Cross-Cut Lean Exhaust Emissions Reduction Simulations

Hydro-Thermal Aging model of NO oxidation on Pt-Pd catalyst

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Advanced Technologies

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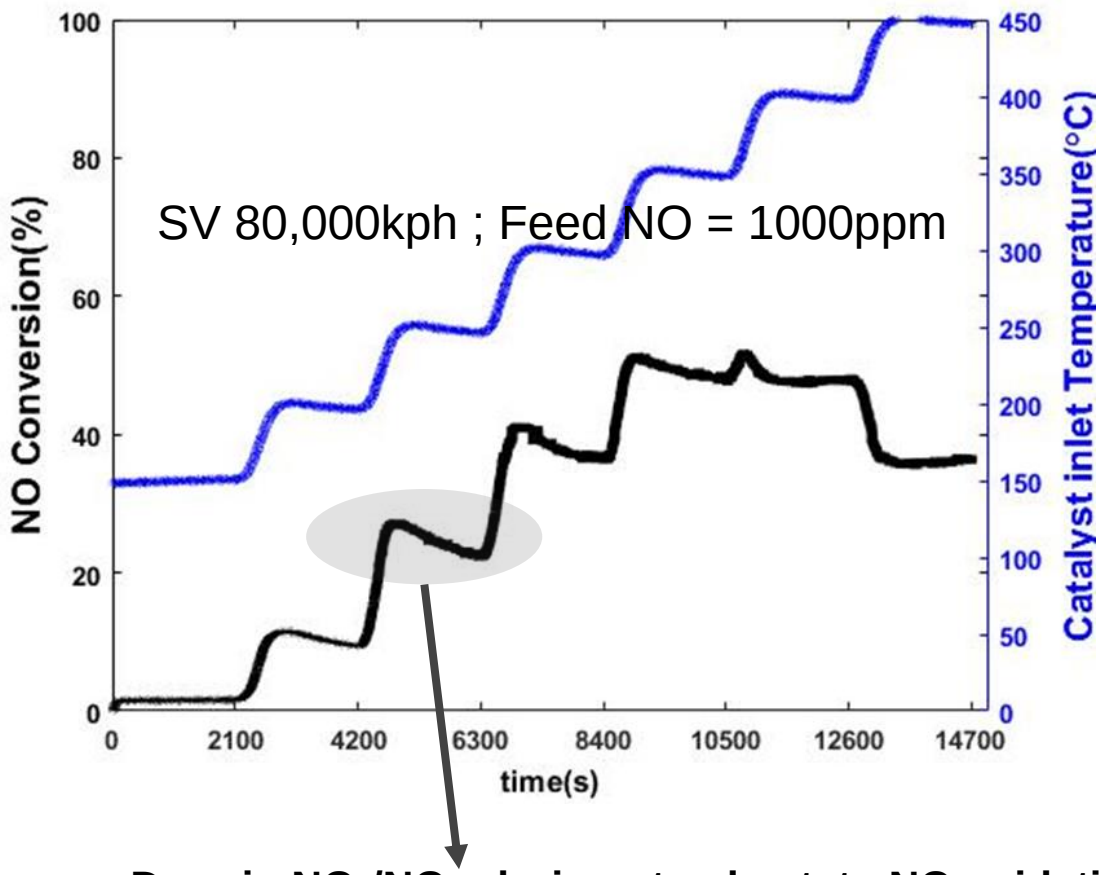
Introduction

- NO oxidation to NO_2 on DOC is a critical reaction since it results in the effective operation of downstream components like DPF and SCR
- Deactivation modes like thermal aging, chemical poisons can cause degradation of oxidation catalyst. Understanding these aging mechanisms is paramount to meet the emissions limits through the life of AT system
- Pt based catalysts are susceptible to sintering of particles during HTA treatment. Sintering of PGM leads to change in intrinsic catalyst activity
- A state-of-the-art DOC was used to investigate HTA stability of NO oxidation. A 1’’(diameter)*3’’(length) monolithic core was used to perform reactor study
- One of the goals of this work is to present a systematic modeling approach to develop a HTA deactivation model for NO oxidation

