Spatio-temporal Features of Periodic Oxidation of H_2 and CO on $Pt/CeO_2/Al_2O_3$

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Outline

- Motivation & objective
- Experimental system
- Spatio-temporal features of H_2 oxidation on $Pt/CeO_2/Al_2O_3$
- Coupling between oxidation of H_2 and CO on $Pt/CeO_2/Al_2O_3$

Background & Motivation

- CO, H_2 are common constituents in vehicle exhaust
- CeO_2 is common ingredient in TWC, LNT converters
- Understanding oxidation of H_2, CO on PGM/CeO_2/Al_2O_3 needed to develop predictive models & to design improved catalytic converters
- Low temperature oxidation is particularly important because of ignition challenges, CO inhibition, etc.
- Coupling known to occur between oxidations of H_2 and CO on Pt/Al_2O_3
  - Advances have been made for steady-state conditions
  - Similar advances needed for transient conditions, especially at low temperature, and with O supplied from CeO_2

Pt-Catalyzed Oxidation of H_2 and CO

- Reactions among most studied of all catalytic reactions

- H_2 oxidation

$H_2 + 2X \leftrightarrow 2\,H\text{-}X$

$O_2 + 2X \leftrightarrow 2\,O\text{-}X$

$H\text{-}X + O\text{-}X \rightarrow OH\text{-}X$

$H\text{-}X + OH\text{-}X \rightarrow H_2O\text{-}X + X$

$H_2O\text{-}X \leftrightarrow H_2O + X$

Positive order w/r H_2 & O_2

20-40 kJ/mole

CO oxidation

$CO + X \leftrightarrow CO\text{-}X$

$O_2 + X \leftrightarrow O_2\text{-}X$

$O_2\text{-}X + X \leftrightarrow 2\,O\text{-}X$

$CO\text{-}X + O\text{-}X \rightarrow CO_2\text{-}X$

$CO_2\text{-}X \leftrightarrow CO_2 + X$

$R \sim A\, e^{-E_d/RT}\, p_{O2}/p_{CO}$

E_d = 120-180 kJ/mole

Peden and Goodman, J. Phys. Chem. (1988)

Co-oxidation of CO & H_2 on Pt: Some Interesting Steady-State Effects

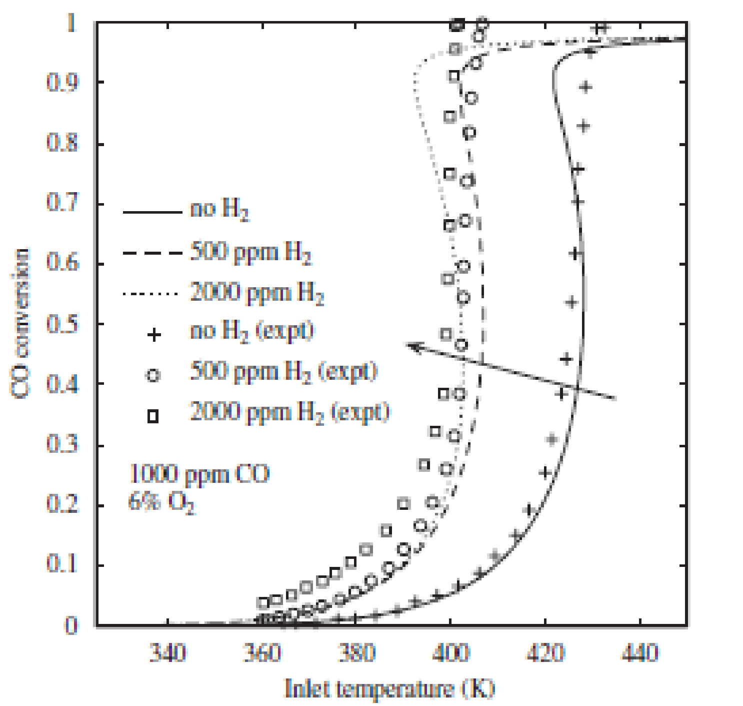


Fig. 10. Comparison of experimental data (Salomons et al., 2006) with simulation results to study the effect of H_2.

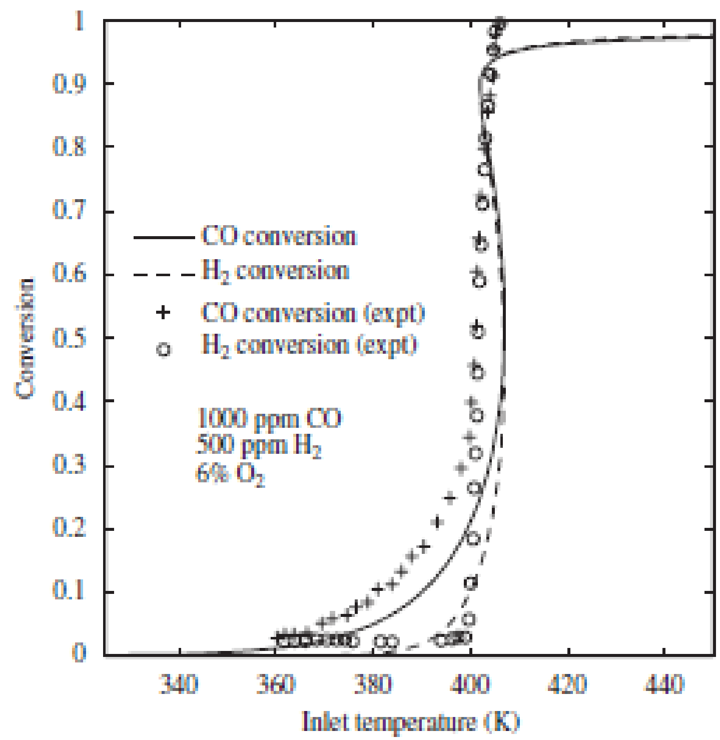


Fig. 12. Comparison of experimental data (Salomons et al., 2006) and modeling results to study the ignition order in a CO–H_2–O_2 system.

Enhancement of CO oxidation by H_2

Ignition of CO before H_2

*Salomons et al., Appl. Catal. B., **70**, 305 (2007)*

*Bhatia et al., Chem. Eng. Sci., **64**, 1544 (2009)*

UNIVERSITY OF HOUSTON Founded 1927

Co-oxidation of CO & H_2 on Pt

Potential phenomenological effects of H_2 enhancing the rate of CO oxidation at low temperature:

- Enhancement of CO oxidation via HCO-Pt complex, reducing CO desorption energy: $E_{d,CO} = E_{d,CO} - \varepsilon\, \theta_H$

Bhatia et al., Chem. Eng. Sci., ***64****, 1544 (2009)*

- Possible second reaction pathway involving COOH-Pt:

$$\text{CO-Pt} + \text{OH-Pt} \rightarrow \text{COOH-Pt} + \text{Pt}$$

with lower activation barrier than

$$\text{CO-Pt} + \text{O-Pt} \rightarrow CO_2 + 2\,\text{Pt}$$

Hauptman et al., Appl. Catal. A., ***174,*** *397 (2011)*

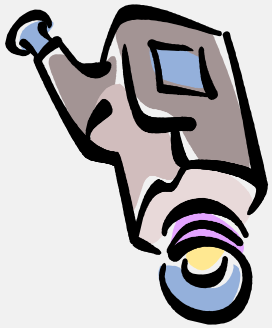
Objective of Study

Carry out the transient oxidations of H_2 and CO and co-oxidation of H_2/CO on Pt/CeO_2/Al_2O_3 to elucidate spatio-temporal effects & coupling between the reactions.

