Experimental Analysis and Kinetics Development of TWC Oxygen Storage

Wednesday, April 10th, 2013

Acknowledgements

Oxygen Storage Redox Process

½ O_2 or NO + VOSC $\rightarrow$ Os + N$_?$

CO or H_2 + O_s $\rightarrow$ CO_2 or H_2O + V_{OSC}

where V_{OSC} indicates a vacant oxygen site and O_s indicates the occupied oxygen site.

O_2 and NO are oxidants for the VOSC and are ultimately reduced

CO and H_2 are reductants for the O_s and are ultimately oxidized

GOAL: Determine competitive rate parameters for these processes on a commercial TWC

The catalyst used is an engine aged (100 hours) commercial three-way catalyst, containing platinum and rhodium (14 g/ft^3 Pt and 3.5 g/ft^3 Rh) with a cell density of 600 cpi. CeZrO$_x$ was the oxygen storage material at a loading of 75g/L or 2124g/ft^3

Experimental Approach

Cyclic steps (leading edge of each step is used for kinetics development):

- O_2 – Ar - CO (Chalmers reactor)
- O_2 – Ar – H_2 (Chalmers reactor)
- NO – He – CO (GM reactor)

Leading edge for kinetics development

Ar purge
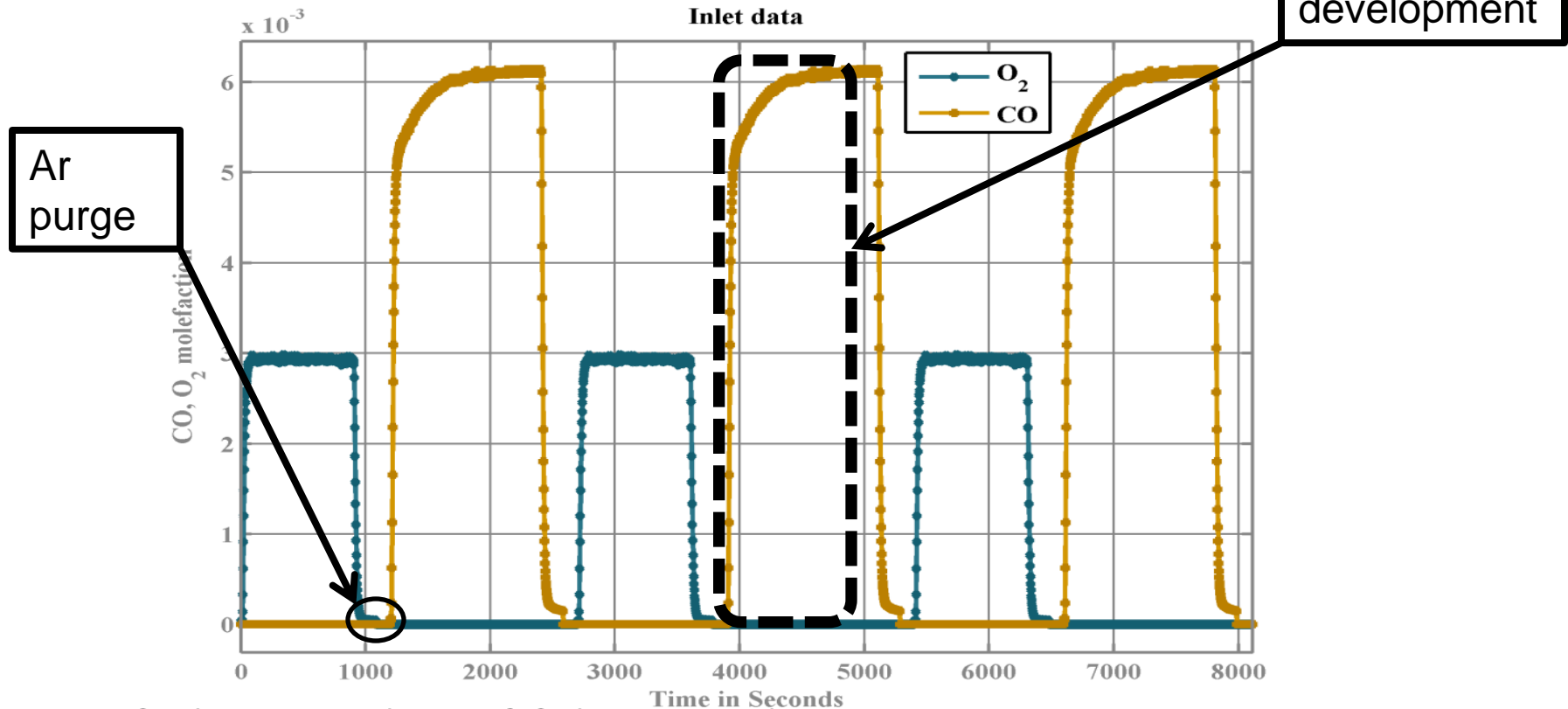
O_2 (3000 ppm) and CO (6000 ppm) mole fractions versus time. Ar flowed through the reactor between pulses as a purge.

Oxygen Storage Mechanism
(Two site model formulation)

Measured

| Reaction	Mechanism	ox/red	site	ΔH
r_1	$2Ce_2O_3(S1) + O_2 \rightarrow 4CeO_2(S1)$	ox	S1	$-200\ kJ/mol$
r_2	$Ce_2O_3(S1) + NO \rightarrow 2CeO_2(S1) + 0.5N_2$	ox	S1	$-190\ kJ/mol$
r_3	$2Ce_2O_3(S2) + O_2 \rightarrow 4CeO_2(S2)$	ox	S2	$-200\ kJ/mol$
r_4	$Ce_2O_3(S2) + NO \rightarrow 2CeO_2(S2) + 0.5N_2$	ox	S2	$-190\ kJ/mol$
r_5	$2CeO_2(S1) + CO \rightarrow Ce_2O_3(S1) + CO_2$	red	S1	$-183\ kJ/mol$
r_6	$2CeO_2(S1) + H_2 \rightarrow Ce_2O_3(S1) + H_2O$	red	S1	$-142\ kJ/mol$
r_7	$2CeO_2(S2) + CO \rightarrow Ce_2O_3(S2) + CO_2$	red	S2	$-183\ kJ/mol$
r_8	$2CeO_2(S2) + H_2 \rightarrow Ce_2O_3(S2) + H_2O$	red	S2	$-142\ kJ$