Experimental Procedure



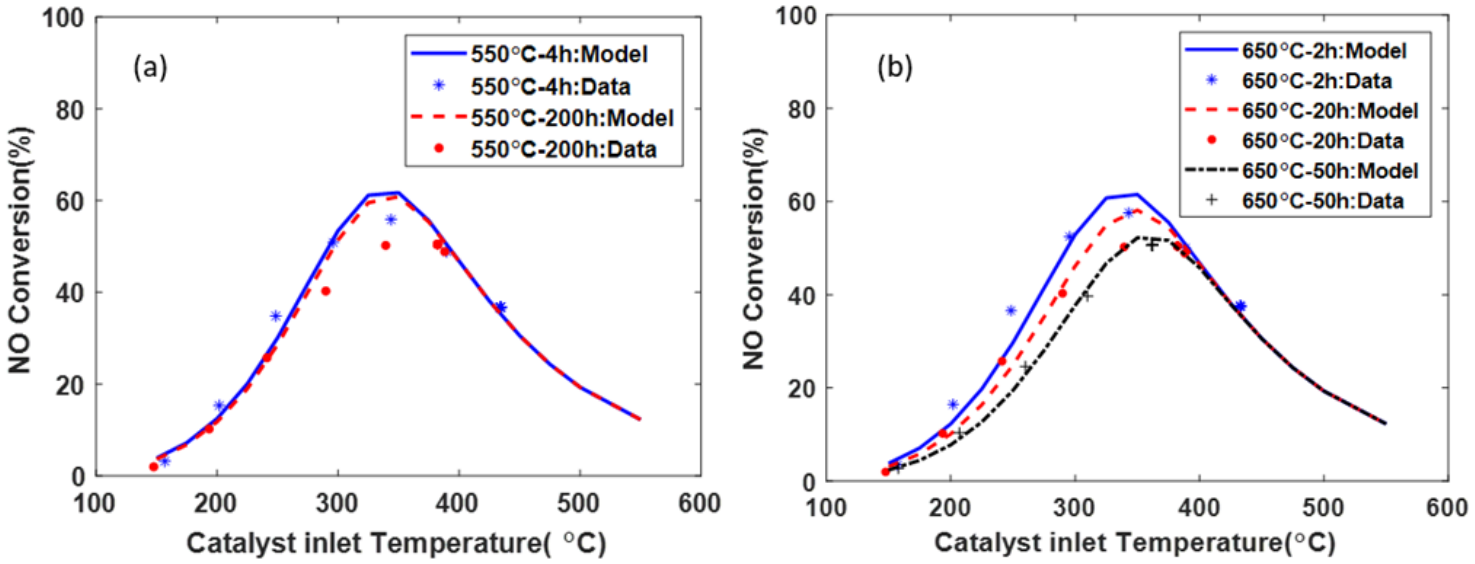
Drop in NO_2/NOx during steady-state NO oxidation

- Degreening at 550°C-4h in the base feed (10% O_2, 7% H_2O, 0% CO2, N2)
- Cool down from 550°C to 150°C and NO is fed after cooling down to 150C
- Steady-state NO oxidation test is performed at different catalyst temperatures, starting from 150°C till 450°C (50°C increment). Hold time at each temperature is 0.5h

Underlying theory

- Metallic Pt is oxidized to PtOx in the presence of oxidizing agents, NO_2 and oxygen in this case
- PtOx is less active than metallic Pt for NO oxidation
- NO_2 formed during the course of NO oxidation oxidizes metallic Pt to PtOx, resulting in the decrease in NO oxidation activity of PGM

Model Based Normalized Activity



$$\frac{r_{HTA}}{r_{ref}} = \frac{k_{HTA}}{k_{ref}} = \frac{A_{HTA}\exp\left(\frac{-E_{HTA}}{RT}\right)}{A_{ref}\exp\left(\frac{-E_{ref}}{RT}\right)}$$

