Investigation of NO Oxidation Rate as a Function of LNT Loading

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Introduction

- Rob Middleton: New Ph.D. Student working on catalyst modeling
  - About 1 year into study of catalysts
  - Work partially supported by Michigan 21st Century Jobs Fund
- Focus on NO Oxidation as it is the rate limiting step for LNT lean phase operation
- Literature seems to be sparse on comparisons of varying catalysts between large groups

Objective

- Correlate global kinetic LNT model parameters to catalyst formulation and loading
- Goal is to reduce parameter fitting time for new catalysts
  - Hold as many terms constant as possible
  - Pick good initial values for non-constant terms
- Useful for improving formulations / performance

Existing Catalyst Model

- Model developed by Depcik, Assanis, Bevan
  - A one-dimensional lean NO_X trap model with a global kinetic mechanism that includes NH_3 and N_2O, *Int. J. Engine Res*. Vol. 9, 2008
- Uses custom C++/Fortran code
  - Optimization of parameters performed via MATLAB (fmincon)

Gas Species: $\cancel{\frac{\partial \bar{C}_{g,j}}{\partial t}} + u\frac{\partial \bar{C}_{g,j}}{\partial x} = \frac{-k_{m,j}G_a}{\varepsilon}\left(\bar{C}_{g,j} - \bar{C}_{s,j}\right)$

Gas Energy: $\rho_g c_{p,g}\left(\frac{1}{\gamma}\cancel{\frac{\partial T_g}{\partial t}} + u\frac{\partial T_g}{\partial x}\right) = \frac{-h_g G_a}{\varepsilon}\left(T_g - T_m\right)$

Fluid Motion: $\cancel{\frac{d\bar{C}_{s,j}}{dt}} = \frac{k_{m,j}G_a}{1-\varepsilon}\left(\bar{C}_{g,j} - \bar{C}_{s,j}\right) - \frac{G_{ca}R_j}{1-\varepsilon}$

Surface Intermediates: $\frac{d\Theta_m}{dt} = \frac{\dot{s}_m}{\Gamma}$

Surface Energy: $\rho_m c_m \frac{dT_m}{dt} = \lambda_m \frac{\partial^2 T_m}{\partial x^2} + \frac{h_g G_a}{1-\varepsilon}\left(T_g - T_m\right) + \frac{G_{ca}}{1-\varepsilon}\sum_{j=1}^{NM} R_j h_j + \cancel{\dot{q}} + \cancel{\frac{Q_{i\to m}}{1-\varepsilon}V_{cat}}$

Existing Catalyst Model

- NO Oxidation reaction $\mathrm{NO} + \frac{1}{2}\mathrm{O_2} \Leftrightarrow \mathrm{NO_2}$

Rate expression [mol/m^3-s]: $$\mathbf{R} = \frac{k \exp\left(-\frac{E}{R_u T_m}\right) X_{s,\mathrm{NO}} X_{s,\mathrm{O_2}}^{0.5} - X_{s,\mathrm{NO_2}} / K_{eq}}{G}$$

$$G = T_m \left(1 + K_{\mathrm{NO}} \exp\left(-\frac{\Delta H_{NO}}{R_u T_m}\right) X_{s,\mathrm{NO}}^{0.7}\right)^2 \left(1 + K_{\mathrm{H_2O}} \exp\left(-\frac{\Delta H_{H_2O}}{R_u T_m}\right) X_{s,\mathrm{H_2O}}\right)$$

Fit Parameters: k, E, K_{NO}, H_{NO}, K_{H2O}, H_{H2O}

- Origin of Inhibition terms:
  - NO site occupancy from Voltz (1973)
  - H_2O estimated functional dependence from literature

Method

- Used literature data
  - 13 papers surveyed, 25 sets of data
  - 10 different catalyst formulations, varying loading / dispersion
    - Al_2O_3-CeO-SiO_2 supports
    - With and without Barium
    - Pd, Pt and Rh as PGM

- Some papers only partially report the reactor setup
  - Assumptions are needed for simulation