Not measured

Total Site Density = $a = a_{S1} + a_{S2}$ where

$$a_{S1} = \gamma a \qquad a_{S2} = (1 - \gamma)a$$

γ = disproportion ratio where $0 \le \gamma \le 1$

O₂ consumption profile

- 200 °C experiment with 6000 ppm inlet oxygen
- Inlet oxygen profile comes from an empty reactor experiment

$$OSC = \int_0^{t_{inf}} w \; x_{g,O2}\Big|_{z=L}^{z=0} \, dt$$
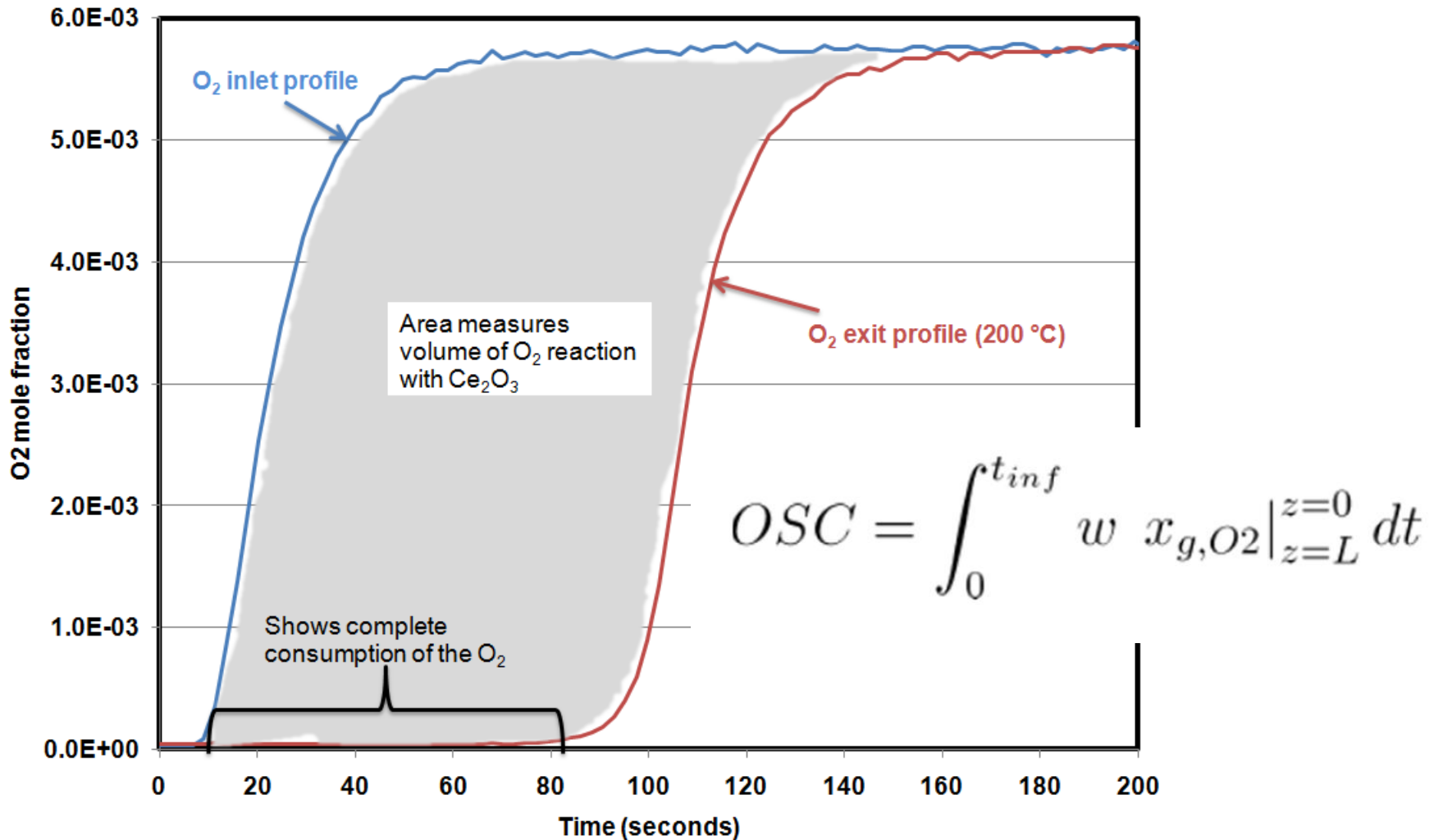
Experimental Oxygen Storage Capacity

Concentration pulse expmts	200 ºC	300 ºC	400 ºC	500 ºC
1.5k 6k	117.12	130.62	125.69	117.80
3k 3k	128.56	127.74	125.23	119.96
3k 6k	105.46	119.18	112.31	115.72
6k 6k	122.20	126.63	119.20	127.43

- Experimental nomenclature e.g. step of 1500 ppm CO and 6000 ppm O_2
- The value of 121 mole-sites/m^3 is used as the characteristic value for this catalyst.
- Standard deviation is 6.8 mole-site/m^3 which is an encouraging consistency over the 16 sets of oxidation experiments.

Oxygen Storage Surface Rates
(Two site model formulation)

$$r_j = k_j c_{s,i} (1 - \theta_{Sk})$$ Oxidation (O_2 and NO)