$$if\ E_{HTA} = E_{ref}$$

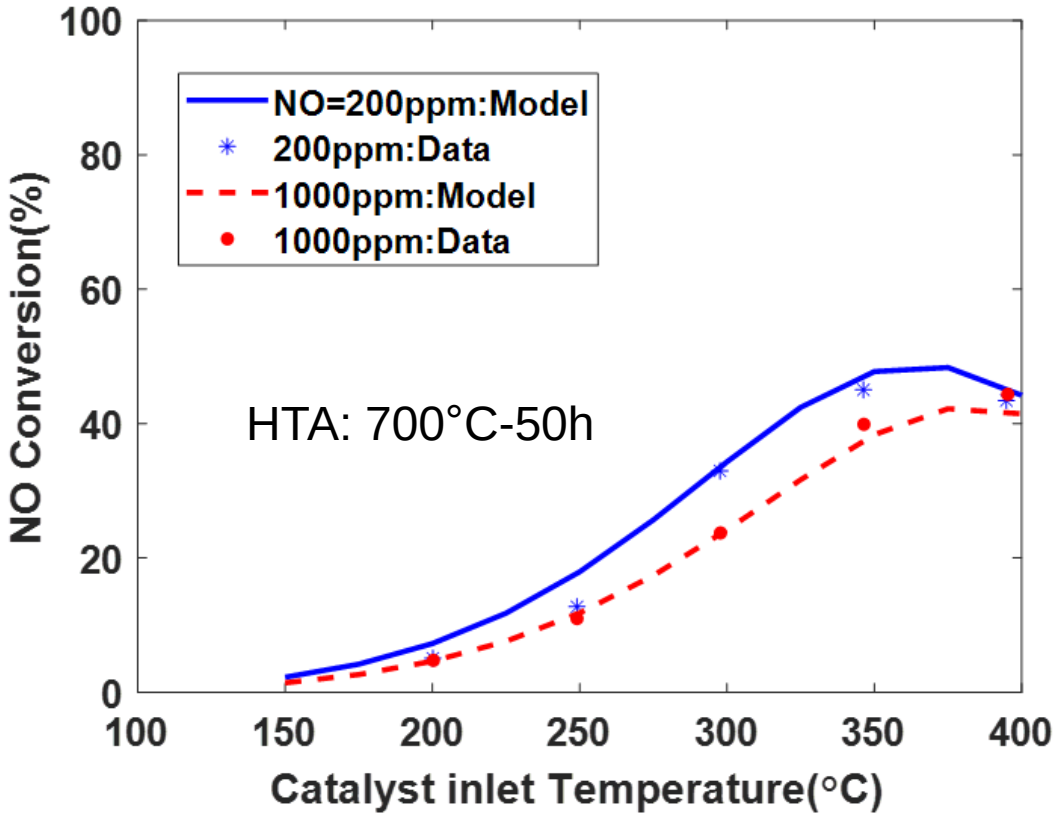
Normalized Activity (Ψ)

$$\Psi = \frac{A_{HTA}}{A_{ref}}$$

- Bell shaped curves were obtained by averaging final 30s data at all catalyst temperatures
- Time on stream deactivation is not very significant at catalyst temperatures like 150 or 200°C
- So, steady-state conversion data at these temperatures can be useful gauges of intrinsic NO oxidation activity

$$\Psi = f(HTA\ duration, HTA\ temperature)$$

Self-Inhibition

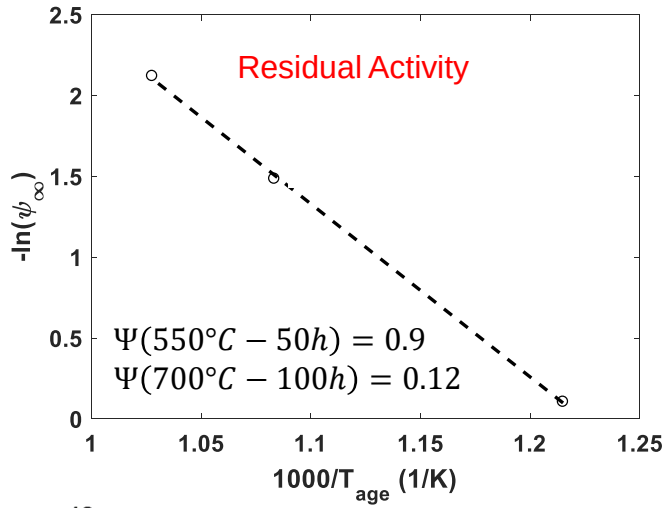


- Global inhibition (NO_2 based) was used to capture self-inhibiting nature of NO oxidation
- Data at multiple HTA conditions could be modeled by using the same inhibition parameters and activation energy