$$H_2 + CeO_2\text{-}O \rightarrow H_2O + CeO_2$$

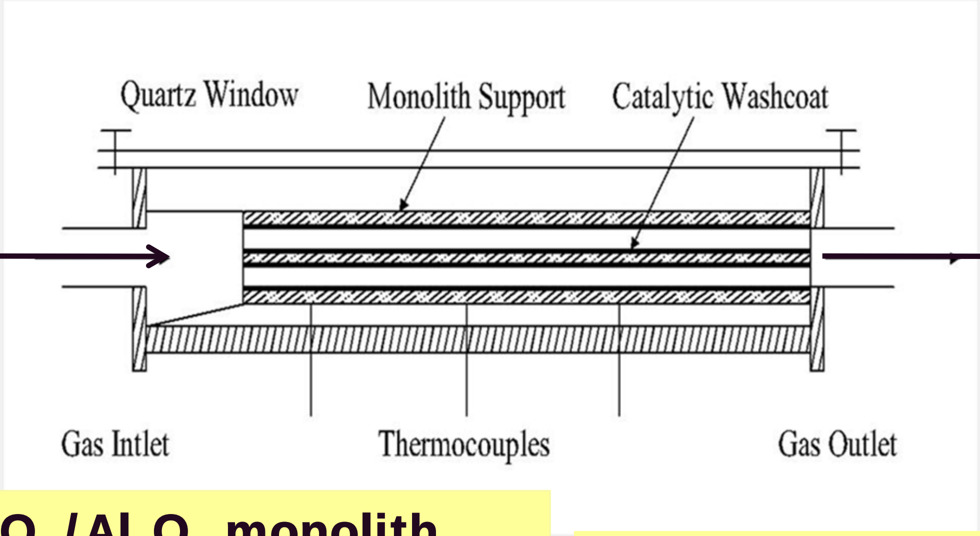
$$CO + CeO_2\text{-}O \rightarrow CO_2 + CeO_2$$

Reactor with IR Imaging & Product Analysis



Capture 2-D temperature profile & product composition during transient reaction

Reactants



Quadrupole Mass Spect.

$Pt/CeO_2/Al_2O_3$ monolith
Washcoat: 2.3 g/in^3 (350 mg)
Pt: 2.78 wt%, 50% dispersion
CeO_2: 15 wt%

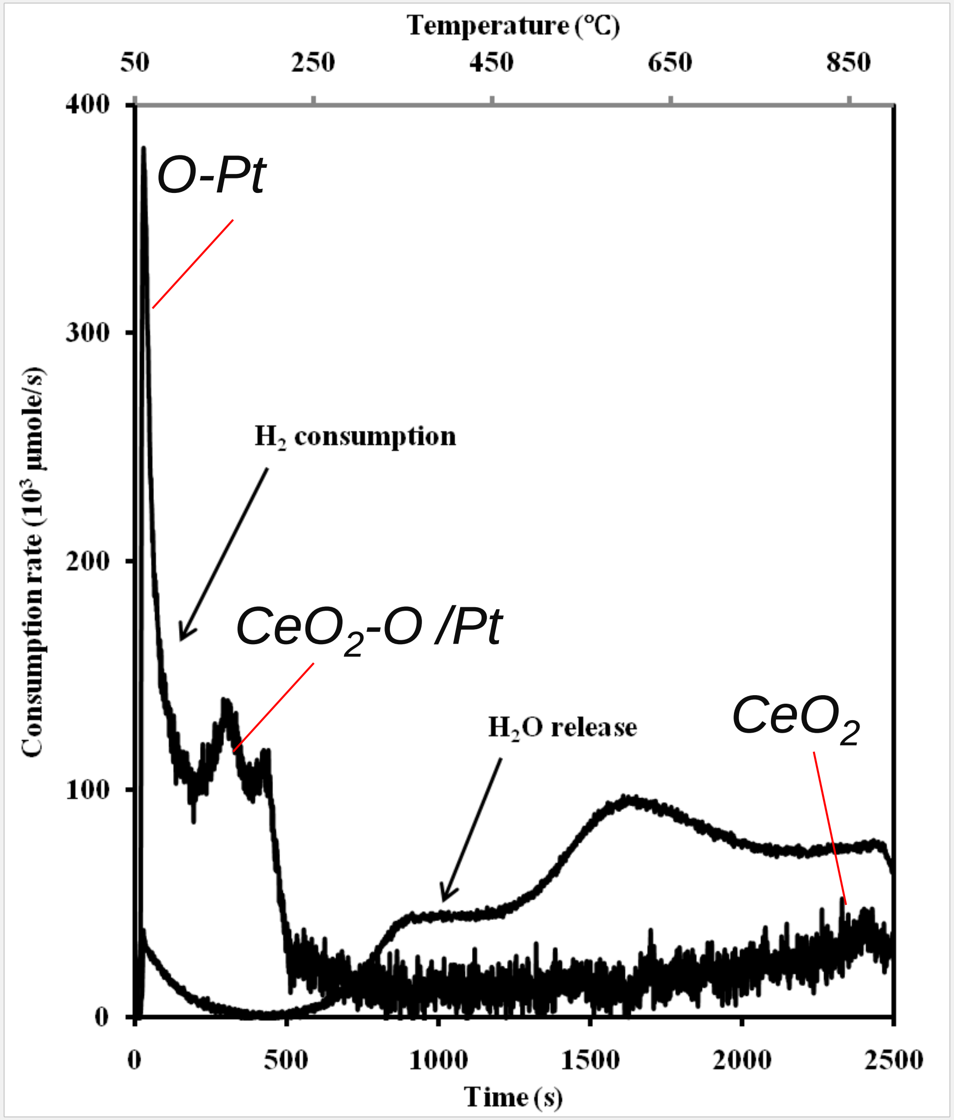
W = 2.1 cm; L = 7.6 cm
2- channels thick
16 channels

Temperature Programmed Reduction

Pre-oxidation: 20% O_2/Ar (500 ^oC, 3 hr)
Sweep with Ar (10 min)
Reduction in 1%H_2/Ar

Several forms of O present:

O-Pt (O:Pt ~ 2)
CeO_2-O (O:Pt ~ 2.5)
$CeO_2 \rightarrow Ce_2O_3$



Co-oxidation of CO & H_2 on Pt

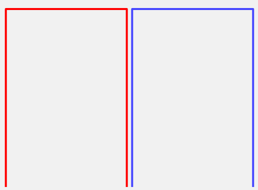
Conditions

Space Velocity: 100,000 hr^{-1}

Lean phase: 5% O_2 in Ar for 100 s
Rich phase: 2% H_2 (or CO) in Ar for 20 s

Temp: 100 to 400 ^{o}C

Transient Effluent Concentrations

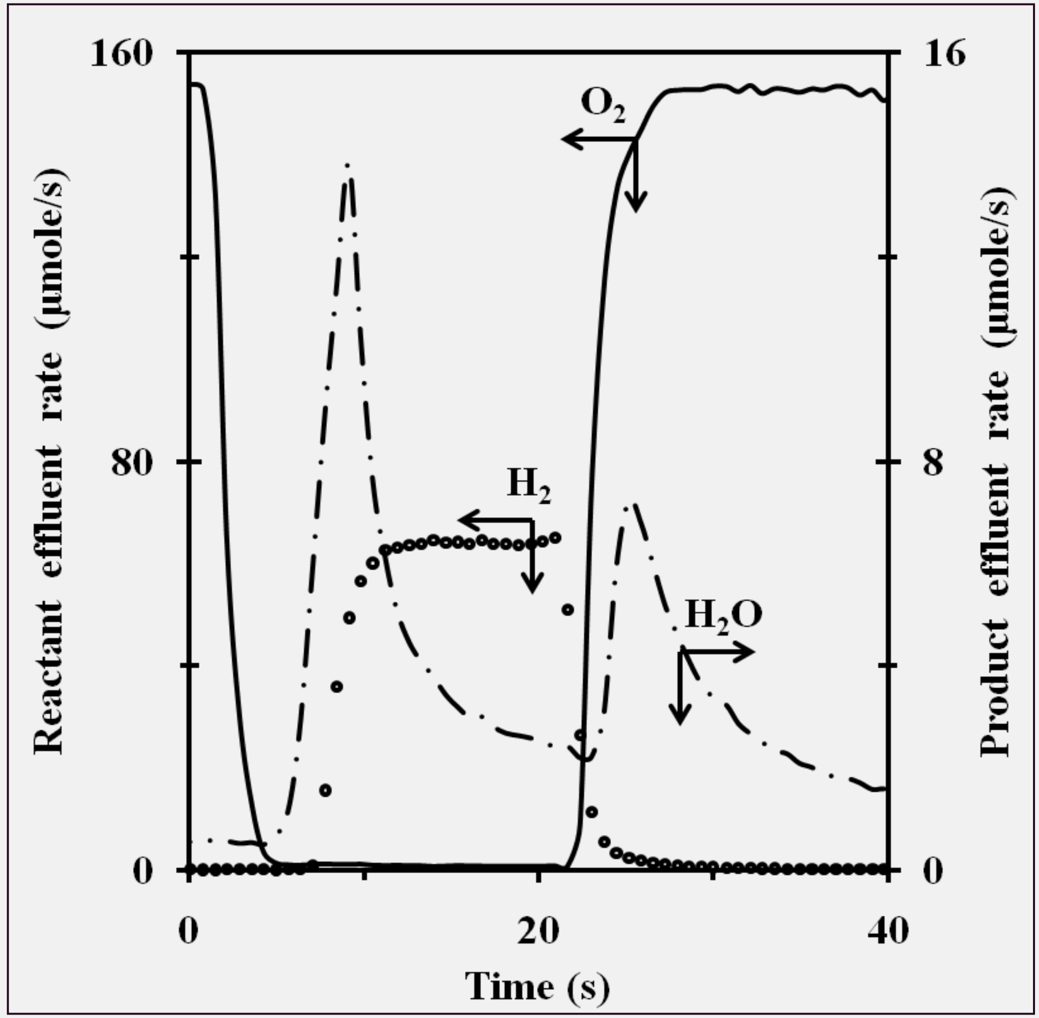


H_2 O_2

20s / 20s

2% 5%

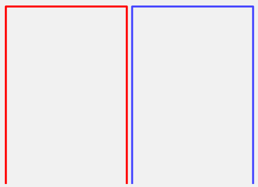
350 ^oC



Nothing unusual with transient response?

Quantification of H2 + O2 Consumption

LR cycle:

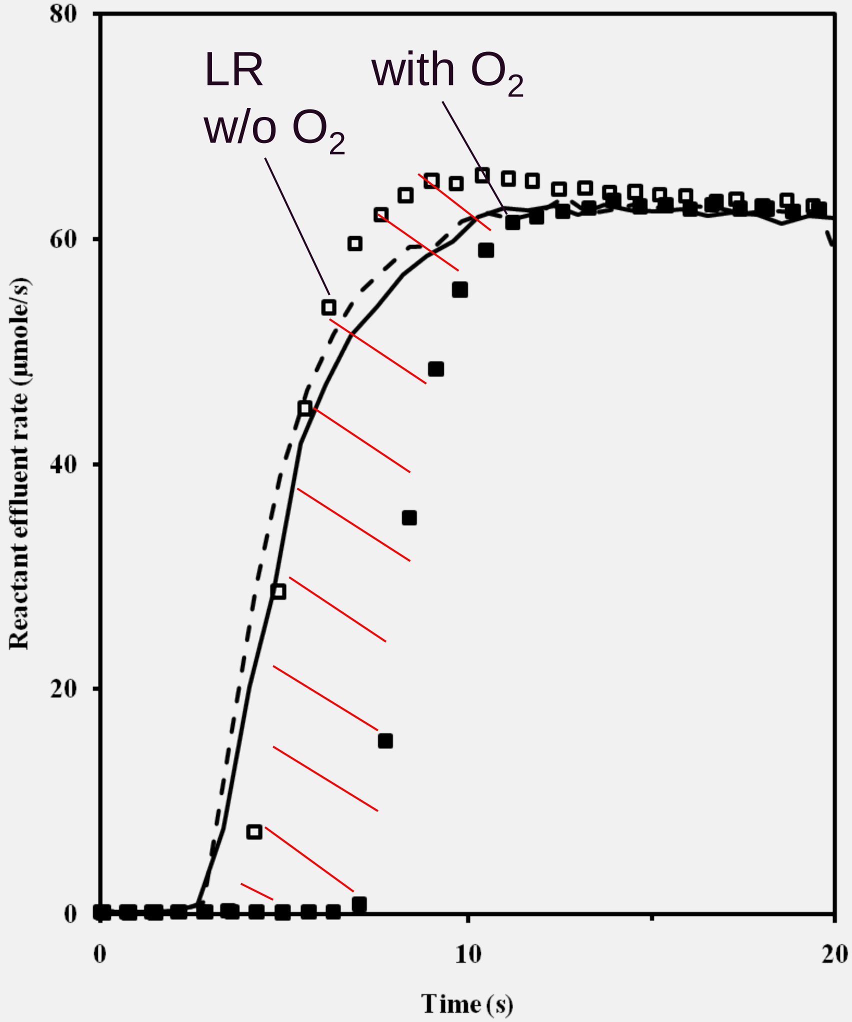


H_2 O_2

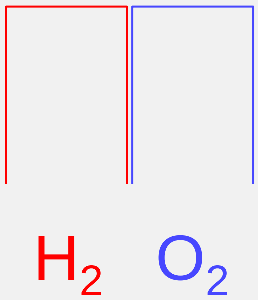
20s / 20s

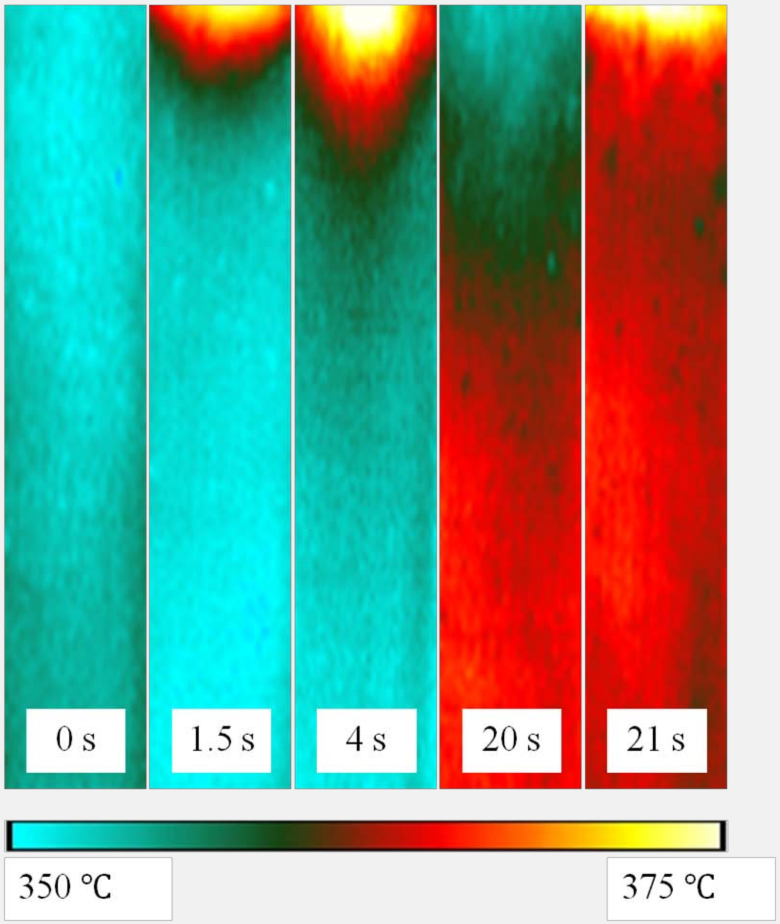
2% 5%

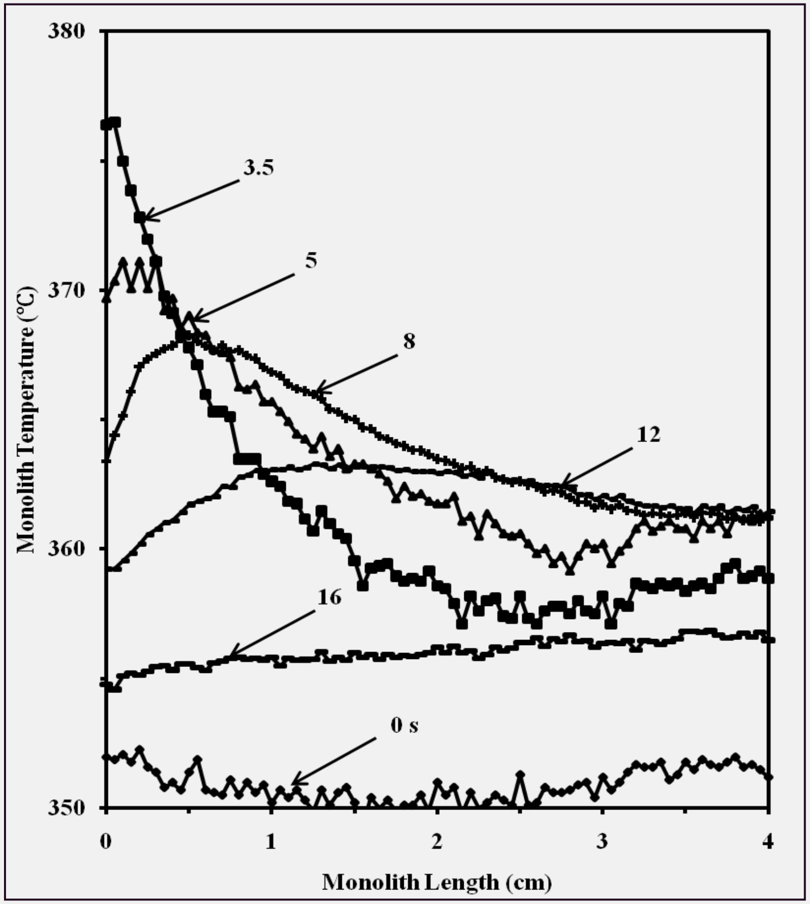
350 °C



Transient Temperature

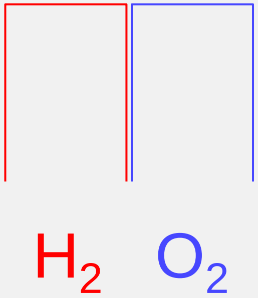


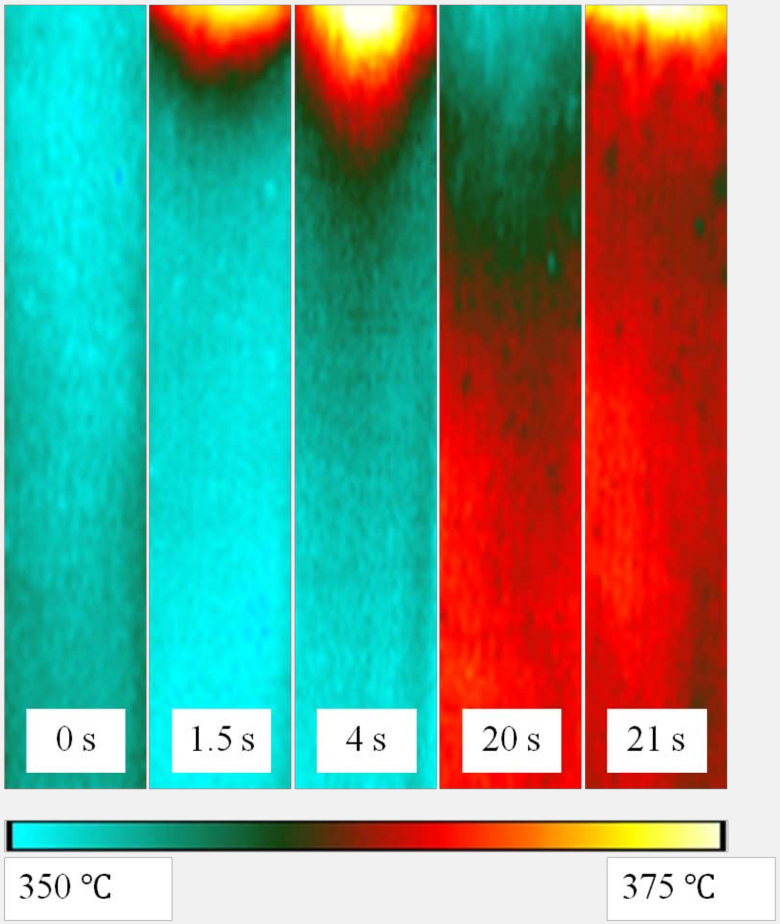


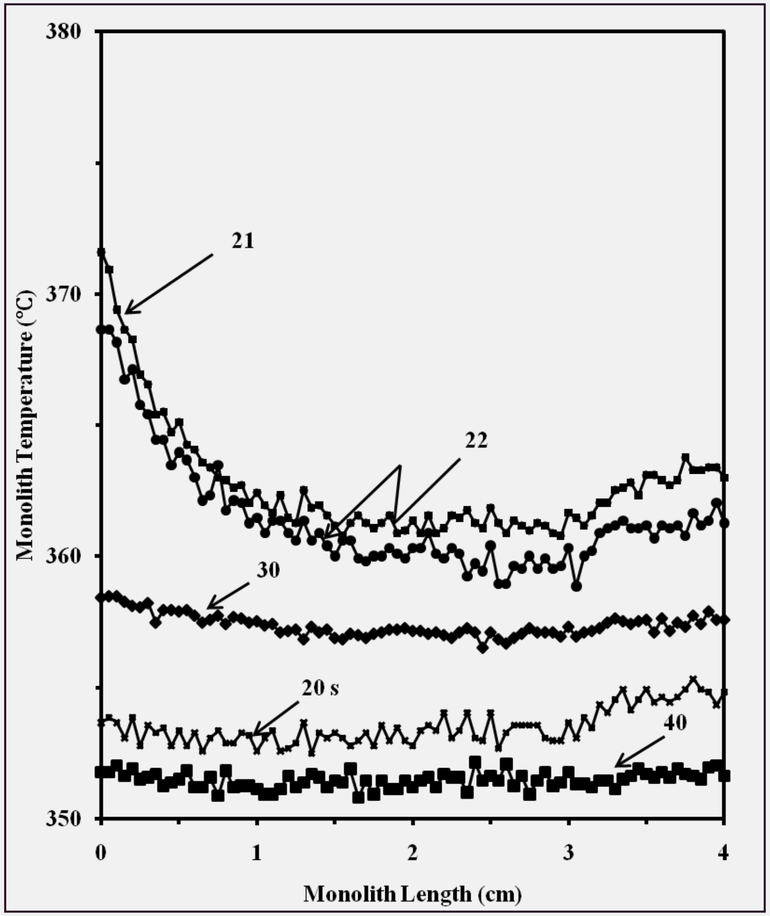


Appreciable spatial nonuniformity in temperature

Transient Temperature