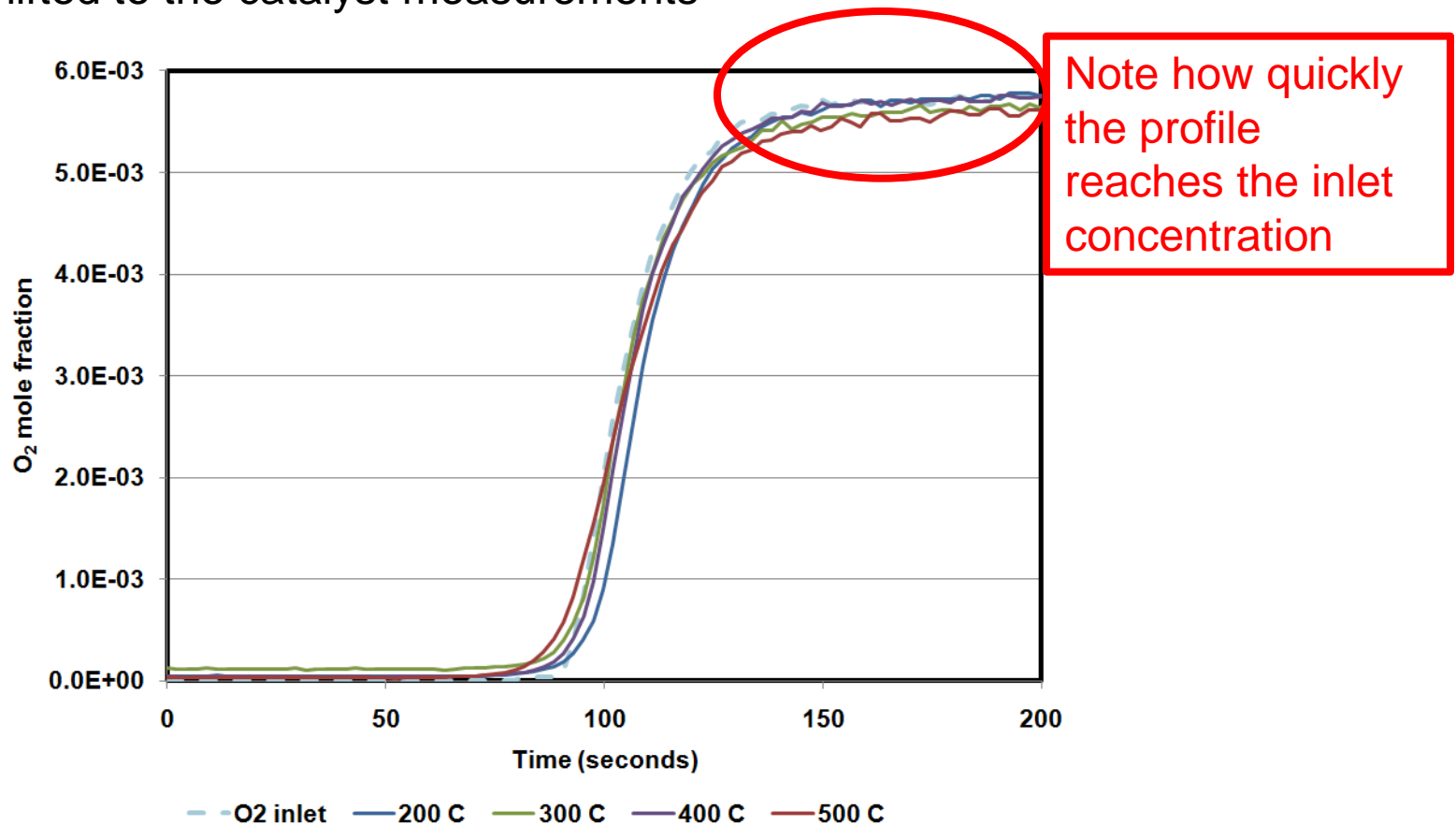$$r_j = k_j c_{s,i} \theta_{Sk}$$ Reduction (CO and H_2)

$$c_{s,i} = c x_{s,i}$$ Concentration of the reactant

$$\theta_{Sk} = \frac{\text{moles } CeO_2 (Sk)}{\text{moles } CeO_2 (Sk) + 2 \text{moles } Ce_2 O_3 (Sk)}$$ $$Sk = S1, S2$$

O₂ emission profiles

- Temperatures from 200-500 °C
- 6000 ppm inlet oxygen
- Inlet O₂ profile comes from an empty reactor experiment and is shifted to the catalyst measurements