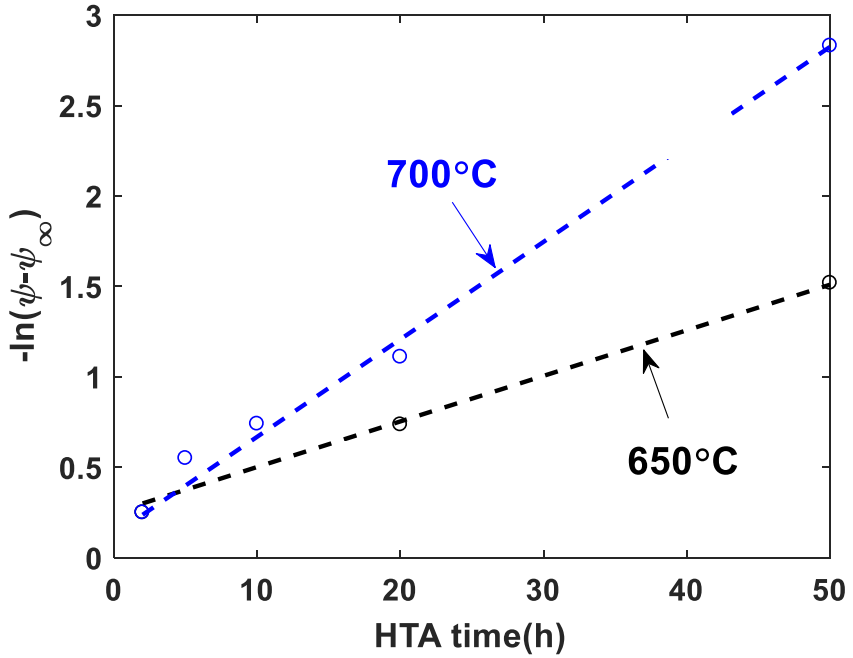
$$R = \frac{k * [NO] * [O_2]^{0.5} * (1-\beta)}{1 + K * [NO_2]}$$

$$K = A_{in} * \exp(-\frac{\Delta H}{RT}) \qquad \beta = \frac{1}{K_{eq}} * \frac{Y_{NO_2}}{Y_{NO} * Y_{O_2}{}^{0.5}}$$

Arrhenius Plots



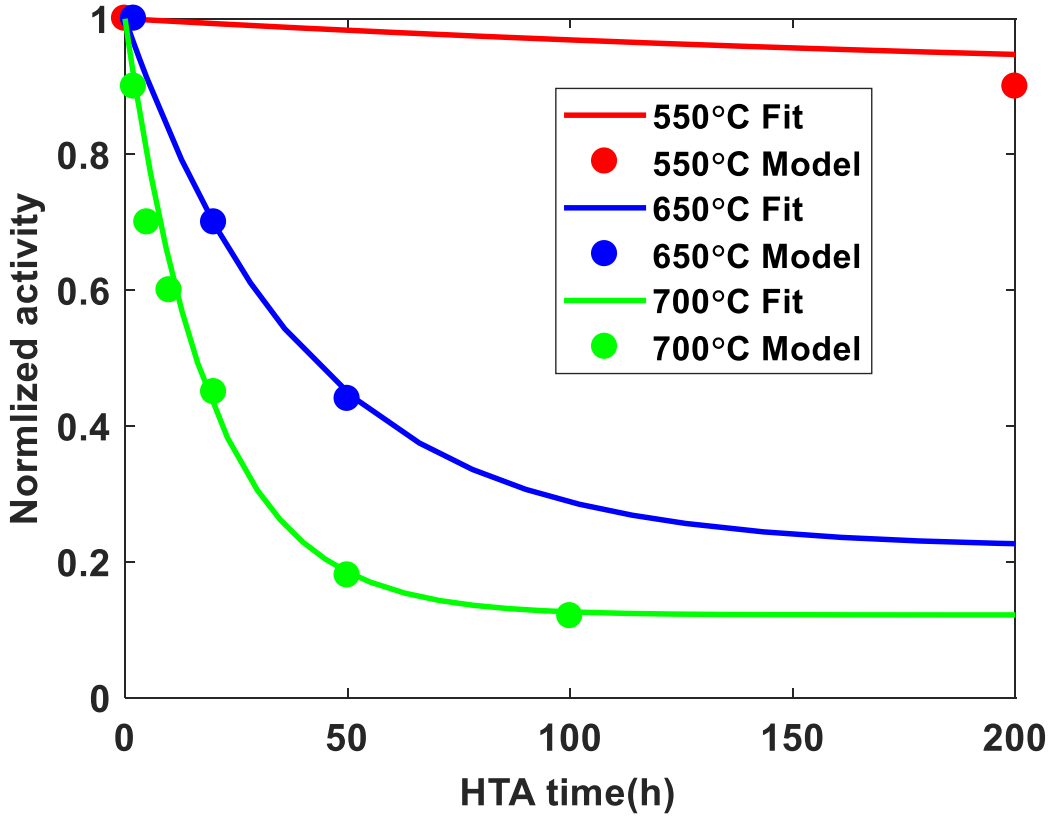
First order Deactivation model with residual activity captured normalized activity as a function of HTA with desired accuracy



