Development of an LNT reaction mechanism for the BMW 120i LNT catalyst, Phase 1

NOx Adsorption and Oxygen Storage

Acknowledgements

- This work was a joint collaboration among

GT Gamma Technologies

OAK RIDGE National Laboratory

N_2 KINETICS RESEARCH

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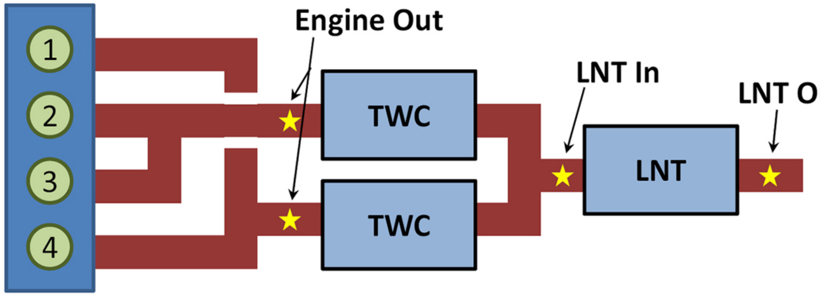
Background

- ORNL purchased a MY2008 BMW 1-series 120i lean gasoline engine vehicle with a N43B20 2.0-liter, 4-cylinder engine with direct injection
- The vehicle was characterized on a chassis dynamometer
- Engine measurement results are available on the CLEERS database
- A core from the LNT was made available for ORNL laboratory testing



Lean Gasoline Engine Reductant Chemistry During Lean NOx Trap Regeneration

James E. Parks, Vitaly Prikhodko, William Partridge, Jae-Soon Choi, Kevin Norman, Shean Huff and Paul Chambon
Oak Ridge National Laboratory

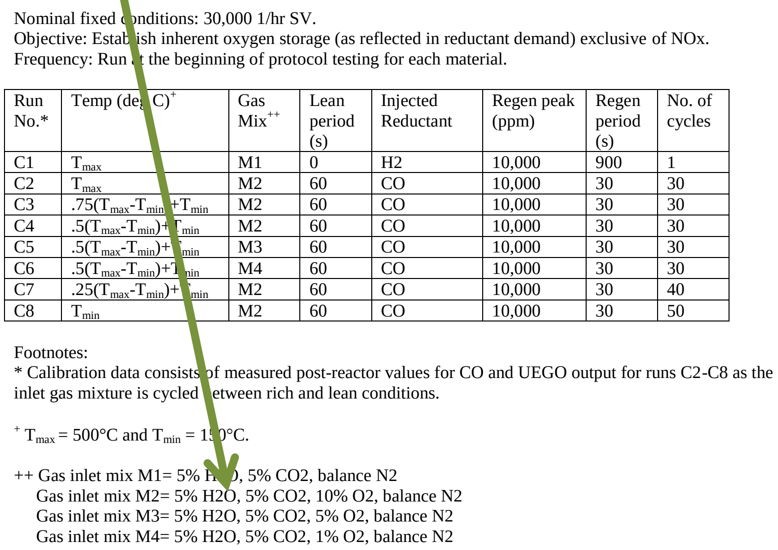
SAE, 2010-01-2267

CLEERS LNT Protocol

Includes water and CO2 so WGS is active

Max 10 minute lean cycle for protocol

Oxygen Storage



Nominal fixed conditions: 30,000 1/hr SV.
Objective: Establish inherent oxygen storage (as reflected in reductant demand) exclusive of NOx.
Frequency: Run at the beginning of protocol testing for each material.

Run No.*	Temp (deg C)[+]	Gas Mix[++]	Lean period (s)	Injected Reductant	Regen peak (ppm)	Regen period (s)	No. of cycles
C1	T_{max}	M1	0	H2	10,000	900	1
C2	T_{max}	M2	60	CO	10,000	30	30
C3	$.75(T_{max}-T_{min})+T_{min}$	M2	60	CO	10,000	30	30
C4	$.5(T_{max}-T_{min})+T_{min}$	M2	60	CO	10,000	30	30
C5	$.5(T_{max}-T_{min})+T_{min}$	M3	60	CO	10,000	30	30
C6	$.5(T_{max}-T_{min})+T_{min}$	M4	60	CO	10,000	30	30
C7	$.25(T_{max}-T_{min})+T_{min}$	M2	60	CO	10,000	30	40
C8	T_{min}	M2	60	CO	10,000	30	50

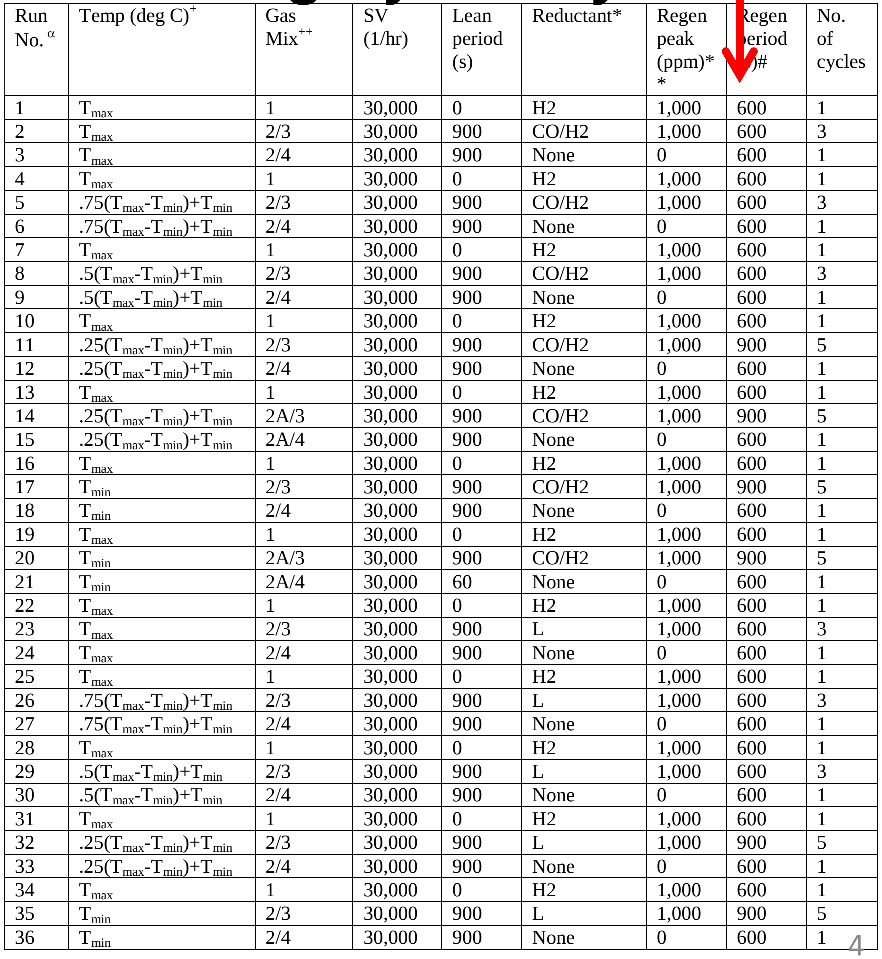
Footnotes:
* Calibration data consists of measured post-reactor values for CO and UEGO output for runs C2-C8 as the inlet gas mixture is cycled between rich and lean conditions.

[+] T_{max} = 500°C and T_{min} = 150°C.

++ Gas inlet mix M1= 5% H2O, 5% CO2, balance N2
Gas inlet mix M2= 5% H2O, 5% CO2, 10% O2, balance N2
Gas inlet mix M3= 5% H2O, 5% CO2, 5% O2, balance N2
Gas inlet mix M4= 5% H2O, 5% CO2, 1% O2, balance N2

http://cleers.org/focus_groups/private/Lean-NOx/files/1113847174LNTmap_7_18_05.pdf