Note how quickly the profile reaches the inlet concentration

No discernible temperature dependence

CO consumption profile

- 500 °C experiment
- 6000 ppm inlet carbon monoxide
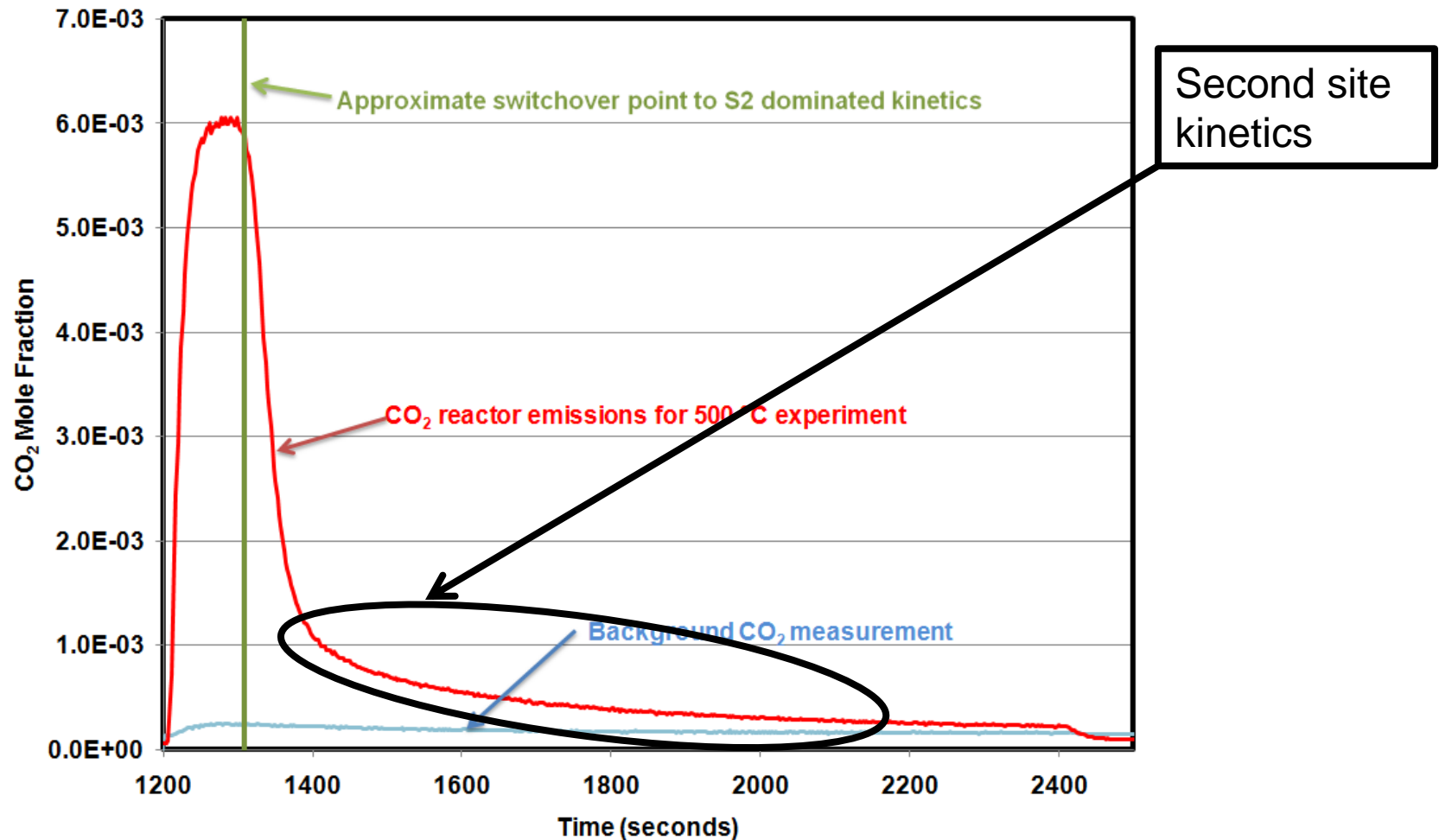- Inlet CO profile comes from an empty reactor experiment
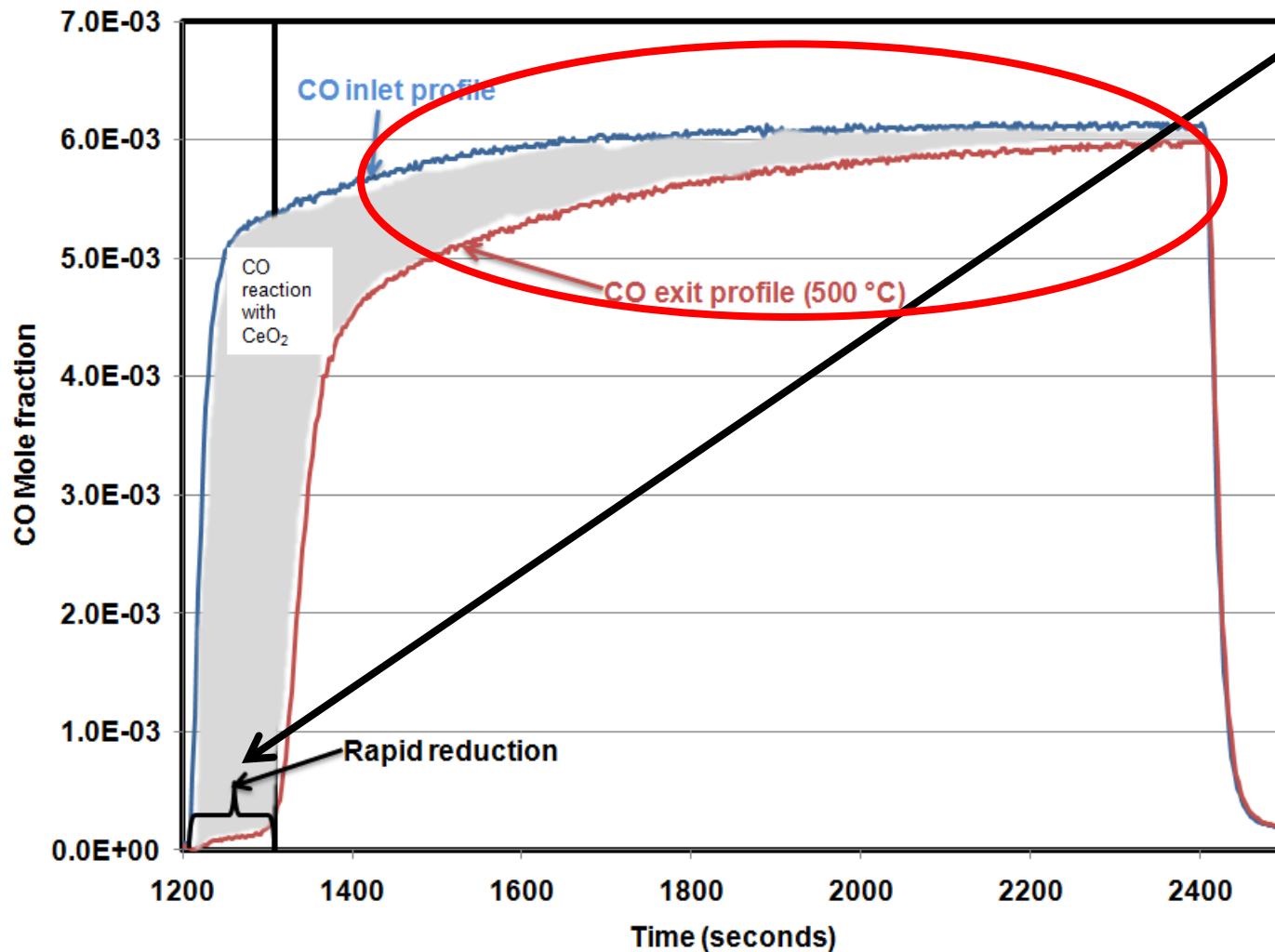
Fast site reaction

Note how slowly the profile reaches the inlet concentration

CO$_2$ formation profile

- 500 °C experiment
- 6000 ppm inlet carbon monoxide
- Background CO$_2$ profile comes from an empty reactor experiment.

Second site kinetics

Approximate switchover point to S2 dominated kinetics

CO$_2$ reactor emissions for 500 °C experiment

Background CO$_2$ measurement

CO$_2$ Mole Fraction

Time (seconds)

Calculated and Experimental CO$_2$ Profiles (200-500 °C with 6000 ppm inlet CO)

