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Imaging the Gas Phase above a Reacting Surface: Partial Oxidation of Methanol Catalyzed by Silver

Jonathan Frank

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

Collaborators

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

Nils Hansen, David Osborn, Erxiong Huang, Raybel Almeida – Sandia National Laboratories

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

Johan Zetterberg - Lund University

Recent publication
ACS Catalysis 11:155-168 (2021)

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Probing Coupled Gas-Phase and Surface Chemistry

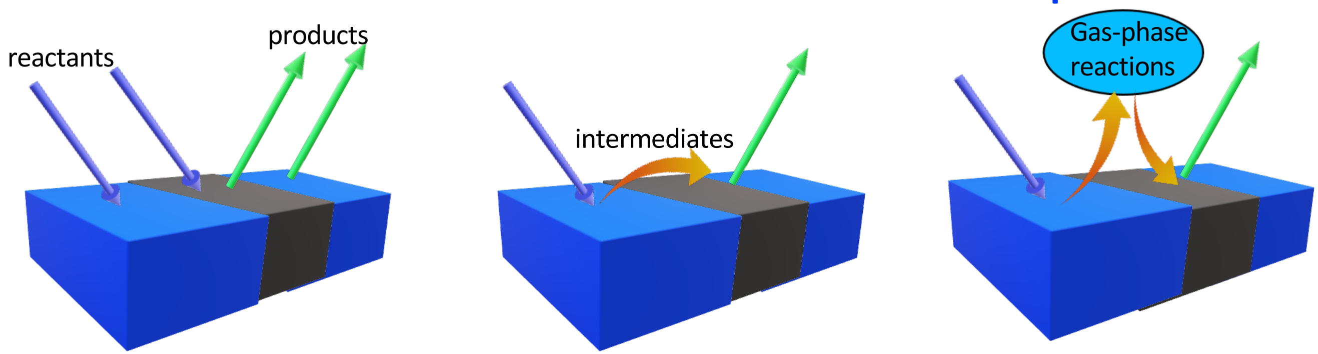
Combine Tools of Gas Phase Chemical Physics with Surface Science → Fundamental Mechanistic Insight

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

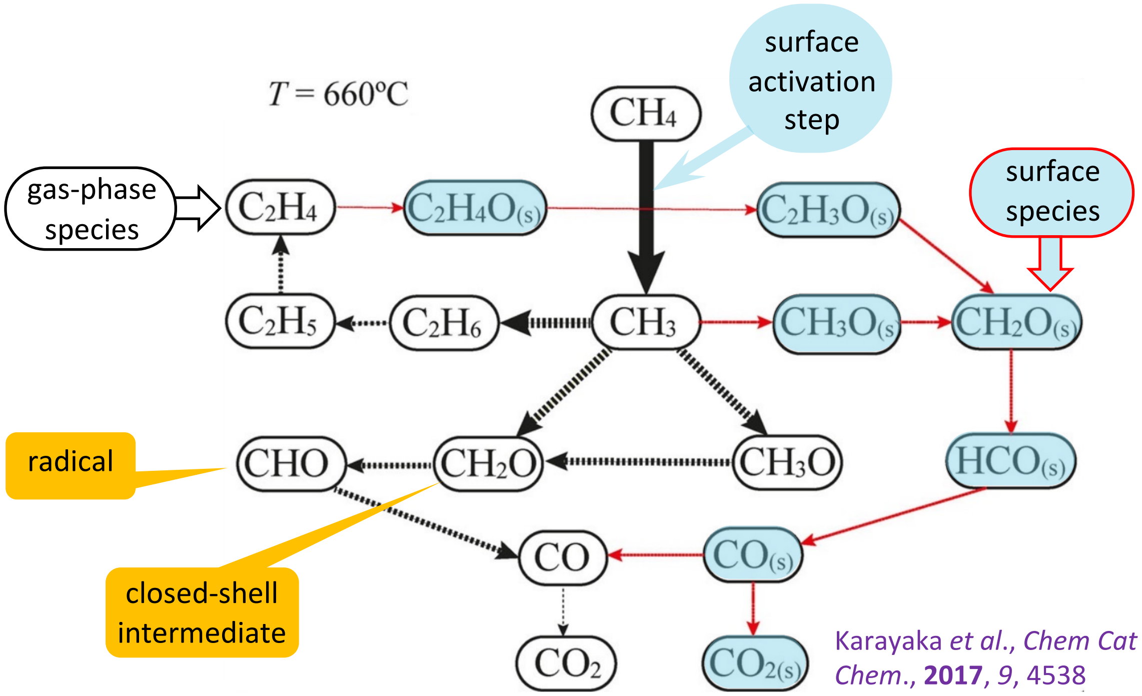
Increasing complexity of gas-phase interactions with multidomain reactive surface

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



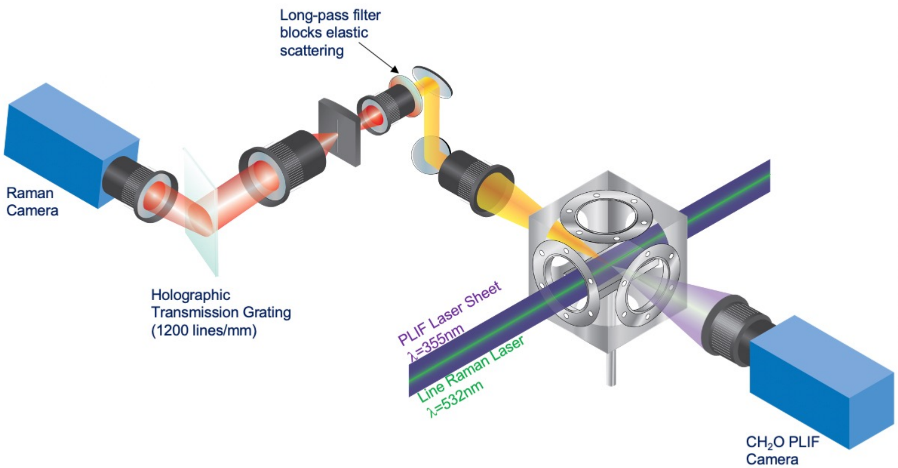
Karayaka *et al.*, *Chem Cat Chem.*, **2017**, *9*, 4538