Long cycle Cycles



Run No. [α]	Temp (deg C)[+]	Gas Mix[++]	SV (1/hr)	Lean period (s)	Reductant*	Regen peak (ppm)**	Regen period (s)#	No. of cycles
1	T_{max}	1	30,000	0	H2	1,000	600	1
2	T_{max}	2/3	30,000	900	CO/H2	1,000	600	3
3	T_{max}	2/4	30,000	900	None	0	600	1
4	T_{max}	1	30,000	0	H2	1,000	600	1
5	$.75(T_{max}-T_{min})+T_{min}$	2/3	30,000	900	CO/H2	1,000	600	3
6	$.75(T_{max}-T_{min})+T_{min}$	2/4	30,000	900	None	0	600	1
7	T_{max}	1	30,000	0	H2	1,000	600	1
8	$.5(T_{max}-T_{min})+T_{min}$	2/3	30,000	900	CO/H2	1,000	600	3
9	$.5(T_{max}-T_{min})+T_{min}$	2/4	30,000	900	None	0	600	1
10	T_{max}	1	30,000	0	H2	1,000	600	1
11	$.25(T_{max}-T_{min})+T_{min}$	2/3	30,000	900	CO/H2	1,000	900	5
12	$.25(T_{max}-T_{min})+T_{min}$	2/4	30,000	900	None	0	600	1
13	T_{max}	1	30,000	0	H2	1,000	600	1
14	$.25(T_{max}-T_{min})+T_{min}$	2A/3	30,000	900	CO/H2	1,000	900	5
15	$.25(T_{max}-T_{min})+T_{min}$	2A/4	30,000	900	None	0	600	1
16	T_{max}	1	30,000	0	H2	1,000	600	1
17	T_{min}	2/3	30,000	900	CO/H2	1,000	900	5
18	T_{min}	2/4	30,000	900	None	0	600	1
19	T_{max}	1	30,000	0	H2	1,000	600	1
20	T_{min}	2A/3	30,000	900	CO/H2	1,000	900	5
21	T_{min}	2A/4	30,000	60	None	0	600	1
22	T_{max}	1	30,000	0	H2	1,000	600	1
23	T_{max}	2/3	30,000	900	L	1,000	600	3
24	T_{max}	2/4	30,000	900	None	0	600	1
25	T_{max}	1	30,000	0	H2	1,000	600	1
26	$.75(T_{max}-T_{min})+T_{min}$	2/3	30,000	900	L	1,000	600	3
27	$.75(T_{max}-T_{min})+T_{min}$	2/4	30,000	900	None	0	600	1
28	T_{max}	1	30,000	0	H2	1,000	600	1
29	$.5(T_{max}-T_{min})+T_{min}$	2/3	30,000	900	L	1,000	600	3
30	$.5(T_{max}-T_{min})+T_{min}$	2/4	30,000	900	None	0	600	1
31	T_{max}	1	30,000	0	H2	1,000	600	1
32	$.25(T_{max}-T_{min})+T_{min}$	2/3	30,000	900	L	1,000	900	5
33	$.25(T_{max}-T_{min})+T_{min}$	2/4	30,000	900	None	0	600	1
34	T_{max}	1	30,000	0	H2	1,000	600	1
35	T_{min}	2/3	30,000	900	L	1,000	900	5
36	T_{min}	2/4	30,000	900	None	0	600	1

Protocol Issues

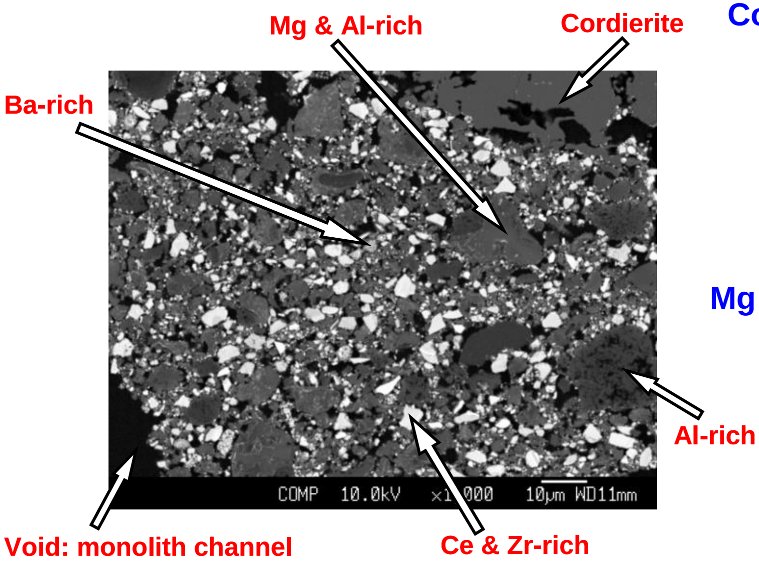
- Original protocol evaluation, Epling, Currier and Yezerets http://www.cleers.org/workshop8/presentations/epling.pdf
- Temperatures ranging from 150 – 550°C equally spaced in 1/T [K] to facilitate better reaction modeling
  - 150°C, 209°C, 286°C, 393°C, 550°C
- For this application 600 seconds lean was not sufficient to get complete NOx storage at all temperatures
  - Josh reran the long POx protocol and adjusted storage times to reach full NOx storage

New Generation Lean GDI LNT

(benchmarking against CLEERS reference catalyst)

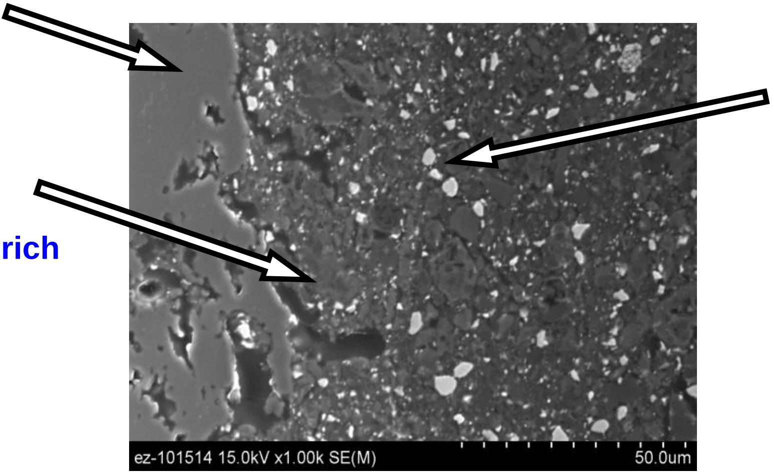
CLEERS reference

Lean GDI, 2004, provided by Umicore



New LNT

Lean GDI, 2009, from BMW 120i vehicle



New generation is more highly dispersed for most components

CLEERS LNT versus BMW LNT

	FULL	SIZE	BRICKS
Property	**CLEERS ref**	**BMW**	**Units**
cell density	625	413	cells/in^2
	97	64	cells/cm^2
mass	465.83	853.24	g
area	109.36	117.24	cm^2
length	7.5	11	cm
volume	820	1290	cm^3
	0.820	1.290	L
density	567.9	661.6	g/L

