SAND2022-2220C

Operando Near-Surface Imaging of the Multi-Component Gas Phase above a Catalyst

Jonathan Frank

Combustion Research Facility
Sandia National Laboratories
Livermore, CA
jhfrank@sandia.gov

Nils Hansen, David Osborn, Erxiong Huang, Angie Zhang – Sandia National Laboratories

Coleman Kronawitter, Ambarish Kulkarni, Sadi Gurses – University of California Davis

Bo Zhou – Sandia National Laboratories, Southern University of Science and Technology

Recent publications
ACS Catalysis 11:155-168 (2021)
J. Phys. Chem. Lett. 12:11252-11258 (2021)

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Probing Coupled Gas-Phase and Surface Chemistry

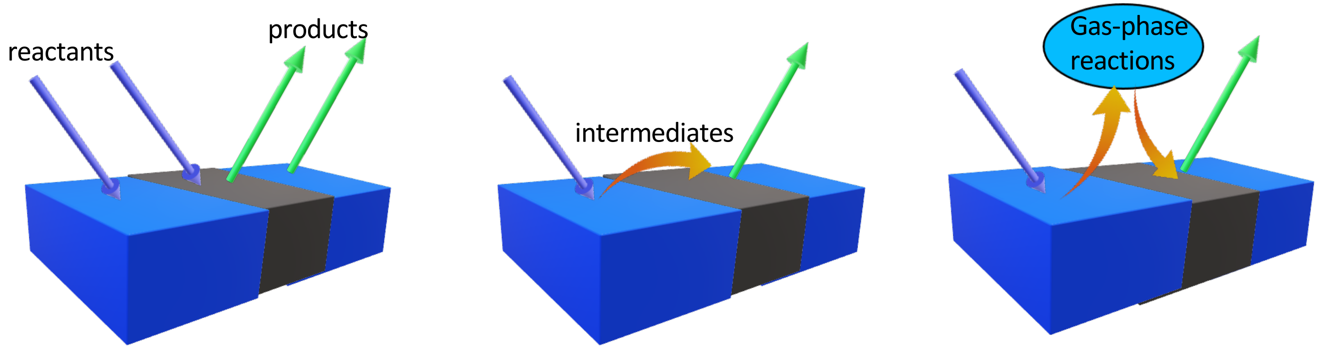
Combine Tools of Gas Phase Chemical Physics with Surface Science → Fundamental Mechanistic Insight

Gas: Laser-Induced Fluorescence, Spontaneous and Coherent Raman, Molecular Beam Mass Spectrometry

Surface: ambient pressure x-ray photoelectron spectroscopy, sum-frequency generation vibrational spectroscopy

Which reaction steps happen on surface vs. in gas phase?

Can we use the gas phase as a spatially resolved reporter of surface activity?



Surface-mediated reactions

Gas-phase transport of reaction intermediates

Coupling of gas-phase reactions and surface reactions

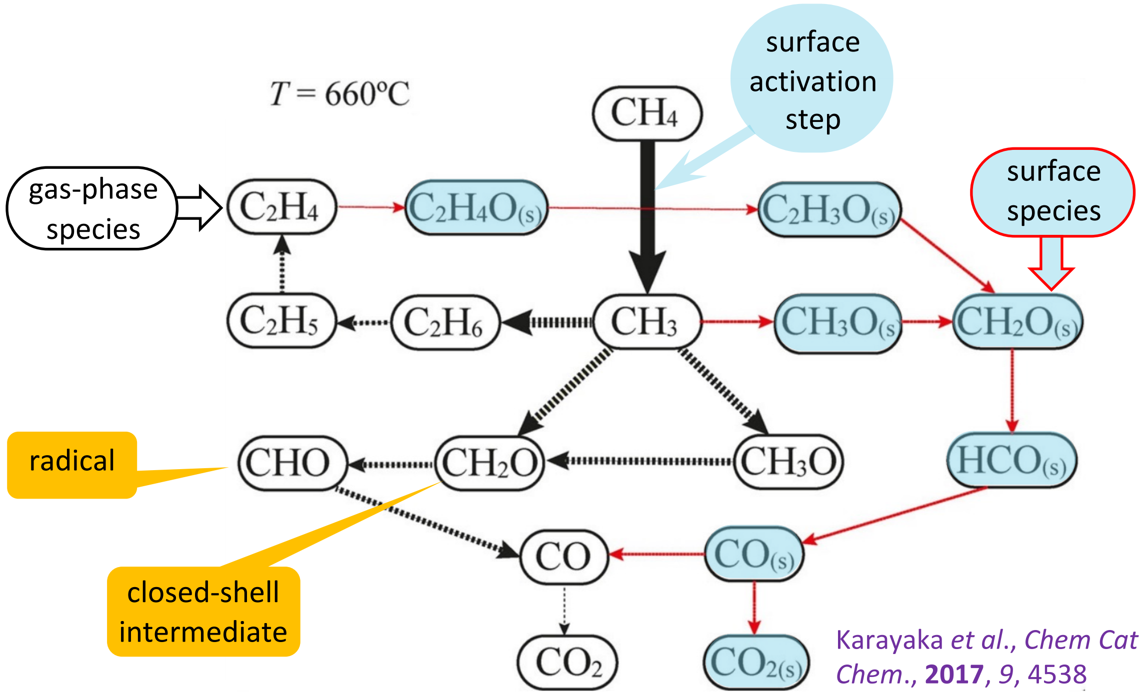
Increasing complexity of gas-phase interactions with multidomain reactive surface

Are reactive intermediates transported in gas phase or on the surface?

Can we validate micro-kinetic mechanisms against detailed species maps?