- γ =0.3 (Optimized for CO$_2$)
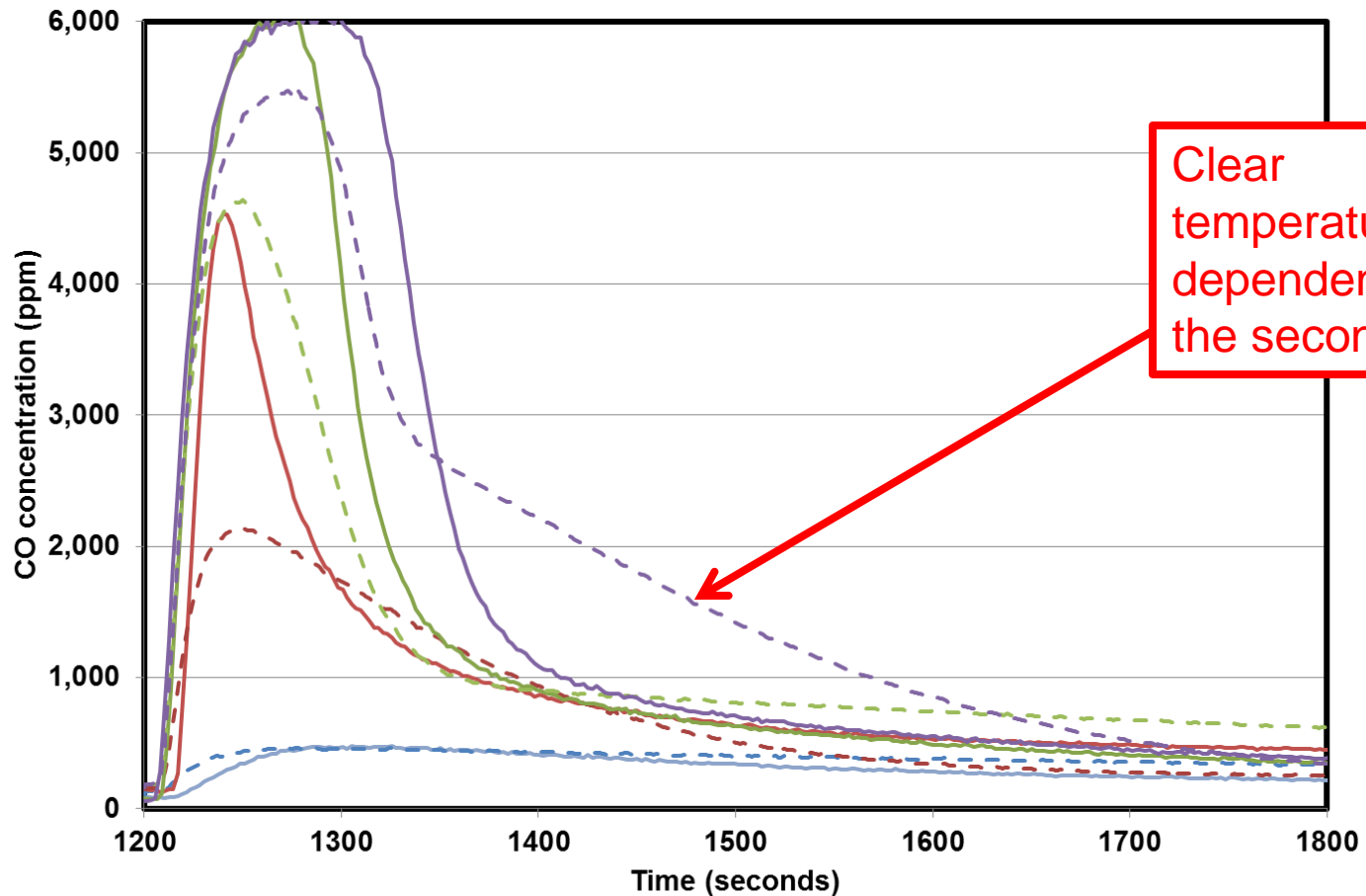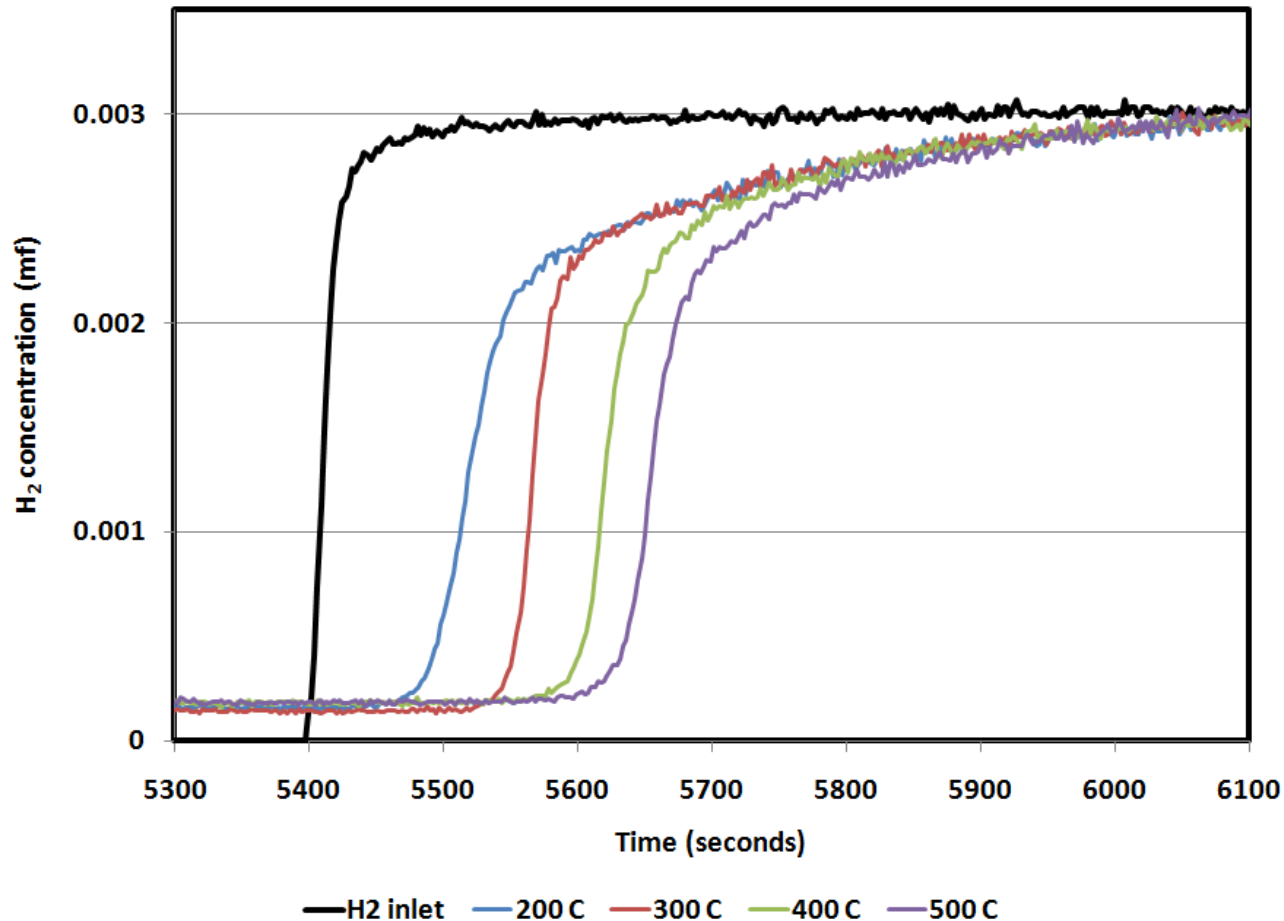