Ceria slightly less

PGM similar

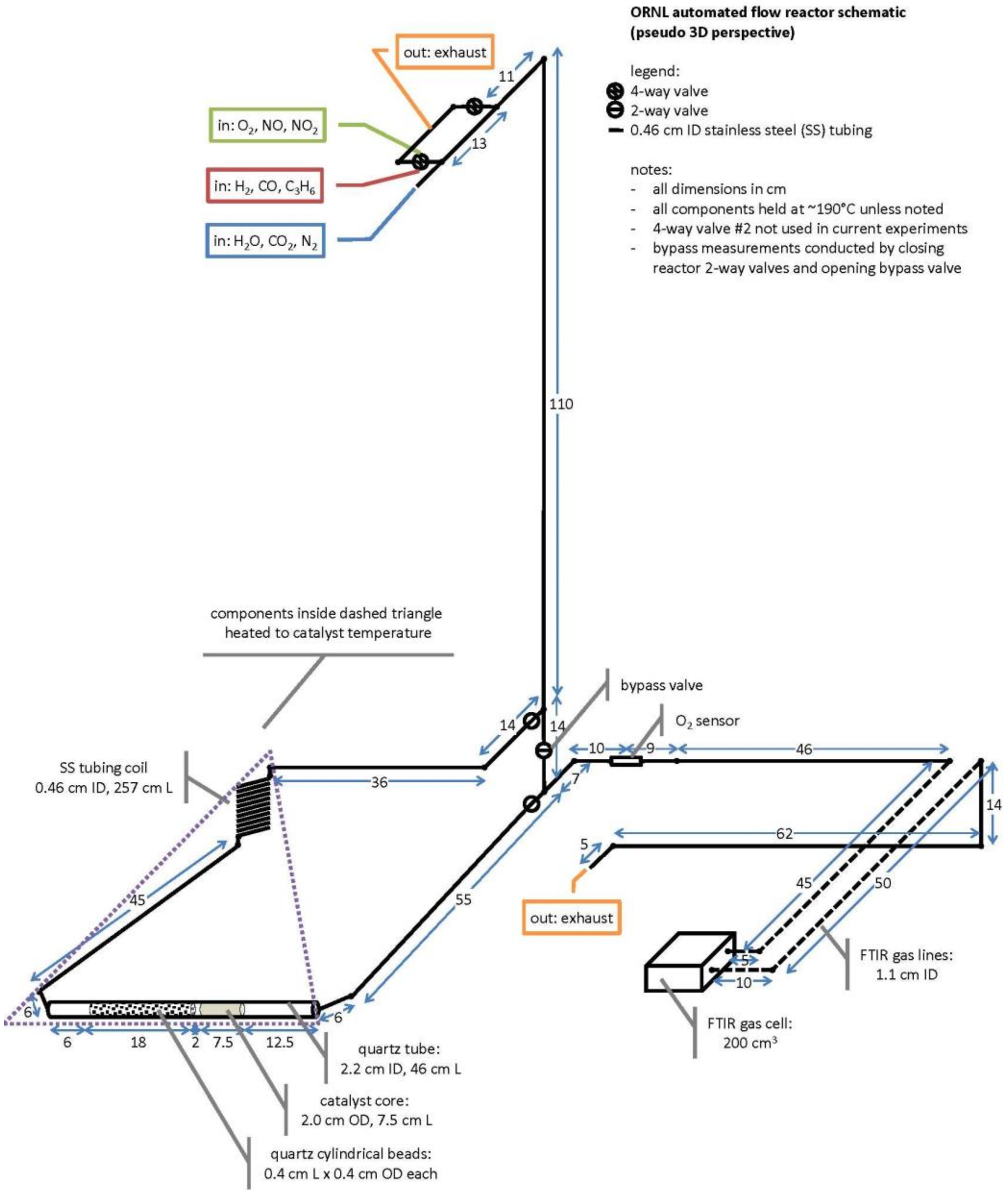
Common NOx storage components

Element	CLEERS ref	BMW	Units
Ba	14.88	19.98	g/L
Ce	67.36	55.51	g/L
Zr	5.11	4.32	g/L
La	2.84	2.45	
Pt	2.45	2.18	
Pd	0.77	0.85	
Rh	0.30	0.30	g/L
PGM	3.52	3.32	g/L
K	0.06	0.04	g/L
Sr	0.34	0.39	g/L
Na	0.03	0.07	g/L
Ca	N/A	0.09	g/L

Dispersion and cell density most significant differences

ORNL Laboratory Reactor Architecture

- Flow simulations were used to calculate measurement delays
- Measurement delays were calculated to vary from 0.1 second to 0.7 seconds
- For efficiency, the full flow architecture was not used for mechanism development



ORNL automated flow reactor schematic
(pseudo 3D perspective)

legend:
⊗ 4-way valve
⊖ 2-way valve
— 0.46 cm ID stainless steel (SS) tubing

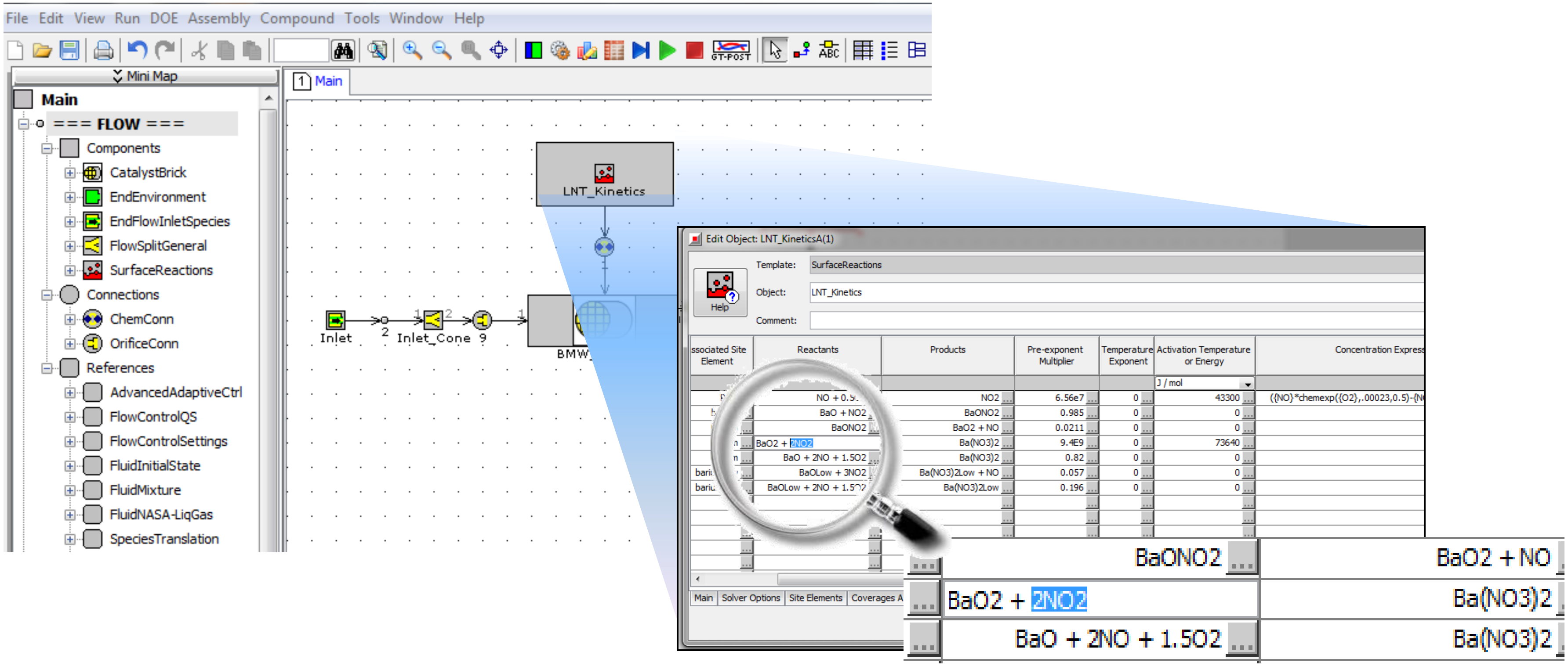
notes:
- all dimensions in cm
- all components held at ~190°C unless noted
- 4-way valve #2 not used in current experiments
- bypass measurements conducted by closing reactor 2-way valves and opening bypass valve

ORNL Laboratory Setup

JOSH

Modeling Approach

- GT-SUITE software
- 1D, quasi-steady flow solution
- GTI's Advanced Adaptive chemistry solver



Edit Object: LNT_KineticsA(1)

Template: SurfaceReactions

Object: LNT_Kinetics

Comment:

ssociated Site Element	Reactants	Products	Pre-exponent Multiplier	Temperature Exponent	Activation Temperature or Energy	Concentration Express
					J / mol	
P	NO + 0.5	NO2	6.56e7	0	43300	({NO}*chemexp({O2},.00023,0.5)-{N
b	BaO + NO2	BaONO2	0.985	0	0	
	BaONO2	BaO2 + NO	0.0211	0	0	
n	BaO2 + 2NO2	Ba(NO3)2	9.4E9	0	73640	
n	BaO + 2NO + 1.5O2	Ba(NO3)2	0.82	0	0	
bari	BaOLow + 3NO2	Ba(NO3)2Low + NO	0.057	0	0	
baric	BaOLow + 2NO + 1.5O2	Ba(NO3)2Low	0.196	0	0	

BaONO2	BaO2 + NO
BaO2 + 2NO2	Ba(NO3)2
BaO + 2NO + 1.5O2	Ba(NO3)2

Ref: SAE 2007-01-4127

GT-SUITE Advanced Adaptive Chemistry Solver

- Chemical kinetics creates stiff systems. To solve these systems robustly and accurately, the solver must be highly