Coupled Gas-Surface Chemistry

Oxidative coupling of CH_4 over La_2O_3/CeO_2 catalyst

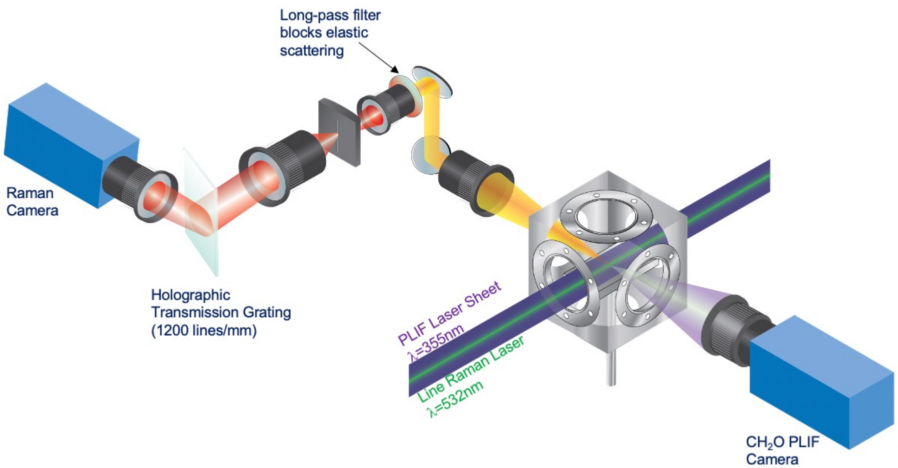


Karayaka *et al.*, *Chem Cat Chem.*, **2017**, *9*, 4538

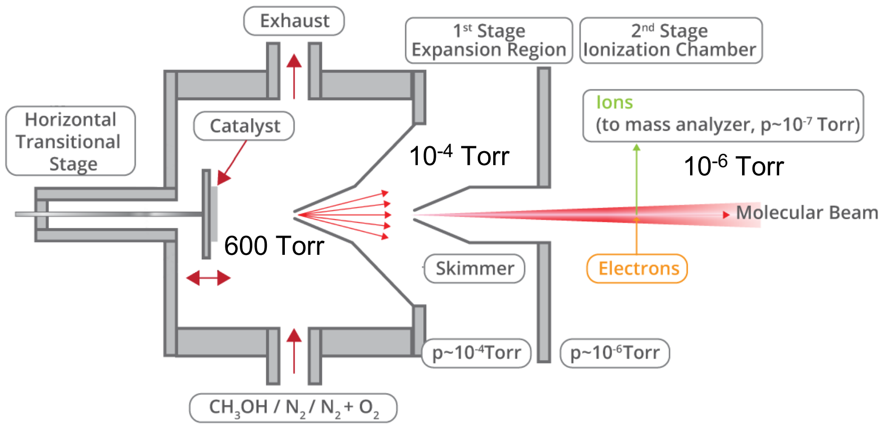
Red arrows = surface reactions
Black dashes = gas-phase reactions

LIF/Raman Imaging and MBMS of Near-Surface Gas-Phase

Planar Laser-Induced Fluorescence/Raman Imaging



Near-Surface Molecular Beam Mass Spectrometry

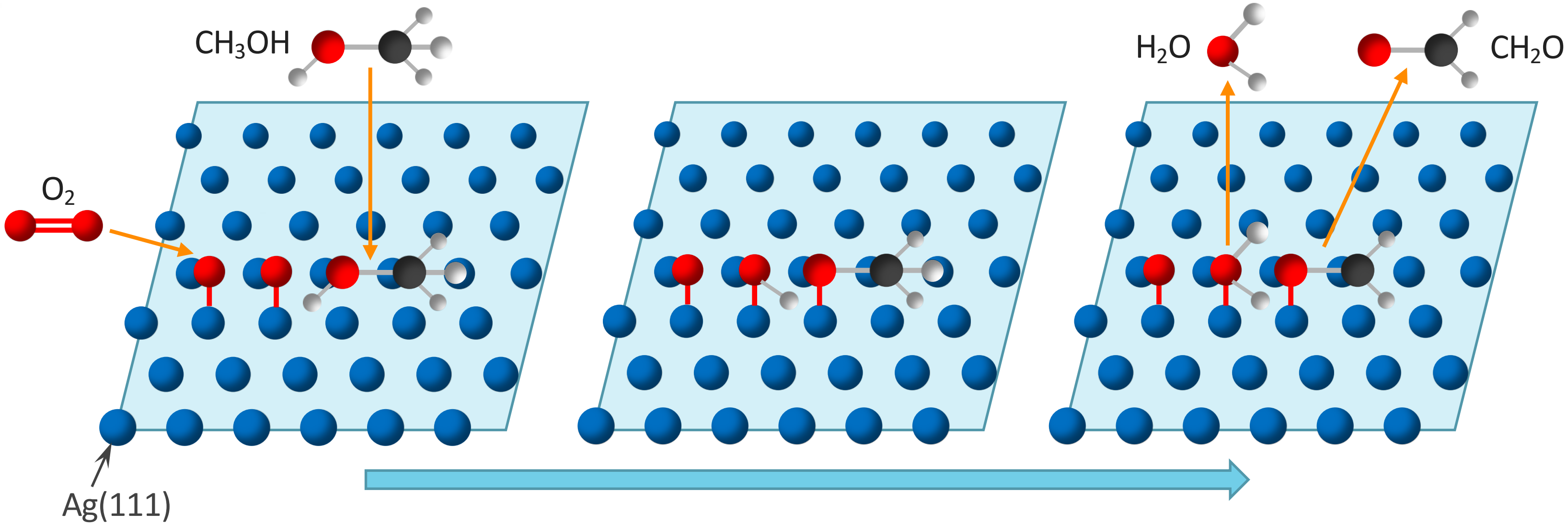


Test Case: Formaldehyde Production by Partial Oxidation of Methanol over a Silver Catalyst

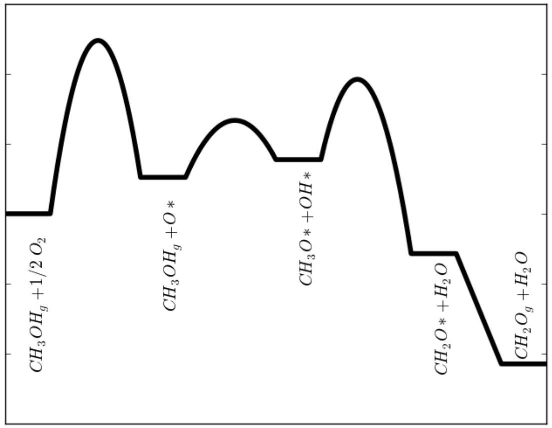
$$CH_3OH + \frac{1}{2}O_2 \rightarrow CH_2O + H_2O \quad \Delta H = -38 \text{ kcal/mol}$$

