Carbon Monoxide Oxidation with Nitric Oxide Resistance on Pd/Cu Catalyst Part 3

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Outline

1. Motivation
2. **Chemistry and Kinetics**
3. DFT and microkinetics background
4. Characterization
5. Testing
6. **Modeling**

Motivation

- Diesel engines are becoming more efficient → lower exhaust temperature
- Still require CO oxidation - target 90% conversion at 150°
- NO inhibits CO oxidation on Pt/Pd catalyst
- Identified Pd/Cu as low inhibition catalyst via simulation
  - Test of powder looked promising
  - Test on monoliths had challenges
- Have new source of consistent catalysts

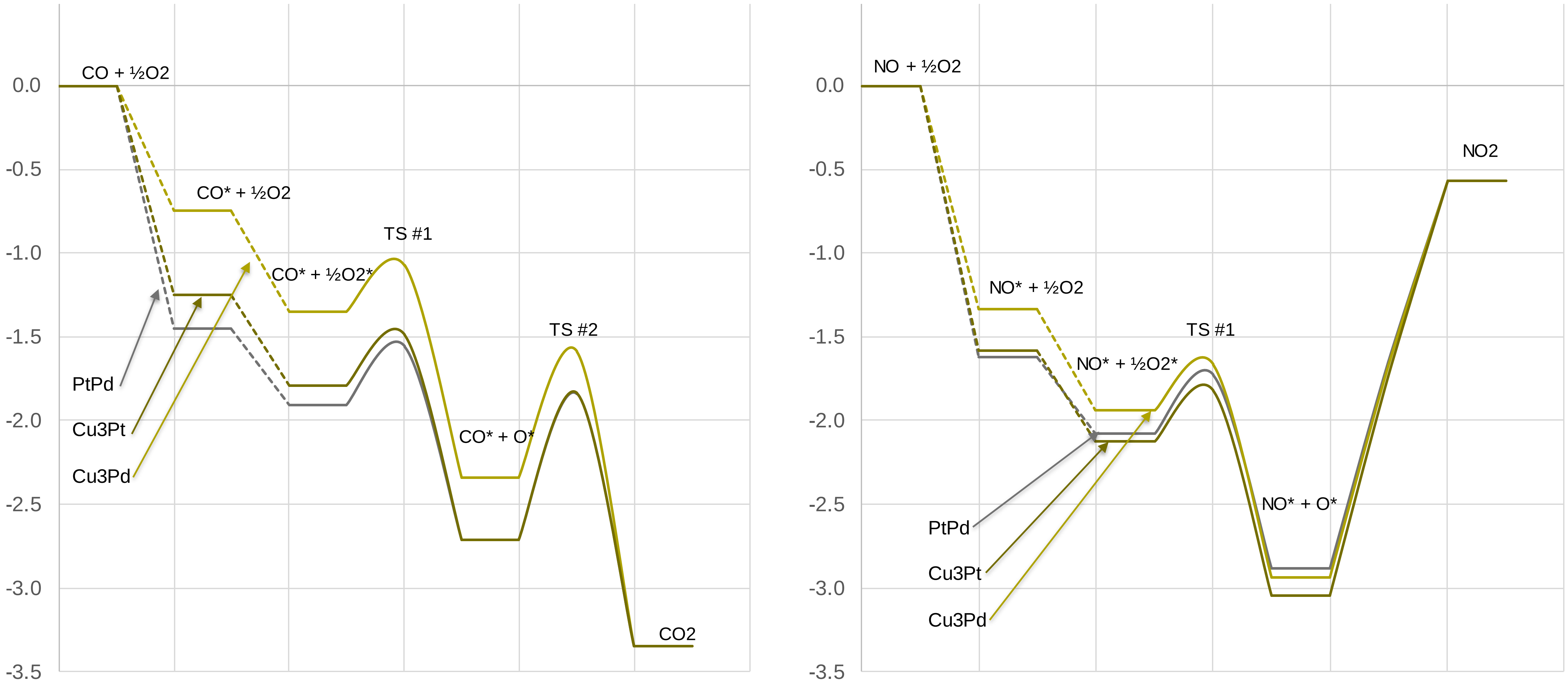
Compound (vol%)	Typical
Nitrogen	76%
Oxygen	10%
Water	7%
Carbon monoxide	500 - 5000
Carbon dioxide	6%
Nitric oxide	100 – 500 ppm
Nitrogen oxide	Not reported
Diesel	Not in scope

Chemistry and Kinetics

- Carbon Monoxide Oxidation $$CO + \frac{1}{2}O_2 \rightarrow CO_2$$
- Nitric Oxide Oxidation $$NO + \frac{1}{2}O_2 \rightarrow NO_2$$

- Carbon Monoxide / Nitrogen Dioxide Redox $$CO + NO_2 \rightarrow CO_2 + NO$$
- Water Gas Shift $$CO + H_2O \rightleftarrows CO_2 + H_2$$
- Water Formation $$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

Energy Levels for CO and NO Oxidation



DFT / Microkinetics Results

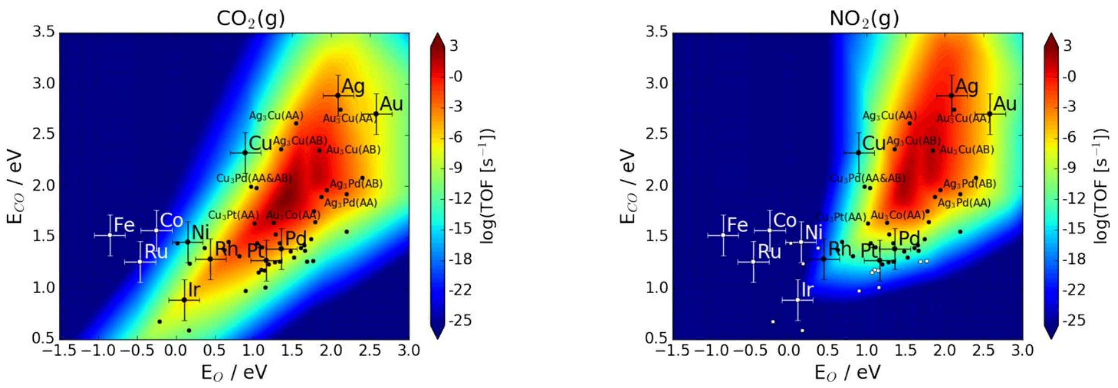


Figure 3. CO_2 and NO_2 production rate contour plots as a function of E_O and E_{CO}. The feed composition is 5000 ppm of CO, 100 ppm of NO, and 10% O_2. An error bar of 0.2 eV is included for each metal, which is approximately the DFT calculation accuracy using the RPBE functional.[35] (a) High temperature condition (T = 600 K, P = 1 atm). (b) LTC engine exhaust temperature (T = 425 K, P = 1 atm). The black/white dots represent selected binary alloys in the descriptor space.

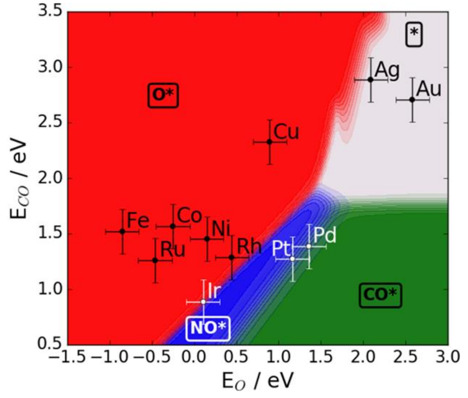


Figure 4. Steady-state coverage plots as a function of EO and ECO. The feed composition is 5000 ppm of CO, 100 ppm of NO, and 10% O2. The O* coverage is shown in red; NO* coverage is shown in blue, and CO* coverage is shown in green. The gray area represents the low coverage region) LTC engine exhaust temperature (T = 425 K, P = 1 atm).

Activity Trends for Catalytic CO and NO Co-Oxidation at Low Temperature Diesel Emission Conditions
Yuying Song and Lars C. Grabow
Industrial & Engineering Chemistry Research **2018** *57* (38), 12715-12725

- Three reactant system (O_2, CO, NO)

- For CO_2 production
Cu_3Pt > Cu_3Pd > PtPd >> Cu

- For NO_2 production
Cu_3Pt > Cu_3Pd >> PtPd > Cu

- Dominant coverage
  - O* for Cu
  - NO* for PtPd
  - O* and NO* for Cu_3Pt & Cu_3Pd

Testing – Fixed Bed Powder

wt%	Blank	PdPt	PdCu	PtCu	Cu only
Cu	0.00%	0.00%	0.49%	0.49%	0.98%
Pd	0.00%	0.27%	0.27%	0.00%	0.00%
Pt	0.00%	0.50%	0.00%	0.50%	0.00%
Al_2O_3	balance	balance	balance	balance	balance