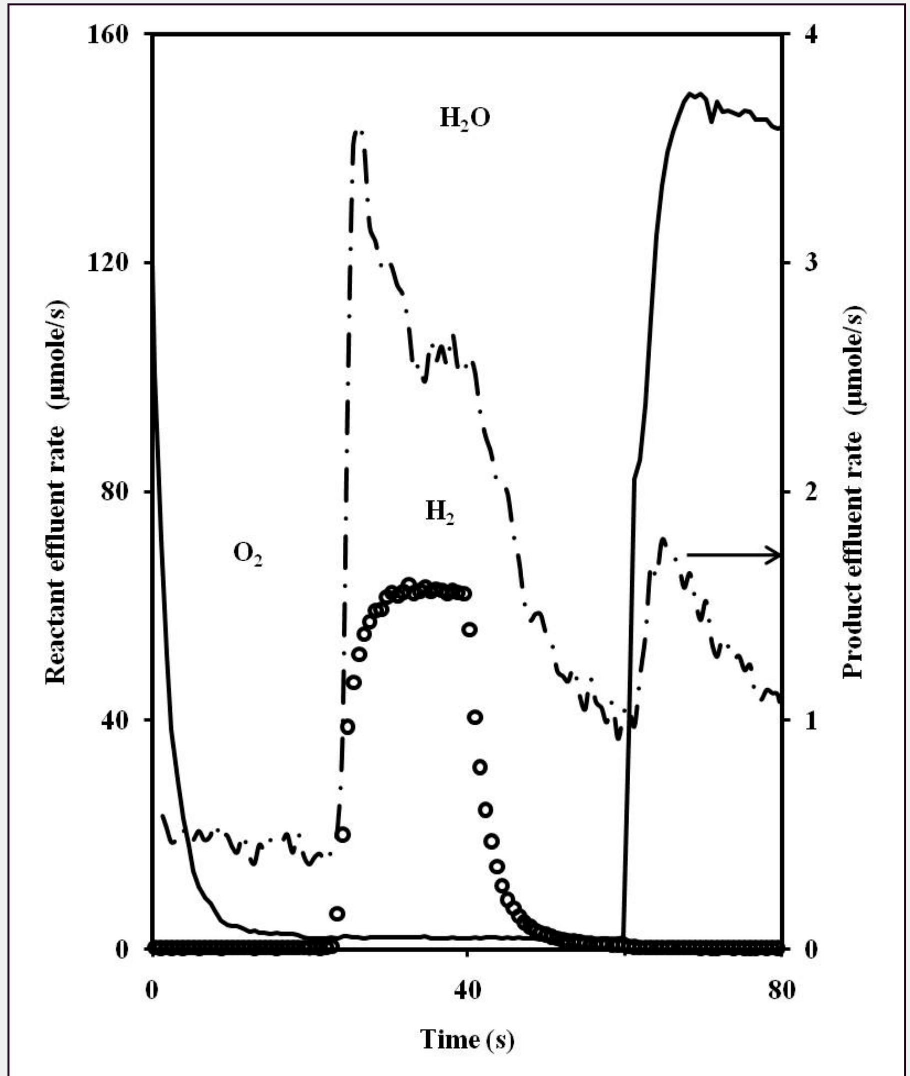


Transient Effluent Concentrations with N_2 Sweep

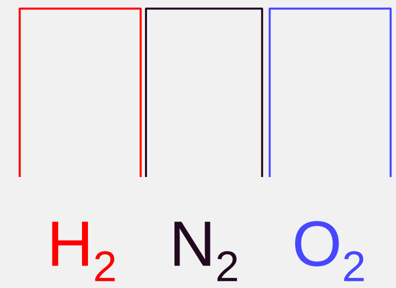
H_2 N_2 O_2

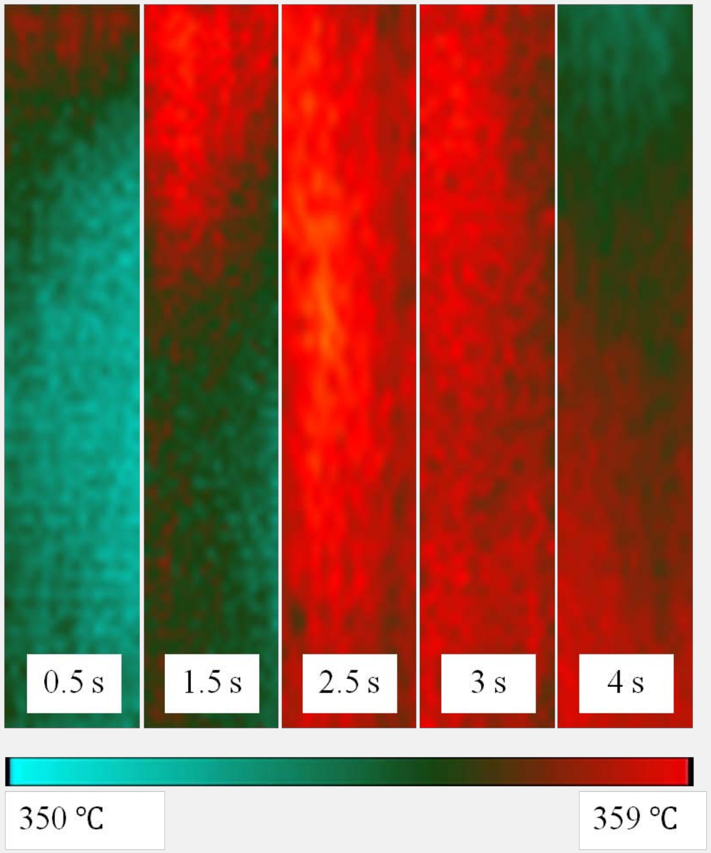
20s / 20s / 20s

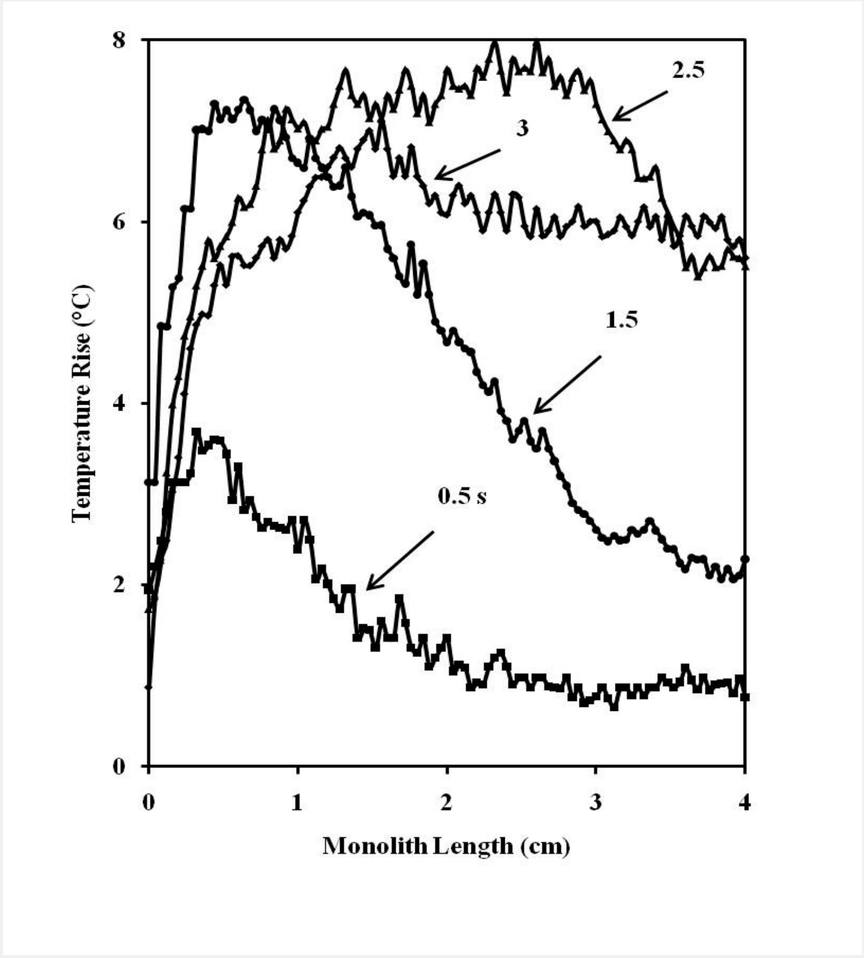
2% 5%



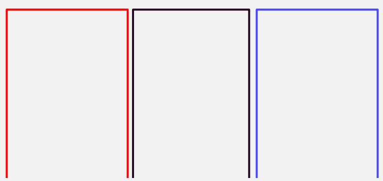
Transient Temperature with N_2 Sweep







Transient Effluent Concentrations with N_2 Sweep



H_2 N_2 O_2

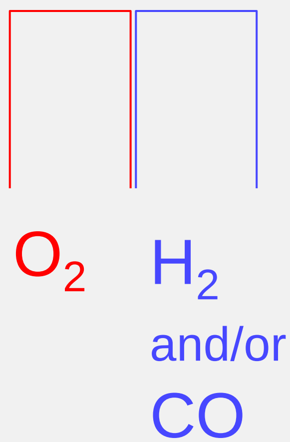
20s / τ / 20s

2% 5%