$$CH_3OH \rightarrow CH_2O + H_2 \quad \Delta H = 20 \text{ kcal/mol}$$

Literature Mechanism for Partial Dehydrogenation of CH_3OH

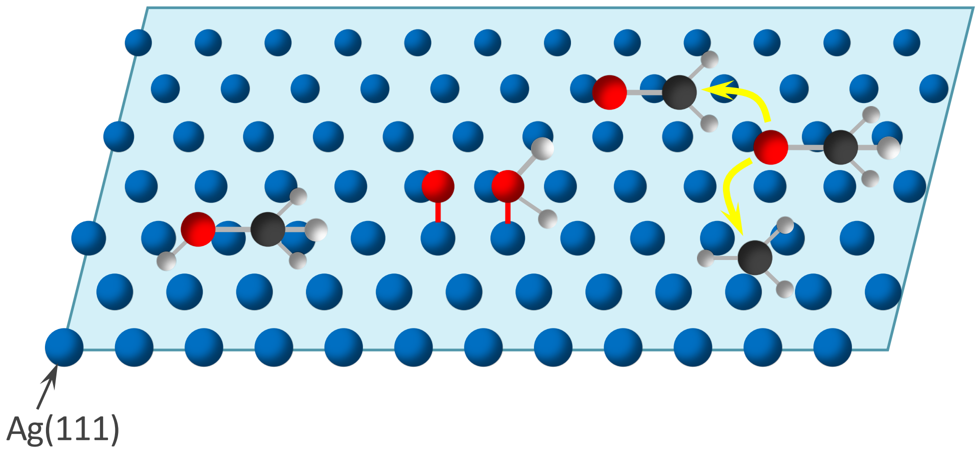


Oxidative reaction pathway for Ag(111) at 630 C

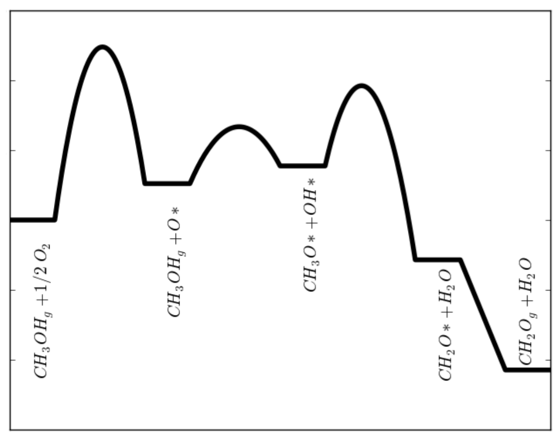


Aljama, Yoo, Nørskov, Abild-Pedersen, Studt, ChemCatChem 8, 3621-3625 (2016)

New Chemistry in Partial Dehydrogenation of CH_3OH

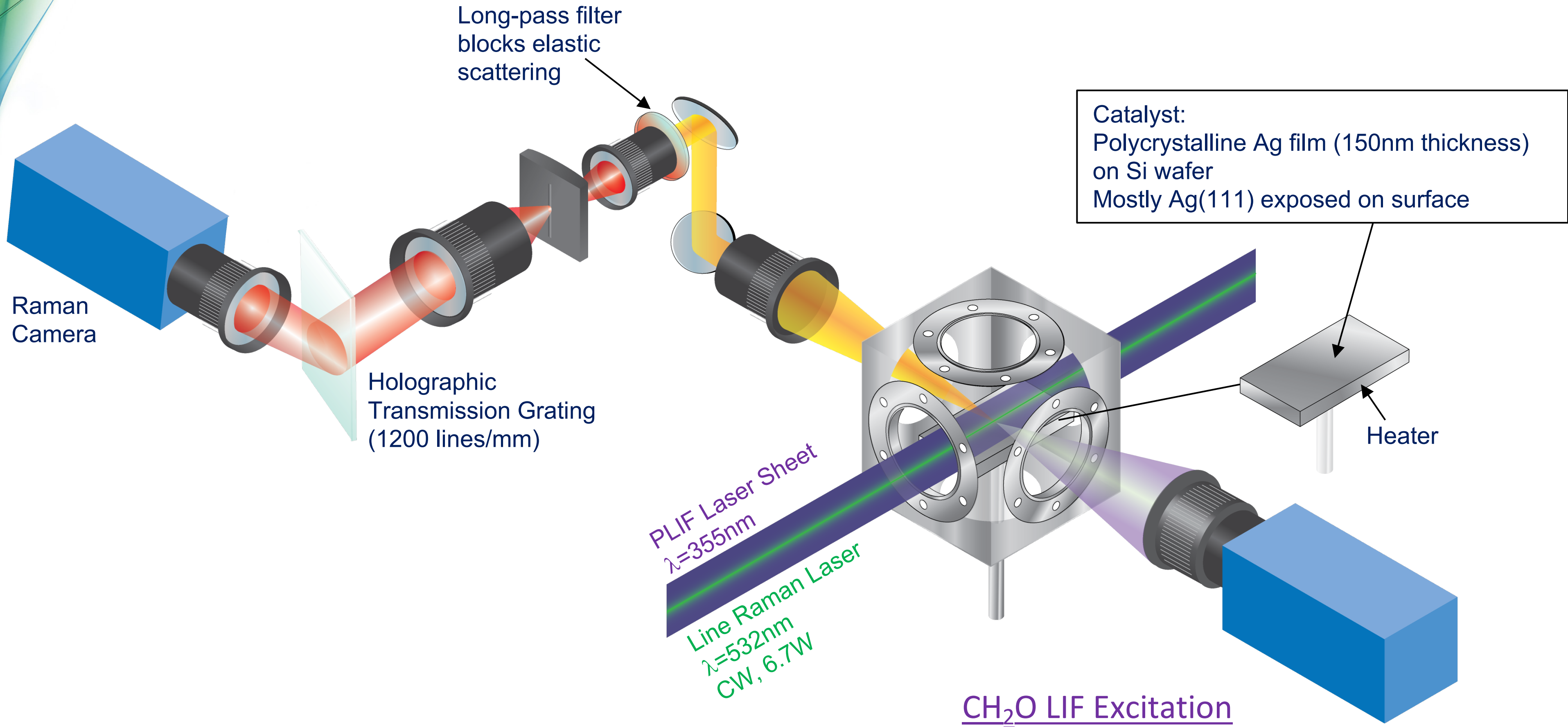


Oxidative reaction pathway for Ag(111) at 630 C



Aljama, Yoo, Nørskov, Abild-Pedersen, Studt,
ChemCatChem 8, 3621-3625 (2016)

1D Raman and 2D Laser-Induced Fluorescence Imaging of Near-Surface Gas-Phase



<u>CH_2O LIF Excitation</u>

λ = 355 nm

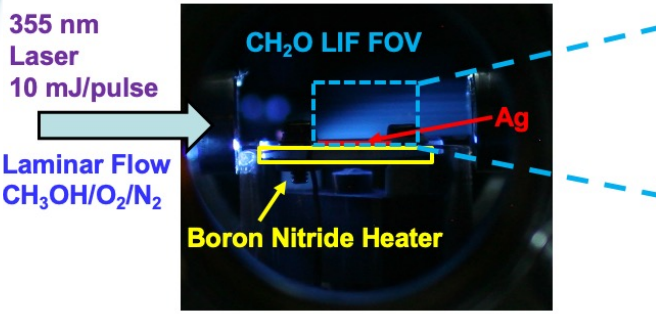
10 ns pulse, 10 mJ/pulse

4_0^1 band of

$\tilde{A}^1A_2 \leftarrow \tilde{X}^1A_1$ system

Formaldehyde LIF Imaging Captures Distribution of Catalysis Products in Boundary Layer Flow