Red arrows = surface reactions

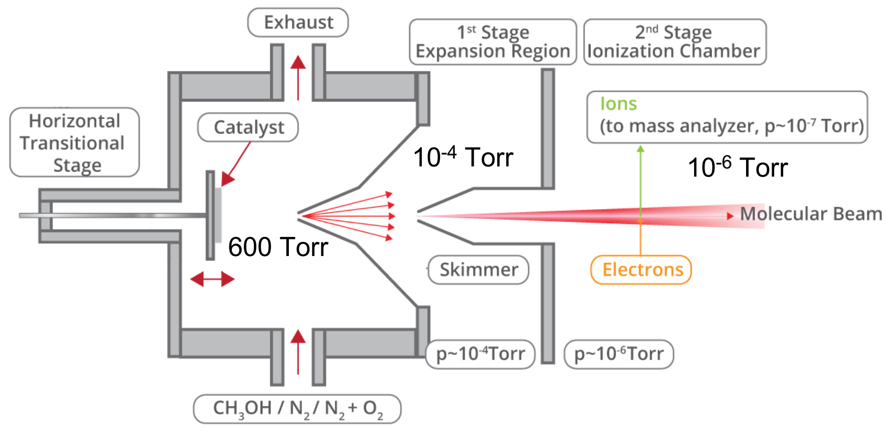
Black dashes = gas-phase reactions

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

Planar Laser-Induced Fluorescence/Raman Imaging



Near-Surface Molecular Beam Mass Spectrometry

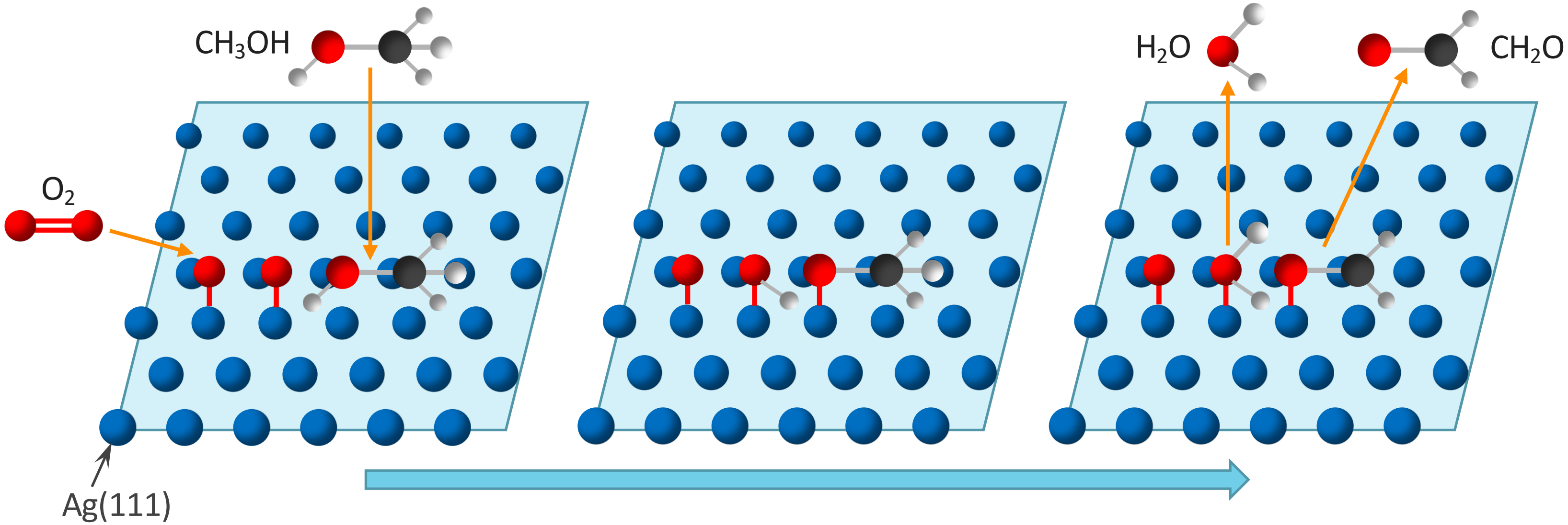


Test Case: Formaldehyde Production by Partial Oxidation of Methanol over a Silver Catalyst

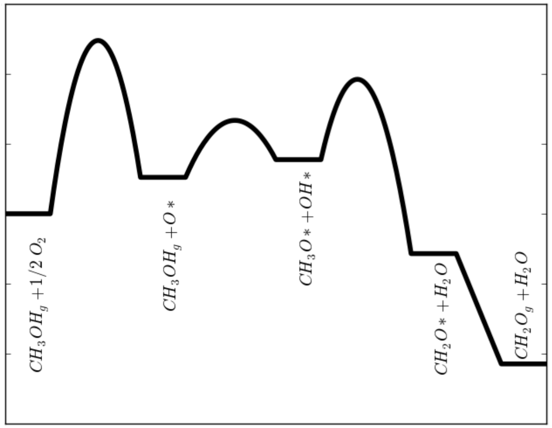
$$CH_3OH + \frac{1}{2}O_2 \rightarrow CH_2O + H_2O \qquad \Delta H = -38 \text{ kcal/mol}$$

