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Design and Characterization of a Small Volume Reactor for the High Pressure Invacuo Study of Catalytic Surface Reactions

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Christopher H. Clark, Jack E. Fulton, Timothy W. Adams
Egor Podgornov, and Francisco Zaera

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Outline

- Introduction
  - Surface Science in catalysis (the big picture)
  - Why design a high pressure-invacuo reactor?
  - What is a high pressure-invacuo reactor and how does it work?
- Results
  - Computational Fluid Dynamics (CFD)
  - Kinetic studies on CO oxidation
- Summary (Experiment-Model-Design Change)

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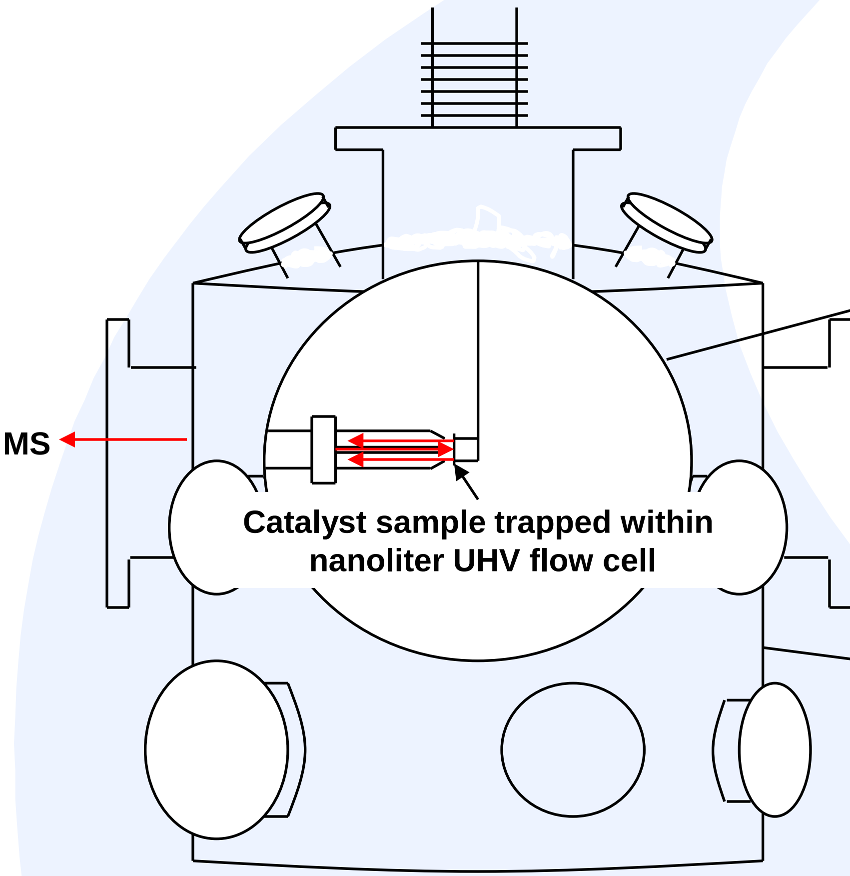
Surface Science in Catalysis (The Big Picture)

- Catalysis is an old field (1880s) integral in modern life
- Catalytic problems still lie at the heart of fuel cell problems
- Nature of the catalytic active site is still an enigma
- Two approaches to catalysis:
  - Theorists (catalytic theory from quantum mechanics)
  - Experimentalists (scanning thousands of catalysts)
- Surface science in catalysis attempts to bridge the gap between these two groups

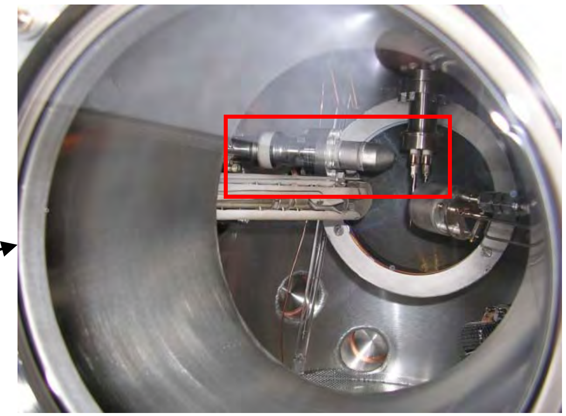
Why Design a high pressure-invacuo reactor?