90% N_2
7.5% CH_3OH
2.5% O_2



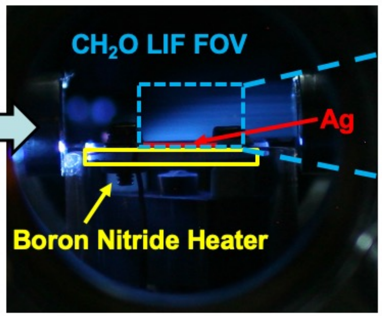
P=600 Torr
$T_{catalyst}$ *= 407 C*

Formaldehyde LIF Imaging Captures Distribution of Catalysis Products in Boundary Layer Flow

90% N_2
7.5% CH_3OH
2.5% O_2

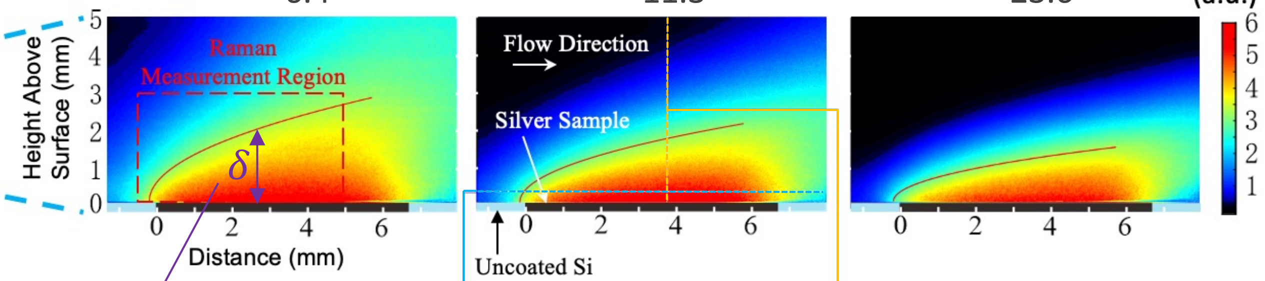
355 nm Laser 10 mJ/pulse

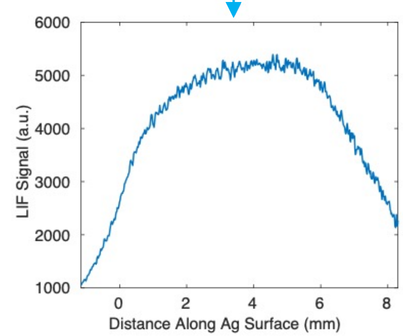
Laminar Flow $CH_3OH/O_2/N_2$

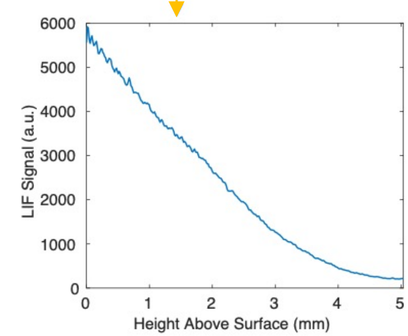


P=600 Torr
$T_{catalyst} = 407\ C$

Increasing flow rate







Blasius solution to Navier-Stokes equations for boundary layer flow

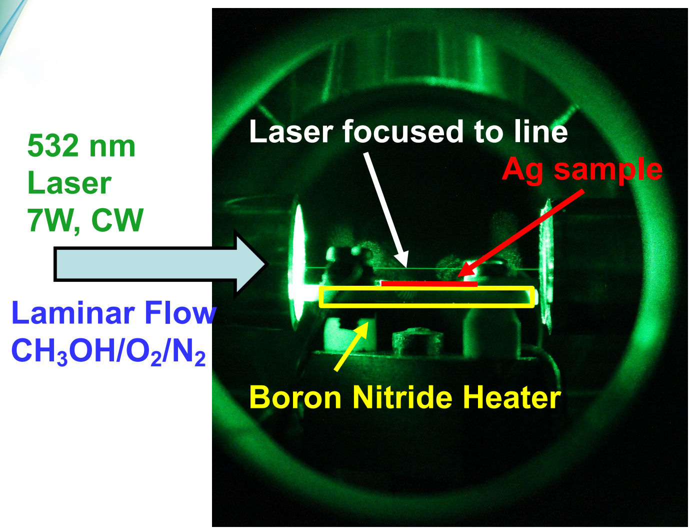
Boundary Layer Thickness: $\delta \propto \sqrt{Dx/u}$