Power law equation when n=1, written in algebraic form:

$$-ln(\Psi - \Psi_\infty) = -ln(1 - \Psi_\infty) + k_d t_{age}$$

HTA model



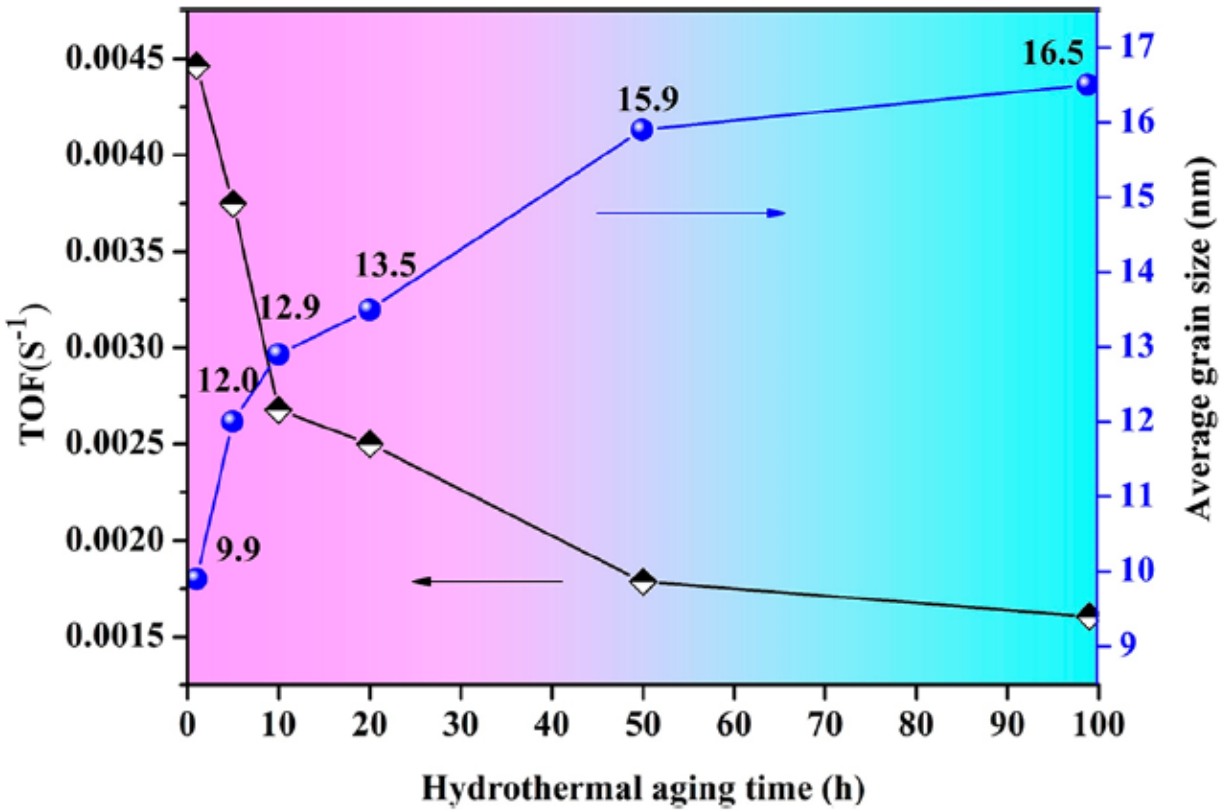
$$\frac{d\Psi}{dt} = -A_d * \exp\left(-\frac{E_d}{R_g T_{age}}\right)(\Psi - \Psi_\infty);$$

$$\Psi_\infty = A_\infty * \exp\left(-\frac{E_\infty}{R_g T_{age}}\right)$$

$$+ \text{Constraint}: \ \Psi_\infty <= 1$$

Constraint was added to ensure activity stays at 1 for all the temperatures below 500°C, regardless of the time spent at that temperature

TOF & Active sites



$$\frac{d\Psi}{dt} = -k_d(\Psi - \Psi_\infty)^n; \Psi_\infty = A_\infty \exp\left(-\frac{E_\infty}{R_g T_{age}}\right)$$

Sintering models

$$r(HTA) = TOF(HTA) * n_a(HTA)$$

- Change in number of number of active sites are typically described by sintering models
- Deactivation model presented here captures the change in macroscopic NO oxidation rate
- Change in rate is due to combination of change in TOF and number of catalytic active sites