- The nature of the catalytic reactive site remains a mystery
- Surface techniques such as Auger Electron Spectroscopy (AES), X-ray Photoelectron Spectroscopy (XPS), and Mass Spectrometry require ultra-high vacuum (UHV).
- Such a reactor could mimic industrial conditions on the catalyst surface with high localized pressure, but use UHV surface techniques
- Catalysis literature reveals a pressure gap where ethylene hydrogenation is shown to have one set of kinetics under UHV conditions and another under industrial conditions such a system could bridge this gap

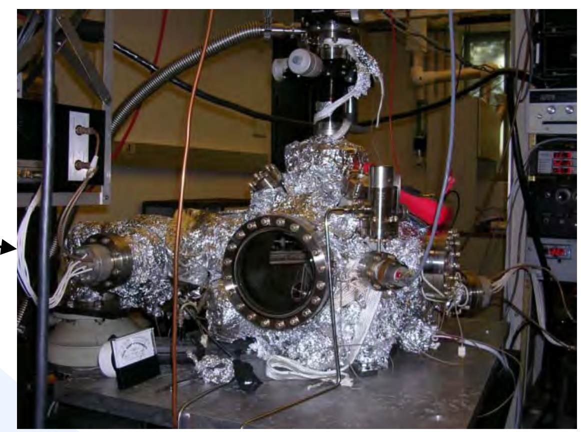
High Pressure-invacuo Reactor



Cartoon of main UHV chamber and doser flow

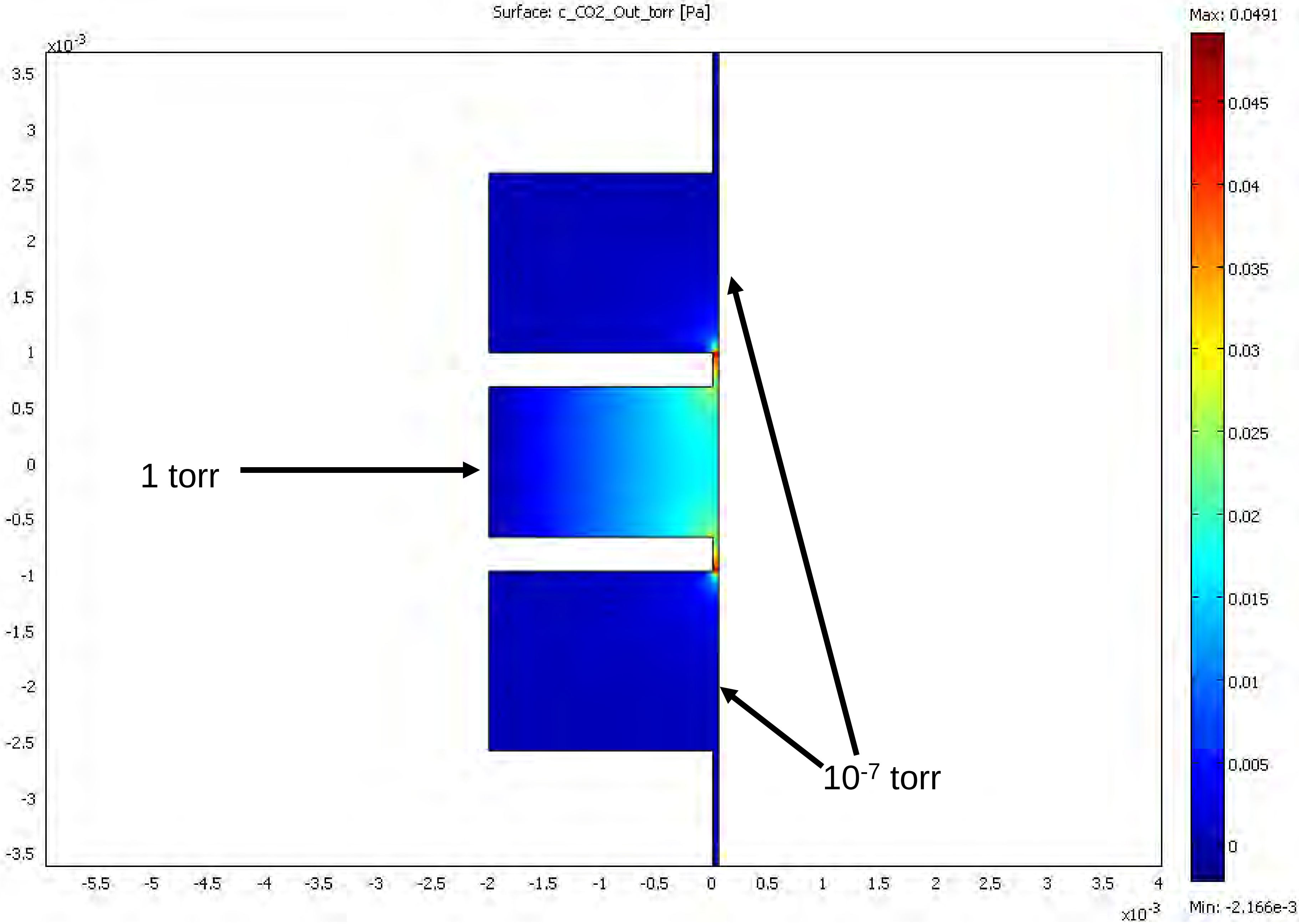


Inner View of main UHV Chamber (with doser prominent)