Method

- Optimize *k*, *E*, K_{NO}, H_{NO}, K_{H2O}, H_{H2O} for all data
  - Analyze K_{NO}, H_{NO}, K_{H2O}, H_{H2O}
  - Hold values constant
- Optimize *k*, *E* using constant values for inhibition
  - Look for trends in *E*
  - Hold *E* constant – either globally or per material
- Optimize *k* alone using constant values for other terms
  - Look for trends in *k*
  - Compare trends to those in the literature

Our Assumptions

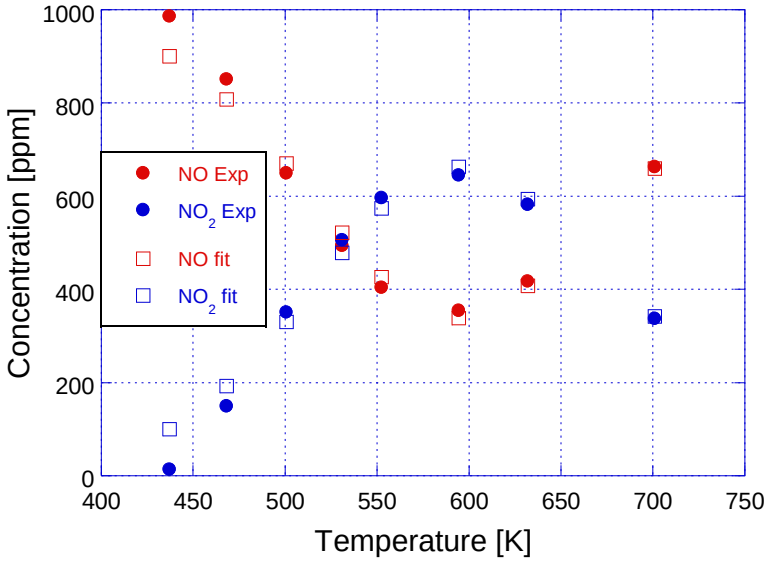
- Literature results can be replicated with a monolith
  - Used the geometry from Olsson ‘99 (clearest definition)
- Inlet velocity is constant
- Flow rates STP

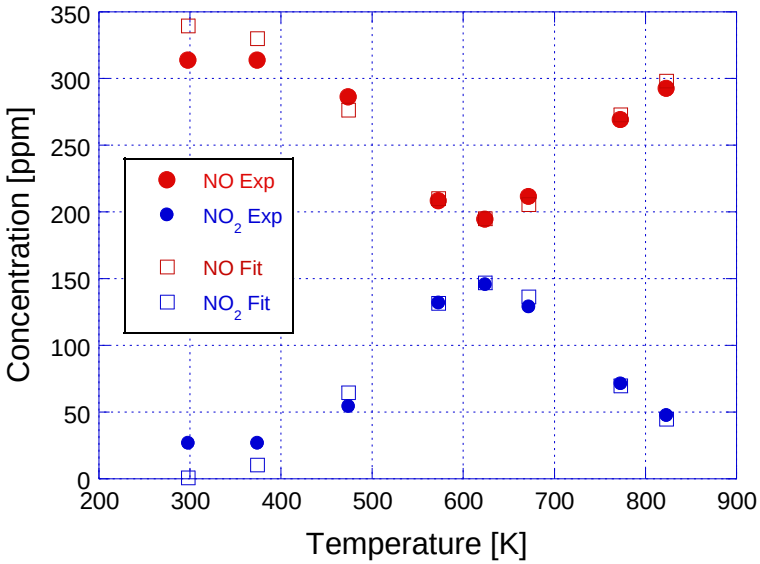
- Assumptions make it hard to compare pre-exponentials
  - Focus on trends under the same set of assumptions
  - Benard ‘05 shows the effect of Pt dispersion
  - Huang ‘01 shows the effect of precious metal

- Can still compare activation energies and inhibition terms

Optimizing All 6 Parameters

- The model matches experimental results well
  - Even matches catalysts with unclear descriptions requiring many assumptions
  - Yentikakis ‘05 has varying flow rates, crushed powder
  - Rodrigues ‘00 has no geometry reported – no reactor type