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Reaction scheme

$$R1\text{: } NO + 0.5O_2 \leftrightarrow NO_2$$

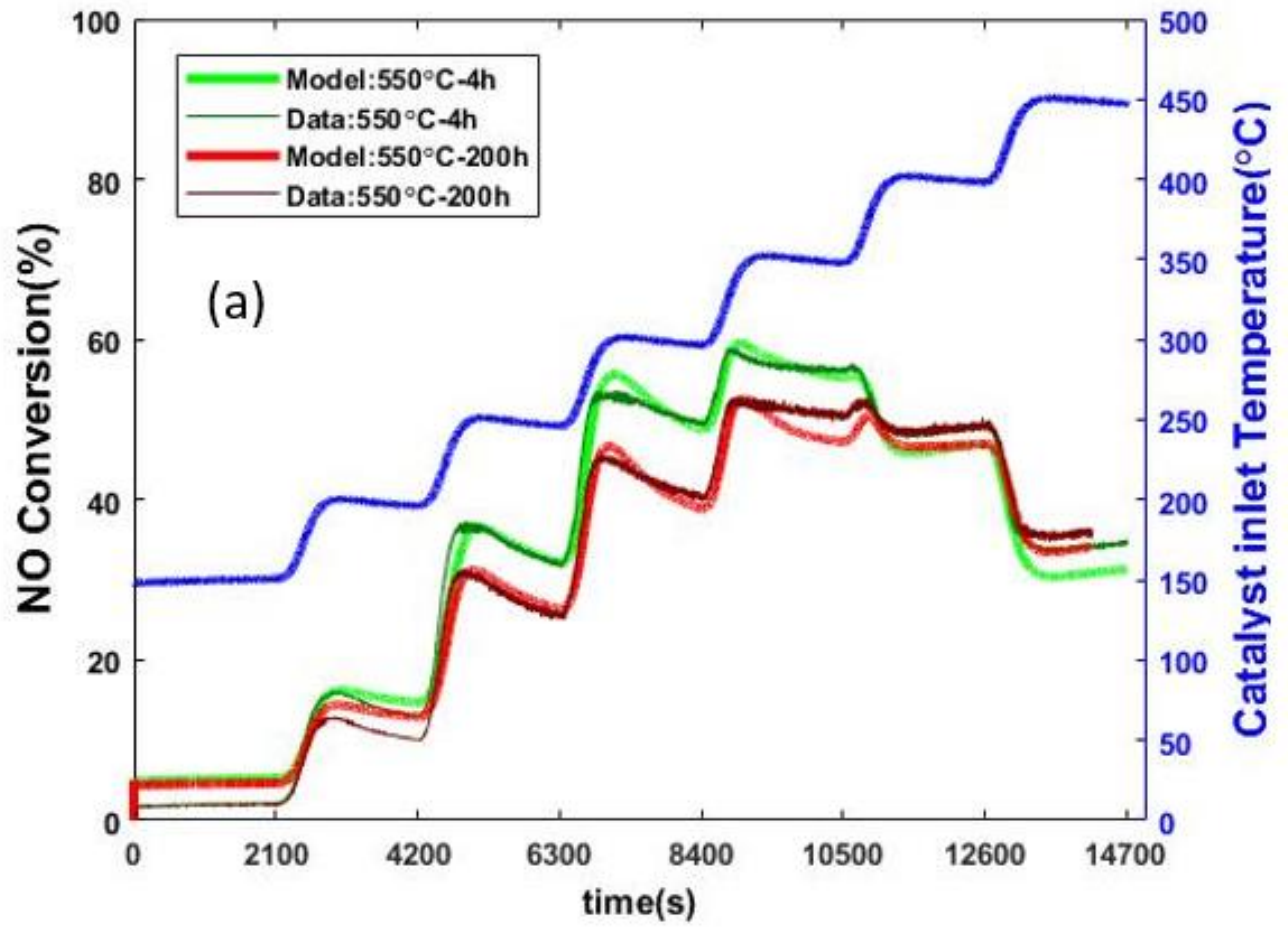
$$R2\text{: } Pt + NO_2 \leftrightarrow PtO + NO$$

$$R3\text{: } Pt + 0.5O_2 \leftrightarrow PtO$$

- PtO is model representative of all Pt oxides
- Above reaction scheme is a global way incorporate change in Pt oxidation state during NO oxidation

- The Reaction scheme shown in the left is used to capture the change in PGM oxidation state during NO oxidation
- R2 is used to model change in PGM oxidation state during NO oxidation. Forward reaction and Backward reactions correspond to oxidation and reduction of PGM, respectively
- R3 is also fundamentally reversible. However, PGM oxidation is way more favorable in the presence of NO_2 than in the presence of O_2