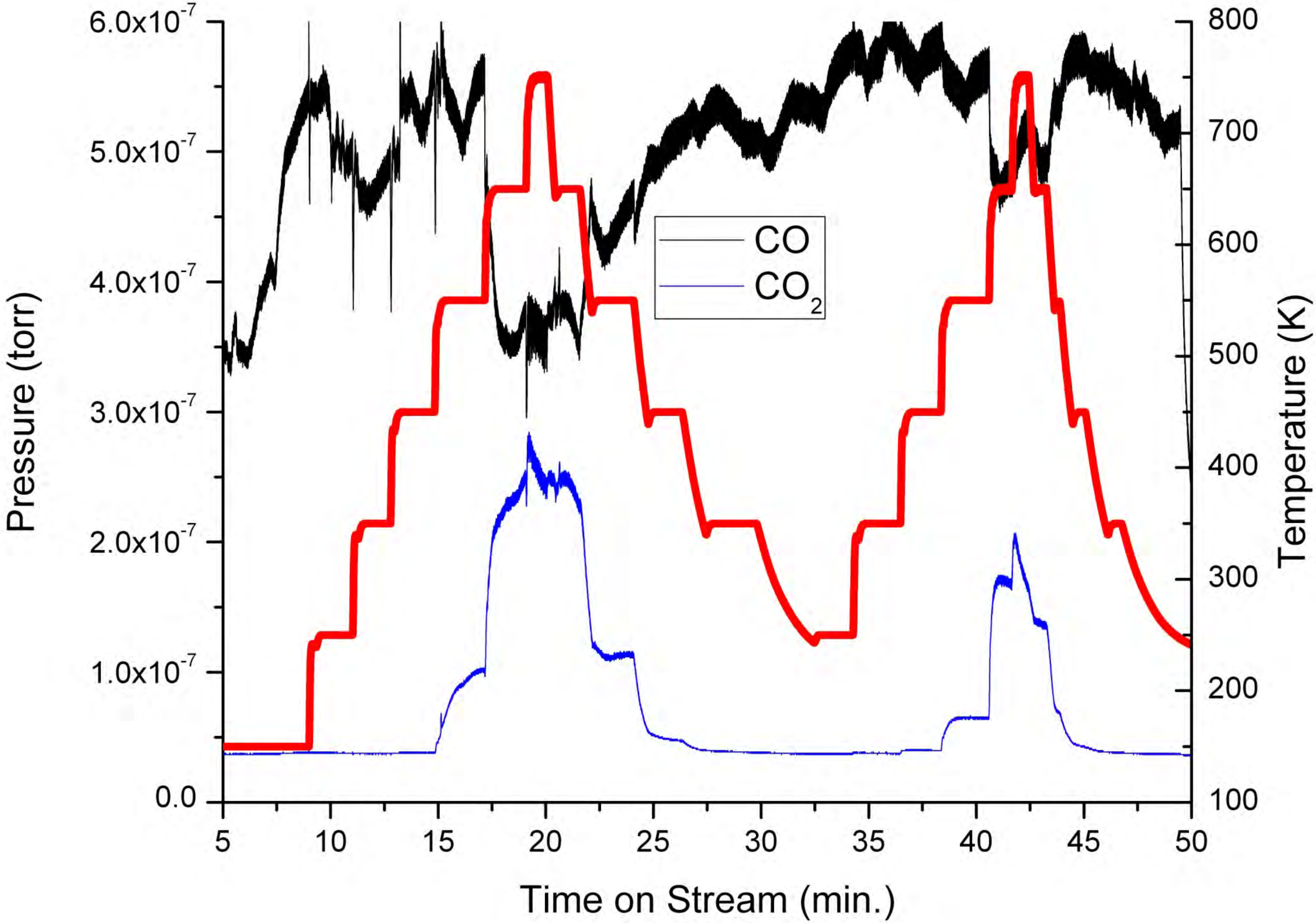


Two chamber differentially pumped UHV system

Concentric tube conical doser

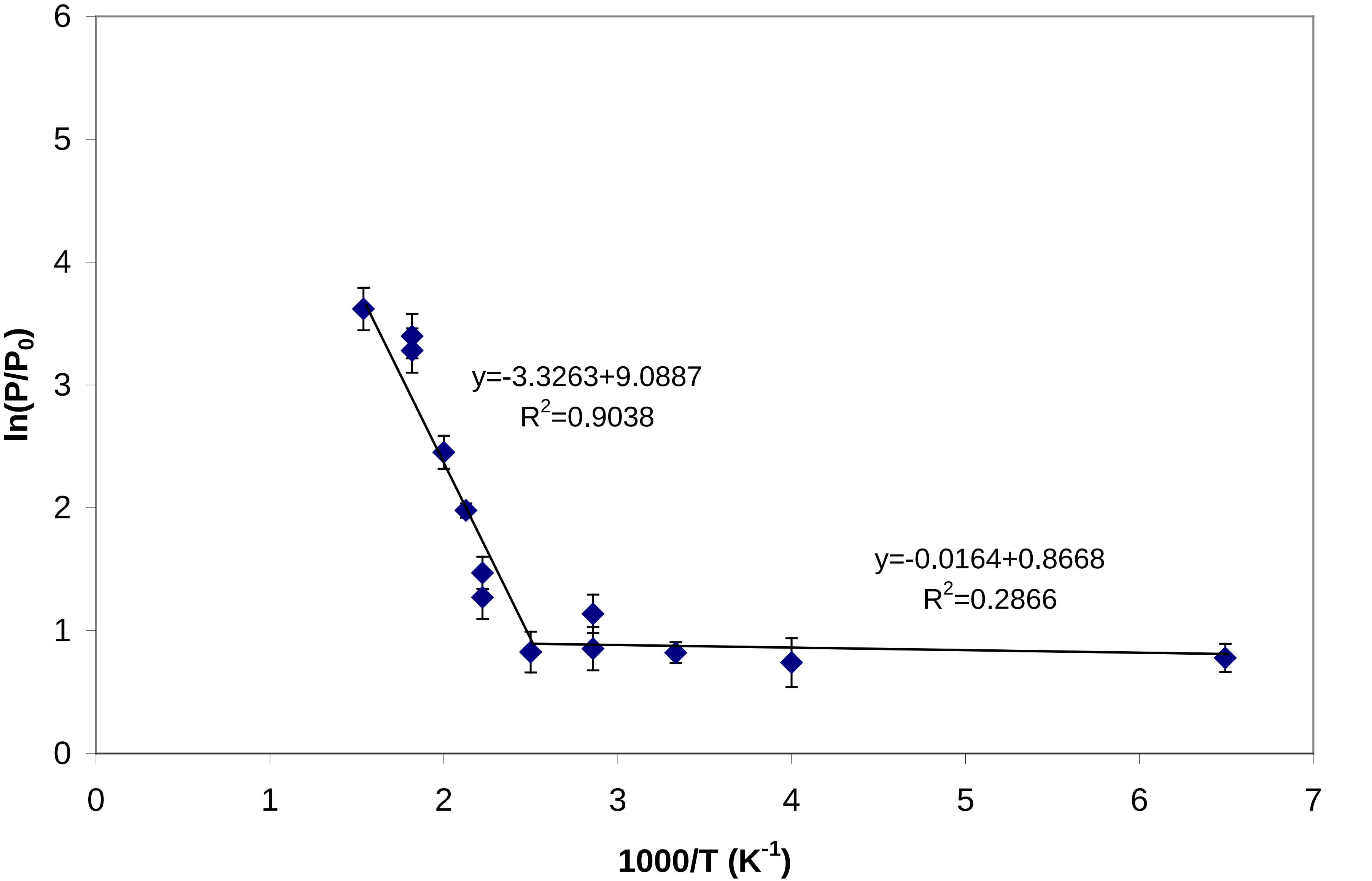


Surface: c_CO2_Out_torr [Pa]
Max: 0.0491