ADAPTIVE

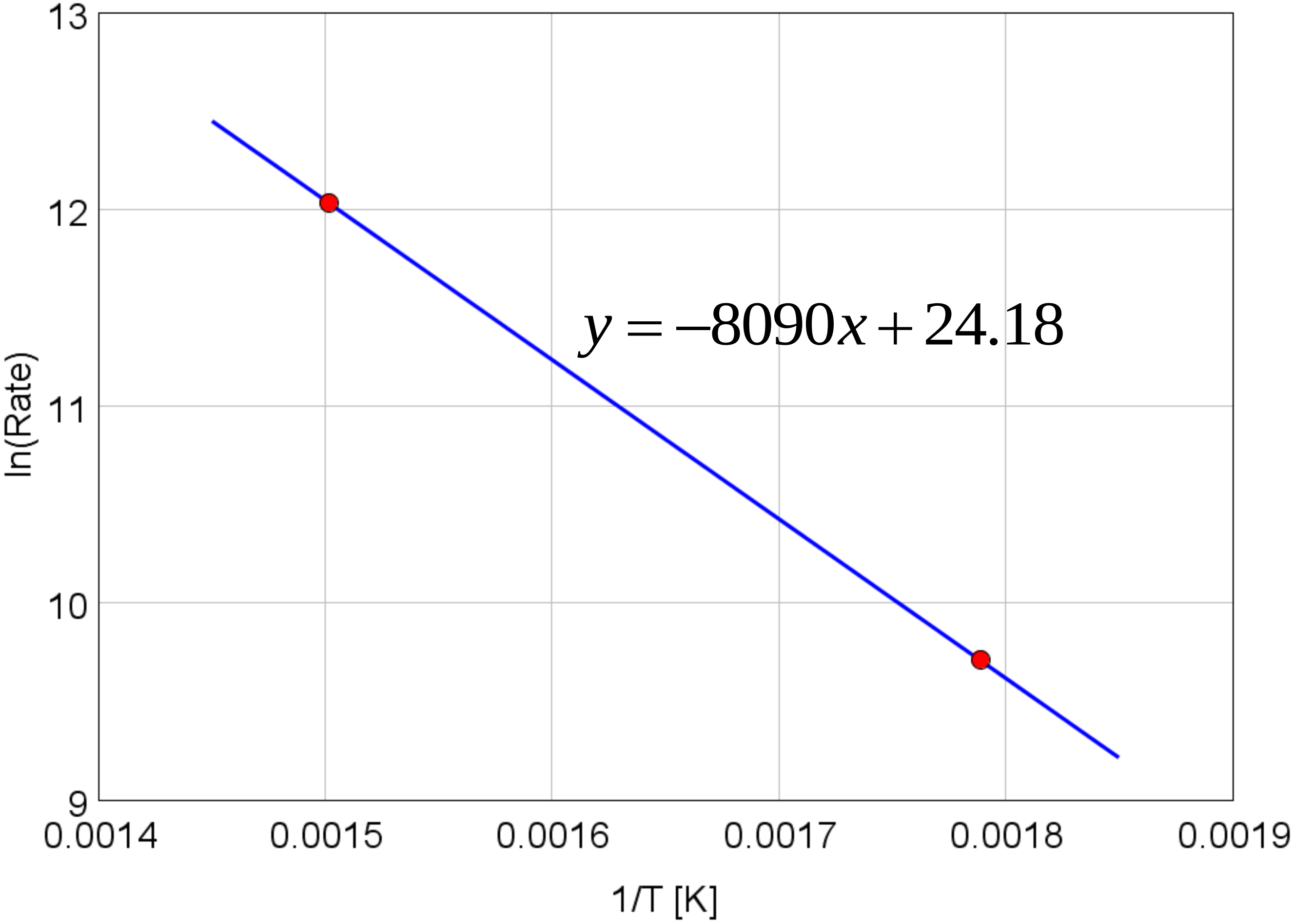
- The solver uses adaptive :
  - Time steps
  - Axial steps
  - Non-linear iterations

Especially helpful for transients

- Highest stability standards are applied:
  - Fully coupled, no lagging
  - BDF (Backward Differentiation Formula) integration methods
- Numerically efficient:
  - 20 – 2000 times faster than real time depending on kinetics and inlet boundary conditions

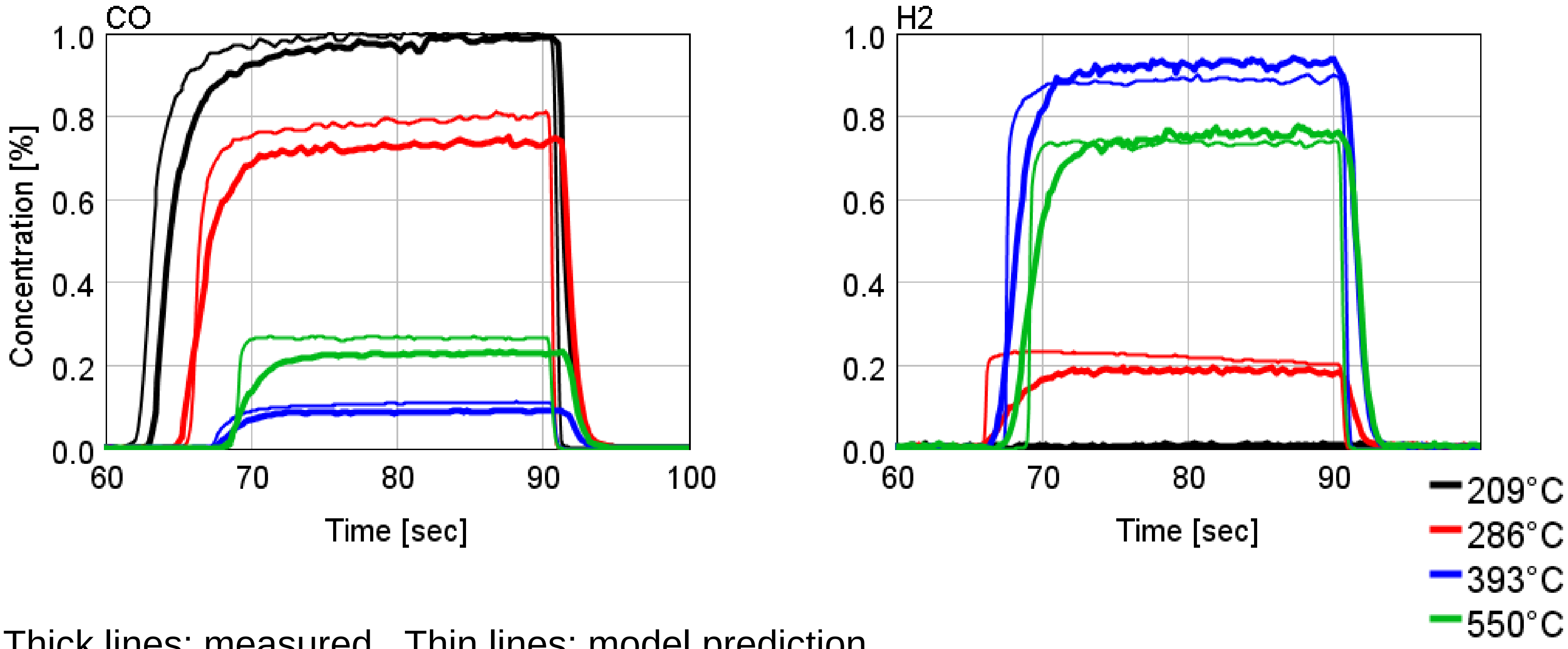
Water-Gas-Shift Reaction Calibration

- WGS calibrated at 286°C and 393°C to match steady-state CO/H_2 ratio
  - Inactive at 150°C and 209°C; at chemical equilibrium at 550°C
- Ahrrenius plot of ln(rate) vs. 1/T gave kinetic rate constant fit



Oxygen Storage Protocol Measurements

- 60 second 10% O_2 storage, 30 second reduction by 1% CO
- Balance of OSC reaction and WGS shows a temperature-dependent oxygen storage capacity
- Water-gas-shift reaction calibrated to match steady-state CO/H_2 ratio



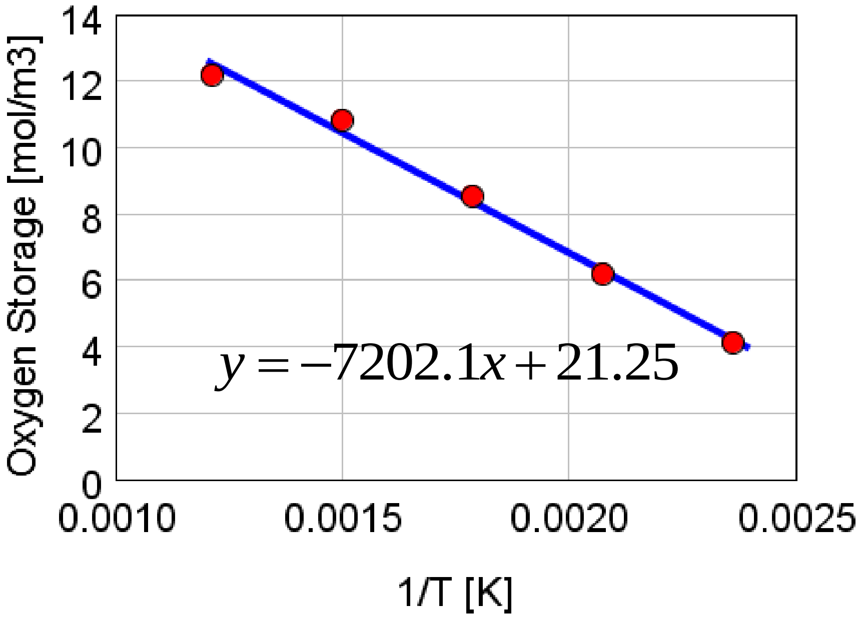
Thick lines: measured   Thin lines: model prediction