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

Literature Mechanism for Partial Dehydrogenation of CH_3OH

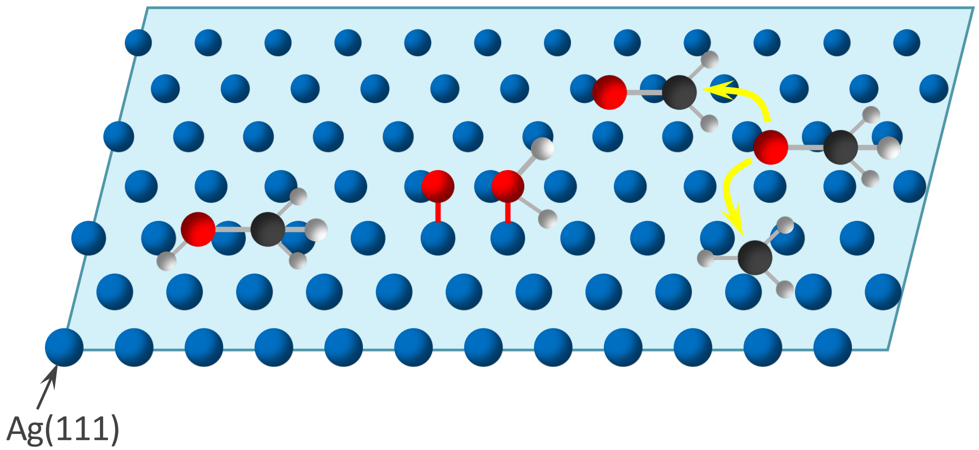


Oxidative reaction pathway for Ag(111) at 630 C



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

New Chemistry in Partial Dehydrogenation of CH_3OH



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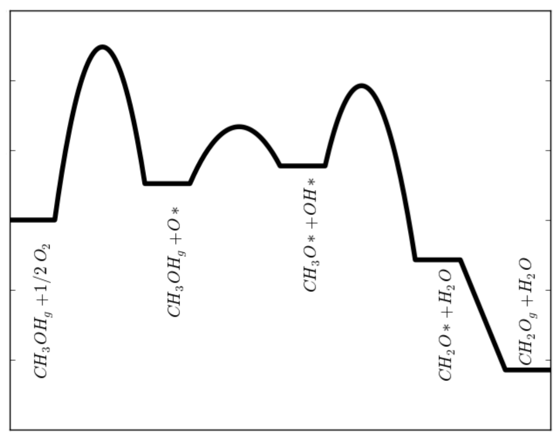
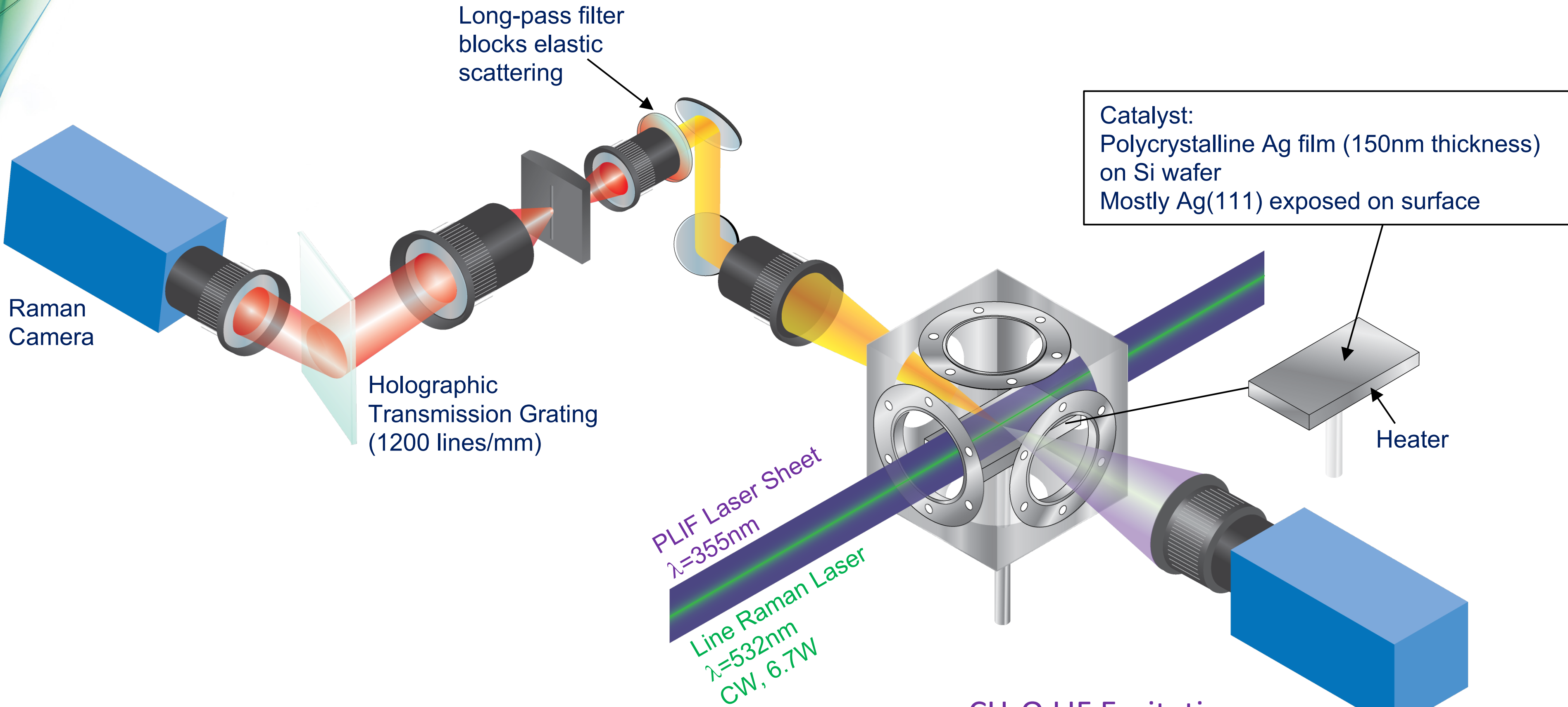