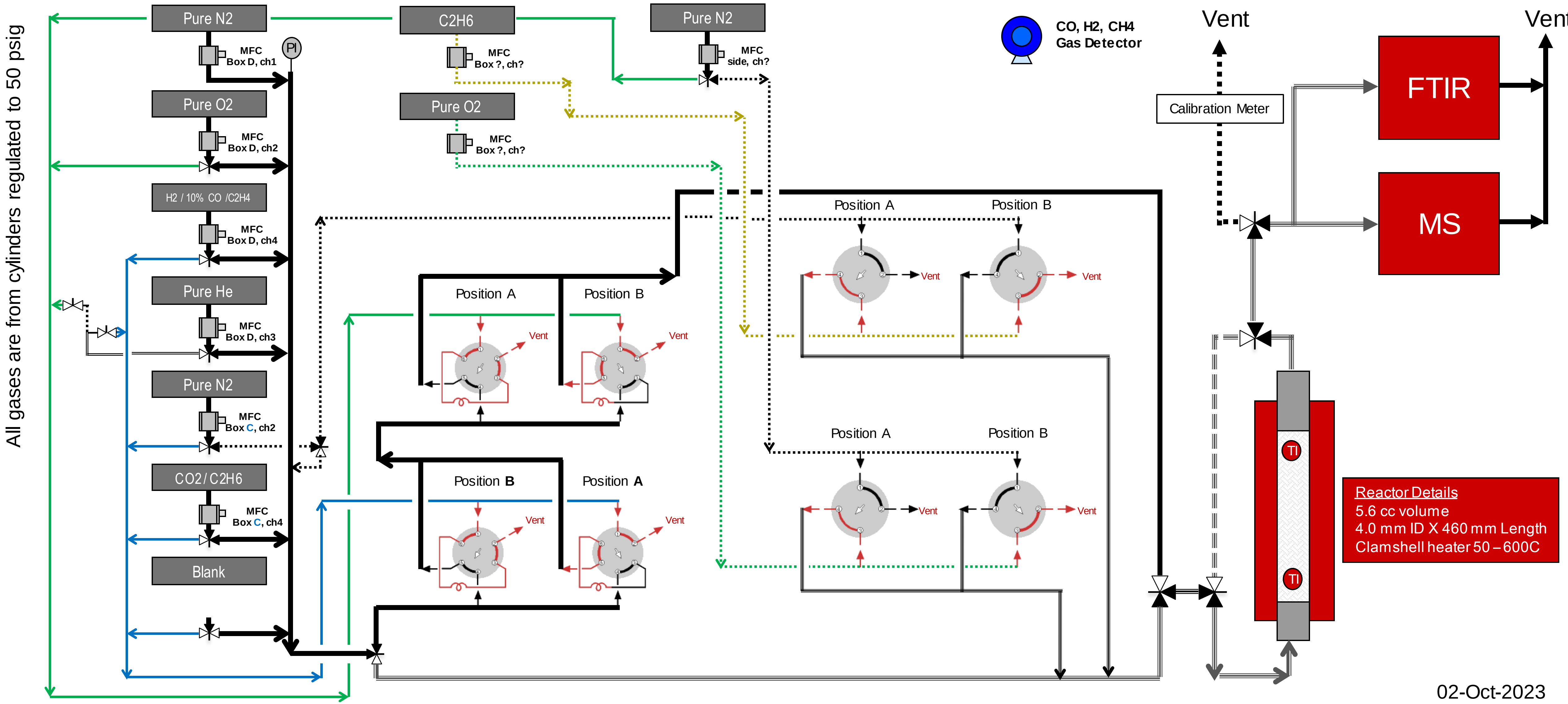
- Commercial Manufacturer
  - 35 years of environmental catalysts
  - γ-Al_2O_3 carrier
- Five samples of powder
  - Enough to run nearly any test

Characterization

- Physisorption
  - N_2 based BET
- Chemisorption
  - H_2 – conventional but may not translate to oxidation
  - CO – more applicable to CO oxidation?
  - O_2 – unconventional and needs method
  - CO_2 – available for physisorption?
  - NO, NO_2 – needs complete method development

		Blank	Pt/Pd	Pd/Cu	Pt/Cu	Cu only
BET SA	m^2/g powder	153	131	128	127	125
H2 SA	m^2/g metal	-	227	106	45	51
CO SA	m^2/g metal	-	203	-	-	-
CO2		-	-	-	-	-
NO		-	-	-	-	-
NO2		-	-	-	-	-

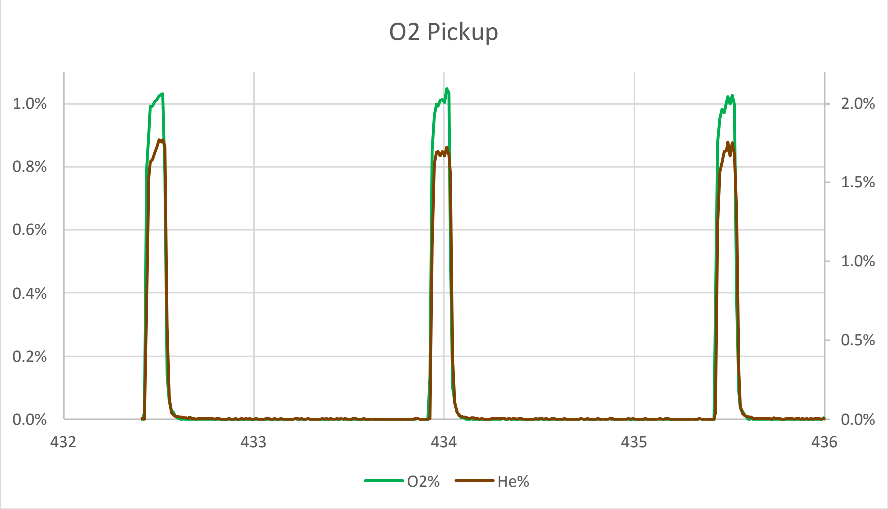
Dynamic Oxygen Storage Capacity rig in S347



02-Oct-2023

DOSC Results – O2

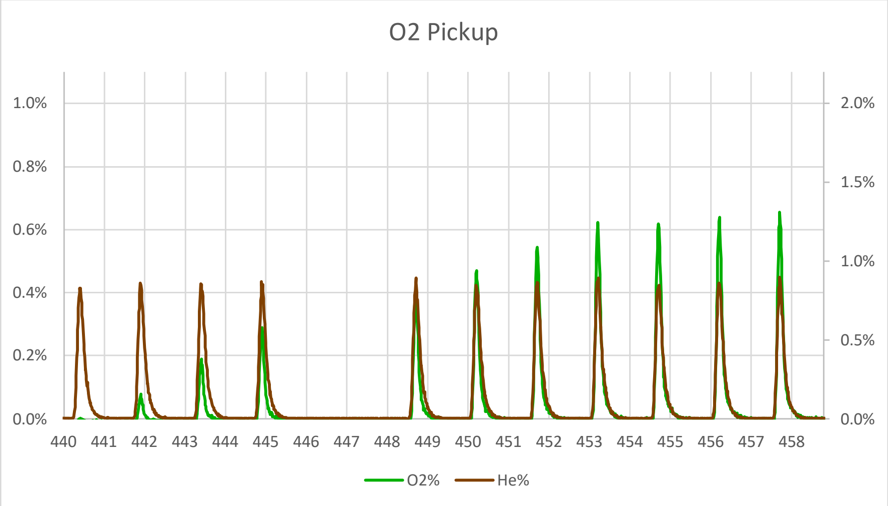
Bypass



	He (µL)	O2(µL)
	93.2	50.3
	92.4	50.1
	91.6	49.9
Average	**92.4**	**50.1**

0.90 g powder loaded
46.1 µmol PGM

Pt/Pd Powder



He (µL)	O2(µL)	He% pickup	O2 % pickup
87.9	-7.7	5%	115%
88.5	-0.7	4%	101%
89.8	8.8	3%	83%
89.2	18.3	3%	63%
90.0	28.2	3%	44%
89.4	35.4	3%	29%
90.3	42.2	2%	16%
91.1	48.9	1%	2%
90.5	50.3	2%	0%
91.1	51.8	1%	-3%
91.2	52.4	1%	-5%

	He (µL)	O2(µL)
Output	625.1	124.4
Input	646.8	350.8
Pickup	21.7	226.4
	3%	**65%**

0.219 O2:PGM (mol)

DOSC rig Results

- Chemisorption
  - H_2 – 35°C, → 0 Pa
- Dosing on the DOSC
  - 150°C, → 101 kPa
  - O_2 includes H_2 adsorbed
  - H_2 includes O_2 adsorbed
  - CO lost to reaction with water

µmol/g cat	Blank	Pt/Pd	Pd/Cu	Pt/Cu	Cu only
H2 from Chemisorption	-1.8	18.3	9.5	5.2	6.7
Metal loading	0	52	103	103	154
O2 dose	0	11.2			
H2 dose	0	15.8			
CO dose					
CO + NO dose					

Testing will be restarted after:

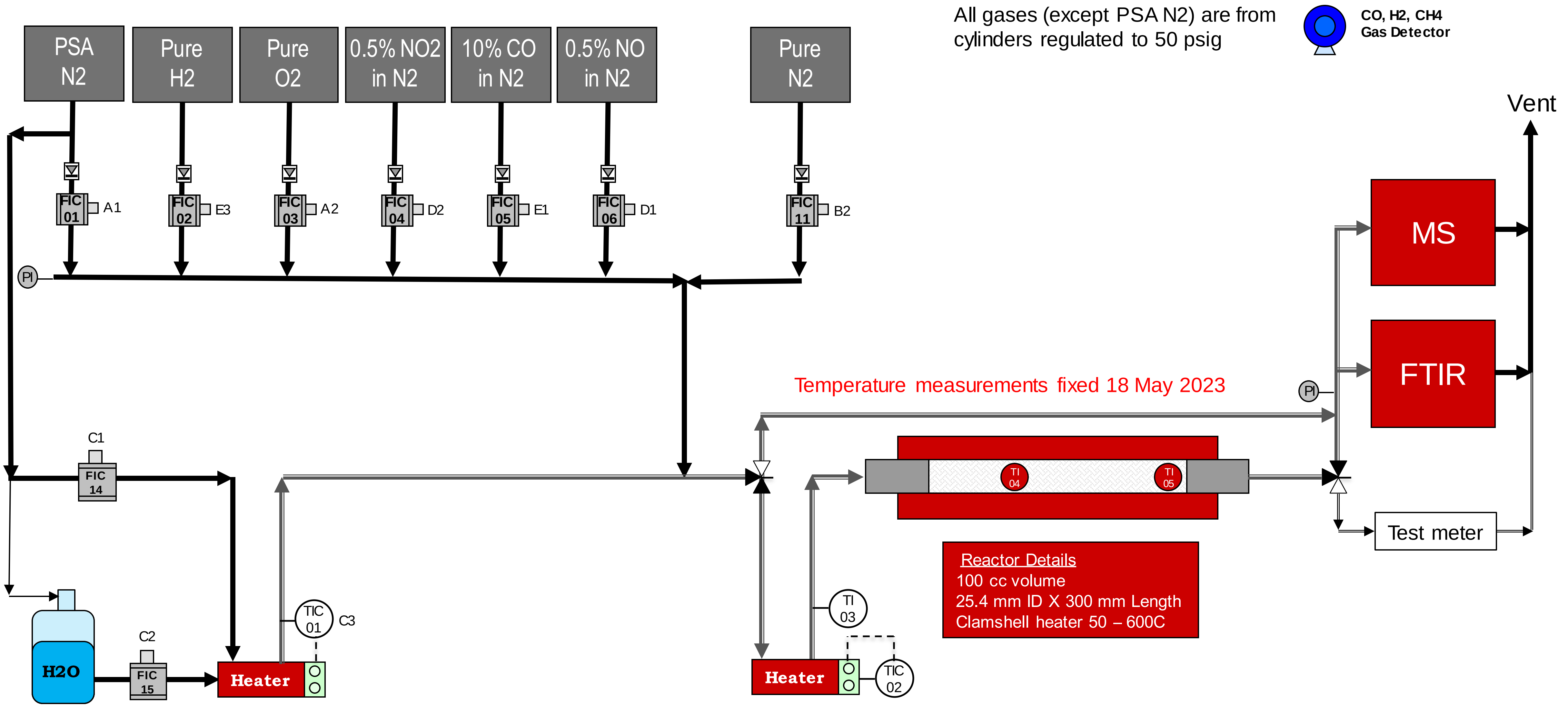
- The O2 leak is found and fixed.
- Add drying step after O2 and H2 probes.
- Switch to mass spec only for analysis.
  - Change the balance gas to Argon because N2 has the same mass as CO.
  - Obtain new probe gas (CO, NO, CO2, NO2) in argon (all currently in N2)

New Catalyst Samples

wt%	PdPt	PdCu	PtCu	Cu only	Blank
Cu		0.49%	0.49%	0.98%	0.00%
Pd	0.27%	0.27%			0.00%
Pt	0.50%		0.50%		0.00%
total	0.77%	0.76%	0.99%	0.98%	0.00%

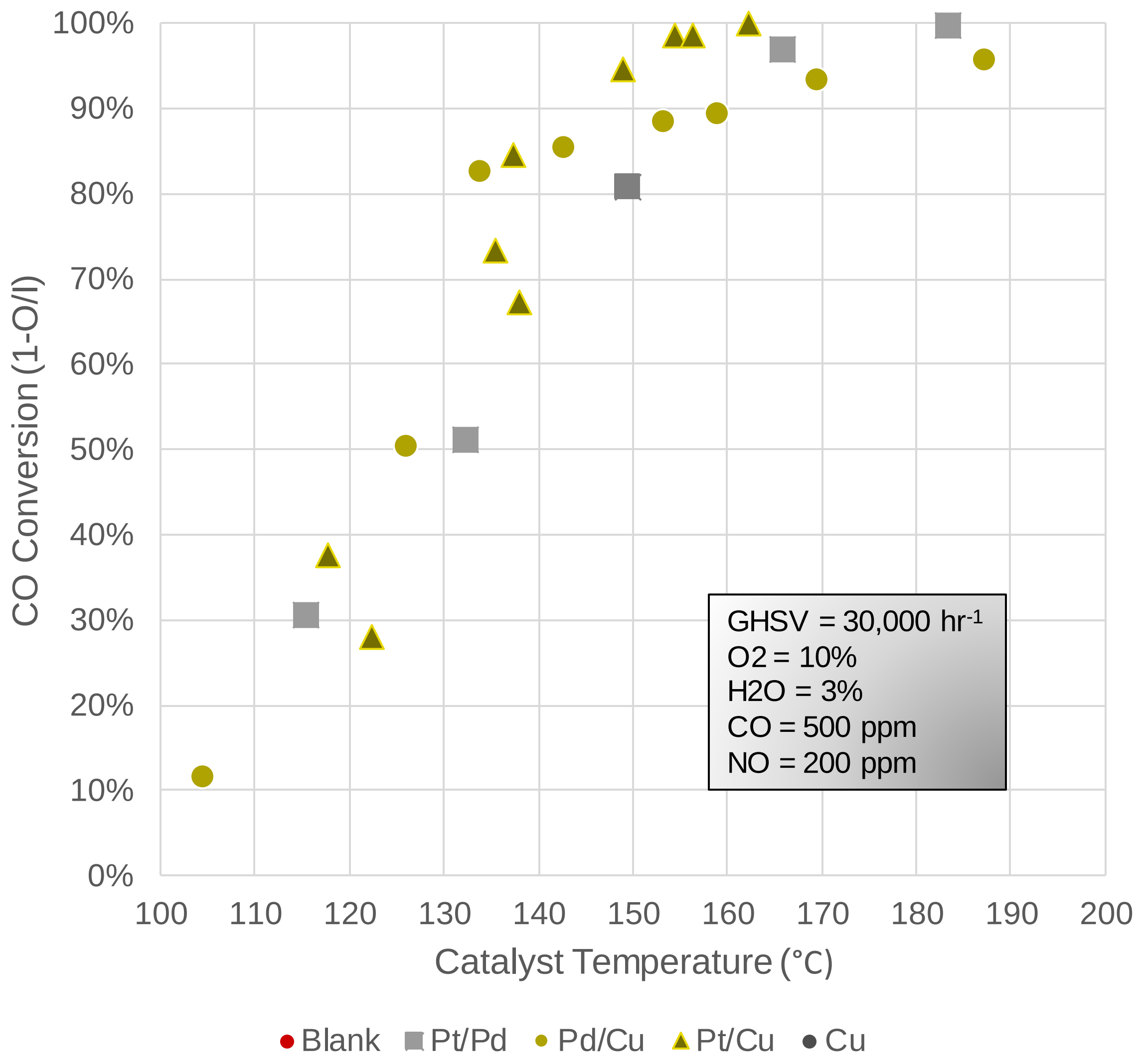
- Commercial Manufacturer
  - 35 years of environmental catalysts
  - γ-Al_2O_3 on FeCrAl alloy
- 4 samples of monolith + blank
  - 2.35 g powder/ci (0.14 g/mL)
  - Same powder as samples
  - Fits 1” quartz reactor
  - 22 mL (1.35 ci)