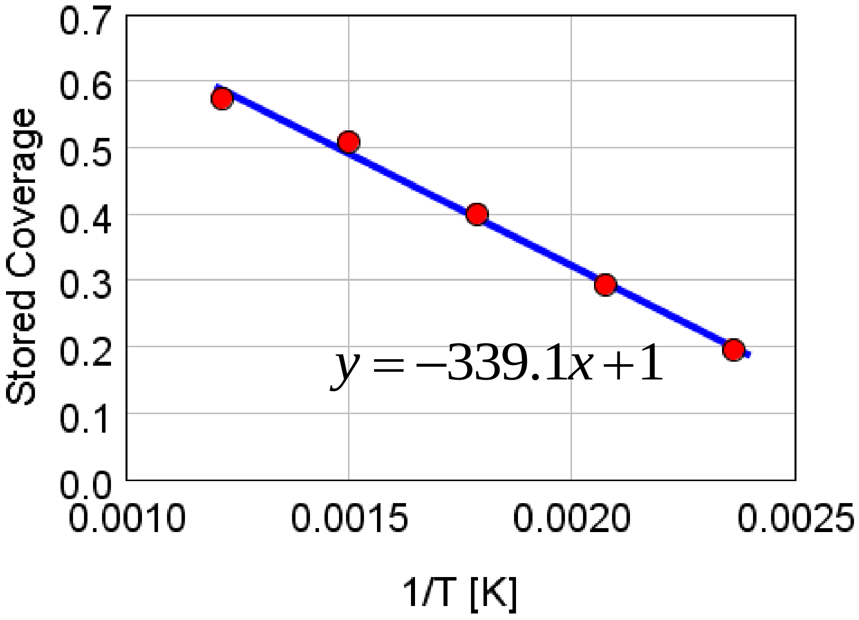
Oxygen Storage and Reduction Modeling

- Oxygen storage capacity increases with increasing balance with WGS reactions
- Maximum storage estimated from extrapolation → 2
- Temperature-dependent equilibrium coverage controls storage capacity

I am not sure that there is any substantiation in the literation for this

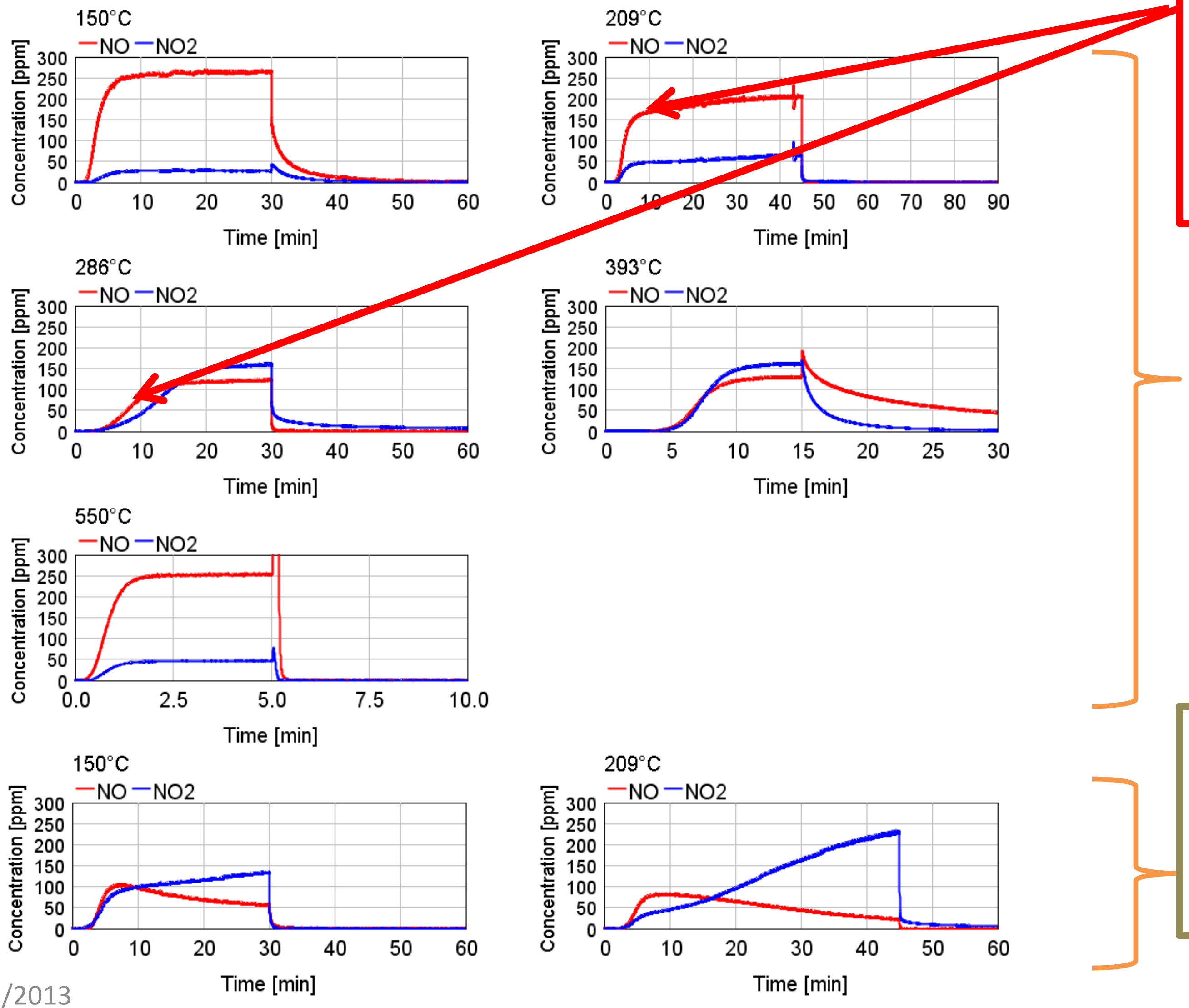
$$\theta_{Ce_2O_4}(T) = 1 - \frac{339}{\max(T, 339)}$$





NOx Storage Experimental Data

Measurements available for 7 different cases



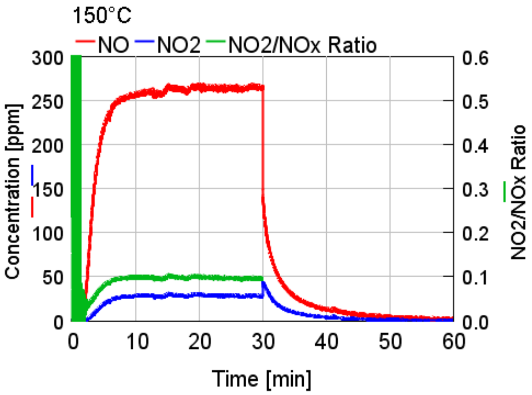
Not equilibrated at 10 minutes

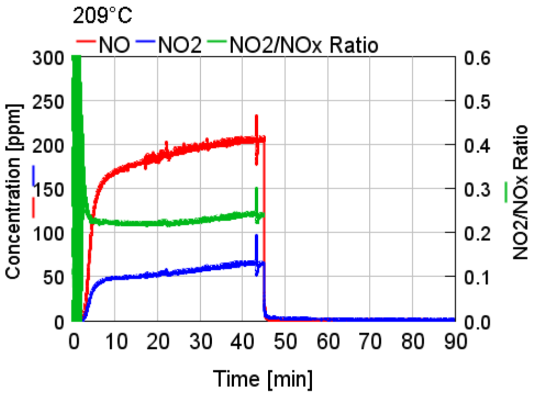
300 ppm NO

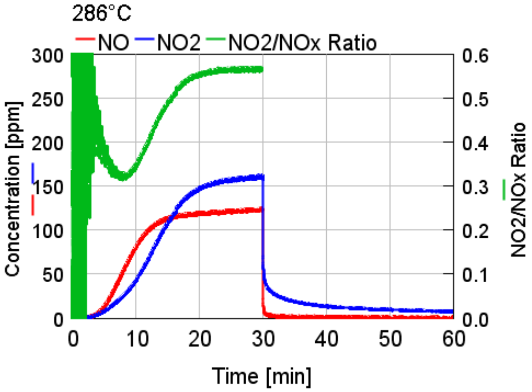
10 minutes not sufficient to stabilize NO_2 concentration