Aljama, Yoo, Nørskov, Abild-Pedersen, Studt,
ChemCatChem 8, 3621-3625 (2016)

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



<u>CH_2O LIF Excitation</u>

λ = 355 nm

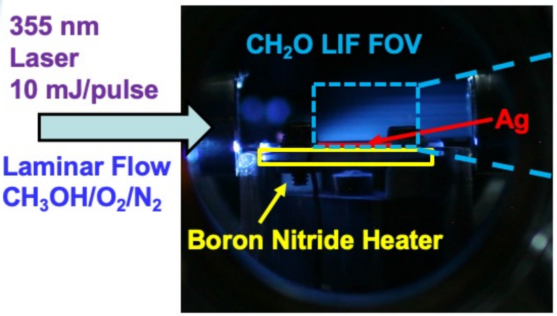
10 ns pulse, 10 mJ/pulse

4^1_0 band of

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

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

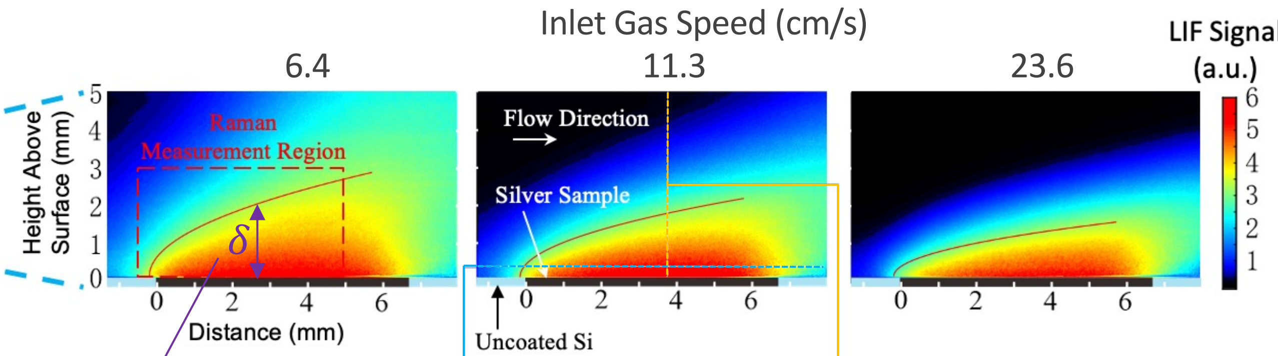
90% N_2
7.5% CH_3OH
2.5% O_2

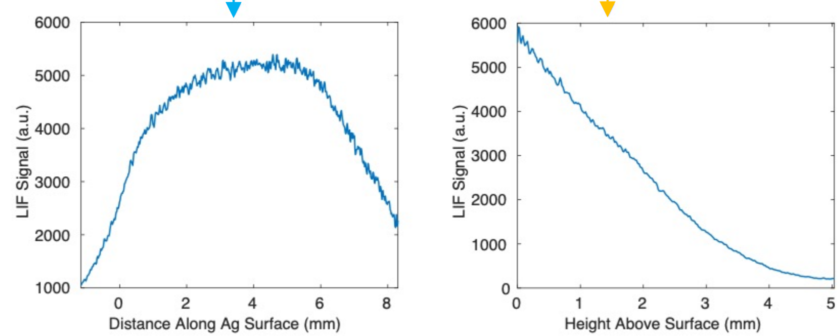


P=600 Torr

$T_{catalyst} = 407\ C$

Increasing flow rate





Blasius solution to Navier-Stokes equations for boundary layer flow

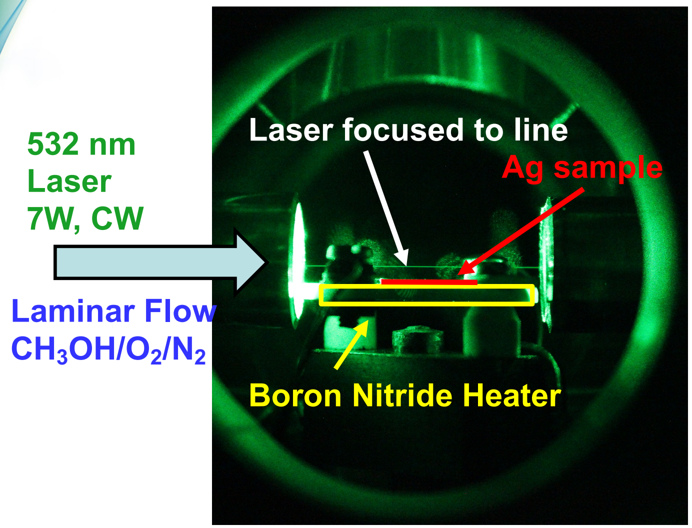
Boundary Layer Thickness: $\delta \propto \sqrt{Dx/u}$