Impact of HTA



$$R2:\ Pt + NO_2 \leftrightarrow PtO + NO$$

$$R2 = k_f * \theta_{Pt} * Y_{NO_2} - k_b * (1 - \theta_{Pt}) * Y_{NO}$$

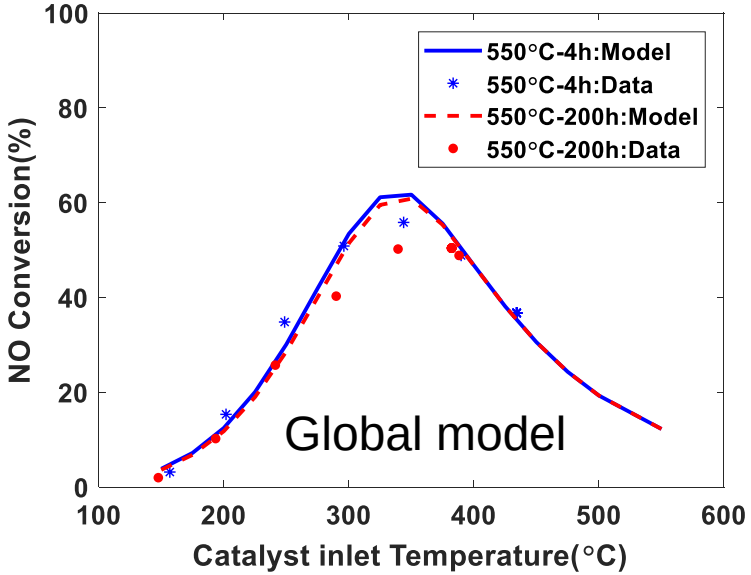
$$k_f = A_f * \exp(-\frac{E_f}{RT})$$

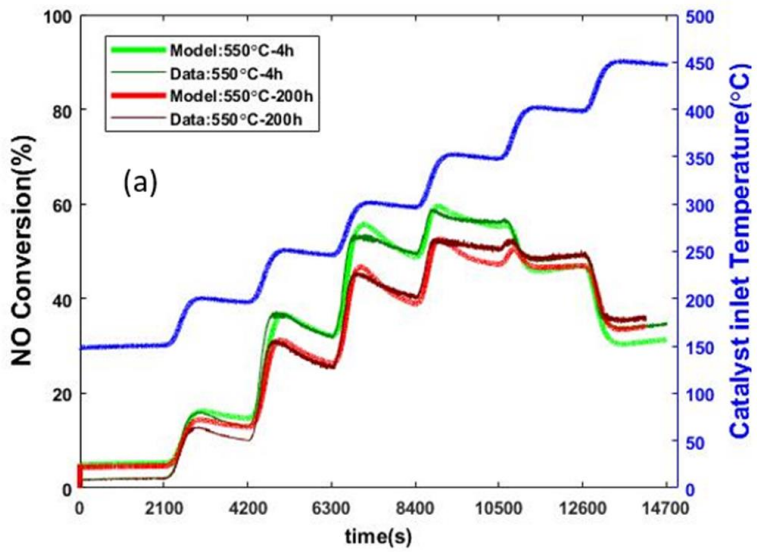
$$R = \frac{k * [NO] * [O_2]^{0.5} * (1 - \beta)}{1 + K * [NO_2]}$$

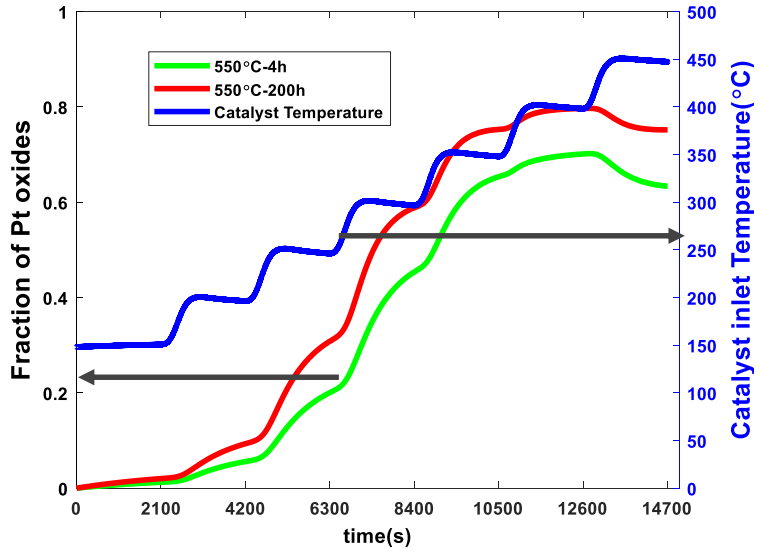
$$k = A * \exp(-\frac{E_f}{RT})$$

A_f and A are the only two kinetic parameters tuned for HTA conditions. All other kinetic parameters are kept constant