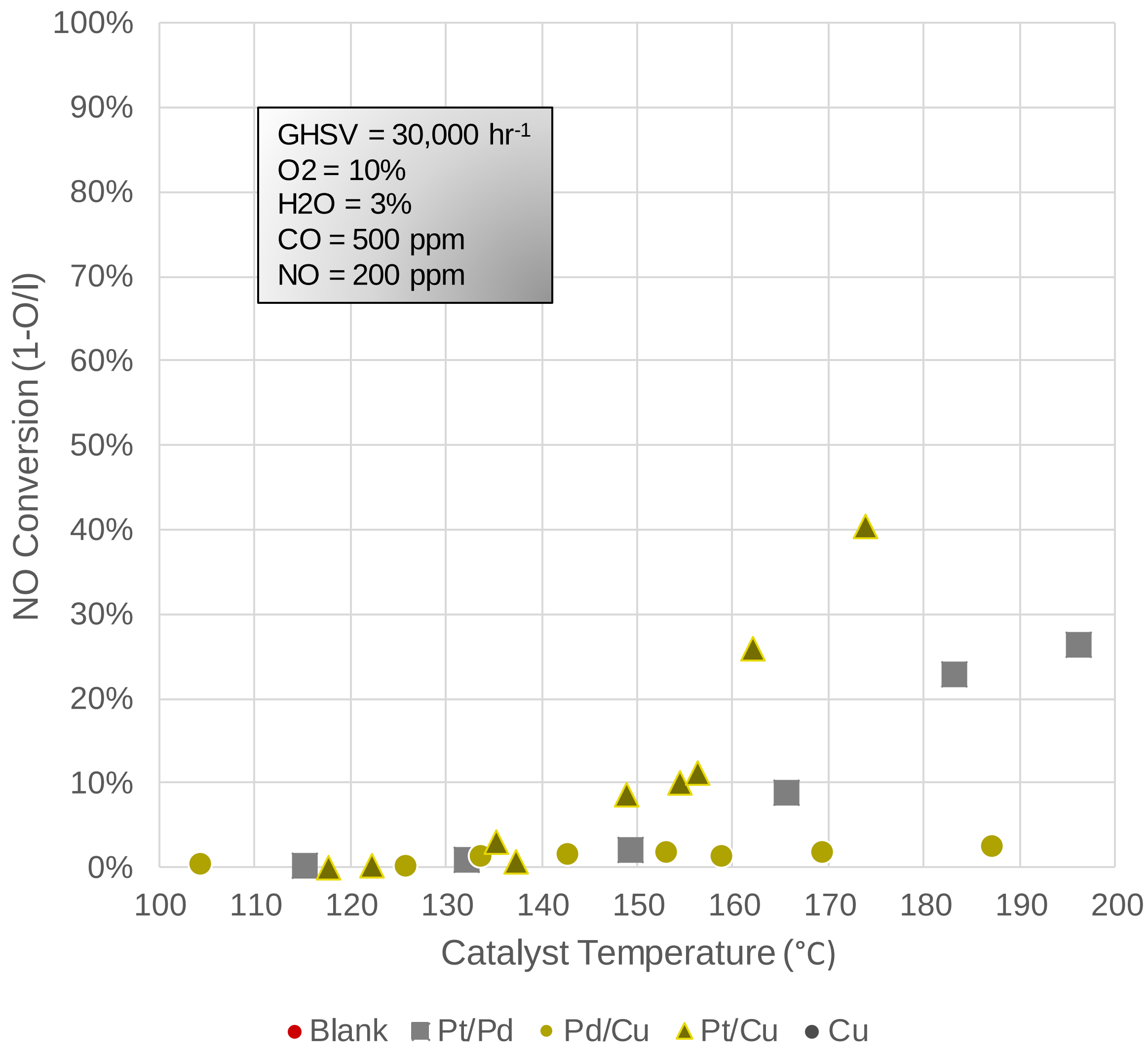
Monolith Reactor in S347



15-Feb-2023

Results – Conversion vs Temperature





Summary of Results

wt%	Blank	PdPt	PdCu	PtCu	Cu only
Cu	0.00%	0.00%	0.49%	0.49%	0.98%
Pd	0.00%	0.27%	0.27%	0.00%	0.00%
Pt	0.00%	0.50%	0.00%	0.50%	0.00%
Al_2O_3	balance	balance	balance	balance	balance
	Conversion at standard conditions				
CO	0%	82%	86%	95%	<5%
50% conv. Temp (℃)	NA	131°	126°	122°	NA
NO	0%	2%	1%	9%	<5%
SS points	-	66	64	68	-

Parameter	Parametric Study
GHSV	30,000 /hr ±5%
Temperature	100 – **150** - 200°C
Nitrogen	Balance
Oxygen	0% or **10%**
Water	0% or **3%**
Carbon monoxide	0 , **500** or 1000 ppm
Nitric oxide	0, 100 or **200** ppm
Carbon dioxide	0%
Nitrogen dioxide	0%

Modeling

- Redo contour plots with revised composition
  - CO 5000 → 500 ppm
  - NO 100 → 200 ppm
  - H2O 0 → 3% (?)
- Elementary Reactions
  - Assume RCS
  - Psudo-equilibrium
  - Overall reaction rate
  - Conventional model fitting from differential equations (Euler)
- Microkinetic modelling
  - Adsorption from DFT
  - Activity from 2-reactant test
  - Compare results!

Component (vol%)	Original	Base	MBal
Nitrogen	Balance	Balance	Balance
Oxygen	10%	10%	10%
Water	0%	3%	7%
Carbon monoxide	5 000 ppm	500 ppm	? ppm
Nitric oxide	100 ppm	200 ppm	? ppm
Carbon dioxide	0%	0%	6%

Elementary Reactions

Carbon Monoxide Oxidation $CO + ½\ O_2 \rightarrow CO_2$ (Rx1)

$CO(g) + * \rightleftarrows CO*$	$r_1 = k_1^+ \cdot P_{CO} \cdot \theta_* - k_1^- \cdot \theta_{CO}$
$O_2(g) + * \rightleftarrows O_2*$	$r_2 = k_2^+ \cdot P_{O2} \cdot \theta_* - k_2^- \cdot \theta_{O2}$
$O_2* + * \rightleftarrows 2O*$	$r_3 = k_3^+ \cdot \theta_{O2} \cdot \theta_* - k_3^- \cdot \theta_O^2$
$CO* + O* \rightleftarrows CO_2* + *$	$r_4 = k_4^+ \cdot \theta_{CO} \cdot \theta_O - k_4^- \cdot \theta_{CO2} \cdot \theta_*$
$CO* + O_2* \rightleftarrows CO_2* + \cancel{\theta_*}$ O	$r_5 = k_5^+ \cdot \theta_{CO} \cdot \theta_{O2} - k_5^- \cdot \theta_{CO2} \cdot \theta_O$
$CO_2* \rightleftarrows CO_2(g) + *$	$r_6 = k_6^+ \cdot \theta_{CO2} - k_6^- \cdot P_{CO2} \cdot \theta_*$

Nitric Oxide Oxidation $NO + ½\ O2 \rightarrow NO2$ (Rx2)

$NO(g) + * \rightleftarrows NO*$	$r_7 = k_7^+ \cdot P_{NO} \cdot \theta_* - k_7^- \cdot \theta_{NO}$
$\cancel{O_2(g) + * \rightleftarrows O_2*}$	$\cancel{r_2 = k_2^+ \cdot P_{O2} \cdot \theta_* - k_2^- \cdot \theta_{O2}}$
$\cancel{O_2* + * \rightleftarrows 2O*}$	$\cancel{r_3 = k_3^+ \cdot \theta_{O2} \cdot \theta_* - k_3^- \cdot \theta_O^2}$
$NO* + O* \rightleftarrows NO_2* + *$	$r_8 = k_8^+ \cdot \theta_{NO} \cdot \theta_O - k_8^- \cdot \theta_{NO2} \cdot \theta_*$
$NO* + O_2* \rightleftarrows NO_2* + O_*$	$r_9 = k_9^+ \cdot \theta_{NO} \cdot \theta_{O2} - k_9^- \cdot \theta_{NO2} \cdot \theta_O$
$NO_2* \rightleftarrows NO_2(g) + *$	$r_{10} = k_{10}^+ \cdot \theta_{NO2} - k_{10}^- \cdot P_{NO2} \cdot \theta_*$

Reduction / Oxidation $CO + NO2 \rightarrow CO2 + NO$ (Rx3)

$\cancel{CO(g) + * \rightleftarrows CO*}$	$\cancel{r_1 = k_1^+ \cdot P_{CO} \cdot \theta_* - k_1^- \cdot \theta_{CO}}$
$\cancel{NO_2(g) + * \rightleftarrows NO_2*}$	$\cancel{r_{10r} = -k_{10}^+ \cdot \theta_{NO2} + k_{10}^- \cdot P_{NO2} \cdot \theta_*}$
$\cancel{NO_2* + * \rightleftarrows NO* + O*}$	$\cancel{r_{8r} = -k_8^+ \cdot \theta_{NO} \cdot \theta_O + k_8^- \cdot \theta_{NO2} \cdot \theta_*}$
$\cancel{CO* + O* \rightleftarrows CO_2* + *}$	$\cancel{r_4 = k_4^+ \cdot \theta_{CO} \cdot \theta_O - k_4^- \cdot \theta_{CO2} \cdot \theta_*}$
$\cancel{NO* \rightleftarrows NO(g) + *}$	$\cancel{r_{7r} = -k_7^+ \cdot P_{NO} \cdot \theta_* + k_7^- \cdot \theta_{NO}}$
$\cancel{CO_2* \rightleftarrows CO_2(g) + *}$	$\cancel{r_6 = k_6^+ \cdot \theta_{CO2} - k_6^- \cdot P_{CO2} \cdot \theta_*}$

Water Gas Shift $CO + H_2O \rightarrow CO_2 + H_2$ (Rx4)

$\cancel{CO(g) + * \rightleftarrows CO*}$	$\cancel{r_1 = k_1^+ \cdot P_{CO} \cdot \theta_* - k_1^- \cdot \theta_{CO}}$
$H_2O(g) + * \rightleftarrows H_2O*$	$r_{11} = k_{11}^+ \cdot P_{H2O} \cdot \theta_* - k_{11}^- \cdot \theta_{H2O}$
$H_2O* + * \rightleftarrows H* + OH*$	$r_{12} = k_{12}^+ \cdot \theta_{H2O} \cdot \theta_* - k_{12}^- \cdot \theta_H \cdot \theta_{OH}$
$CO* + OH* \rightleftarrows COOH* + *$	$r_{13} = k_{13}^+ \cdot \theta_{CO} \cdot \theta_{OH} - k_{13}^- \cdot \theta_{COOH} \cdot \theta_*$
$COOH* + * \rightleftarrows CO_2* + H*$	$r_{14} = k_{14}^+ \cdot \theta_{COOH} \cdot \theta_* - k_{14}^- \cdot \theta_{CO2} \cdot \theta_H$
$\cancel{CO_2* \rightleftarrows CO_2(g) + *}$	$\cancel{r_6 = k_6^+ \cdot \theta_{CO2} - k_6^- \cdot P_{CO2} \cdot \theta_*}$
$2H* \rightleftarrows H_2* + *$	$r_{15} = k_{15}^+ \cdot \theta_H^2 - k_{15}^- \cdot \theta_{H2} \cdot \theta_*$
$H_2* \rightleftarrows H_2(g) + *$	$r_{16} = k_{16}^+ \cdot \theta_{H2} - k_{16}^- \cdot P_{H2} \cdot \theta_*$

Hydrogen Oxidation $H_2 + ½\ O_2 \rightarrow H_2O$ (Rx5)

$\cancel{H_2(g) + * \rightleftarrows H_2*}$	$\cancel{r_{16r} = -k_{16}^- \cdot P_{H2} \cdot \theta_* - k_{16}^+ \cdot \theta_{H2}}$
$\cancel{H_2* + * \rightleftarrows 2H*}$	$\cancel{r_{15r} = -k_{15}^- \cdot \theta_{H2} \cdot \theta_* - k_{15}^+ \cdot \theta_H^2}$
$\cancel{O_2(g) + * \rightleftarrows O_2*}$	$\cancel{r_2 = k_2^+ \cdot P_{O2} \cdot \theta_* - k_2^- \cdot \theta_{O2}}$
$\cancel{O_2* + * \rightleftarrows 2O*}$	$\cancel{r_3 = k_3^+ \cdot \theta_{O2} \cdot \theta_* - k_3^- \cdot \theta_O^2}$
$O* + H* \rightleftarrows OH* + *$	$r_{17} = k_{17}^+ \cdot \theta_O \cdot \theta_H - k_{17}^- \cdot \theta_{OH} \cdot \theta_*$
$2OH* \rightleftarrows \cancel{HOH}* + O*$	$r_{18} = k_{18}^+ \cdot \theta_{OH}^2 - k_{18}^- \cdot \theta_{H2O} \cdot \theta_O$ H_2O
$\cancel{H_2O* \rightleftarrows H_2O(g) + *}$	$\cancel{r_{11r} = -k_{11}^- \cdot \theta_{H2O} - k_{11}^+ \cdot P_{H2O} \cdot \theta_*}$