Pulse time (s) τ	H_2 consumption (μmol H_2/ g washcoat)	H_2 conversion (%)	ΔT_{max}(°C)
0	960	29.5	25.1
5	630	19.4	15.6
10	448	13.8	12.3
15	243	7.5	10.1
20	211	6.5	8.4
300	181	5.6	7.8
600	187	5.7	7.7

Rcn. with chemisorbed O from CeO_2

Transient Co-oxidation of H_2 & CO



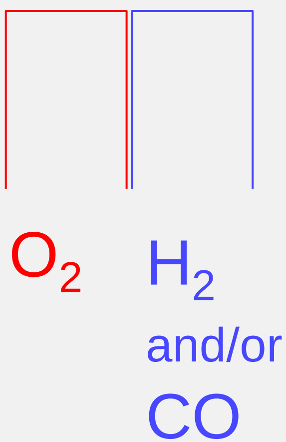
Space Velocity: 100,000 hr^{-1}

Temp: 100 to 400 ^oC

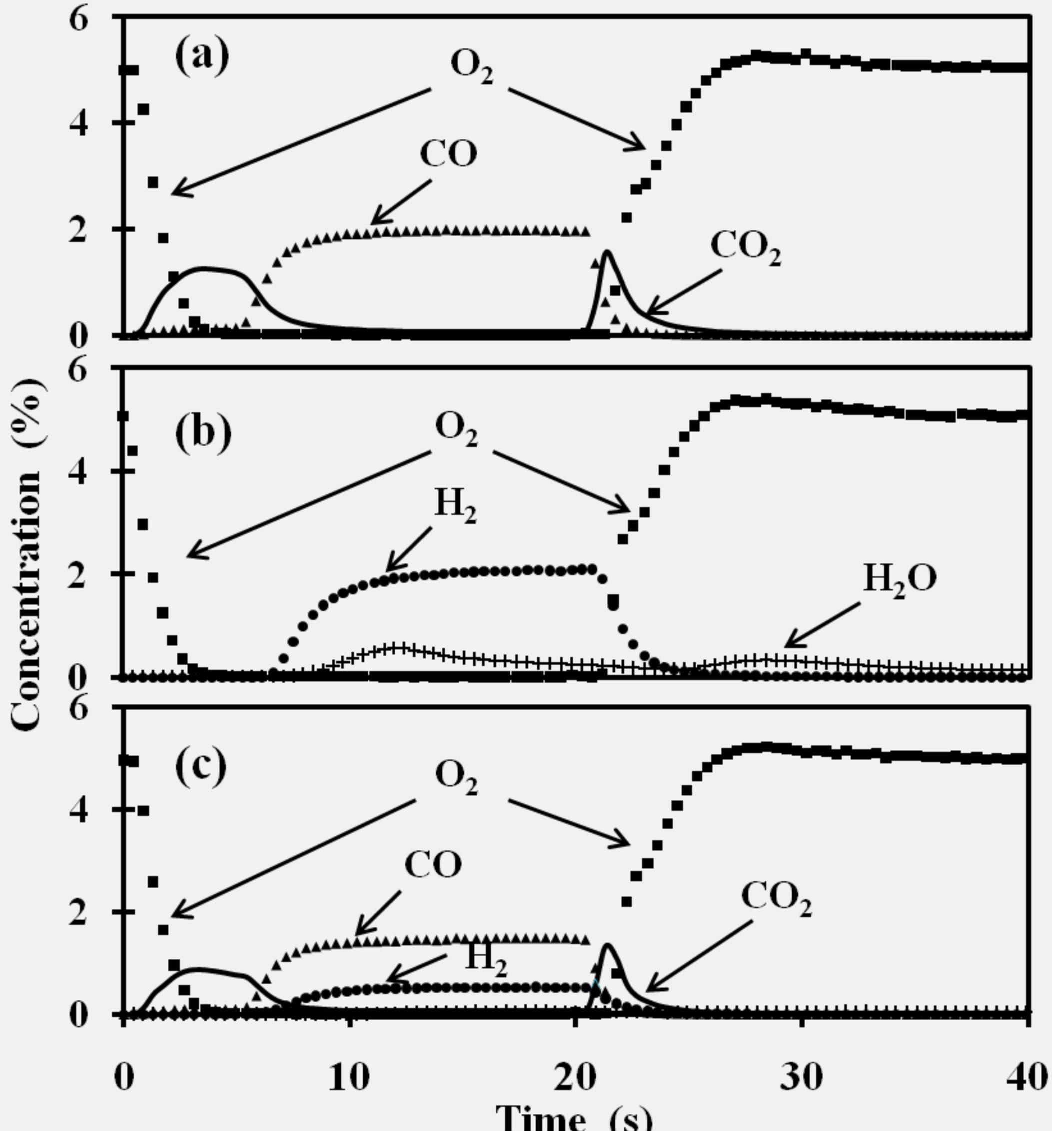
Lean phase: 5% O_2 in Ar (100 s)