Min: -2.166e-3
x10^-3
1 torr
10^-7 torr

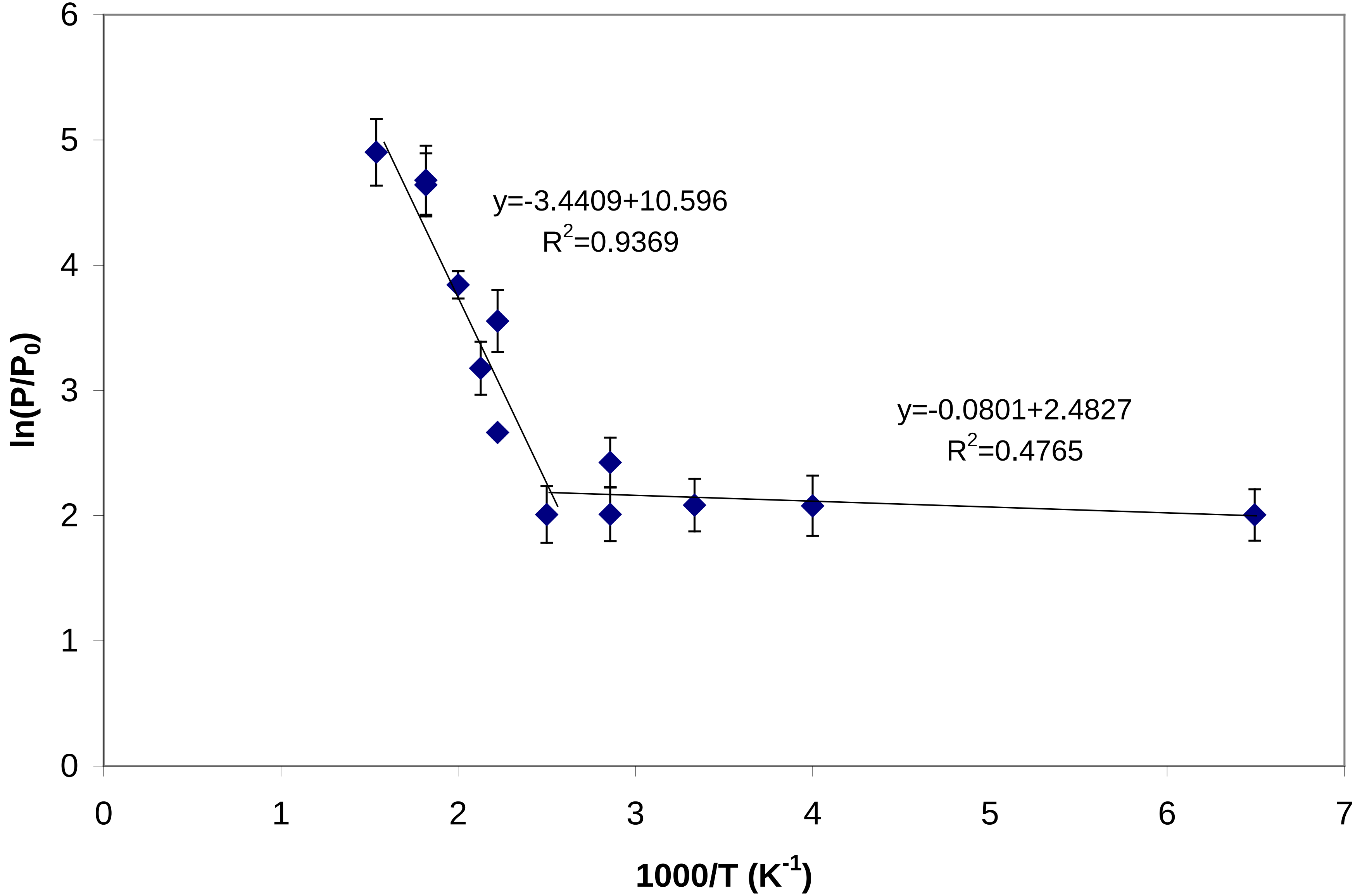


6.0x10-7
5.0x10-7
4.0x10-7
3.0x10-7
2.0x10-7
1.0x10-7
0.0
Pressure (torr)
800
700
600
500
400
300
200
100