Microkinetic Modeling Summary and Plan

- Five (5) overall reactions
  - 2 primary
  - 1 is combination of others
- Eighteen (18) elementary reactions
  - Up to thirty-six (**36**) reaction rates
  - Up to thirty-six (**36**) activation energies
  - Many reactions are irreversible
  - Some reactions are orders of magnitude slower
  - Which are rate controlling steps?
- Twelve (11) adsorbed species
  - 4 reactants (O_2, CO, NO, H_2O)
  - 3 products (CO_2, NO_2, H_2)
  - 4 intermediates (O*, H*, OH*, COOH*)
- 6 Material Balances:
  - 3 reactants
  - 3 products
- 1 surface balance

- →29 (+36) additional equations
- Phase 1 – Pseudo-equilibrium + RCS
  - Assume rate controlling step is 2 adsorbed species
  - 18 – 5 additional equations via equilibrium
  - Calculate equilibrium from surface energy change:

$$K = \frac{k_f}{k_r} = \frac{C^c D^d}{A^a B^b} = \frac{[C]^c [D]^d}{[A]^a [B]^b} = e^{-\Delta G / RT}$$

  - Need 16+ cases for parameter fitting
  - Alternately – more data at 150C.
- Phase 2 – steady state on surface
  - 12 additional equations from surface balance
  - May relax some psudo-equilibrium constraints
  - Need 17+ cases for parameter fitting

CO Oxidation Elementary Reactions

Carbon Monoxide Oxidation $CO + \frac{1}{2} O_2 \rightarrow CO_2$ (Rx1)

1	$CO(g) + * \rightleftarrows CO*$	$r_1 = k_1^+ \cdot P_{CO} \cdot \theta_* - k_1^- \cdot \theta_{CO}$	$K_1 = \frac{k_1^+}{k_1^-} = \frac{\theta_{CO}}{P_{CO} \cdot \theta_*}$	$\theta_{CO} = K_1 \cdot P_{CO} \cdot \theta_*$
2	$O_2(g) + * \rightleftarrows O_2*$	$r_2 = k_2^+ \cdot P_{O2} \cdot \theta_* - k_2^- \cdot \theta_{O2}$	$K_2 = \frac{k_2^+}{k_2^-} = \frac{\theta_{O2}}{P_{O2} \cdot \theta_*}$	$\theta_{O2} = K_2 \cdot P_{O2} \cdot \theta_*$
3	$O_2 * + * \rightleftarrows 2O*$	$r_3 = k_3^+ \cdot \theta_{O2} \cdot \theta_* - k_3^- \cdot \theta_O^2$	$K_3 = \frac{k_3^+}{k_3^-} = \frac{\theta_O^2}{\theta_{O2} \cdot \theta_*}$	$\theta_O = \sqrt{K_2 \cdot K_3 \cdot P_{O2}} \cdot \theta_*$
4	$CO * + O* \rightleftarrows CO_2 * + *$	$r_4 = k_4^+ \cdot \theta_{CO} \cdot \theta_O - k_4^- \cdot \theta_{CO2} \cdot \theta_*$	Rate Controlling Step for CO oxidation	
5	$CO * + O_2 * \rightleftarrows CO_2 * + \theta_*$	$r_5 = k_5^+ \cdot \theta_{CO} \cdot \theta_{O2} - k_5^- \cdot \theta_{CO2} \cdot \theta_O$	Rate Controlling Step for CO oxidation	
6	$CO_2 * \rightleftarrows CO_2(g) + *$	$r_6 = k_6^+ \cdot \theta_{CO2} - k_6^- \cdot P_{CO2} \cdot \theta_*$	$K_6 = \frac{k_6^+}{k_6^-} = \frac{P_{CO2} \cdot \theta_*}{\theta_{CO2}}$	$\theta_{CO2} = \frac{1}{K_6} \cdot P_{CO2} \cdot \theta_*$

CO Oxidation Parallel Rate Controlling Steps

Assume the rate determining (limiting) step is the combining reaction on the surface = r4 & r5. In the absence of other reactants:

$$Rx1 = r_4 + r_5 = k_4^+ \cdot \theta_{CO} \cdot \theta_O - k_4^- \cdot \theta_{CO2} \cdot \theta_* + k_5^+ \cdot \theta_{CO} \cdot \theta_{O2} - k_5^- \cdot \theta_{CO2} \cdot \theta_O$$

$$Rx1 = k_4^+ \cdot K_1 \cdot P_{CO} \cdot \theta_* \cdot \sqrt{K_2 \cdot K_3 \cdot P_{O2}} \cdot \theta_* + k_5^+ \cdot K_1 \cdot P_{CO} \cdot \theta_* \cdot K_2 \cdot P_{O2} \cdot \theta_* - k_4^- \cdot \frac{1}{K_6} \cdot P_{CO2} \cdot \theta_* \cdot \theta_* - k_5^- \cdot \frac{1}{K_6} \cdot P_{CO2} \cdot \theta_* \cdot \sqrt{K_2 \cdot K_3 \cdot P_{O2}} \cdot \theta_*$$

$$Rx1 = \theta_*^2 \left(k_4^+ \cdot K_1 \cdot \sqrt{K_2 \cdot K_3} \cdot P_{CO} \cdot \sqrt{P_{O2}} + k_5^+ \cdot K_1 \cdot K_2 \cdot P_{CO} \cdot P_{O2} - k_4^- \cdot \frac{1}{K_6} \cdot P_{CO2} - k_5^- \cdot \frac{1}{K_6} \cdot \sqrt{K_2 \cdot K_3} \cdot \sqrt{P_{O2}} \cdot P_{CO2} \right)$$

$$1 = \theta_* + \theta_{CO} + \theta_{O2} + \theta_O + \theta_{CO2}$$

$$1 = \theta_* \left(1 + K_1 \cdot P_{CO} + K_2 \cdot P_{O2} + \sqrt{K_2 \cdot K_3 \cdot P_{O2}} + \frac{1}{K_6} \cdot P_{CO2} \right)$$

$$\theta_*^2 = \frac{1}{\left(1 + K_1 \cdot P_{CO} + K_2 \cdot P_{O2} + \sqrt{K_2 \cdot K_3 \cdot P_{O2}} + \frac{1}{K_6} \cdot P_{CO2} \right)^2}$$

$$Rx1 = \frac{\left(k_4^+ \cdot K_1 \cdot \sqrt{K_2 \cdot K_3} \cdot P_{CO} \cdot \sqrt{P_{O2}} + k_5^+ \cdot K_1 \cdot K_2 \cdot P_{CO} \cdot P_{O2} - k_4^- \cdot \frac{1}{K_6} \cdot P_{CO2} - k_5^- \cdot \frac{1}{K_6} \cdot \sqrt{K_2 \cdot K_3} \cdot \sqrt{P_{O2}} \cdot P_{CO2} \right)}{\left(1 + K_1 \cdot P_{CO} + K_2 \cdot P_{O2} + \sqrt{K_2 \cdot K_3 \cdot P_{O2}} + \frac{1}{K_6} \cdot P_{CO2} \right)^2}$$

$Parameters: \quad k_4^+, k_4^-, k_5^+, k_5^-, K_1, K_2, K_3, K_6$

$Variables: \quad P_{CO}, P_{O2}, P_{CO2}$

- Need 16 cases at single temperature
- Need 32 cases at range of temperatures
- Have parametric study of 2 of C_{CO} and 5 of T_{cat}.
- may not resolve k4 vs k5
- Key test: Feed CO2
    - Does X_{CO} change with C_{CO2}?
    - Is any CO or O2 formed if CO2 feed only?

NO Oxidation Elementary Reactions

Nitric Oxide Oxidation NO + ½ O_2 → NO_2 (Rx2)

7	$NO(g) + * \rightleftarrows NO*$	$r_7 = k_7^+ \cdot P_{NO} \cdot \theta_* - k_7^- \cdot \theta_{NO}$	$K_7 = \frac{k_7^+}{k_7^-} = \frac{\theta_{NO}}{P_{NO} \cdot \theta_*}$	$\theta_{NO} = K_7 \cdot P_{NO} \cdot \theta_*$
2	$O_2(g) + * \rightleftarrows O_2 *$	$r_2 = k_2^+ \cdot P_{O2} \cdot \theta_* - k_2^- \cdot \theta_{O2}$	$K_2 = \frac{k_2^+}{k_2^-} = \frac{\theta_{O2}}{P_{O2} \cdot \theta_*}$	$\theta_{O2} = K_2 \cdot P_{O2} \cdot \theta_*$
3	$O_2 * + * \rightleftarrows 2O*$	$r_3 = k_3^+ \cdot \theta_{O2} \cdot \theta_* - k_3^- \cdot \theta_O^2$	$K_3 = \frac{k_3^+}{k_3^-} = \frac{\theta_O^2}{\theta_{O2} \cdot \theta_*}$	$\theta_O = \sqrt{K_2 \cdot K_3 \cdot P_{O2}} \cdot \theta_*$
8	$NO* + O* \rightleftarrows NO_2 * + *$	$r_8 = k_8^+ \cdot \theta_{NO} \cdot \theta_O - k_8^- \cdot \theta_{NO2} \cdot \theta_*$	Rate Controlling Step for NO oxidation	
9	$NO* + O_2 * \rightleftarrows NO_2 * + O_*$	$r_9 = k_9^+ \cdot \theta_{NO} \cdot \theta_{O2} - k_9^- \cdot \theta_{NO2} \cdot \theta_O$	Rate Controlling Step for NO oxidation	
10	$NO_2 * \rightleftarrows NO_2(g) + *$	$r_{10} = k_{10}^+ \cdot \theta_{NO2} - k_{10}^- \cdot P_{NO2} \cdot \theta_*$	$K_{10} = \frac{k_{10}^+}{k_{10}^-} = \frac{P_{NO2} \cdot \theta_*}{\theta_{NO2}}$	$\theta_{NO2} = \frac{1}{K_{10}} \cdot P_{NO2} \cdot \theta_*$