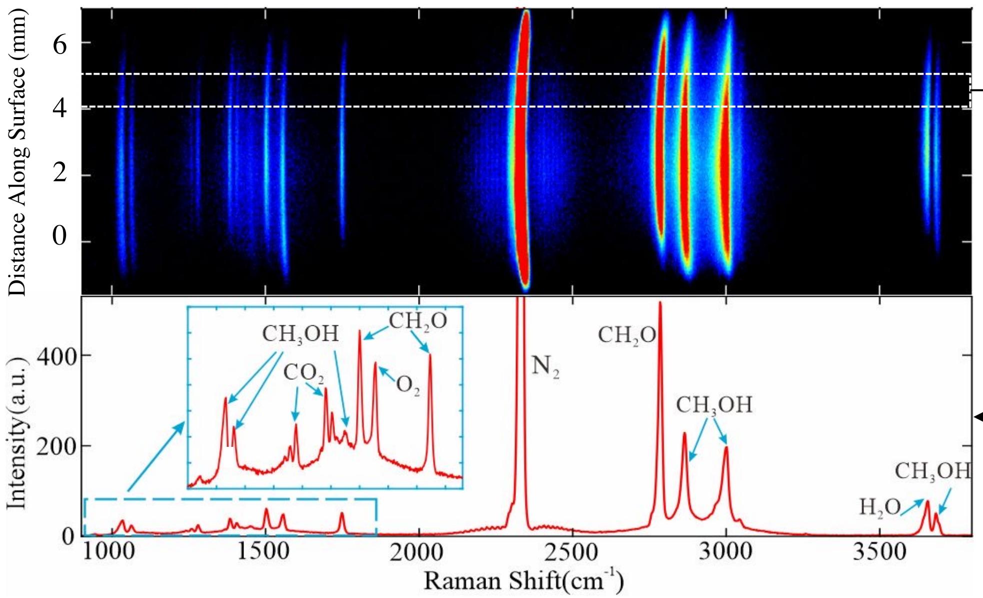
D = Diffusion Coefficient

x = Streamwise Distance

u = Streamwise Velocity

1D Raman Scattering Measurements

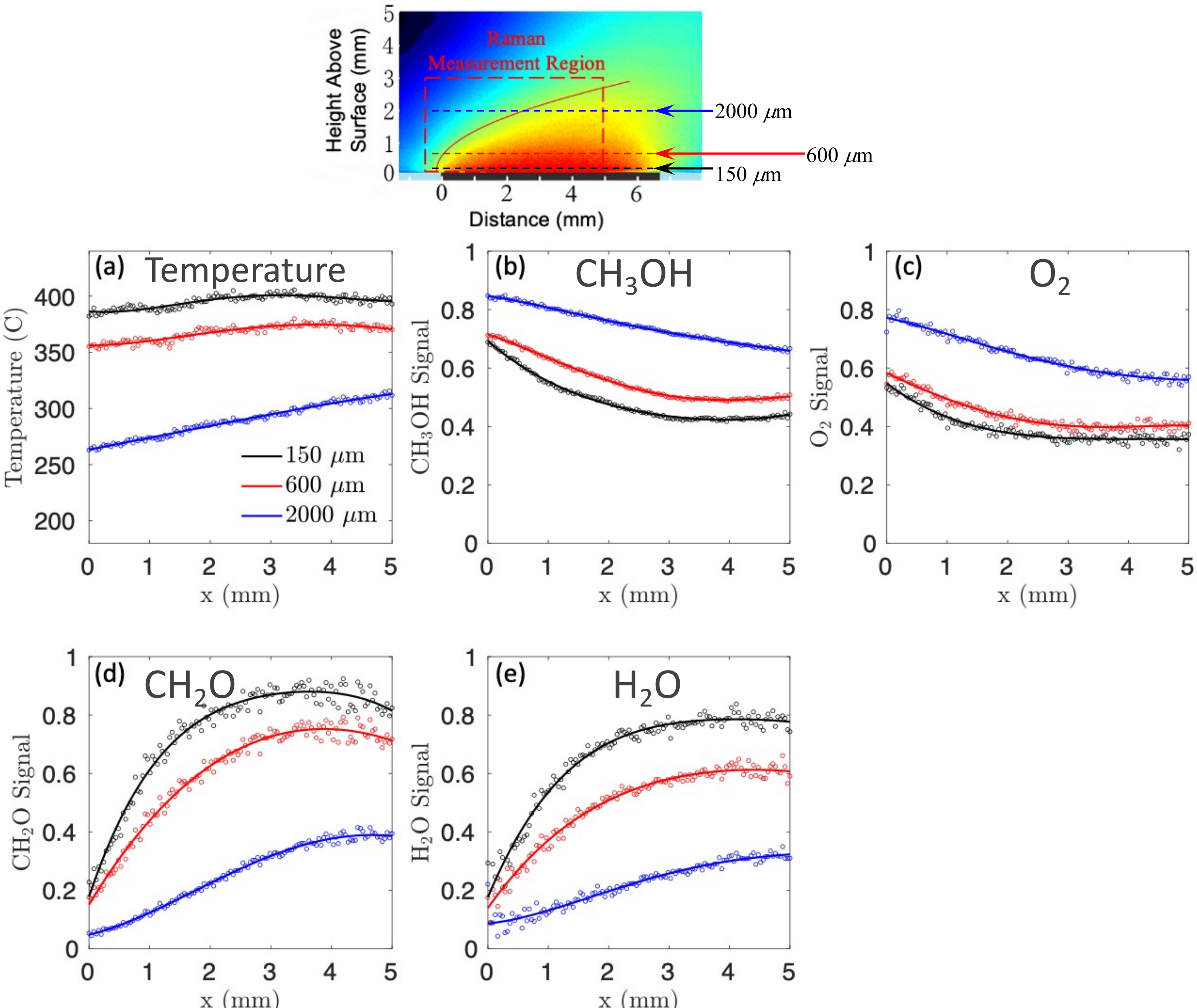




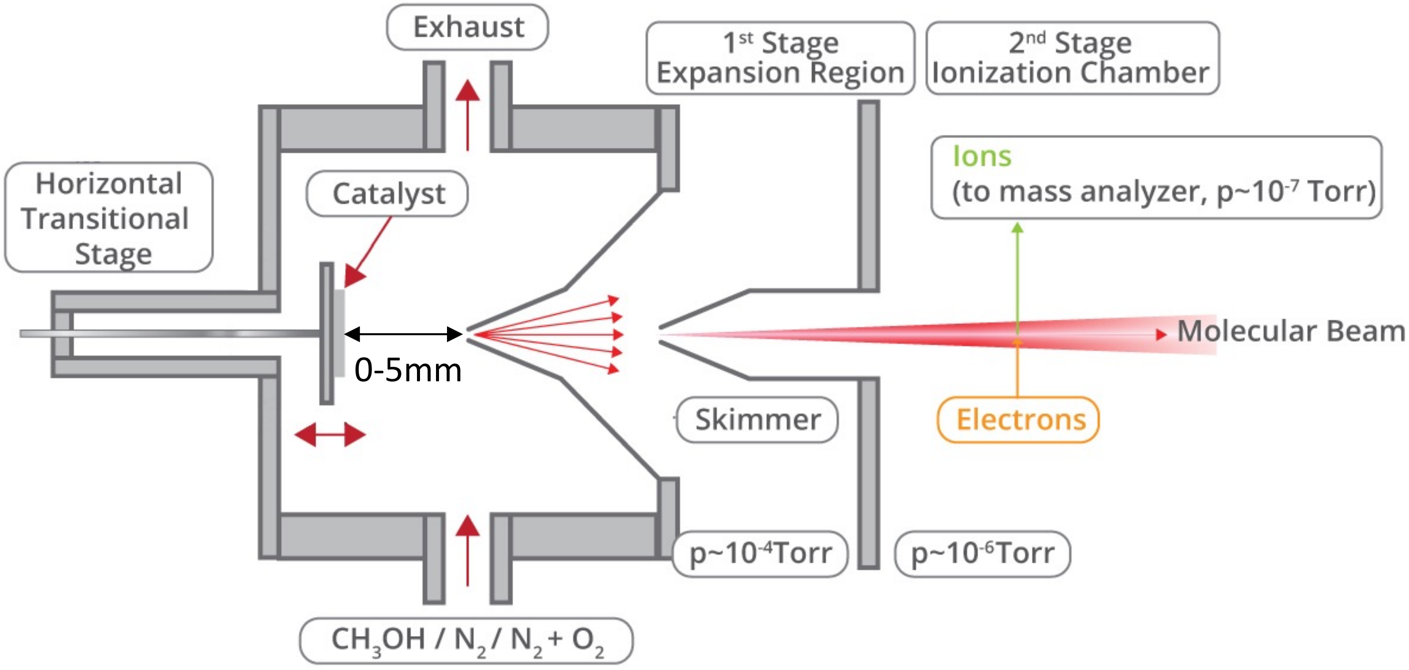
1D Raman imaging spectrum for 60-second integration