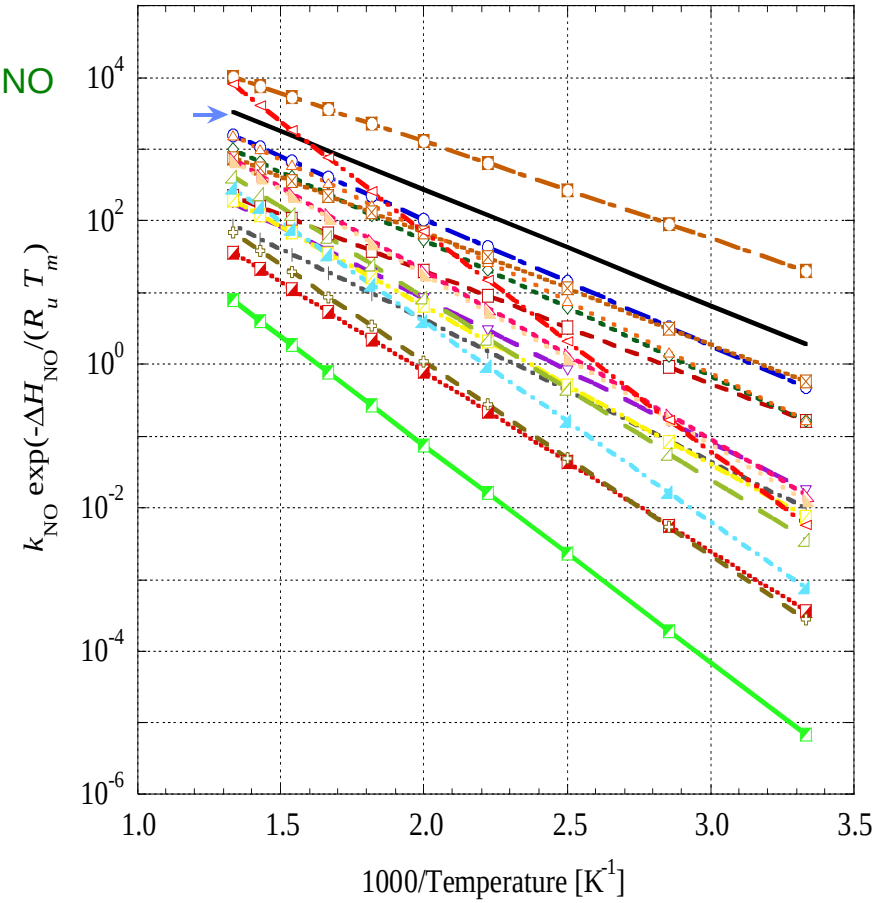


Averaging the NO Inhibition

- K_{NO} is less than reported by Voltz

$$1 + K_{NO} \exp\left(-\frac{\Delta H_{NO}}{R_u T_m}\right) X_{s,NO}^{0.7}$$

  - Large variations seen in K_{NO} and H_{NO}
  - Ideally one H_{NO} per material and K_{NO} correlated to loading
  - Used average values:
    - $K_{NO} = 4.7 \times 10^5$
    - $H_{NO} = 41.3$ [KJ/mol]