NO Oxidation Parallel Rate Controlling Steps

Assume the rate controlling step is the combining reaction on the surface = r8 & r9. In the absence of other reactants:

$$Rx2 = r_8 + r_9 = k_8^+ \cdot \theta_{NO} \cdot \theta_O - k_8^- \cdot \theta_{NO2} \cdot \theta_* + k_9^+ \cdot \theta_{NO} \cdot \theta_{O2} - k_9^- \cdot \theta_{NO2} \cdot \theta_O$$

$$Rx2 = k_8^+ \cdot K_1 \cdot P_{CO} \cdot \theta_* \cdot \sqrt{K_2 \cdot K_3 \cdot P_{O2}} \cdot \theta_* + k_9^+ \cdot K_1 \cdot P_{NO} \cdot \theta_* \cdot K_2 \cdot P_{O2} \cdot \theta_* - k_8^- \cdot \frac{1}{K_{10}} \cdot P_{NO2} \cdot \theta_* \cdot \theta_* - k_9^- \cdot \frac{1}{K_{10}} \cdot P_{NO2} \cdot \theta_* \cdot \sqrt{K_2 \cdot K_3 \cdot P_{O2}} \cdot \theta_*$$

$$Rx2 = \theta_*^2 \left(k_8^+ \cdot K_7 \cdot \sqrt{K_2 \cdot K_3} \cdot P_{NO} \cdot \sqrt{P_{O2}} + k_9^+ \cdot K_7 \cdot K_2 \cdot P_{NO} \cdot P_{O2} - k_8^- \cdot \frac{1}{K_{10}} \cdot P_{NO2} - k_9^- \cdot \frac{1}{K_{10}} \cdot \sqrt{K_2 \cdot K_3} \cdot \sqrt{P_{O2}} \cdot P_{NO2} \right)$$

$$1 = \theta_* + \theta_{NO} + \theta_{O2} + \theta_O + \theta_{NO2}$$

$$1 = \theta_* \left(1 + K_7 \cdot P_{NO} + K_2 \cdot P_{O2} + \sqrt{K_2 \cdot K_3 \cdot P_{O2}} + \frac{1}{K_{10}} \cdot P_{CO2} \right)$$

$$\theta_*^2 = \frac{1}{\left(1 + K_7 \cdot P_{NO} + K_2 \cdot P_{O2} + \sqrt{K_2 \cdot K_3 \cdot P_{O2}} + \frac{1}{K_{10}} \cdot P_{NO2} \right)^2}$$

$$Rx2 = \frac{\left(k_8^+ \cdot K_7 \cdot \sqrt{K_2 \cdot K_3} \cdot P_{NO} \cdot \sqrt{P_{O2}} + k_9^+ \cdot K_7 \cdot K_2 \cdot P_{NO} \cdot P_{O2} - k_8^- \cdot \frac{1}{K_{10}} \cdot P_{NO2} - k_9^- \cdot \frac{1}{K_{10}} \cdot \sqrt{K_2 \cdot K_3} \cdot \sqrt{P_{O2}} \cdot P_{NO2} \right)}{\left(1 + K_7 \cdot P_{NO} + K_2 \cdot P_{O2} + \sqrt{K_2 \cdot K_3 \cdot P_{O2}} + \frac{1}{K_{10}} \cdot P_{NO2} \right)^2}$$

$Parameters: \quad k_8^+, k_8^-, k_9^+, k_9^-, K_2, K_3, K_7, K_{10}$

$Variables: \quad P_{NO}, P_{O2}, P_{NO2}$

- Need 16 cases at single temperature
- Need 32 cases at range of temperatures
- Have parametric study of 2 of C_{CO} and 5 of T_{cat}.
- K2 and K3 should be the same as CO oxidation test
- may not resolve k8 vs k9
- Key test: Feed NO2
  - Does X_{NO} change with C_{NO2}?
  - Is any NO or O2 formed if NO2 feed only?

Adding terms from both CO and NO to surface coverage:

$$\theta_*^2 = \frac{1}{\left(1 + K_1 \cdot P_{CO} + K_2 \cdot P_{O2} + \sqrt{K_2 \cdot K_3 \cdot P_{O2}} + \frac{1}{K_6} \cdot P_{CO2} + K_7 \cdot P_{NO} + \frac{1}{K_{10}} \cdot P_{NO2} \right)^2}$$

Parameter fit with combined CO, NO, and O2?

RedOx Elementary Reactions

Carbon Monoxide / Nitrogen Dioxide RedOx $CO + NO_2 \rightarrow CO_2 + NO$ (Rx3)

1	$CO(g) + * \rightleftarrows CO*$	$r_1 = k_1^+ \cdot P_{CO} \cdot \theta_* - k_1^- \cdot \theta_{CO}$	$K_1 = \frac{k_1^+}{k_1^-} = \frac{\theta_{CO}}{P_{CO} \cdot \theta_*}$	$\theta_{CO} = K_1 \cdot P_{CO} \cdot \theta_*$
10r	$NO_2(g) + * \rightleftarrows NO_2*$	$r_{10r} = -k_{10}^+ \cdot \theta_{NO2} + k_{10}^- \cdot P_{NO2} \cdot \theta_*$	$K_{10} = \frac{k_{10}^+}{k_{10}^-} = \frac{P_{NO2} \cdot \theta_*}{\theta_{NO2}}$	$\theta_{NO2} = \frac{1}{K_{10}} \cdot P_{NO2} \cdot \theta_*$
8r	$NO_2 * + * \rightleftarrows NO * + O*$	$r_{8r} = -k_8^+ \cdot \theta_{NO} \cdot \theta_O + k_8^- \cdot \theta_{NO2} \cdot \theta_*$	$K_8 = \frac{k_8^+}{k_8^-} = \frac{\theta_{NO2} \cdot \theta_*}{\theta_{NO} \cdot \theta_O}$	$\theta_O = \frac{P_{NO2}}{K_7 \cdot K_8 \cdot K_{10} \cdot P_{NO}} \cdot \theta_*$
4	$CO * + O* \rightleftarrows CO_2 * + *$	$r_4 = k_4^+ \cdot \theta_{CO} \cdot \theta_O - k_4^- \cdot \theta_{CO2} \cdot \theta_*$	Rate determining (limiting) step for CO oxidation	
7r	$NO* \rightleftarrows NO(g) + *$	$r_{7r} = -k_7^+ \cdot P_{NO} \cdot \theta_* + k_7^- \cdot \theta_{NO}$	$K_7 = \frac{k_7^+}{k_7^-} = \frac{\theta_{NO}}{P_{NO} \cdot \theta_*}$	$\theta_{NO} = K_7 \cdot P_{NO} \cdot \theta_*$
6	$CO_2 * \rightleftarrows CO_2(g) + *$	$r_6 = k_6^+ \cdot \theta_{CO2} - k_6^- \cdot P_{CO2} \cdot \theta_*$	$K_6 = \frac{k_6^+}{k_6^-} = \frac{P_{CO2} \cdot \theta_*}{\theta_{CO2}}$	$\theta_{CO2} = \frac{1}{K_6} \cdot P_{CO2} \cdot \theta_*$

RedOx Parallel Rate Controlling Step(s)

Assume the rate controlling step is the combining reaction on the surface = 17. In the absence of other reactants:

$$Rx3 = r_4 = k_4^+ \cdot \theta_{CO} \cdot \theta_O - k_4^- \cdot \theta_{CO2} \cdot \theta_*$$

$$Rx3 = k_4^+ \cdot K_1 \cdot P_{CO} \cdot \theta_* \cdot \frac{1}{K_7 \cdot K_8 \cdot K_{10}} \cdot \frac{P_{NO2}}{P_{NO}} \cdot \theta_* - k_4^- \cdot \frac{1}{K_6} \cdot P_{CO2} \cdot \theta_* \cdot \theta_*$$

$$Rx3 = \theta_*^{\,2} \left(k_4^+ \cdot \frac{K_1}{K_7 \cdot K_8 \cdot K_{10}} \cdot \frac{P_{NO2} \cdot P_{CO}}{P_{NO}} - k_4^- \cdot \frac{1}{K_6} \cdot P_{CO2} \right)$$

$$1 = \theta_* + \theta_{CO} + \theta_{NO2} + \theta_O + \theta_{NO} + \theta_{CO2}$$

$$1 = \theta_* + K_1 \cdot P_{CO} \cdot \theta_* + \frac{1}{K_{10}} \cdot P_{NO2} \cdot \theta_* + \frac{1}{K_7 \cdot K_8 \cdot K_{10}} \cdot \frac{P_{NO2}}{P_{NO}} \cdot \theta_* + K_7 \cdot P_{NO} \cdot \theta_* + \frac{1}{K_6} \cdot P_{CO2} \cdot \theta_*$$

$$1 = \theta_* \left(1 + K_1 \cdot P_{CO} + \frac{1}{K_{10}} \cdot P_{NO2} + \frac{1}{K_7 \cdot K_8 \cdot K_{10}} \cdot \frac{P_{NO2}}{P_{NO}} + K_7 \cdot P_{NO} + \frac{1}{K_6} \cdot P_{CO2} \right)$$

$$Rx3 = \frac{k_4^+ \cdot \frac{K_1}{K_7 \cdot K_8 \cdot K_{10}} \cdot \frac{P_{NO2} \cdot P_{CO}}{P_{NO}} - k_4^- \cdot \frac{1}{K_6} \cdot P_{CO2}}{\left(1 + K_1 \cdot P_{CO} + \frac{1}{K_{10}} \cdot P_{NO2} + \frac{1}{K_7 \cdot K_8 \cdot K_{10}} \cdot \frac{P_{NO2}}{P_{NO}} + K_7 \cdot P_{NO} + \frac{1}{K_6} \cdot P_{CO2} \right)^2}$$

$$Parameters: \quad k_4^+, k_4^-, K_1, K_6, K_7, K_8, K_{10}$$

$$Variables: \quad P_{CO}, P_{NO2}, P_{CO2}, P_{NO}$$

- No new tests (previous -100% NO2 conversion)
- K's should be the same as CO and NO oxidation tests
- Key test: co-feed CO2
  - Does X_{CO} change with C_{CO2}?