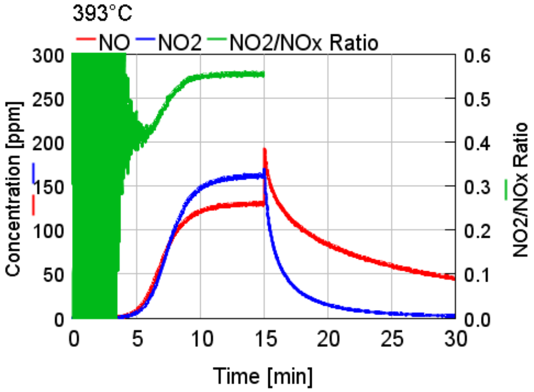
NO Oxidation from NO Inlet Experiments

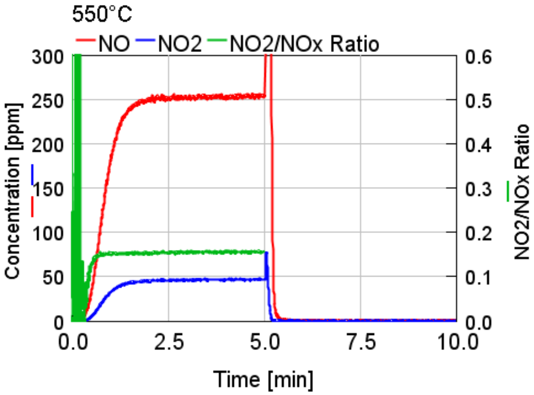
- Protocol does not directly provide NO oxidation information
- NO_2/NOx reaches near steady-state in all cases
- NO oxidation kinetics were calibrated using NO_2/NOx ratio



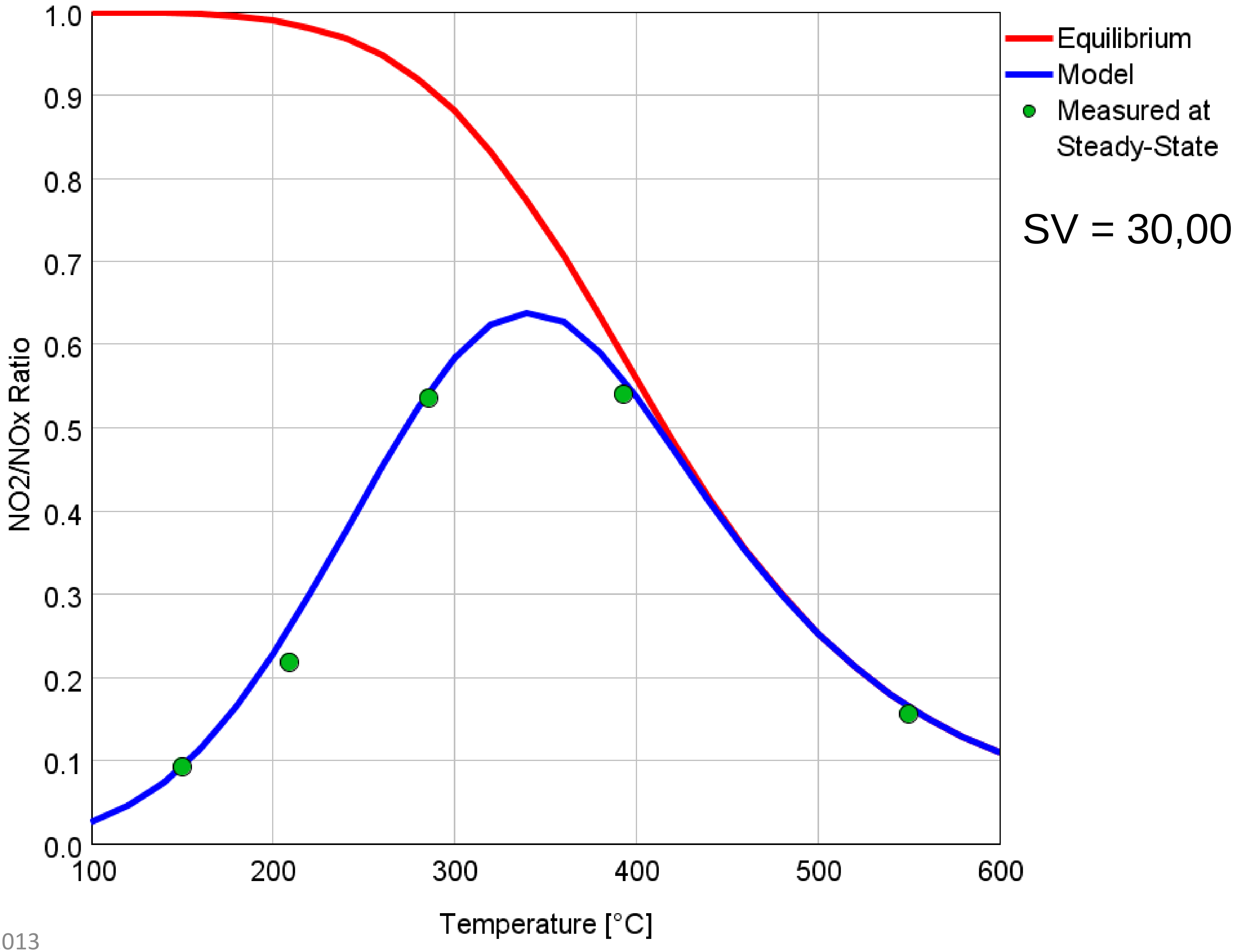








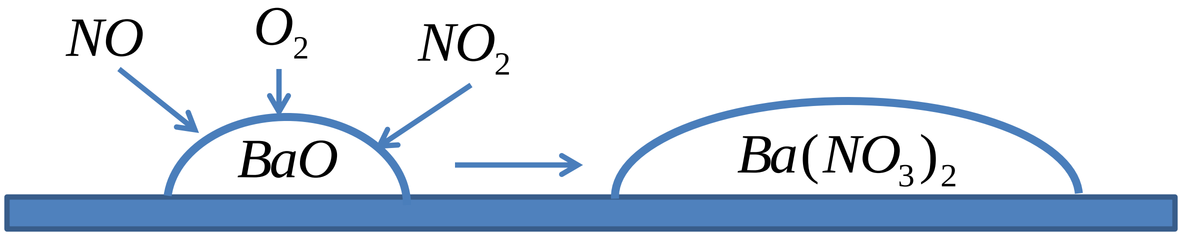
NO Oxidation from NO Inlet



SV = 30,000 1/hr

NOx Storage Modeling

- Equilibrium coverage method for NOx storage modeling has two major flaws



$$R = kC_{NOx}C_{O_2}\,sign\Big(\big(\theta_{eq}(T)-\theta_{NOx}\big)^2,\theta_{eq}(T)-\theta_{NOx}\Big)$$

- When $C_{O_2} = 0$, R = 0, which is not supported by the data
  - NOx clearly releases from the surface when oxygen is absent

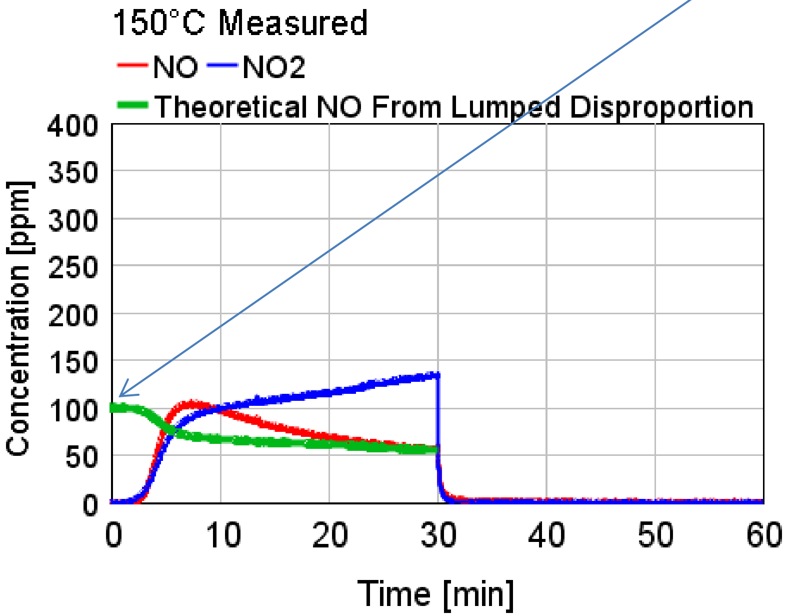
- When $\theta_{eq}(T) < \theta_{NOx}$, R < 0, → net rate is NOx release from surface
  - The net rate is still dependent on C_{NOx}, which is not physical

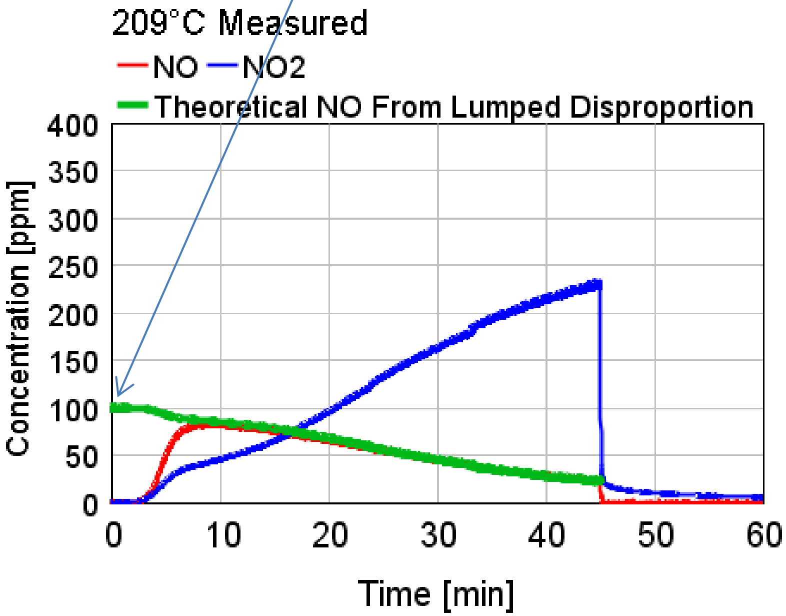
NOx Storage Modeling

Where does the model get NO at time-0??