- 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

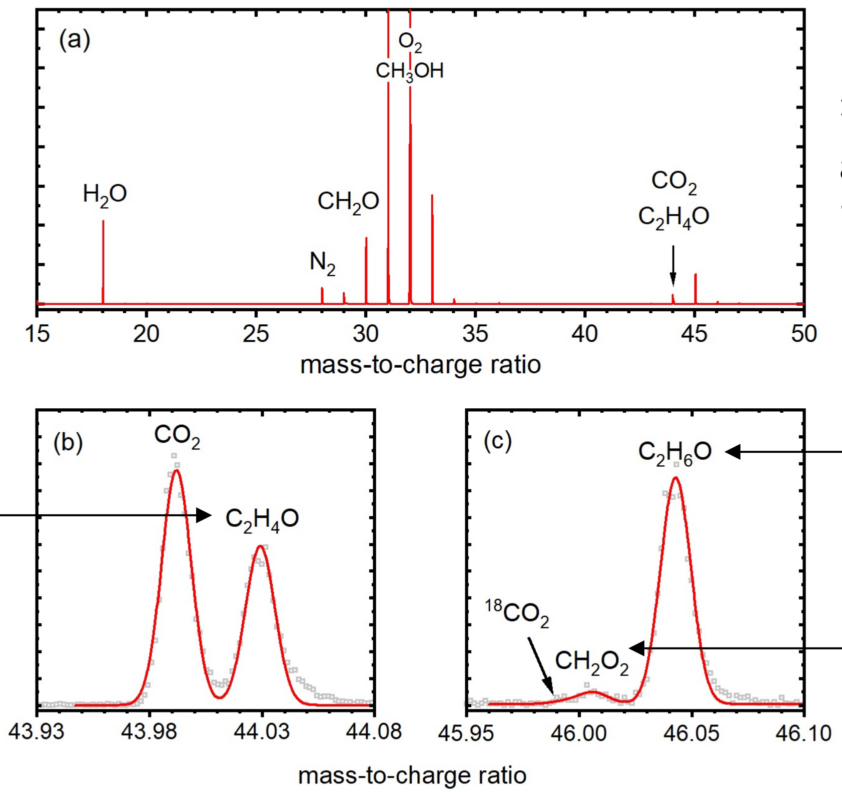


Complementary Molecular Beam Mass Spectrometry of Near-Surface Gas Phase



- 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)

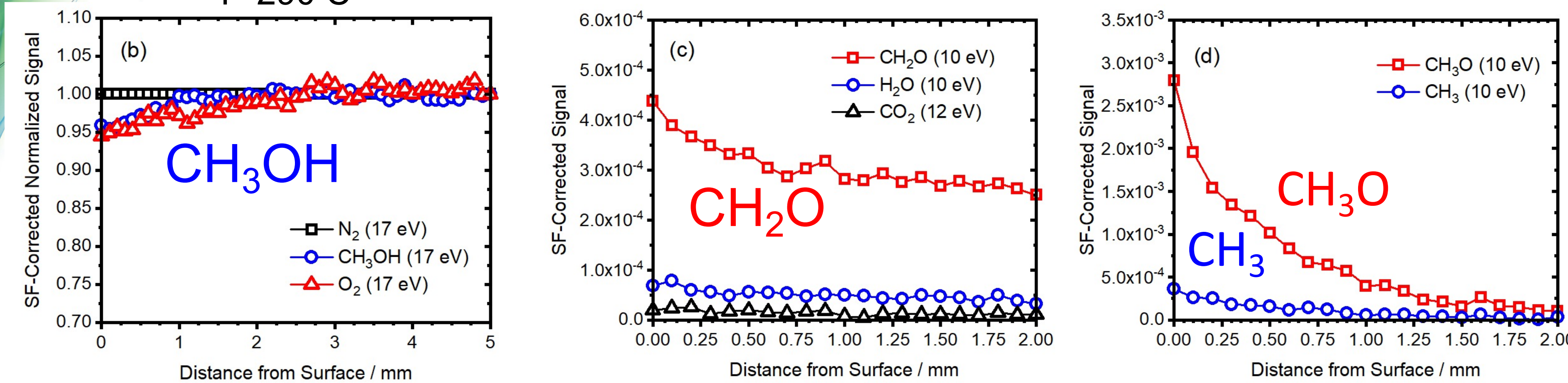
Formic Acid (HCOOH)