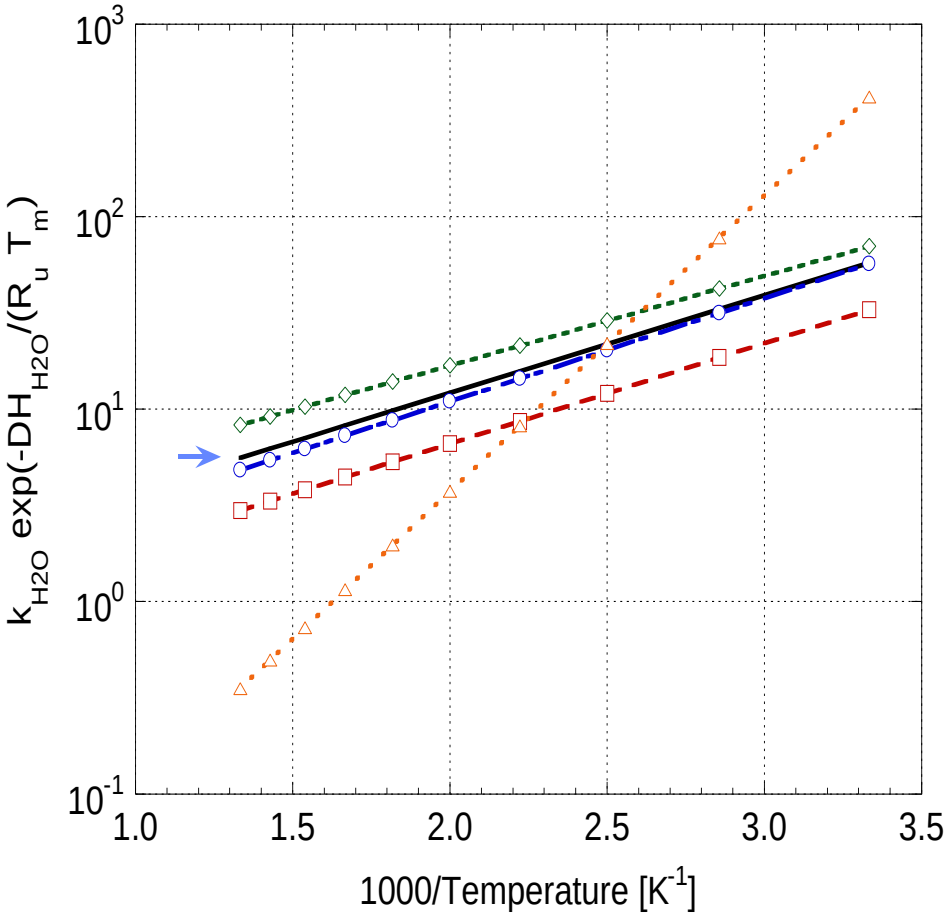


Averaging the H_2O Inhibition

- No literature results for this term

$$1+K_{\mathrm{H_2O}}\exp\left(-\frac{\Delta H_{H_2O}}{R_u T_m}\right)X_{s,\mathrm{H_2O}}^{\ 2}$$

  - Only 4 data sets
  - Negative activation energy
  - Used average values:
    - K_{H2O} = 1.18
    - H_{H2O} = -9.7 [KJ/mol]



Method

- Optimize *k*, *E*, K_{NO}, H_{NO}, K_{H2O}, H_{H2O} for all data
  - Analyze K_{NO}, H_{NO}, K_{H2O}, H_{H2O}
  - Hold values constant

$K_{NO} = 4.7 \times 10^5$
$H_{NO} = 41.3$ [KJ/mol]
$K_{H2O} = 1.18$
$H_{H2O} = -9.7$ [KJ/mol]

- Optimize *k*, *E* using constant values for inhibition
  - Look for trends in *E*
  - Hold *E* constant - globally

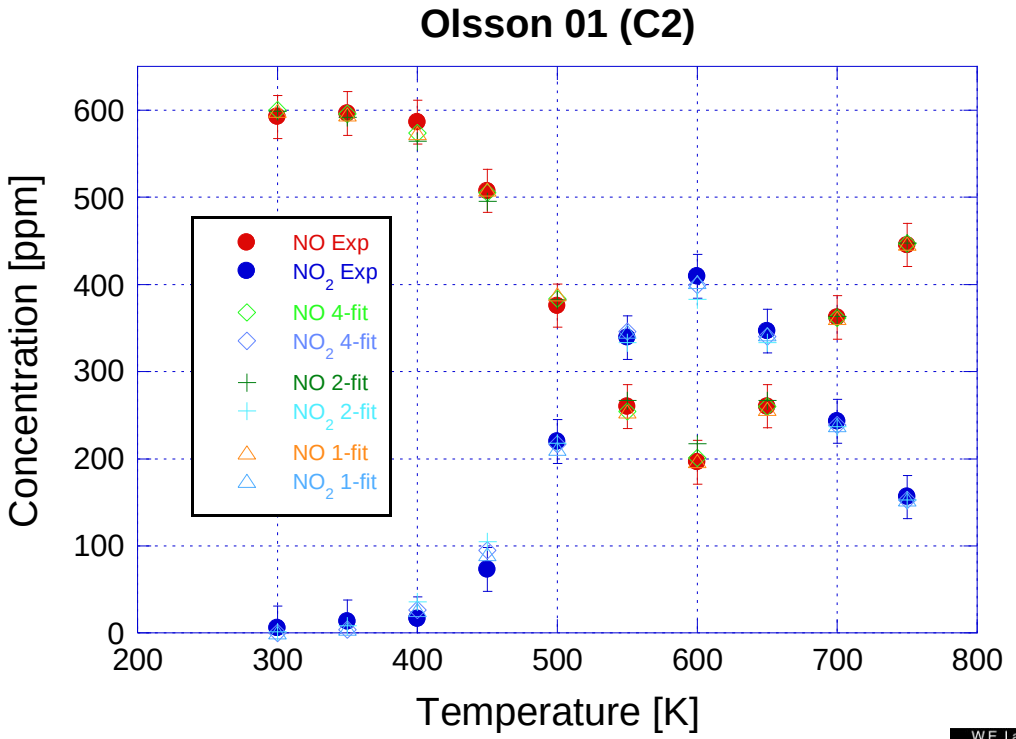
E = 39.72 [KJ/mol]