Clear temperature dependence for the second site

Calculated and Experimental NO Profiles (from 300-600 °C, 2860 ppm inlet NO)

- Two site model
- Inlet profile comes from a tracer helium gas
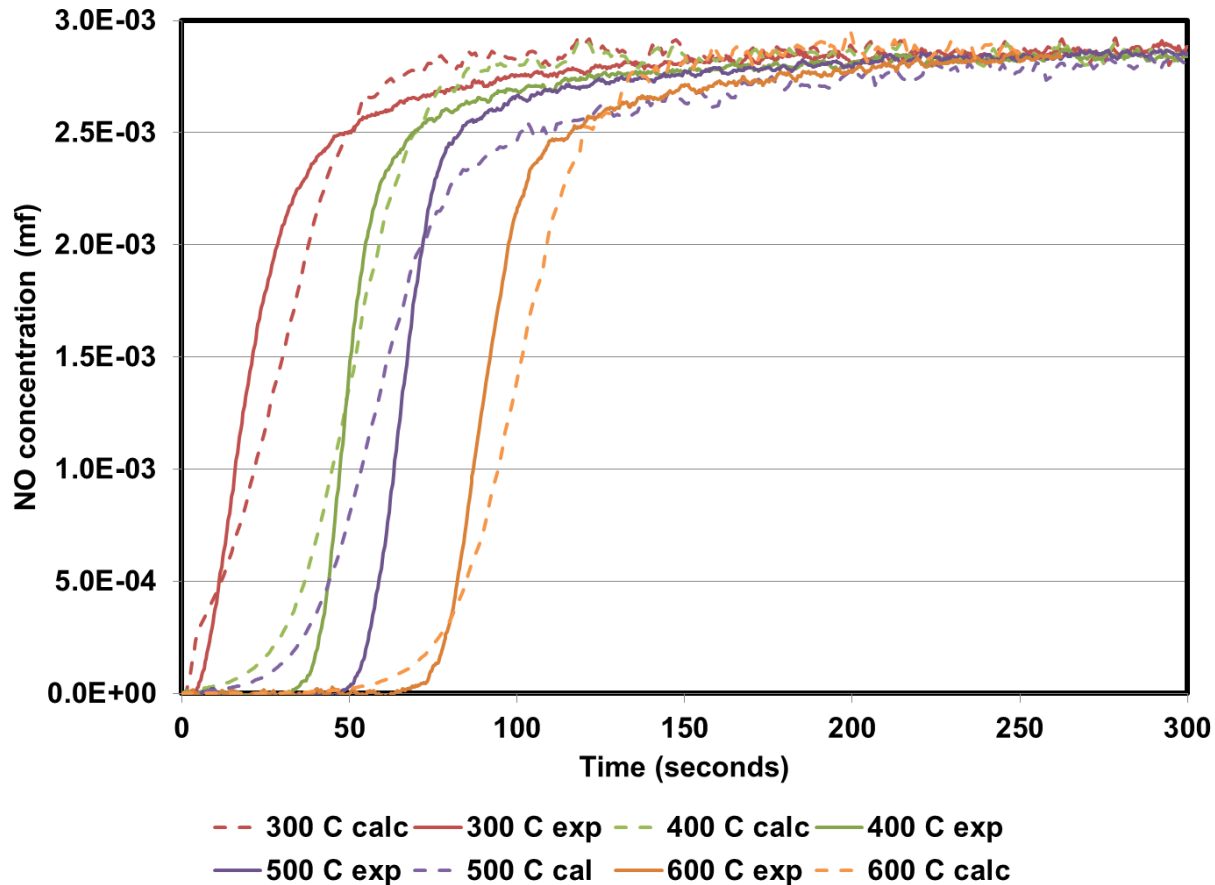
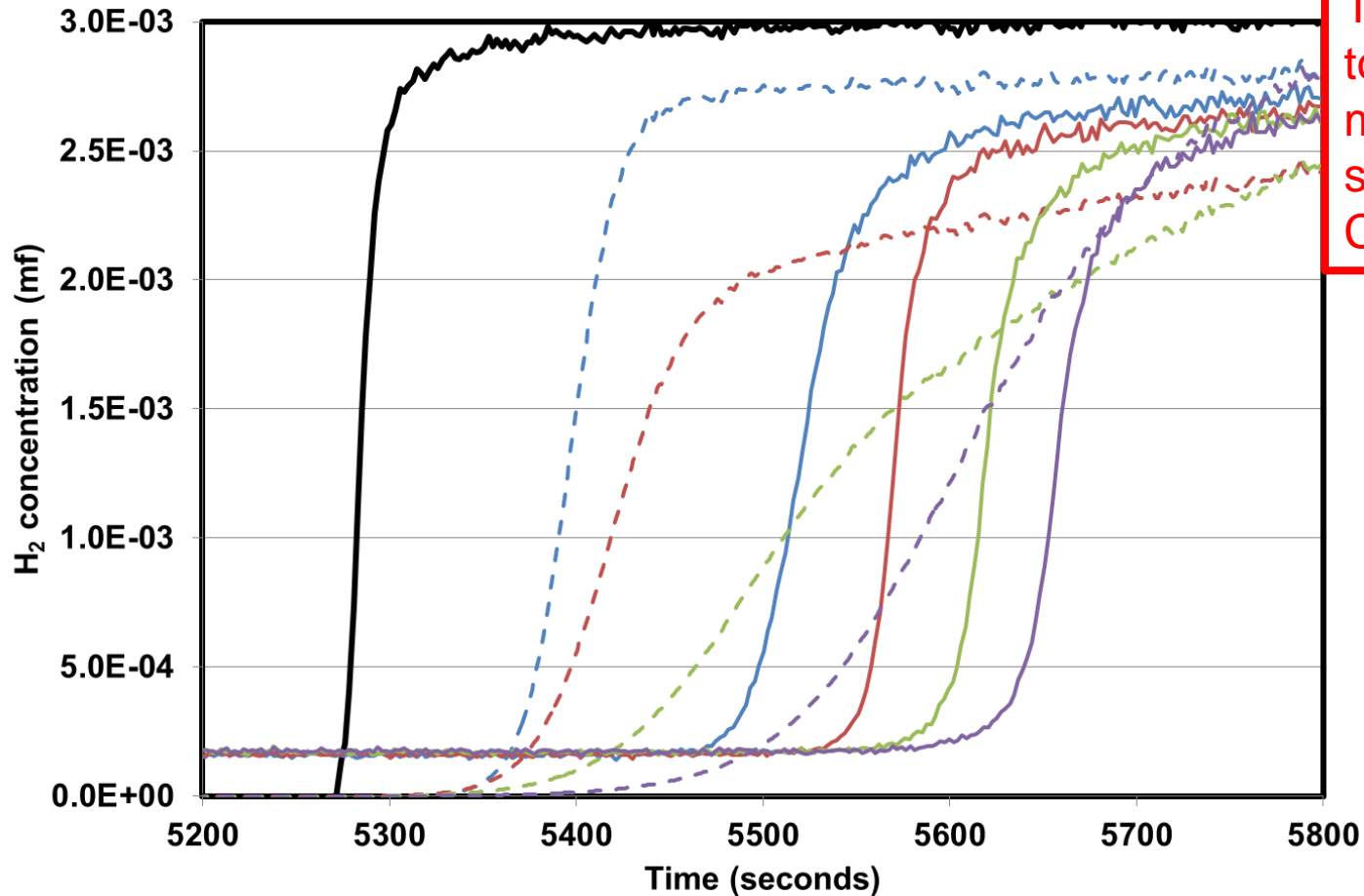# H$_2$ emission profiles