- NO_2 inlet experiments calibrated first
  - Reverse NO oxidation does not occur at 150°C; negligible at 209°C
- One-step disproportion reaction accounts for outlet NO at 209°C; 150°C approaches theoretical value at steady-state

$$\boxed{BaO + 3NO_2 \rightarrow Ba(NO_3)_2 + NO}$$





3 site?

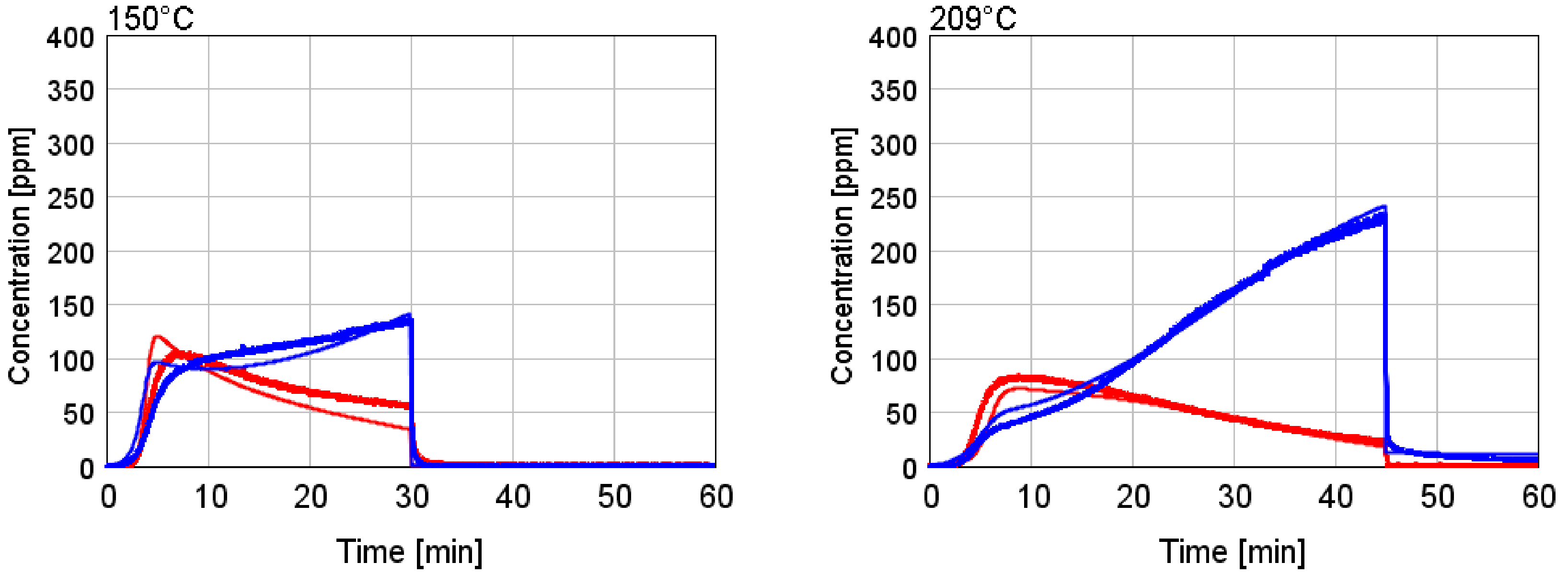
NOx Storage Modeling

- Three-step disproportion needed to match peak NO outlet concentration at 150°C

$$BaO + 3NO_2 \rightarrow Ba(NO_3)_2 + NO \quad \left\{ \begin{array}{l} BaO + NO_2 \rightarrow BaO - NO_2 \\ BaO - NO_2 \rightarrow BaO_2 + NO \\ BaO_2 + 2NO_2 \rightarrow Ba(NO_3)_2 \end{array} \right.$$

→ rate-limited at low temperature

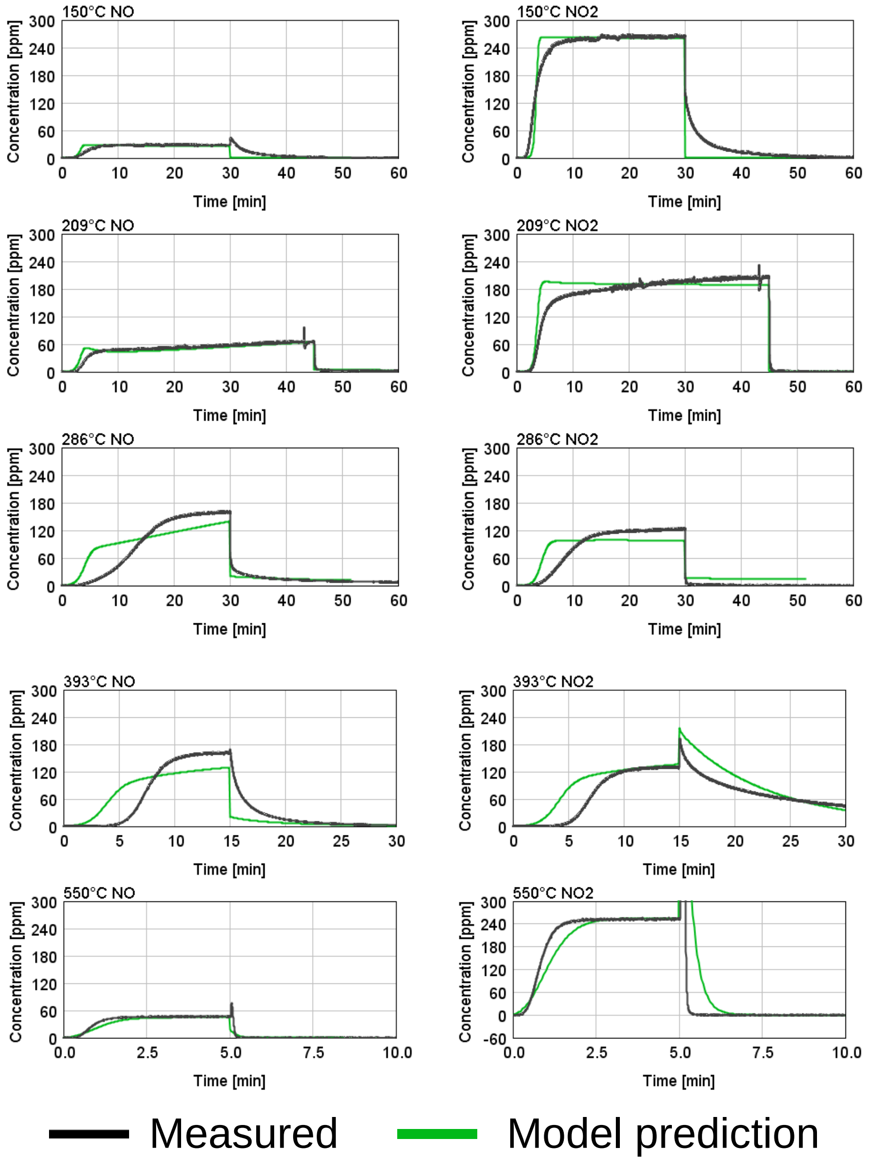
- Two site storage needed for delayed breakthrough
- Quite possibly the low temperature adsorption is on ceria, see Chuan et. al, Applied Catalysis B: Environmental 119–20 (2012) 183–196