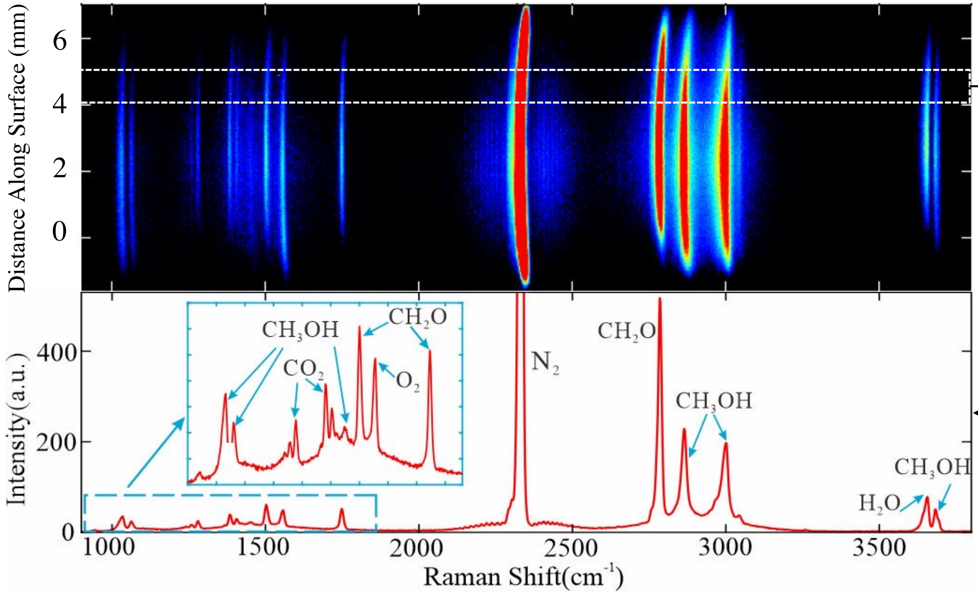
D = Diffusion Coefficient

x = Streamwise Distance

u = Streamwise Velocity

1D Raman Scattering Measurements

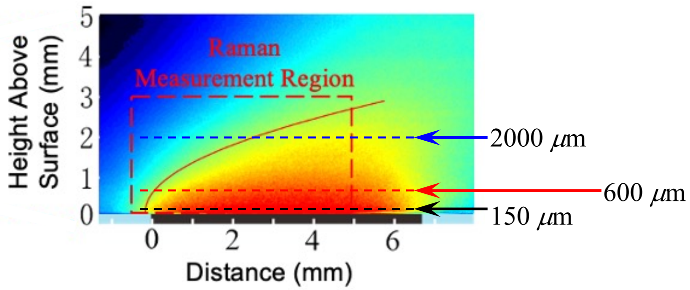


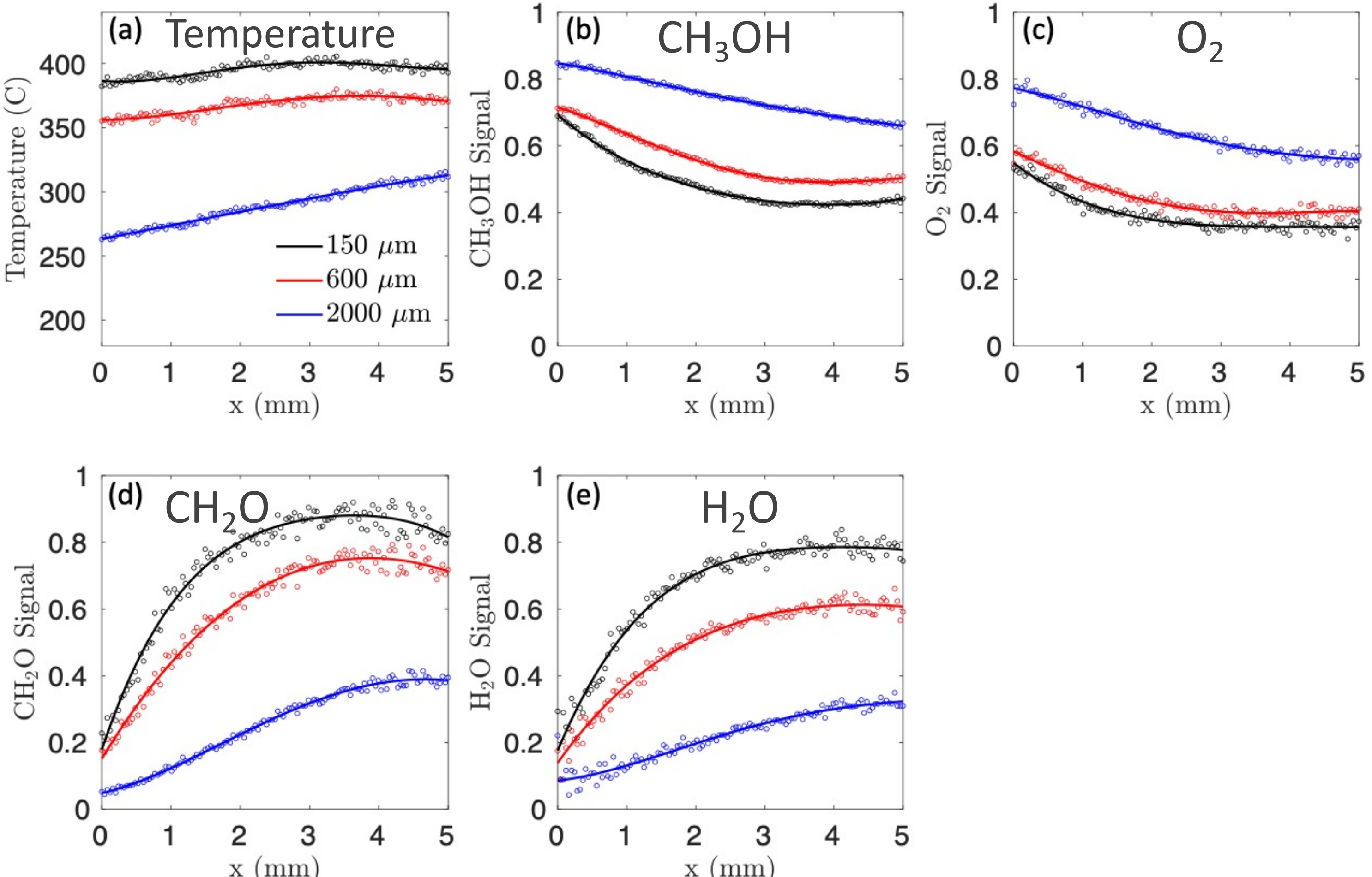


1D Raman imaging spectrum for 60-second integration

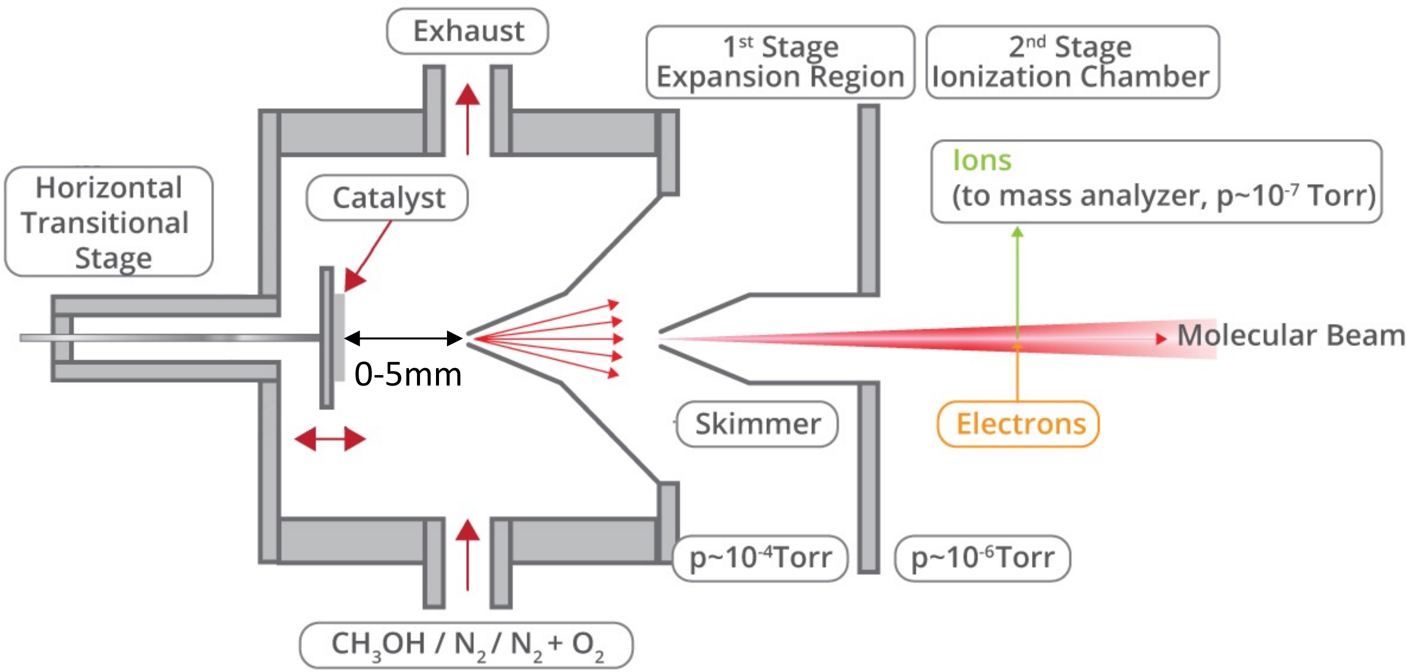
- Measure all major species simultaneously
- Detection to within ~60 µm of surface
- Correct for optical throughput, background, spectral cross-talk, temperature-dependent Raman scattering cross sections