WGS Elementary Reactions

Water Gas Shift CO + H_2O → CO_2 + H_2 (Rx4)

1	$CO(g) + * \rightleftarrows CO*$	$r_1 = k_1^+ \cdot P_{CO} \cdot \theta_* - k_1^- \cdot \theta_{CO}$	$K_1 = \frac{k_1^+}{k_1^-} = \frac{\theta_{CO}}{P_{CO} \cdot \theta_*}$	$\theta_{CO} = K_1 \cdot P_{CO} \cdot \theta_*$
11	$H_2O(g) + * \rightleftarrows H_2O*$	$r_{11} = k_{11}^+ \cdot P_{H2O} \cdot \theta_* - k_{11}^- \cdot \theta_{H2O}$	$K_{11} = \frac{k_{11}^+}{k_{11}^-} = \frac{\theta_{H2O}}{P_{H2O} \cdot \theta_*}$	$\theta_{H2O} = K_{11} \cdot P_{H2O} \cdot \theta_*$
12	$H_2O* + * \rightleftarrows H* + OH*$	$r_{12} = k_{12}^+ \cdot \theta_{H2O} \cdot \theta_* - k_{12}^- \cdot \theta_H \cdot \theta_{OH}$	$K_{12} = \frac{k_{12}^+}{k_{12}^-} = \frac{\theta_H \cdot \theta_{OH}}{\theta_{H2O} \cdot \theta_*}$	
13	$CO* + OH* \rightleftarrows COOH* + *$	$r_{13} = k_{13}^+ \cdot \theta_{CO} \cdot \theta_{OH} - k_{13}^- \cdot \theta_{COOH} \cdot \theta_*$	Rate controlling step for WGS	
14	$COOH* + * \rightleftarrows CO_2* + H*$	$r_{14} = k_{14}^+ \cdot \theta_{COOH} \cdot \theta_* - k_{14}^- \cdot \theta_{CO2} \cdot \theta_H$	$K_{14} = \frac{k_{14}^+}{k_{14}^-} = \frac{\theta_{CO2} \cdot \theta_H}{\theta_{COOH} \cdot \theta_*}$	
6	$CO_2* \rightleftarrows CO_2(g) + *$	$r_6 = k_6^+ \cdot \theta_{CO2} - k_6^- \cdot P_{CO2} \cdot \theta_*$	$K_6 = \frac{k_6^+}{k_6^-} = \frac{P_{CO2} \cdot \theta_*}{\theta_{CO2}}$	$\theta_{CO2} = \frac{1}{K_6} \cdot P_{CO2} \cdot \theta_*$
15	$2H* \rightleftarrows H_2* + *$	$r_{15} = k_{15}^+ \cdot \theta_H^2 - k_{15}^- \cdot \theta_{H2} \cdot \theta_*$	$K_{15} = \frac{k_{15}^+}{k_{15}^-} = \frac{\theta_{H2} \cdot \theta_*}{\theta_H^2}$	
16	$H_2* \rightleftarrows H_2(g) + *$	$r_{16} = k_{16}^+ \cdot \theta_{H2} - k_{16}^- \cdot P_{H2} \cdot \theta_*$	$K_{16} = \frac{k_{16}^+}{k_{16}^-} = \frac{P_{H2} \cdot \theta_*}{\theta_{H2}}$	$\theta_{H2} = \frac{1}{K_{16}} \cdot P_{H2} \cdot \theta_*$

WGS Rate Controlling Step

Assume the rate controlling step is the combining reaction on the surface = r13. In the absence of other reactants:

$$Rx4 = r_{13} = k_{13}^{+} \cdot \theta_{CO} \cdot \theta_{OH} - k_{13}^{-} \cdot \theta_{COOH} \cdot \theta_{*}$$

$$Rx4 = k_{13}^{+} \cdot K_{1} \cdot P_{CO} \cdot \theta_{*} \cdot K_{11} \cdot K_{12} \cdot \sqrt{K_{15} \cdot K_{16}} \cdot \frac{P_{H2O}}{\sqrt{P_{H2}}} \cdot \theta_{*} - k_{13}^{-} \cdot \frac{1}{K_{6} \cdot K_{14} \cdot \sqrt{K_{15} \cdot K_{16}}} \cdot P_{CO2} \cdot \sqrt{P_{H2}} \cdot \theta_{*} \cdot \theta_{*}$$

$$1 = \theta_{*} + \theta_{CO} + \theta_{H2O} + \theta_{OH} + \theta_{COOH} + \theta_{CO2} + \theta_{H} + \theta_{H2}$$

$$1 = \theta_{*}\left(1 + K_{1} \cdot P_{CO} + K_{11} \cdot P_{H2O} + K_{11} \cdot K_{12} \cdot \sqrt{K_{15} \cdot K_{16}} \cdot \frac{P_{H2O}}{\sqrt{P_{H2}}} + \frac{1}{K_{6} \cdot K_{14} \cdot \sqrt{K_{15} \cdot K_{16}}} \cdot P_{CO2} \cdot \sqrt{P_{H2}} + \frac{1}{K_{6}} \cdot P_{CO2} + \sqrt{\frac{P_{H2}}{K_{15} \cdot K_{16}}} + \frac{1}{K_{16}} \cdot P_{H2}\right)$$

$$Rx4 = \frac{k_{13}^{+} \cdot K_{1} \cdot K_{11} \cdot K_{12} \cdot \sqrt{K_{15} \cdot K_{16}} \cdot \frac{P_{CO} \cdot P_{H2O}}{\sqrt{P_{H2}}} - k_{13}^{-} \cdot \frac{1}{K_{6} \cdot K_{14} \cdot \sqrt{K_{15} \cdot K_{16}}} \cdot P_{CO2} \cdot \sqrt{P_{H2}}}{\left(1 + K_{1} \cdot P_{CO} + K_{11} \cdot P_{H2O} + K_{11} \cdot K_{12} \cdot \sqrt{K_{15} \cdot K_{16}} \cdot \frac{P_{H2O}}{\sqrt{P_{H2}}} + \frac{1}{K_{6} \cdot K_{14} \cdot \sqrt{K_{15} \cdot K_{16}}} \cdot P_{CO2} \cdot \sqrt{P_{H2}} + \frac{1}{K_{6}} \cdot P_{CO2} + \sqrt{\frac{P_{H2}}{K_{15} \cdot K_{16}}} + \frac{1}{K_{16}} \cdot P_{H2}\right)^{2}}$$

$Parameters: \quad k_{13}^{+}, k_{13}^{-}, K_{1}, K_{6}, K_{11}, K_{12}, K_{14}, K_{15}, K_{16}$

$Variables: \quad P_{CO}, P_{H2O}, P_{H2}, P_{CO2}$

- Rate too low at 150°C to resolve parameters?
- Key test: Feed H2
  - Does X_{CO} change with C_{H2}?

H2 Oxidation Elementary Reactions

Hydrogen Oxidation $H_2 + ½\, O_2 \rightarrow + H_2O$ (Rx5)