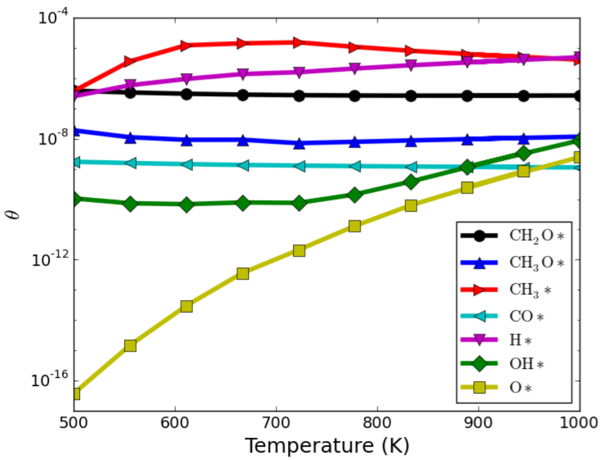
Not shown: peaks at *m/z*=60.021 ($C_2H_4O_2$), *m/z*=62.037 ($C_2H_6O_2$)– assign to methyl formate and methoxymethanol, respectively

* Electron ionization does not provide conclusive isomeric assignments

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

T=290 C



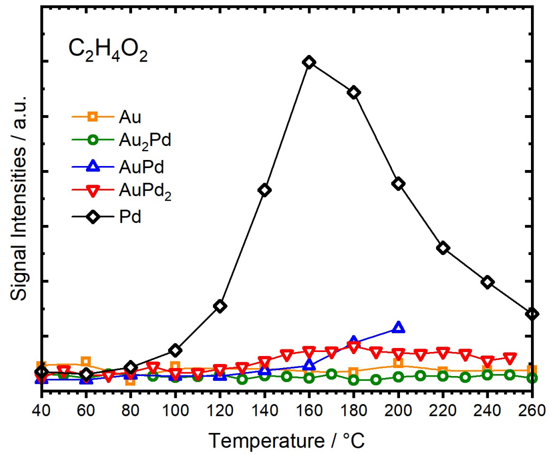


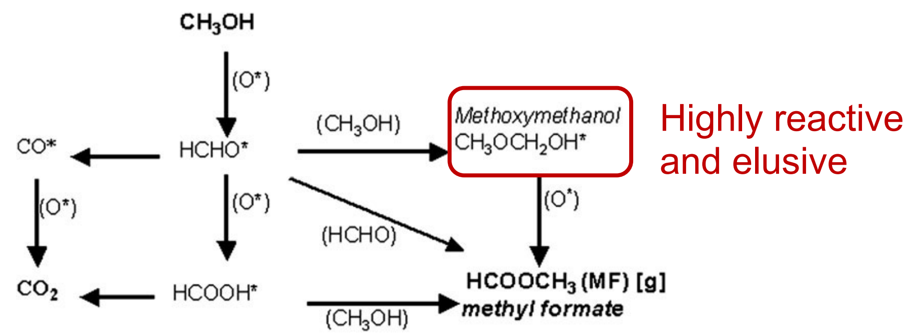
Nørskov group partial methanol oxidation model on Ag(111)

- 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)

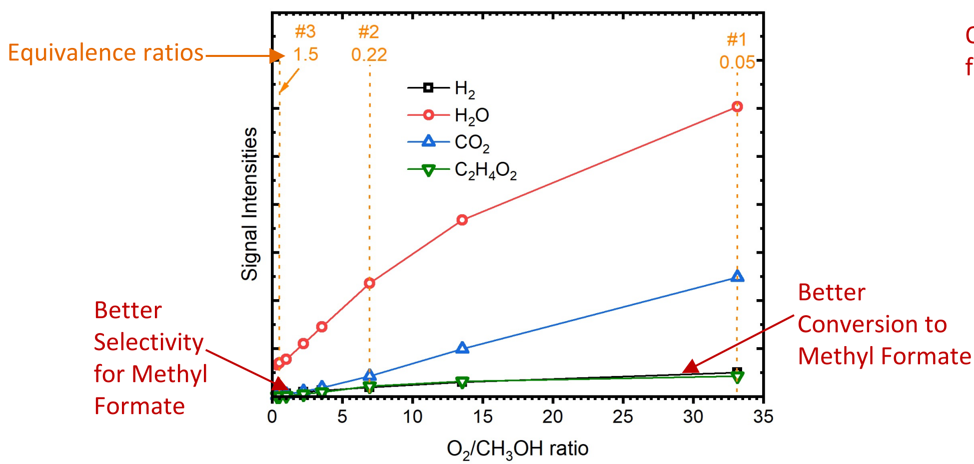
Effects of Catalyst Composition on Methanol Oxidation