Temperature (K)
5
10
15
20
25
30
35
40
45
50
Time on Stream (min.)
CO
CO2

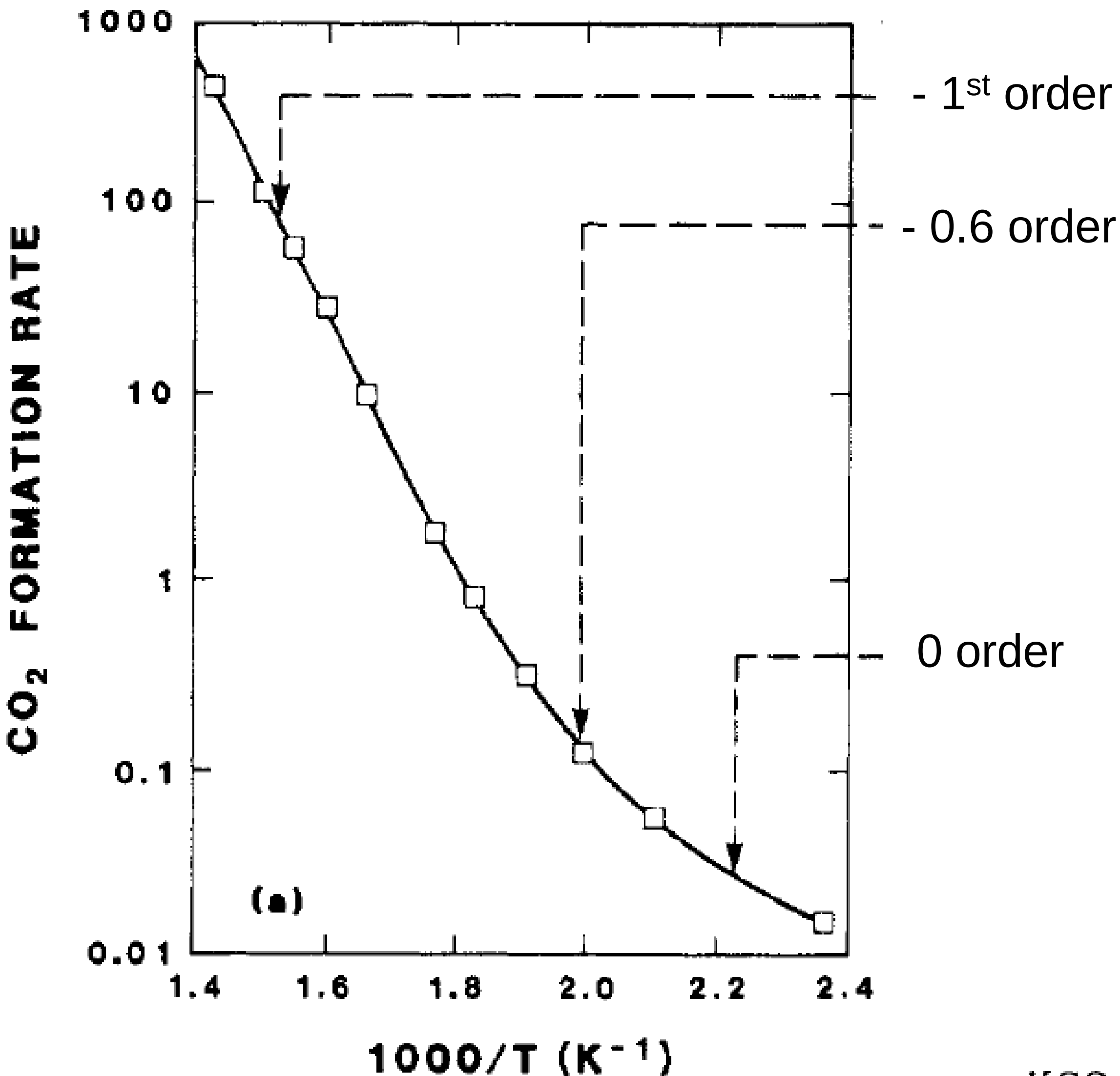
Probe chamber Arrhenius plot of CO oxidation on Pt(111) at a backing pressure of 1 torr