Raman Spectroscopy Probes Consumption and Production Profiles



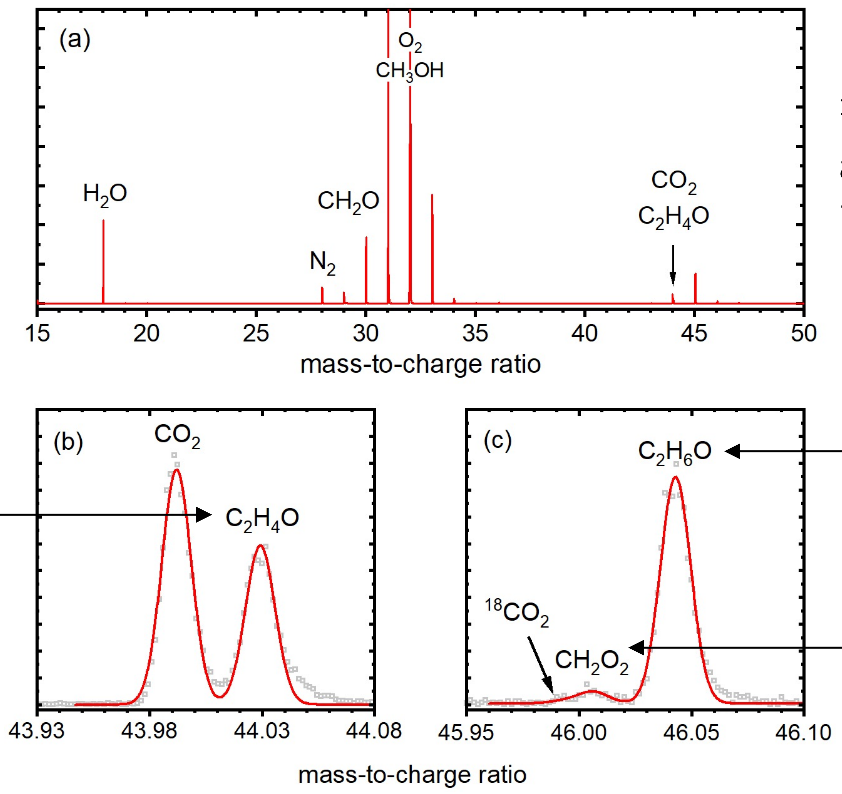


Complementary Molecular Beam Mass Spectrometry of Near-Surface Gas Phase



- Reactor chamber: P = 600 Torr
- Quartz sampling probe with ~50 µm diameter
- Electron ionization with ΔE (FWHM) = 2.2 eV
- Mass resolution m/Δm ~ 3500

Overview of Mass Spectrum
Mass-to-Charge Ratio 15-50 amu



Reactants O_2, CH_3OH with ^{13}C and ^{18}O isotopologues and N_2 buffer along with intermediates/products

Acetaldehyde (CH_3CHO)

Only detected molecule with C-C bond

Dimethyl ether (CH_3OCH_3)

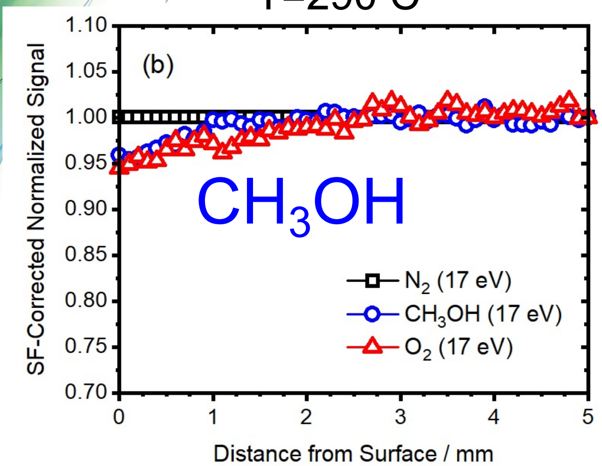
Formic Acid (HCOOH)

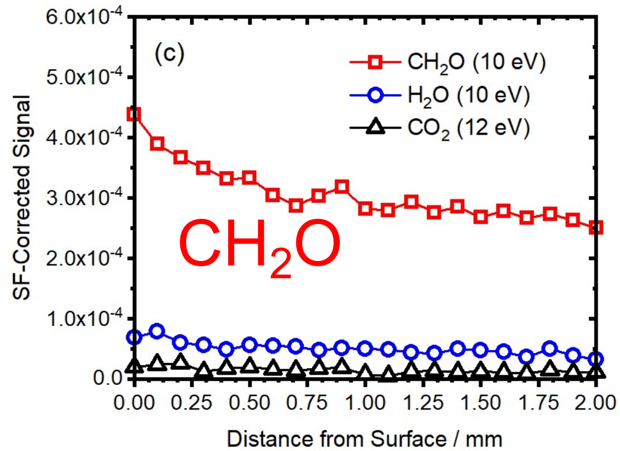
Not shown: peaks at *m/z*=60.021 ($C_2H_4O_2$), *m/z*=62.037 ($C_2H_6O_2$)– assign to methyl formate and methoxy methanol, respectively

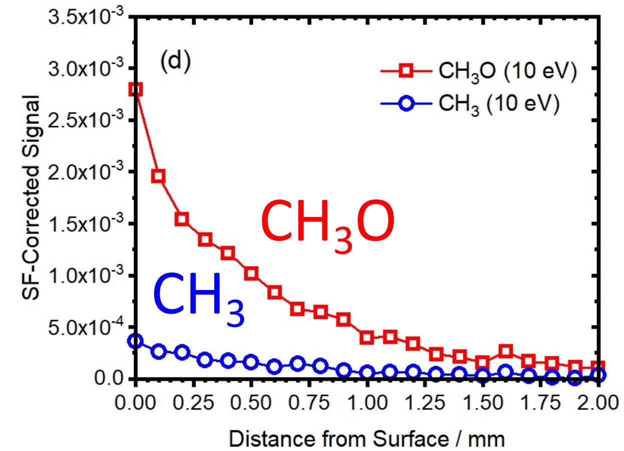
* Electron ionization does not provide conclusive isomeric assignments

