Microkinetic Model Development of NOx Storage and Reduction over Pt/BaO/Al2O3 Catalysts using Temporal Analysis of Products

A. Kumar, V. Medhekar, V. Balakotiah*, and M. P. Harold**
Department of Chemical and Biomolecular Engineering
University of Houston, Houston, TX 77204 (USA)
* bala@uh.edu, **mh Harold@uh.edu

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/Al2O3 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/Al2O3 and Pt/Ba/Al2O3 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/Al2O3 catalyst at ~10⁻⁸ torr pressure and temperature range of 150 °C - 400 °C. Two kinds of experiments are performed on TAP, the Storage/Adsorption experiment, in which NO is pulsed with spacing time (τs) and Pump-Probe experiment in which NO/H2 are pulsed with a prescribed delay time (τd) and spacing time (τc). The product gas emerging from the catalyst bed is analyzed by a Quadrupole Mass Spectrometer (QMS) in a separate chamber maintained at ~10⁻⁸ torr. The QMS monitors effluents N2, NO, NH3, N2O, H2 and H2O. The feed intensities are suitably chosen to ensure Knudsen regime. Post-reaction TPD is performed (Tc) 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 N2 as the dominant product. Oxygen adatoms accumulate on the Pt, leading to a decrease in the decomposition rate and breakthrough of NO. Secondary product N2O 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°C.

To get an insight into the reduction chemistry of NO by H2, NO and H2 were pulsed alternately (pump-probe experiments). The temperature (Tc), NO/H2 ratio, and delay time between NO and H2 pulses (τd) affect the selectivity to N2, NH3 and N2O. NH3 selectivity increases with decreasing Tc, NO/H2, and τd. In pump-probe experiments in excess H2 (NO/H2 < 2), NH3 is the major product at 150 °C whereas N2 is the major product at 350 °C. N2O is the major product during NO/H2 pump-probe at 150 °C in excess NO; conditions for which NO decomposition does not occur.

Table 1. Proposed mechanism for NO + H2 on Pt.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Symbols</th>
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<tbody>
<tr>
<td>NO Decomposition</td>
<td></td>
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<tr>
<td>1 NO + Pt ↔ NO–Pt</td>
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</tr>
<tr>
<td>2 NO–Pt + Pt ↔ N–Pt + O–Pt</td>
<td></td>
</tr>
<tr>
<td>3 N–Pt + N–Pt ↔ N2 + 2 Pt</td>
<td></td>
</tr>
<tr>
<td>4 O–Pt + O–Pt ↔ O2 + 2 Pt</td>
<td></td>
</tr>
<tr>
<td>5 NO–Pt + N–Pt ↔ N2O + 2 Pt</td>
<td></td>
</tr>
<tr>
<td>H2 Oxidation</td>
<td></td>
</tr>
<tr>
<td>6 H2 + 2 Pt ↔ 2 H–Pt</td>
<td></td>
</tr>
<tr>
<td>7 NO–Pt + H–Pt ↔ HO–Pt + N–Pt</td>
<td></td>
</tr>
<tr>
<td>8 O–Pt + H–Pt ↔ HO–Pt + Pt</td>
<td></td>
</tr>
<tr>
<td>9 HO–Pt + H–Pt ↔ H2O + Pt</td>
<td></td>
</tr>
<tr>
<td>Ammonia Formation</td>
<td></td>
</tr>
<tr>
<td>10 N–Pt + H–Pt ↔ NH–Pt + Pt</td>
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</tr>
<tr>
<td>11 NH–Pt + H–Pt ↔ NH2–Pt + Pt</td>
<td></td>
</tr>
<tr>
<td>12 NH2–Pt + H–Pt ↔ NH3 + Pt</td>
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</tbody>
</table>

Figure 1. NH3 formation vs. temperature with delay time as parameter

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.