Main Chamber Arrhenius plot of CO oxidation on Pt(111) at a backing pressure of 1 torr



High Pressure Arrhenius Plot for CO oxidation on Pt(100)
(Goodman et al., *J. Phys. Chem.*, 1988)

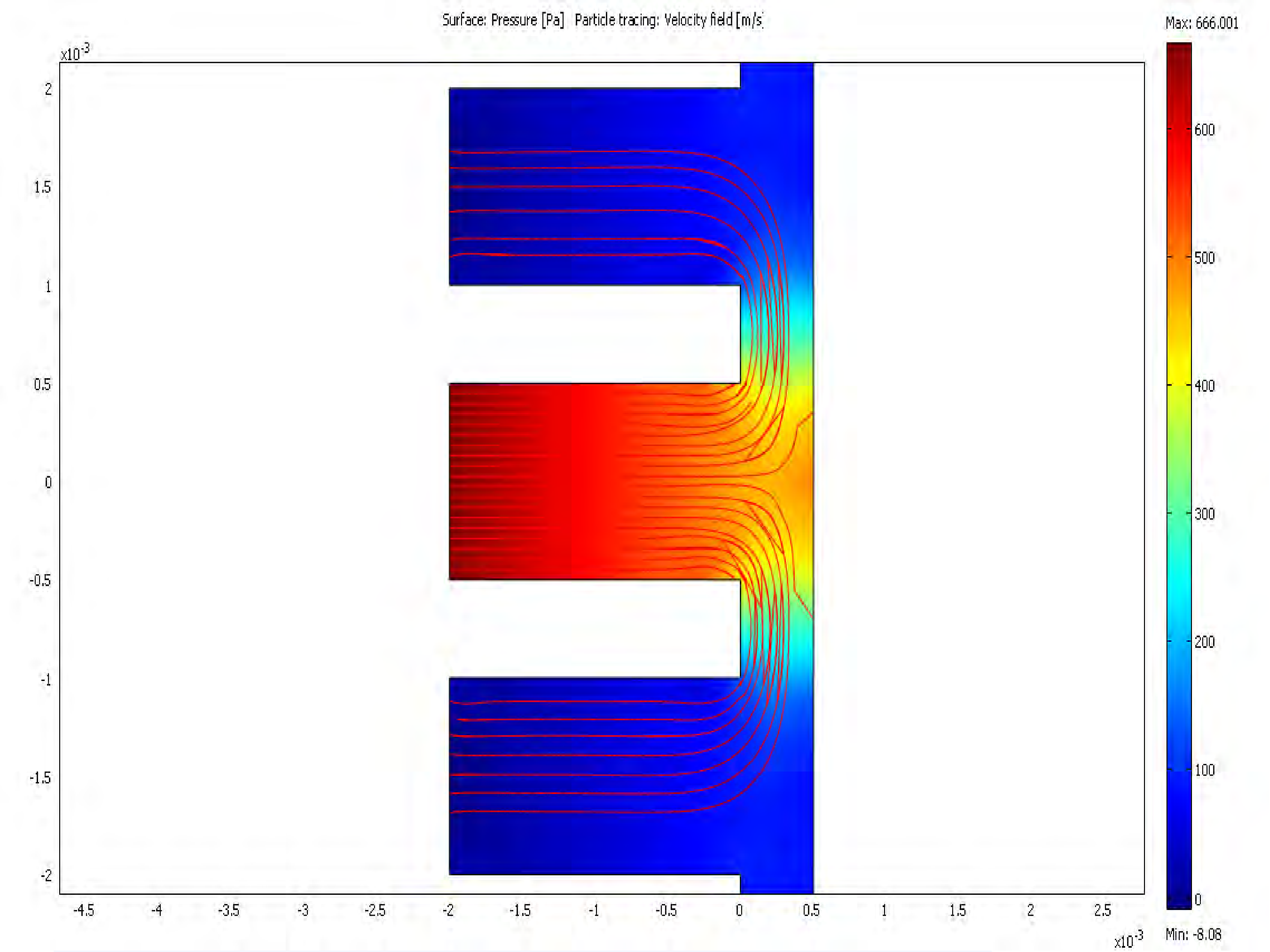


$$CO(g) \leftrightarrow CO(ads)$$

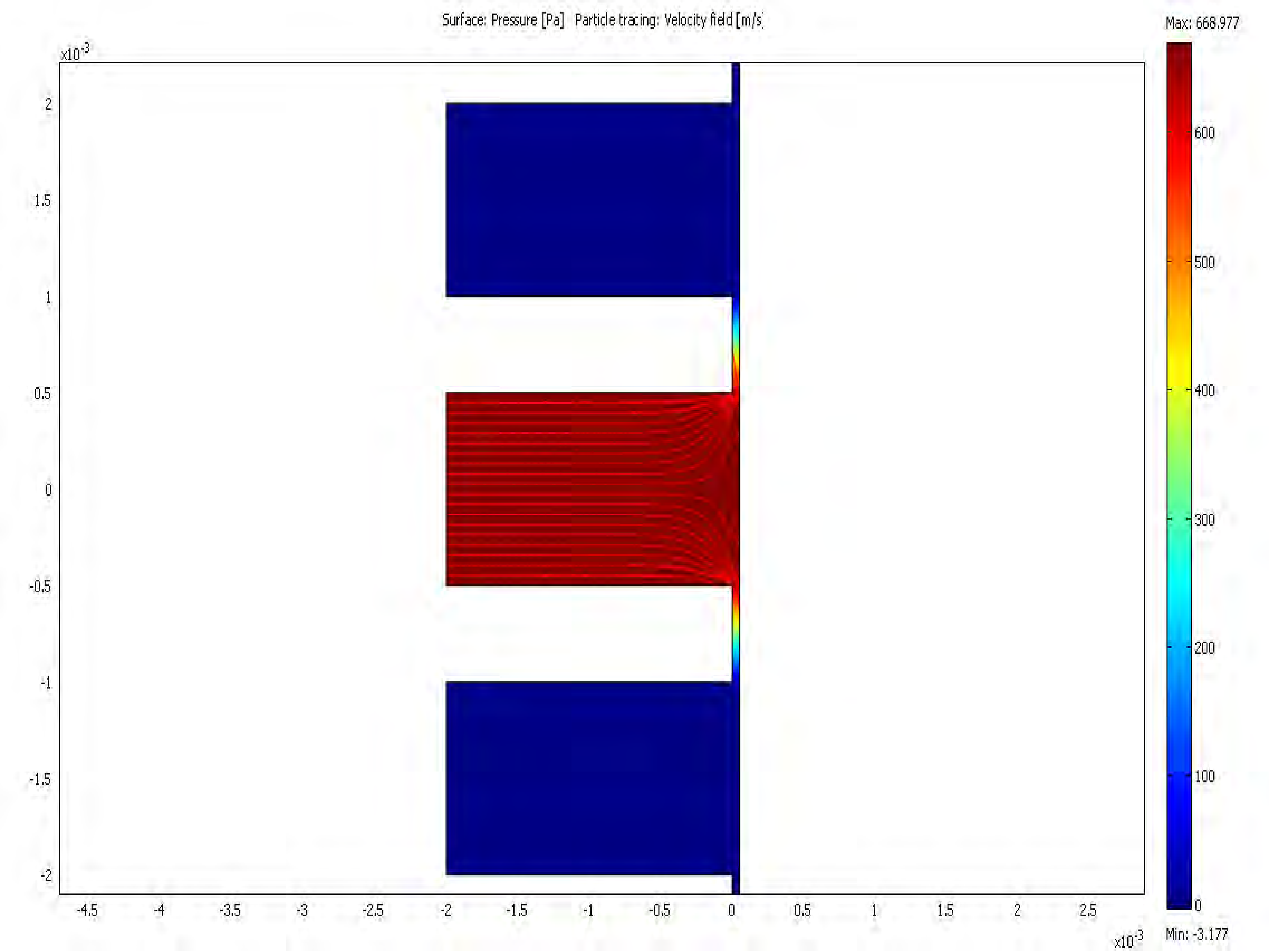
$$O_2(g) \rightarrow 2O(ads)$$

$$CO(ads) + O(ads) \rightarrow CO_2(g)$$

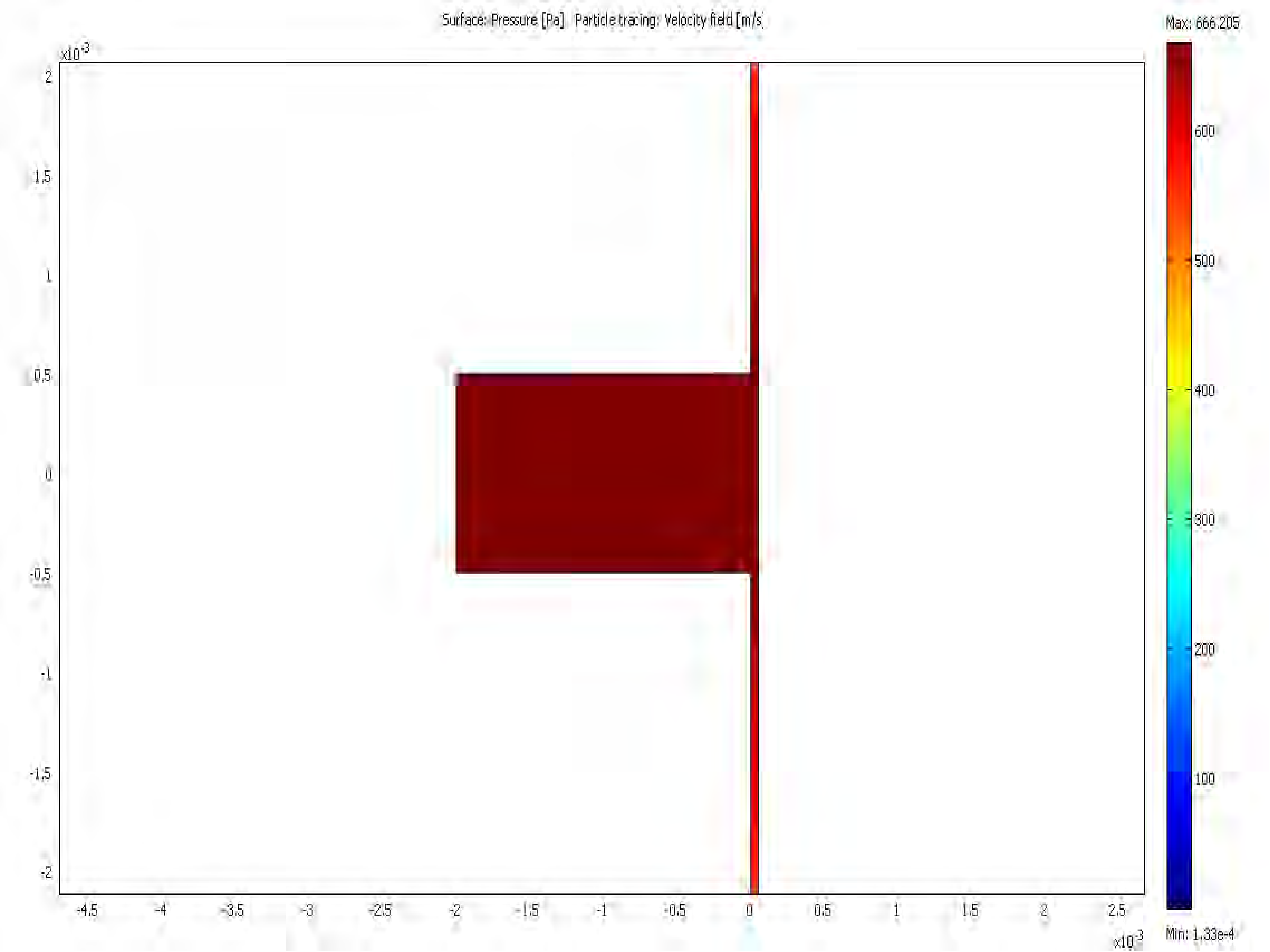
$$d[CO_2]/dt = k \exp(-E_{des,CO}/RT)P_{O_2}/P_{CO}$$



Surface: Pressure [Pa] Particle tracing: Velocity field [m/s]
Max: 666.001
Min: -8.08
x10^-3
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
-4.5
-4
-3.5
-3
-2.5
-2
-1.5
-1
-0.5
0
0.5
1
1.5
2
2.5
x10^-3
600
500
400
300
200
100
0



Surface: Pressure [Pa]   Particle tracing: Velocity field [m/s]
Max: 668.977
Min: -3.177
x10^-3
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
-4.5
-4
-3.5
-3
-2.5
-2
-1.5
-1
-0.5
0
0.5
1
1.5
2
2.5
x10^-3
600
500
400
300
200
100
0



Surface: Pressure [Pa] Particle tracing: Velocity field [m/s
Max: 666.205
600
500
400
300
200
100
Min: 1.33e-4
x10^-3
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
-4.5
-4
-3.5
-3
-2.5
-2
-1.5
-1
-0.5
0
0.5
1
1.5
2
2.5
x10^-3

Summary

- The role of surface science in catalysis as worked on here is to bridge the “pressure gap”
- CO oxidation kinetics generally follow literature values for other high pressure reaction systems and agree with computational models
- CFD has led to an estimates of crystal pressure and some strategies to optimize geometry to improve molecular impingement
- The current reactor design is not optimized for low probability reactions

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