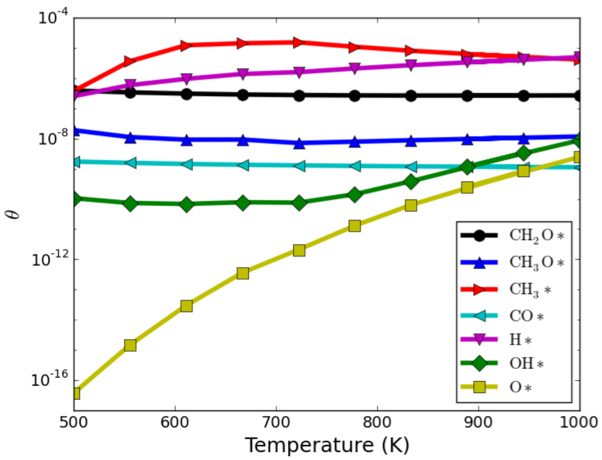
Mapping Reactants, Intermediates, and Products Near-Surface Mass Spectrometry

T=290 C









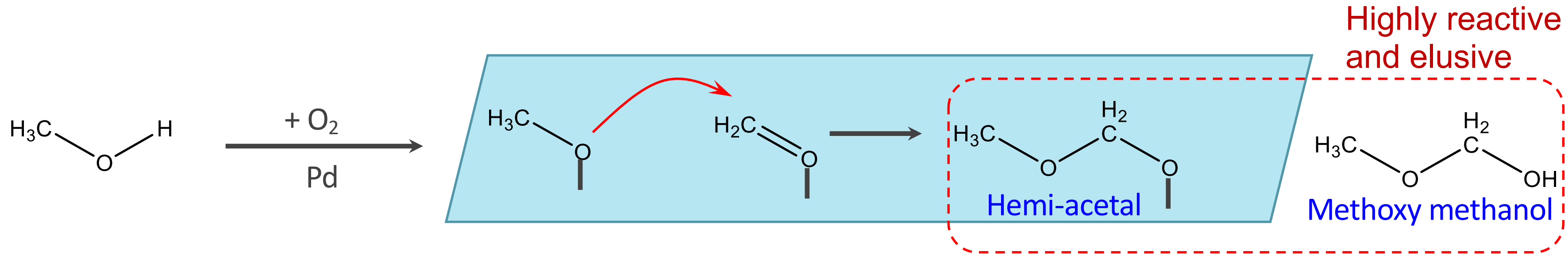
Nørskov group partial methanol oxidation model on Ag(111)

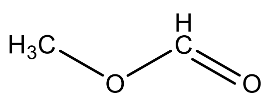
- Surface species: CH_3^*, CH_2O^*, CH_3O^*, CO^*
- CH_3^* has highest surface coverage (200-700 C)
- Production and ejection of CH_3O and CH_3 not previously observed

50-reaction kinetic model: Aljama, Yoo, Nørskov, et al., ChemCatChem 8, 3621-3625 (2016)

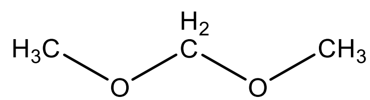
Reactive Intermediates in Partial Oxidation of Methanol over Palladium

Catalytic transformation of methanol is a pathway to many commodity chemicals under mild conditions

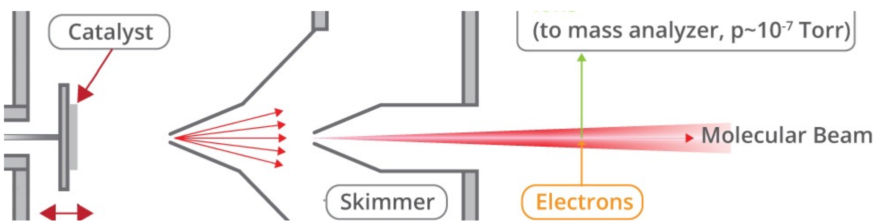




Methyl formate



Dimethoxy methane



Methoxy methanol proposed as a critical intermediate in methyl formate production, but it is rarely detected.

Don’t usually observe intermediate species resulting from initial C-O-C coupling.