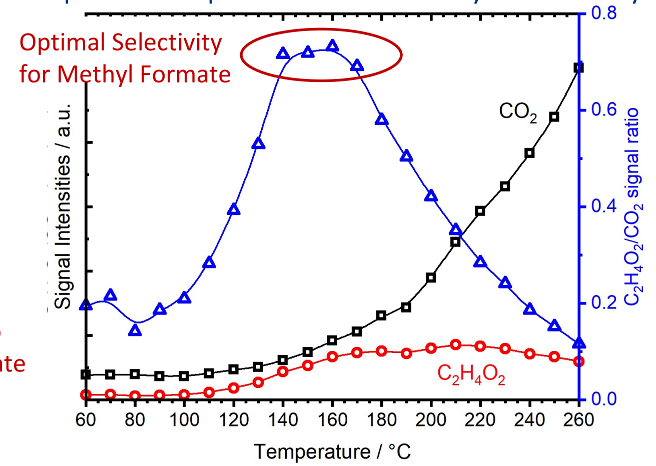


Proposed reaction pathways (* represents adsorbed species)
Lichtenberger, Lee, Iglesia, Phys. Chem. Chem. Phys. 9, 4902 (2007)

Dependence on Reactant Composition for Pd Catalyst

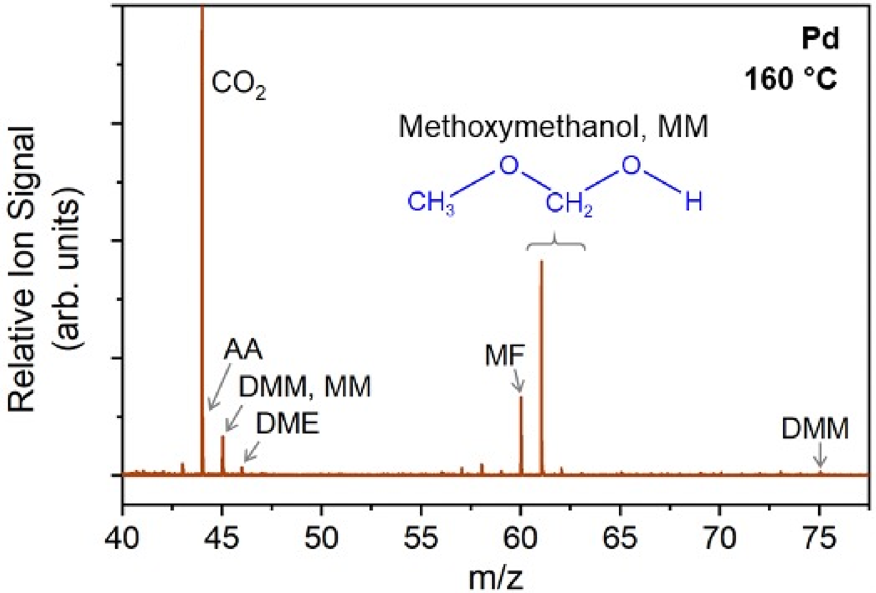


Temperature Dependence of Selectivity for Pd Catalyst



- Provide benchmark data for computations of catalysts from less reactive (Au) to more reactive (Pd) with tradeoffs in conversion rates and selectivity
- Test microkinetic models of C1 chemistry which can include compensating errors
- Predictions of C2 chemistry provide additional challenge to computations

Near-surface Methoxymethanol (CH_3OCH_2OH) Generated by Methanol Oxidation Over Pd-based Catalysts

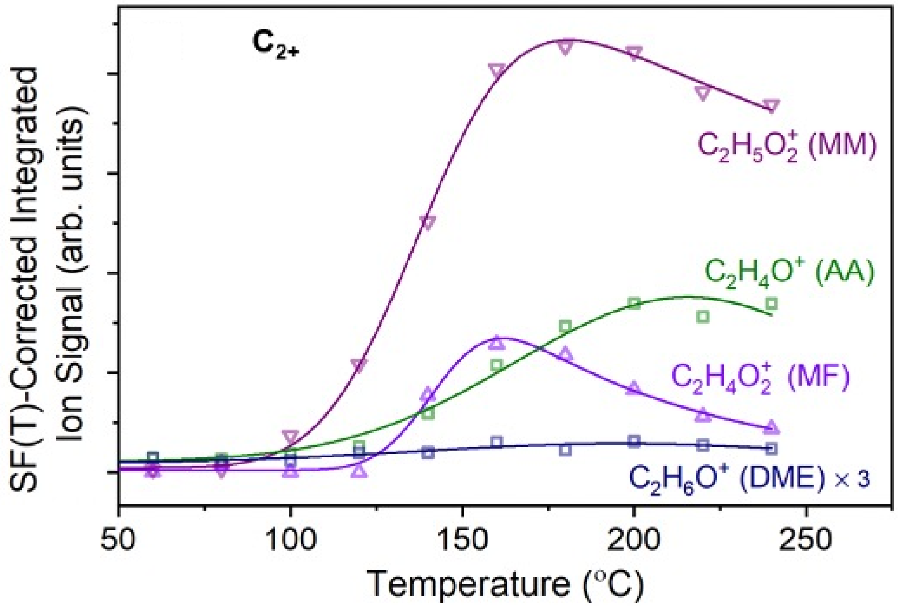


DMM = Dimethoxymethane ($CH_3OCH_2OCH_3$)

MF = Methyl formate (CH_3OCHO)

DME = Dimethyl ether (CH_3OCH_3)

AA = Acetaldehyde (CH_3CHO)



P=600 torr

Reactant mixture: CH_3OH/O_2 = 0.07

Height above surface = 500 µm

- Methoxymethanol proposed as a critical intermediate in methyl formate production
- Methoxymethanol is highly reactive and rarely observed
- Development of catalysts and microkinetic models should account for formation, desorption, adsorption, and surface reactions involving methoxymethanol

Recent publication: *J. Phys. Chem. Lett.* 12:11252 (2021)

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
  - Unexpected species
- Mechanistic insights to inform / validate mechanistic models

Acknowledgments

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