pt | ↔ N–Pt + O–Pt |
| 3 | N–Pt + N–Pt | ↔ **N$_2$** + 2 Pt |
| 4 | O–Pt + O–Pt | ↔ O$_2$ + 2 Pt |
| 5 | NO–Pt + N–Pt | ↔ **N$_2$O** + 2 Pt |
| | **H$_2$ Oxidation** | |
| 6 | H$_2$ + 2 Pt | ↔ 2 H–Pt |
| 7 | NO–Pt + H–Pt | ↔ HO–Pt + N–Pt |
| 8 | O–Pt + H–Pt | ↔ HO–Pt + Pt |
| 9 | HO–Pt + H–Pt | ↔ **H$_2$O** + Pt |
| | **Ammonia Formation** | |
| 10 | N–Pt + H–Pt | ↔ NH–Pt + Pt |
| 11 | NH–Pt + H–Pt | ↔ NH$_2$–Pt + Pt |
| 12 | NH$_2$–Pt + H–Pt | ↔ **NH$_3$** + Pt |



**Figure 1.** NH$_3$ formation vs. temperature with delay time as parameter

These and other results suggest that molecularly adsorbed NO reacts with H$_2$ at 150 °C forming primarily NH$_3$ whereas at 350 °C NO decomposition is favored. Moreover NH$_3$ formation decreases (Figure 1) with increase in delay time ($\tau_d$). TPD for carried out at 150 °C in excess H$_2$ produces a large amount of NH$_3$ whereas in excess NO, more N$_2$ is produced than NH$_3$. At 150 °C, one observes much less N$_2$O confirming that molecularly adsorbed NO does not combine readily to form N$_2$O and that NO bond scission is slow at these temperatures.

Based on the pulse and pump-probe experiments a mechanistic sequence is proposed that comprises NO decomposition, H$_2$ oxidation, and ammonia formation (Table 1). Simulations will be presented that support the proposed sequence. Among other results, the simulations confirm that N$_2$ is inhibited by the accumulating oxygen, resulting in its gradual decrease as well as N$_2$O production achieving a maximum. The simulations also confirm the interesting competition between NO decomposition and hydrogenation as the NO/H$_2$ and temperature are varied.
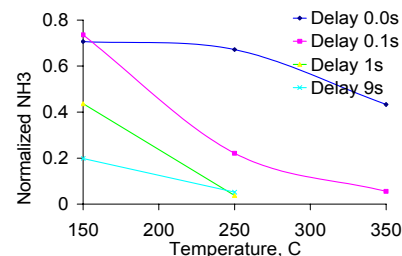
Ongoing experimental results will be presented that compare the performance of Pt and Pt/Ba catalysts having different Pt loadings and dispersions. In particular, we will report results for a series of Pt/Ba catalysts with fixed Pt loading and varied dispersion.

## Significance

There is a great need for reducing NOx emissions in lean burn vehicle exhaust. This work is a step towards understanding the complex catalytic chemistry of NSR through systematic transient experiments, mechanistic modeling, and kinetic parameter estimation.