- Optimize *k* alone using constant values for other terms
  - Look for trends in *k*
  - Compare trends to those in the literature

Change in Accuracy with Constant Terms

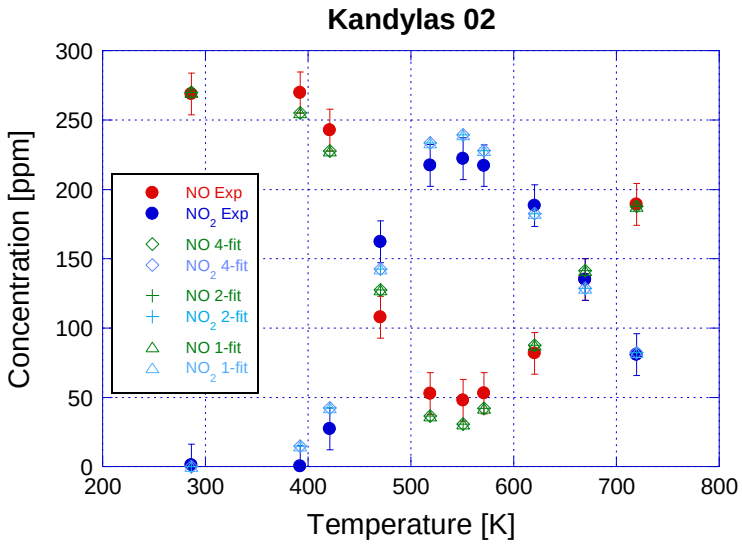
- Reducing the number of fit parameters does not adversely impact the quality of the results
  - Least squares fit increases between ~0.1/pt and 20-40/pt
  - Average increase of 8/pt

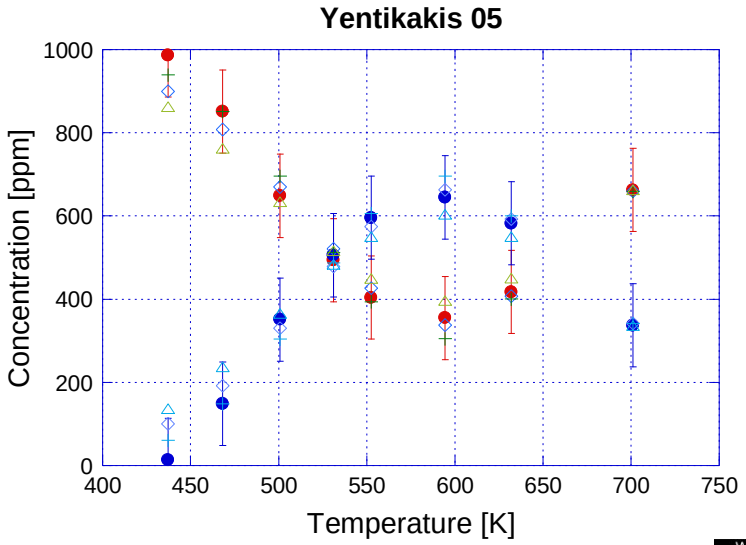
- Results are within the expected error from reading the literature data
  - LSQ *decreased* from 3.5/pt to 3.34/pt
  - Within ± 25 ppm (5% inlet)