- Two site model
- Temperatures from 200-500 °C with 1500 ppm inlet O$_2$ and 3000 ppm inlet H$_2$. The inlet H$_2$ profile comes from an empty reactor experiment.

Calculated and Experimental H$_2$ Emission profiles

- for temperatures from 200-500 °C with 3000 ppm inlet H$_2$.

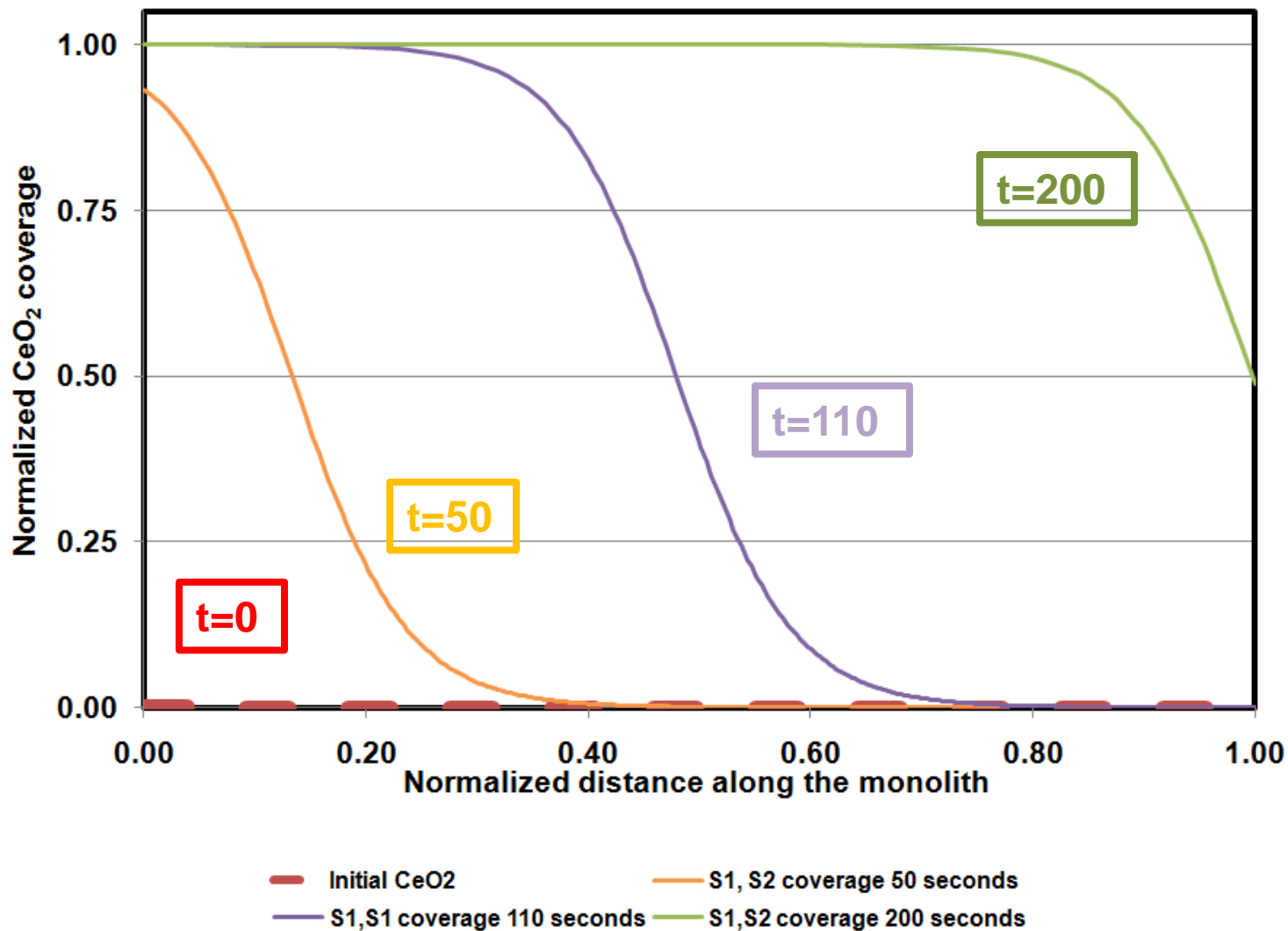This appears to need more S1 sites than CO

Fitted Rate Constants

- O_2
  - $R_{S1}^{O2} = 0.5\,[O_2][1 - \theta_{S1}]$
  - $R_{S2}^{O2} = 0.5\,[O_2][1 - \theta_{S2}]$
- NO
  - $R_{S1}^{NO} = 7.727\,e^{\frac{-1287}{T}}\,[NO][1 - \theta_{S1}]$
  - $R_{S2}^{NO} = 6.936x10^6\,e^{\frac{-13870}{T}}\,[NO][1 - \theta_{S2}]$
- CO
  - $R_{S1}^{CO} = 2.084x10^4\,e^{\frac{-7490}{T}}\,[CO][\theta_{S1}]$
  - $R_{S2}^{CO} = 1.168x10^4\,e^{\frac{-9821}{T}}\,[CO][\theta_{S2}]$
- H_2
  - $R_{S1}^{H_2} = 0.613\,[H_2][\theta_{S1}]$
  - $R_{S2}^{H_2} = 93.44e^{\frac{-5009}{T}}\,[H_2][\theta_{S2}]$