16r	$H_2(g) + * \rightleftarrows H_2*$	$r_{16r} = k_{16}^{-} \cdot P_{H2} \cdot \theta_* - k_{16}^{+} \cdot \theta_{H2}$	$K_{16} = \frac{k_{16}^{+}}{k_{16}^{-}} = \frac{P_{H2} \cdot \theta_*}{\theta_{H2}}$	$\theta_{H2} = \frac{1}{K_{16}} \cdot P_{H2} \cdot \theta_*$
15r	$H_2*+ * \rightleftarrows 2H*$	$r_{15r} = k_{15}^{-} \cdot \theta_{H2} \cdot \theta_* - k_{15}^{+} \cdot \theta_H^2$	$K_{15} = \frac{k_{15}^{+}}{k_{15}^{-}} = \frac{\theta_{H2} \cdot \theta_*}{\theta_H^2}$	$\theta_H = \sqrt{\frac{P_{H2}}{K_{15} \cdot K_{16}}} \cdot \sqrt{\theta_*}$
2	$O_2(g) + * \rightleftarrows O_2*$	$r_2 = k_2^{+} \cdot P_{O2} \cdot \theta_* - k_2^{-} \cdot \theta_{O2}$	$K_2 = \frac{k_2^{+}}{k_2^{-}} = \frac{\theta_{O2}}{P_{O2} \cdot \theta_*}$	$\theta_{O2} = K_2 \cdot P_{O2} \cdot \theta_*$
3	$O_2*+ * \rightleftarrows 2O*$	$r_3 = k_3^{+} \cdot \theta_{O2} \cdot \theta_* - k_3^{-} \cdot \theta_O^2$	$K_3 = \frac{k_3^{+}}{k_3^{-}} = \frac{\theta_O^2}{\theta_{O2} \cdot \theta_*}$	$\theta_O = \sqrt{K_2 \cdot K_3 \cdot P_{O2}} \cdot \theta_*$
17	$O*+ H* \rightleftarrows OH*+*$	$r_{17} = k_{17}^{+} \cdot \theta_O \cdot \theta_H - k_{17}^{-} \cdot \theta_{OH} \cdot \theta_*$	$K_{17} = \frac{k_{17}^{+}}{k_{17}^{-}} = \frac{\theta_* \cdot \theta_{OH}}{\theta_O \cdot \theta_H}$	RCS
18	$2OH* \rightleftarrows HOH*+O*$	$r_{18} = k_{18}^{+} \cdot \theta_{OH}^2 - k_{18}^{-} \cdot \theta_{H2O} \cdot \theta_O$	$K_{18} = \frac{k_{18}^{+}}{k_{18}^{-}} = \frac{\theta_O \cdot \theta_{H2O}}{\theta_{OH}^2}$	$\theta_{OH} = \sqrt{\frac{K_{11} \cdot P_{H2O}}{K_{18}}} \cdot \sqrt[4]{K_2 \cdot K_3 \cdot P_{O2}} \cdot \theta_*$
11r	$H_2O* \rightleftarrows H_2O(g) + *$	$r_{11r} = k_{11}^{-} \cdot \theta_{H2O} - k_{11}^{+} \cdot P_{H2O} \cdot \theta_*$	$K_{11} = \frac{k_{11}^{+}}{k_{11}^{-}} = \frac{\theta_{H2O}}{P_{H2O} \cdot \theta_*}$	$\theta_{H2O} = K_{11} \cdot P_{H2O} \cdot \theta_*$

H2 Oxidation Rate Controlling Step

Assume the rate controlling step is the combining reaction on the surface = 17. In the absence of other reactants:

$$Rx5 = r_{17} = k_{17}^{+} \cdot \theta_O \cdot \theta_H - k_{17}^{-} \cdot \theta_{OH} \cdot \theta_*$$

$$Rx5 = k_{17}^{+} \cdot \sqrt{K_2 \cdot K_3 \cdot P_{O2}} \cdot \theta_* \cdot \sqrt{\frac{P_{H2}}{K_{15} \cdot K_{16}}} \cdot \theta_* - k_{17}^{-} \cdot \sqrt{\frac{K_{11} \cdot P_{H2O}}{K_{18}}} \cdot \sqrt[4]{K_2 \cdot K_3 \cdot P_{O2}} \cdot \theta_* \cdot \theta_*$$

$$Rx5 = \theta_*^{2} \left(k_{17}^{+} \cdot \sqrt{\frac{K_2 \cdot K_3}{K_{15} \cdot K_{16}}} \cdot \sqrt{P_{O2} \cdot P_{H2}} - k_{17}^{-} \cdot \sqrt{\frac{K_{11} \cdot \sqrt{K_2 \cdot K_3}}{K_{18}}} \cdot \sqrt{P_{H2O} \sqrt{P_{O2}}} \right)$$

$$1 = \theta_* + \theta_{H2} + \theta_H + \theta_{O2} + \theta_O + \theta_{OH} + \theta_{H2O}$$

$$1 = \theta_* + \frac{1}{K_{16}} \cdot P_{H2} \cdot \theta_* + \sqrt{\frac{P_{H2}}{K_{15} \cdot K_{16}}} \cdot \theta_* + K_2 \cdot P_{O2} \cdot \theta_* + \sqrt{K_2 \cdot K_3 \cdot P_{O2}} \cdot \theta_* + \sqrt{\frac{K_{11} \cdot P_{H2O}}{K_{18}}} \cdot \sqrt[4]{K_2 \cdot K_3 \cdot P_{O2}} \cdot \theta_* + K_{11} \cdot P_{H2O} \cdot \theta_*$$

$$1 = \theta_* \left(1 + \frac{1}{K_{16}} \cdot P_{H2} + \sqrt{\frac{1}{K_{15} \cdot K_{16}}} \cdot \sqrt{P_{H2}} + K_2 \cdot P_{O2} + \sqrt{K_2 \cdot K_3} \cdot \sqrt{P_{O2}} + \sqrt{\frac{K_{11}\sqrt{K_2 \cdot K_3}}{K_{18}}} \cdot \sqrt{P_{H2O} \cdot \sqrt{P_{O2}}} + K_{11} \cdot P_{H2O} \right)$$

$$\theta_* = \frac{1}{1 + \frac{1}{K_{16}} \cdot P_{H2} + \sqrt{\frac{1}{K_{15} \cdot K_{16}}} \cdot \sqrt{P_{H2}} + K_2 \cdot P_{O2} + \sqrt{K_2 \cdot K_3} \cdot \sqrt{P_{O2}} + \sqrt{\frac{K_{11}\sqrt{K_2 \cdot K_3}}{K_{18}}} \cdot \sqrt{P_{H2O} \cdot \sqrt{P_{O2}}} + K_{11} \cdot P_{H2O}}$$

$$Rx5 = \frac{k_{17}^{+} \cdot \sqrt{\frac{K_2 \cdot K_3}{K_{15} \cdot K_{16}}} \cdot \sqrt{P_{O2} \cdot P_{H2}} - k_{17}^{-} \cdot \sqrt{\frac{K_{11} \cdot \sqrt{K_2 \cdot K_3}}{K_{18}}} \cdot \sqrt{P_{H2O} \sqrt{P_{O2}}}}{\left(1 + \frac{1}{K_{16}} \cdot P_{H2} + \sqrt{\frac{1}{K_{15} \cdot K_{16}}} \cdot \sqrt{P_{H2}} + K_2 \cdot P_{O2} + \sqrt{K_2 \cdot K_3} \cdot \sqrt{P_{O2}} + \sqrt{\frac{K_{11}\sqrt{K_2 \cdot K_3}}{K_{18}}} \cdot \sqrt{P_{H2O} \cdot \sqrt{P_{O2}}} + K_{11} \cdot P_{H2O} \right)^2}$$

- X_{H2} may be too high @150° C to resolve parameters
- Key test: Feed H2O
  - Does X_{H2} change with C_{H2O}?

$Parameters: \quad k_{17}^{+}, k_{17}^{-}, K_2, K_3, K_{11}, K_{15}, K_{16}, K_{18}$

$Variables: \quad P_{H2}, P_{O2}, P_{H2O}$

DFT / MKM compared to experimental parameters

	$CO + \frac{1}{2} O_2 \rightarrow CO_2$	$NO + \frac{1}{2} O_2 \rightarrow NO_2$	$CO + NO_2 \rightarrow CO_2 + NO$	$CO + H_2O \rightarrow CO_2 + H_2$	$H_2 + \frac{1}{2} O_2 \rightarrow + H_2O$
θ_{CO}	$K_1 \cdot P_{CO} \cdot \theta_*$		$K_1 \cdot P_{CO} \cdot \theta_*$	$K_1 \cdot P_{CO} \cdot \theta_*$	
θ_{NO}		$K_7 \cdot P_{NO} \cdot \theta_*$	$K_7 \cdot P_{NO} \cdot \theta_*$		
θ_{O2}	$K_2 \cdot P_{O2} \cdot \theta_*$	$K_2 \cdot P_{O2} \cdot \theta_*$			$K_2 \cdot P_{O2} \cdot \theta_*$
θ_{CO2}	$\frac{1}{K_6} \cdot P_{CO2} \cdot \theta_*$		$\frac{1}{K_6} \cdot P_{CO2} \cdot \theta_*$	$\frac{1}{K_6} \cdot P_{CO2} \cdot \theta_*$	
θ_{NO2}		$\frac{1}{K_{10}} \cdot P_{NO2} \cdot \theta_*$	$\frac{1}{K_{10}} \cdot P_{NO2} \cdot \theta_*$		
θ_{H2O}				$K_{11} \cdot P_{H2O} \cdot \theta_*$	$K_{11} \cdot P_{H2O} \cdot \theta_*$
θ_{H2}				$\frac{1}{K_{16}} \cdot P_{H2} \cdot \theta_*$	$\frac{1}{K_{16}} \cdot P_{H2} \cdot \theta_*$
θ_O	$\sqrt{K_2 \cdot K_3 \cdot P_{O2}} \cdot \theta_*$	$\sqrt{K_2 \cdot K_3 \cdot P_{O2}} \cdot \theta_*$	$\frac{1}{K_7 \cdot K_8 \cdot K_{10}} \cdot \frac{P_{NO2}}{P_{NO}} \cdot \theta_*$		$\sqrt{K_2 \cdot K_3 \cdot P_{O2}} \cdot \theta_*$
θ_H				$\sqrt{\frac{P_{H2}}{K_{15} \cdot K_{16}}} \cdot \theta_*$	$\sqrt{\frac{P_{H2}}{K_{15} \cdot K_{16}}} \cdot \theta_*$
θ_{OH}				$K_{11} \cdot K_{12} \cdot \sqrt{K_{15} \cdot K_{16}} \cdot \frac{P_{H2O}}{\sqrt{P_{H2}}} \cdot \theta_*$	$\sqrt{\frac{K_{11} \cdot P_{H2O}}{K_{18}}} \cdot \sqrt[4]{K_2 \cdot K_3 \cdot P_{O2}} \cdot \theta_*$
θ_{COOH}				$\frac{1}{K_6 \cdot K_{14} \cdot \sqrt{K_{15} \cdot K_{16}}} \cdot P_{CO2} \cdot \sqrt{P_{H2}} \cdot \theta_*$	

Thank You - Questions?

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