Change in Accuracy with Constant Terms

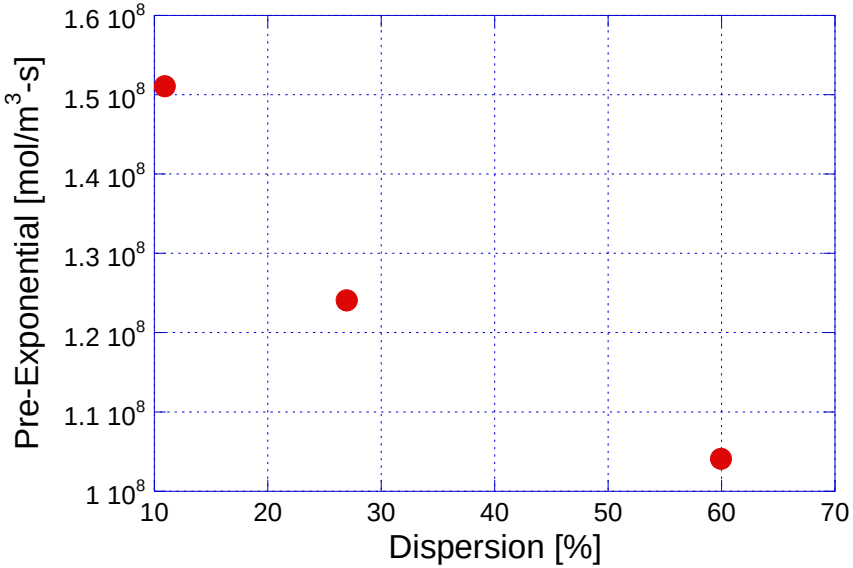
- From Kandylas ‘02:
  - LSQ nearly constant at 55 ppm total
  - Within ± 15ppm (5% of inlet flow)
- From Yentikakis ‘05:
  - LSQ increases from 150 to 240 ppm
  - Within ± 100ppm (10% of inlet flow)
- Reducing the number of fit parameters from 6 to 1 decreased the model accuracy by only 5-15%
  - The optimization search space decreased by 5 dimensions
  - Fit time decreased from ~5 hours to less than 1hour

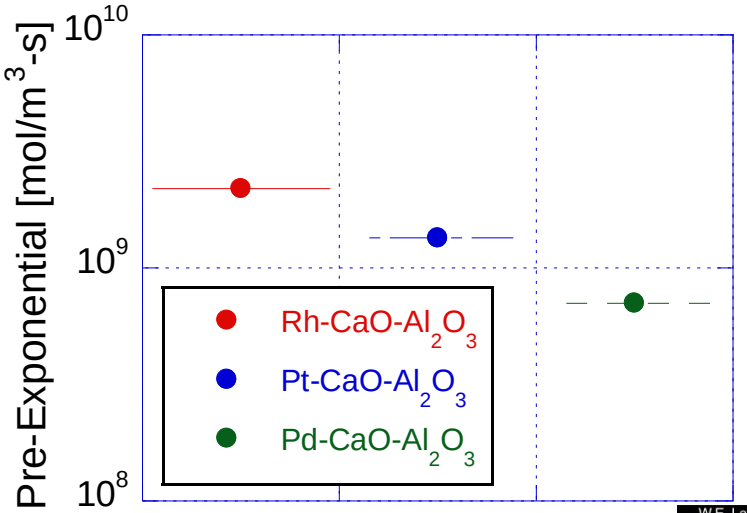




Effect of Dispersion and Metal Selection

- As a reality check …
  - Under the same assumptions
  - Can we match literature trends?
- Benard ‘05 – Pt dispersion
  - Pt-Al_2O_3 – same Pt loading
  - Higher dispersion decreases activity
  - Matches the literature
  - Reportedly due to Pt-O formation
- Huang ’01 – metal selection
  - Activity: Rh > Pt > Pd
  - Matches the literature





Lessons Learned

- Model can fit experimental data well over a wide range of catalysts
- Parameter optimization speed can be increased without significant decrease in accuracy by using average inhibition values
- Method looks promising – will continue to add data
  - From the literature
  - In-house via reactor bench
- Many assumptions are needed to use literature data

Acknowledgements

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Questions

Source Data

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