Rich phase: 2% CO in Ar (20 s)
1.5 % CO in Ar (20 s)
1.5 % CO + 0.5% H_2 in Ar (20 s)
2% H_2 (20 s)

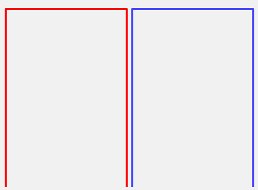
Transient Co-oxidation of H_2 & CO: High Temperature



350 °C

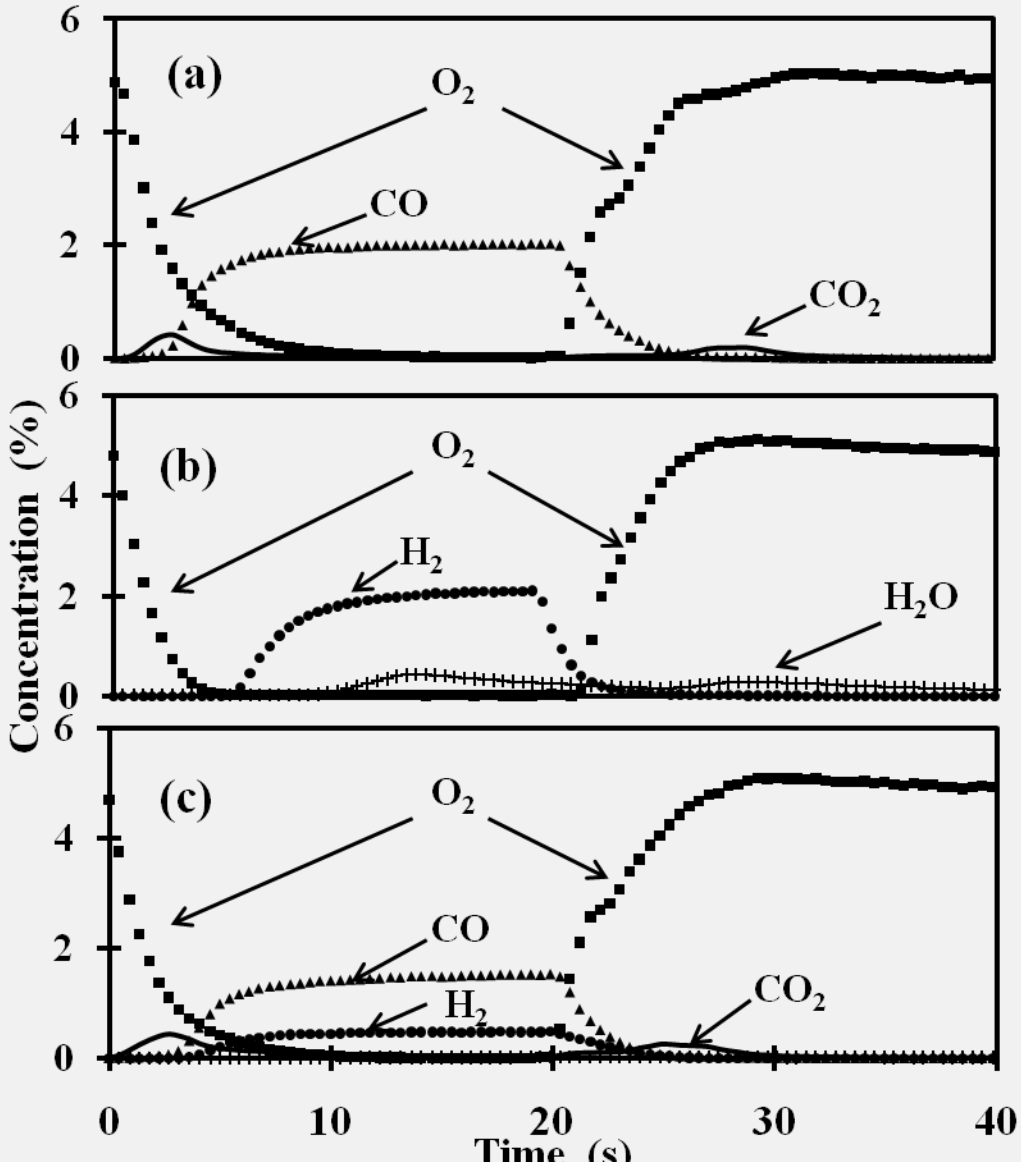


Transient Co-oxidation of H_2 & CO: Low Temperature

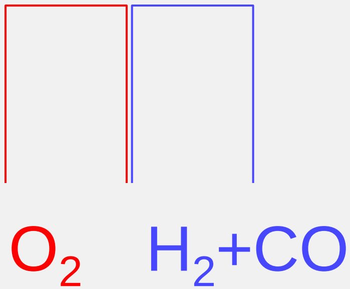


O_2 H_2 and/or CO

100 ^oC

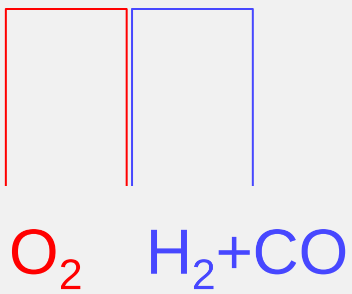


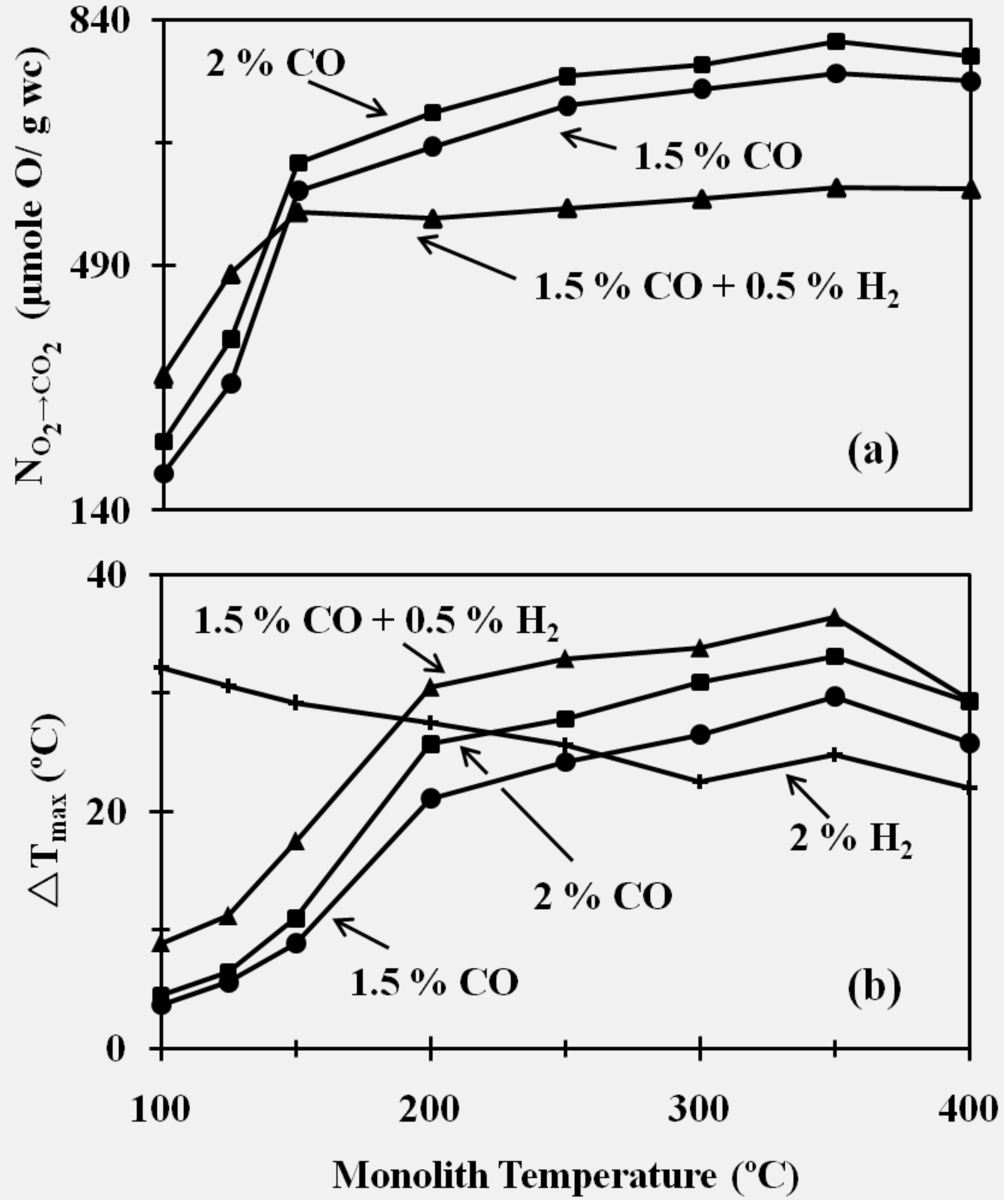
Transient Co-oxidation of H_2 & CO



Temp (°C)		100	125	150	200	250	300	350	400
2 % CO	Delay (s)	2.2	2.5	2.8	4.5	4.7	5	5.2	4.3
	T_{max} (°C)	4.5	6.5	11	25.7	27.8	30.9	33.1	29.3
	N_{O2CO2} (µmole O/ g washcoat)	238	384	635	707	759	776	809	788
2 % H_2	Delay (s)	5.6	5.8	5.8	6.1	6.4	6.7	6.9	6.8
	T_{max} (°C)	32.2	30.6	29.2	27.5	25.6	22.5	24.8	22
	N_{O2H2O} (µmole O/ g washcoat)	886	934	973	978	972	969	960	929
1.5 % CO + 0.5 % H_2	Delay (s)	3	3.2	3.5	4.9	5.1	5.2	5.5	5.1
	T_{max} (°C)	8.9	11.2	17.5	30.5	32.9	33.8	36.4	29.5
	$N_{O2H2O+CO2}$ (µmole O/ g washcoat)	477	648	777	824	852	863	876	845
	From H_2	144	171	212	268	281	279	276	247
	From CO	333	477	565	556	571	584	600	598
1.5 % CO	Delay (s)	2.6	3	3.2	4.7	5	5.2	5.4	4.6
	T_{max} (°C)	3.7	5.6	8.9	21.1	24.2	26.5	29.7	25.8
	N_{O2CO2} (µmole O/ g washcoat)	192	321	596	659	717	741	763	752

Transient Co-oxidation of H_2 & CO





Mechanistic & Kinetic Implications

- H_2 oxidation on Pt