Quantification of Pt oxide coverage using Model

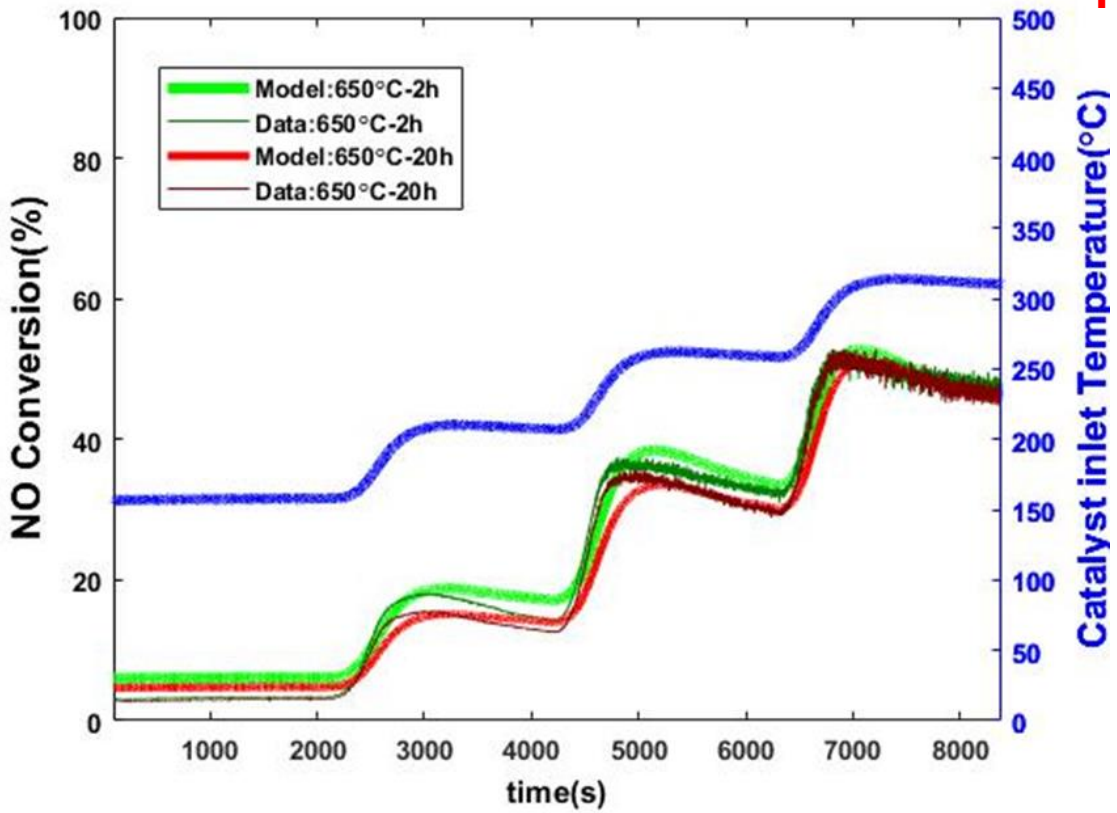






- Model that does not capture change in oxidation state has difficulty predicting ss conversion accurately
- Mechanistically, rate of PGM oxidation changes with HTA in addition to the change in intrinsic NO oxidation rate
- In the above example, change in rate of Pt oxidation is more profound than change in intrinsic NO oxidation rate

Modeling time on stream data as function of HTA



HTA model not changed to explain time on stream data

HTA specification	Reaction pre-exponential factor of PGM oxidation reaction (mol/m^3/s)
550°C-4h	A_f
550°C-200h	2.11 A_f
HTA Temperature = 650°C	1.65 A_f

Aging model + NO oxidation **(GPLE)**, Pt oxidation **(Discrete)**

NO oxidation kinetic model for reference condition

Summary

- Aging model has been developed based on flow-reactor data of NO oxidation
- Modeling the change in PGM oxidation state improves model's accuracy, especially in the temperature range of 250-400°C
- Aging model used in conjunction with reference kinetic model can serve as NO oxidation model as a function of hydro-thermal age
- HTA temperature range used for the model shown here is 550-700°C. Model does not capture non-decreasing rate with increase in particle size (when particle size is too low)
- Model is not be expected to be very accurate under extreme HTA condition that can possibly result in change in sintering mechanism or loss in surface area of washcoat support

Q+A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