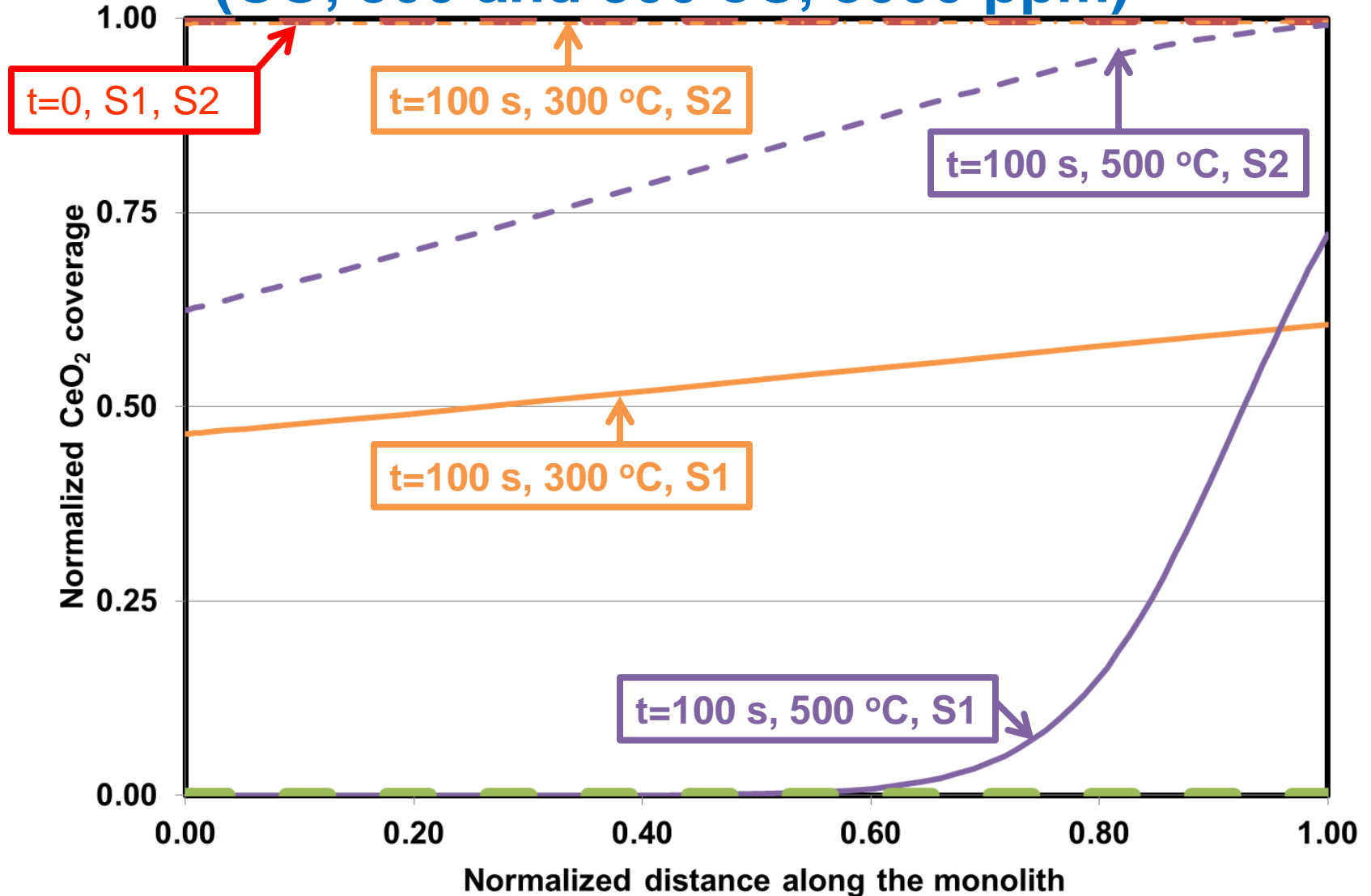Where θ_{S1} and θ_{S2} are the surface coverages of site 1 and site 2 respectively

Calculated Coverage Profiles for both Sites (O$_2$, 300 ^{o}C, 3000 ppm)

Calculated Coverage Profiles
(CO, 300 and 500 oC, 3000 ppm)

t=0, S1, S2

t=100 s, 300 °C, S2

t=100 s, 500 °C, S2

t=100 s, 300 °C, S1

t=100 s, 500 °C, S1

Normalized CeO$_2$ coverage

Normalized distance along the monolith

For the Oxidants

- Oxidation kinetics of O_2 are quite fast and the experiments are able to resolve only a lower limit on the rate constant so a temperature dependence could not be determined.

- NO kinetic parameters are:
    - somewhat faster than the O_2 oxidation rates
    - show a temperature dependence for the second site (S2) rates
    - an apparent temperature dependence for the faster (S1) oxidation rate.

- The spatially dependent oxidation state of the ceria during oxidation shows a front to rear progression

- Surface reactions are so fast that the inlet reactant does not exit until almost all the fast S1 sites along the full length of the catalyst has been either oxidized or reduced.

- Reactions of these exhaust gases in monolith core are dependent on the spatial distribution of the oxidized ceria in the monolith.

For the Reductants

- A two site model is needed to predict the CO_2 experimental profiles measured during the CO reduction step
- Reduction kinetics using CO as the reductant:
  - Show a clear temperature dependence for the reactions on the S1 sites with a fitted E_a of slightly more than 62 kJ/mol.
  - The S2 reactions are slower than the S1 reactions and show a slightly more pronounced E_a of almost 82 kJ/mol.
- For the reduction with H_2:
  - There is little evidence of a temperature dependence for the S1 rates and that rate is similar to the CO rate
  - The S2 rate does show distinct temperature dependence, with a E_a of approximately 42 kJ/mol. This rate is faster than the CO S2 rate
- It is observed that the oxidation rates appear to be uniformly faster than the reduction reactions; however both sets of reactions are quite fast.
- **I speculate that the oxygen storage sites have a continuum of energetics which are monotonic, but not linear**