$H_2 + 2X \leftrightarrow 2\,H\text{-}X$

$O_2 + 2X \leftrightarrow 2\,O\text{-}X$

$H\text{-}X + O\text{-}X \rightarrow OH\text{-}X$

$H\text{-}X + OH\text{-}X \rightarrow H_2O\text{-}X + X$

$H_2O\text{-}X \leftrightarrow H_2O + X$

- CO oxidation on Pt

$CO + X \leftrightarrow CO\text{-}X$

$O_2 + X \leftrightarrow O_2\text{-}X$

$O_2\text{-}X + X \leftrightarrow 2\,O\text{-}X$

$CO\text{-}X + O\text{-}X \rightarrow CO_2\text{-}X$

$CO_2\text{-}X \leftrightarrow CO_2 + X$

- H_2 + CO co-oxidation on Pt ???

Proposed Schemes for Co-oxidation

Scheme 1

H-X + CO-X ←→ HCO-X + X

HCO-X + O-X ←→ CO_2-X + H-X

H-X + CO-X + O-X ←→ CO_2-X + H-X

H_2 + 2 X ←→ 2 H-X

O_2 + 2 X ←→ 2 O-X

H-X + O-X → OH-X

H-X + OH-X → H_2O-X + X

H_2O-X ←→ H_2O + X

Scheme 2

H-X + O-X → OH-X + X

OH-X + CO-X ←→ COOH-X + X

COOH-X + X ←→ CO_2-X + H-X

H-X + CO-X + O-X ←→ CO_2-X + H-X

CO + X ←→ CO-X

O_2 + X ←→ O_2-X

O_2-X + X ←→ 2 O-X

CO-X + O-X → CO_2-X

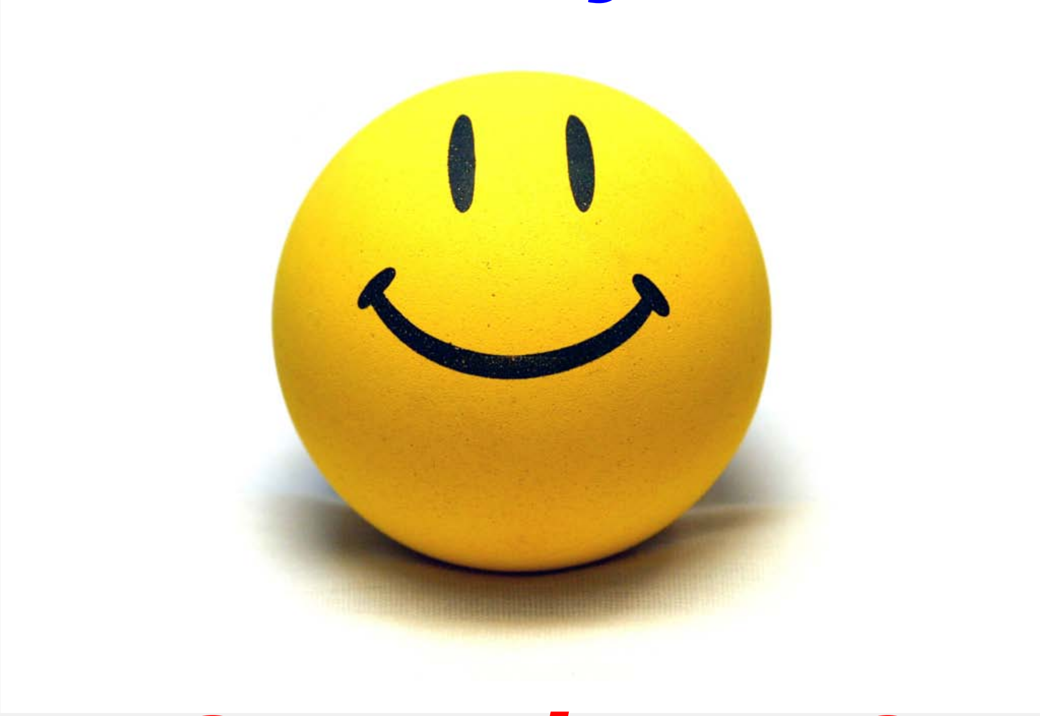
CO_2-X ←→ CO_2 + X

Hauptman et al., Appl. Catal. A., ***174,*** *397 (2011)*

Conclusions

- Low temperature oxidation remains challenging problem in vehicle exhaust abatement
- Complex spatio-temporal temperature features during transient oxidation of H_2 on Pt/CeO_2
- Enhancement of CO oxidation by H_2 at low temperature requires further development of new kinetic model

Thank you!



Questions ?