Reactive intermediates provide mechanistic insight in the near-surface region

$\frac{CH_3OH}{O_2} = 0.07$

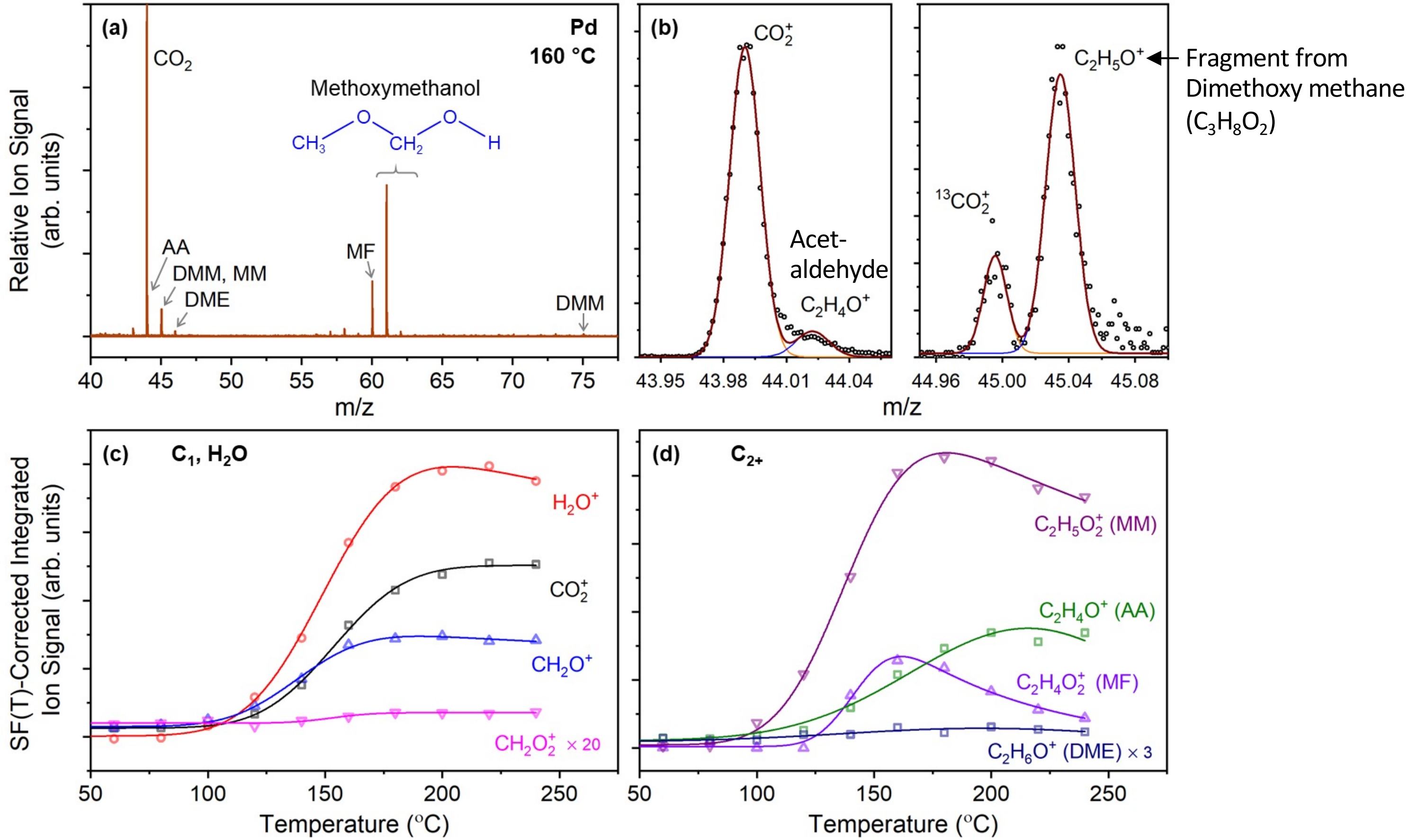
Diluent N_2

Pd(111)

P = 600 Torr

500 μm above surface

Elec. K.E. = 17 eV



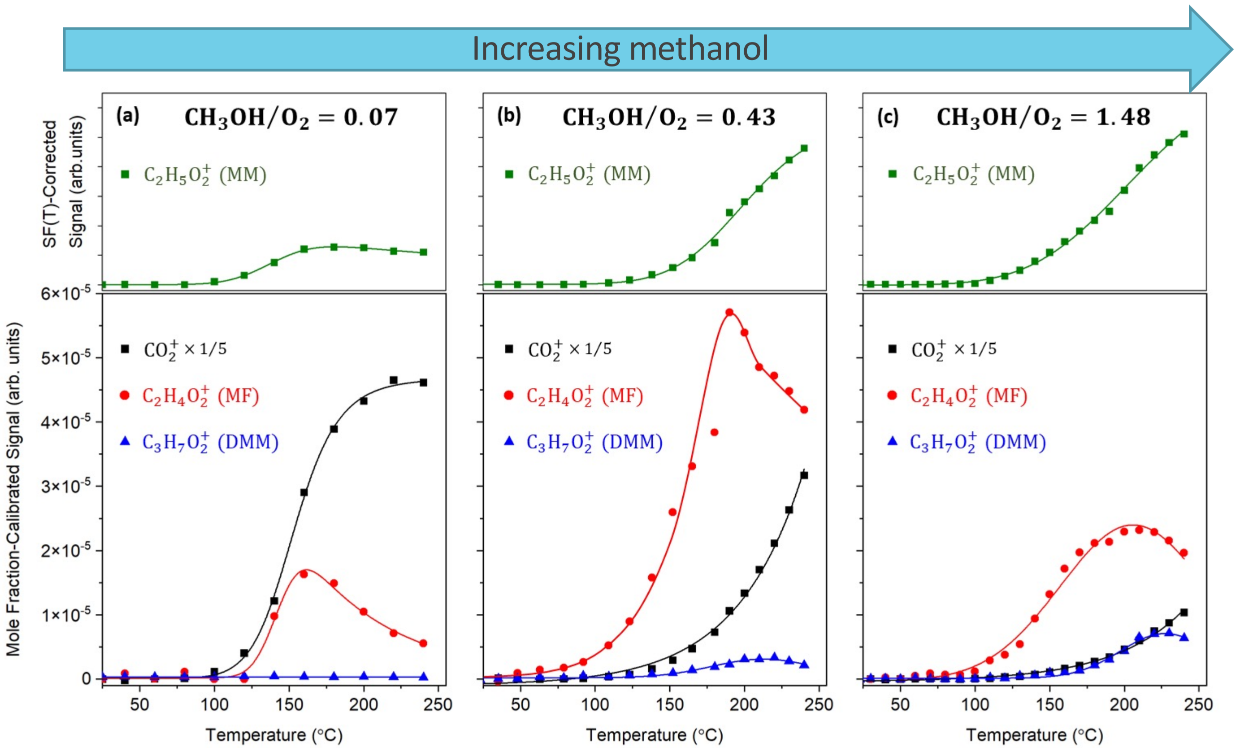
DMM = Dimethoxymethane ($CH_3OCH_2OCH_3$)

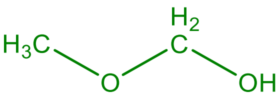
MF = Methyl formate (CH_3OCHO)

DME = Dimethyl ether (CH_3OCH_3)

AA = Acetaldehyde (CH_3CHO)

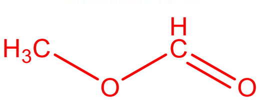
Reactive intermediates provide mechanistic insight in the near-surface region



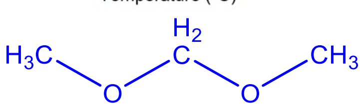


Methoxy methanol

- Complete oxidation to CO_2 decreases
- C-O-C coupling to dimethoxy methane always increases
- C-O-C coupling to methyl formate reaches a maximum



Methyl formate



Dimethoxy methane

Summary

- Diagnostics to investigate coupled chemistry at real-world conditions
- Optical approaches:
  - good spatial / temporal resolution
  - 1D and 2D imaging
- Near-surface mass spectrometry
  - Universal probing
  - Detect elusive species
- Mechanistic insights to inform / validate mechanistic models
  - Development of catalysts and microkinetic models should account for formation, desorption, adsorption, and surface reactions involving methoxymethanol

Acknowledgments

Nils Hansen, David Osborn, Erxiong Huang, Angie Zhang – Sandia National Laboratories

Coleman Kronawitter, Ambarish Kulkarni, Sadi Gurses – University of California Davis

Bo Zhou – Sandia National Laboratories, Southern University of Science and Technology

U.S. Department of Energy (DOE), Office of Basic Energy Sciences (BES), Division of Chemical Sciences, Geosciences and Biosciences

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. DOE's National Nuclear Security Administration under contract DE-NA0003525. This presentation describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the presentation do not necessarily represent the views of the U.S. DOE or the U.S. Government.