Thick lines: measured   Thin lines: model prediction

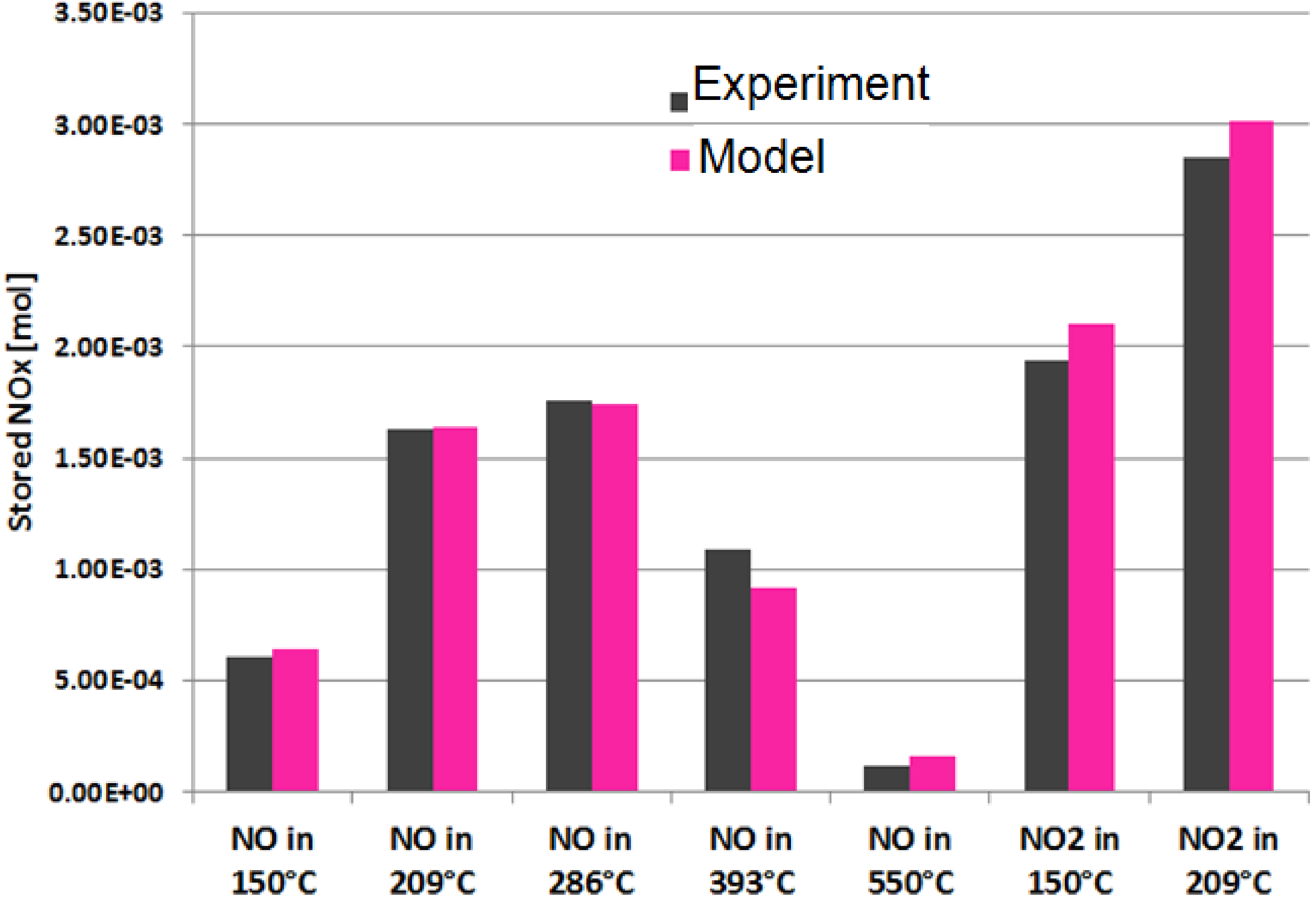
NOx Storage Modeling – NO Inlet Experiments

- Current mechanism
  - Two storage sites
  - Storage + release of both NO and NO_2
  - Retains satisfactory results with NO_2 experiments
- Additional work needed
  - Release at 150°C
  - Breakthroughs at 286°C and 393°C



Equilibrium NOx Storage Capacity

- Current model predicts storage capacity both quantitatively and qualitatively



Current Mechanism

$$R1: NO + 0.5O_2 \leftrightarrow NO_2$$

$$R2: BaO + NO_2 \rightarrow BaO - NO_2$$

$$R3: BaO - NO_2 \rightarrow BaO_2 + NO$$

$$R4: BaO_2 + 2NO_2 \rightarrow Ba(NO_3)_2$$

$$R5: BaO + 2NO + 1.5O_2 \rightarrow Ba(NO_3)_2$$

$$R6: Ba(NO_3)_2 \rightarrow BaO + 2NO + 1.5O_2$$

$$R7: Ba(NO_3)_2 \rightarrow BaO + 2NO_2 + 0.5O_2$$

$$R8: Ba'O + 3NO_2 \rightarrow Ba'(NO_3)_2 + NO$$

$$R9: Ba'O + 2NO + 1.5O_2 \rightarrow Ba'(NO_3)_2$$

$$R10: Ba'(NO_3)_2 \rightarrow Ba'O + 2NO + 1.5O_2$$

$$R11: Ba'(NO_3)_2 \rightarrow Ba'O + 2NO_2 + 0.5O_2$$

$$R12: H_2O + CO \leftrightarrow H_2 + CO_2$$

$$R13: Ce_2O_3 + 0.5O_2 \rightarrow Ce_2O_4$$

$$R14: Ce_2O_4 + CO \rightarrow Ce_2O_3 + CO_2$$

$$R15: Ce_2O_4 + H_2 \rightarrow Ce_2O_3 + H_2O$$

Active Site Densities (moles/m^3 total catalyst volume)	
PGM	2.02
Ba	64
Ba’	11
cerium	84

Current Mechanism

All rates are turnover number based

All concentrations in mol/m³

Reaction	A	T_a (K)
R1	6.56E7	5212
R2	0.23	0
R3	35.5	0
R4	1.1E10	10350
R5	0.001	0
R6	120900	12360
R7	2.2	5220
R8	3.55	0
R9	5.65	0
R10	231000	12360
R11	1.45	5220
R12	3.175E10	8090
R13	0.1	See Rate Form
R14	20000	See Rate Form
R15	53060	See Rate Form

$$R1 = Ae^{-T_a/T}\left(C_{NO}C_{O_2}^{0.5} - \frac{C_{NO_2}}{K_{eq}}\right)/G$$

$$R12 = Ae^{-T_a/T}\left(C_{H_2O}C_{CO} - \frac{C_{H_2}C_{CO_2}}{K_{eq}}\right)/G$$

$$R13 = AC_{O_2}\max\left(0{,}1 - \frac{339.1}{\max(T,344.25)} - \theta_{Ce_2O_4}\right)$$

$$R14 = AC_{CO}e^{\left(\frac{-4500\left(1-1.775\theta_{Ce_2O_4}+2\theta_{Ce_2O4}^2\right)}{T}\right)}$$

$$R15 = AC_{H_2}e^{\left(\frac{-9595\left(1-3.03\theta_{Ce_2O_4}+1.64\theta_{Ce_2O4}^2\right)}{T}\right)}$$

All other rate forms:

$$R_j = Ae^{-T_a/T}\prod C_i \prod \theta_i$$

(order 1 concentrations and coverages)

Summary

- Experimental results at 150 ^{o}C provide significant additional information about the low temperature storage process
- The oxygen storage protocol is quite sufficient for developing kinetics; however, a two site storage model might be needed especially when the short cycle effects are modeled
- A three site model for NOx storage is needed perhaps due to NOx storage on ceria
- For this catalyst lean cycle times greater than 600 seconds are needed to reach steady state. In some cases times in excess of 2700 seconds seem to be needed
- At low temperature NO and NO_2 adsorption do not seem to be strongly connected through the NO oxidation step. NO and NO_2 have vastly different storage pathways
- Prediction of the temperature dependent NO and NO_2 storage appears to be good
- High temperature NOx adsorption appears to be a one site process
- This mechanism appears to describe both the NO and the NO_2 adsorption at low temperature; however, experiments for NO_2 storage in the absence of O_2 would be very informative

Future Work

- TPR experiment for NO oxidation for better transient modeling
- Refine the NOx storage kinetic parameters with additional modeling
- Calibrate NOx reduction by CO, H_2, and C_3H_6
- Model the short cycle lab experiments for transient kinetics development
- Simulation of the engine results may be considered

Current Mechanism

$$G = T(1+K_1 y_{CO} + K_2 y_{C_3H_6})^2 (1+K_3 y_{CO}^2 y_{C_3H_6}^2)(1+K_4 y_{NO})$$

$$K_1 = 65.5\exp(961/T)$$

$$K_2 = 2080\exp(361/T)$$

$$K_3 = 3.98\exp(11611/T)$$

$$K_4 = 479000\exp(-3733/T)$$

y_j : mole fraction