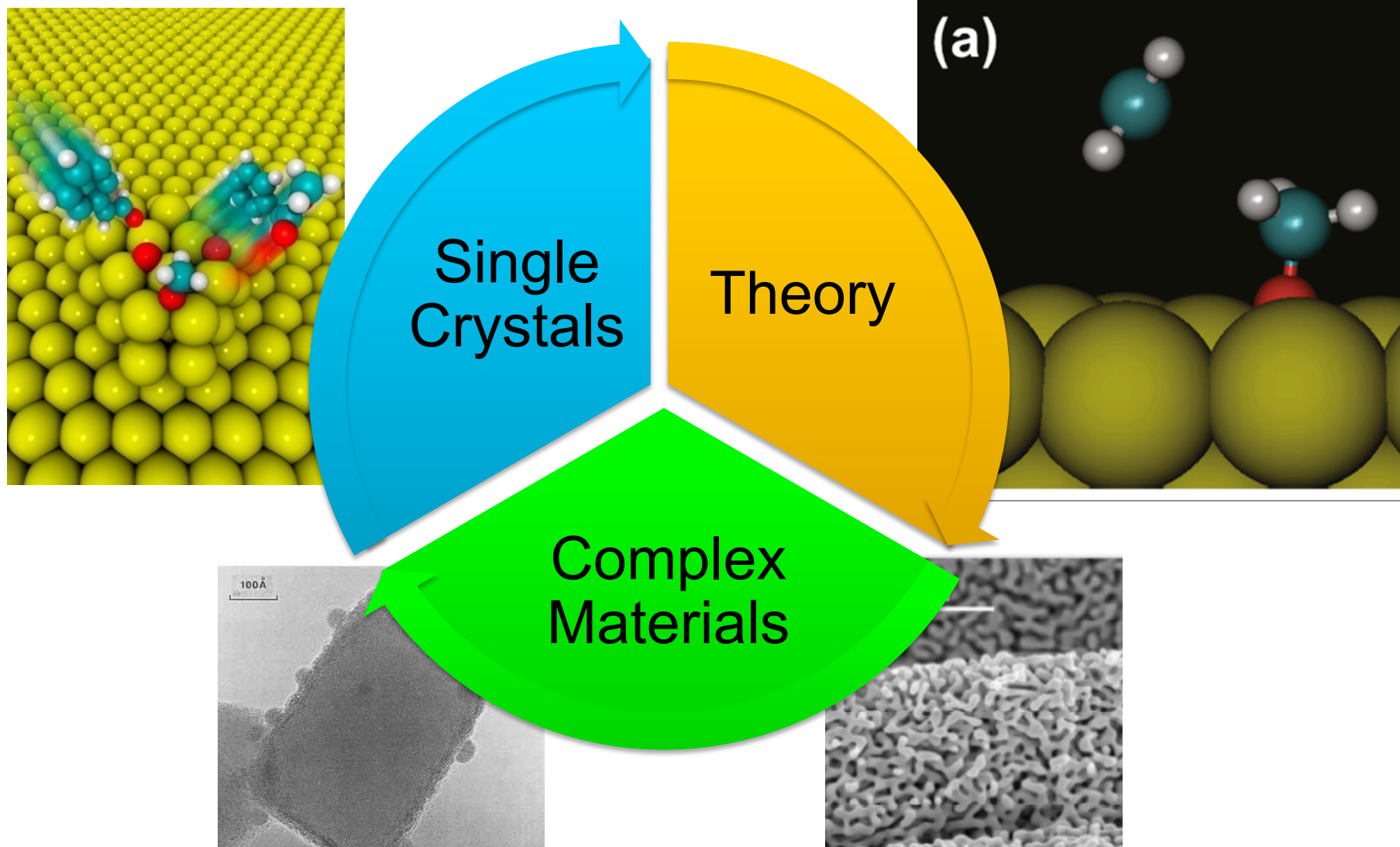


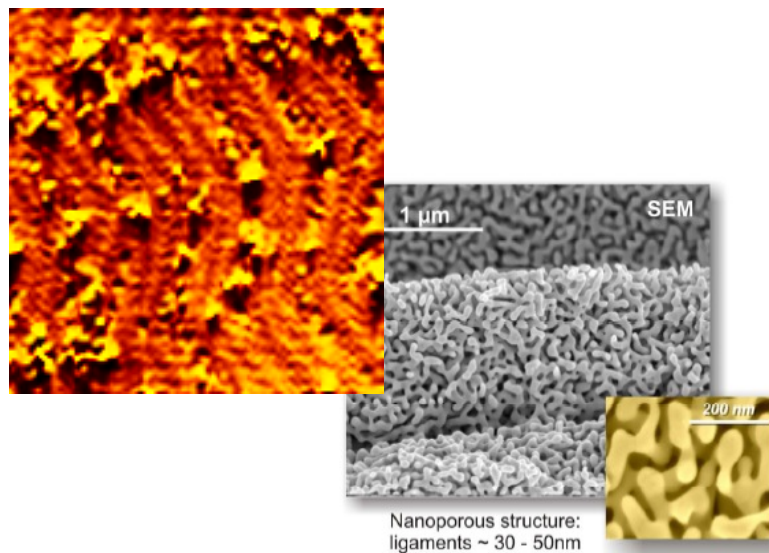
Our goal: To design new, efficient catalytic processes based on fundamental understanding of bonding and reactivity.



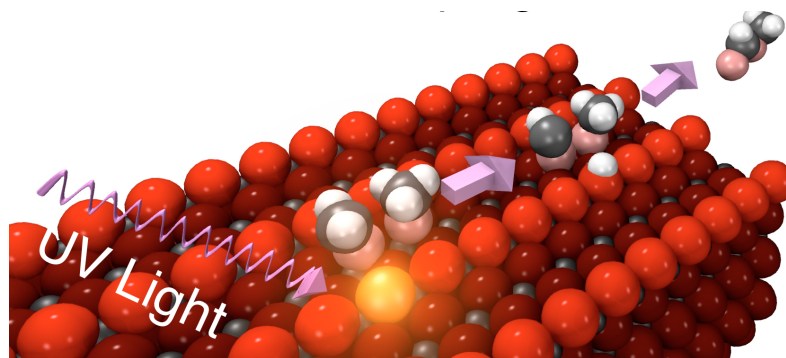


# Two primary research areas

1. Selective oxidation induced by coinage metals (Au and Ag) —bridging the pressure and materials gaps.



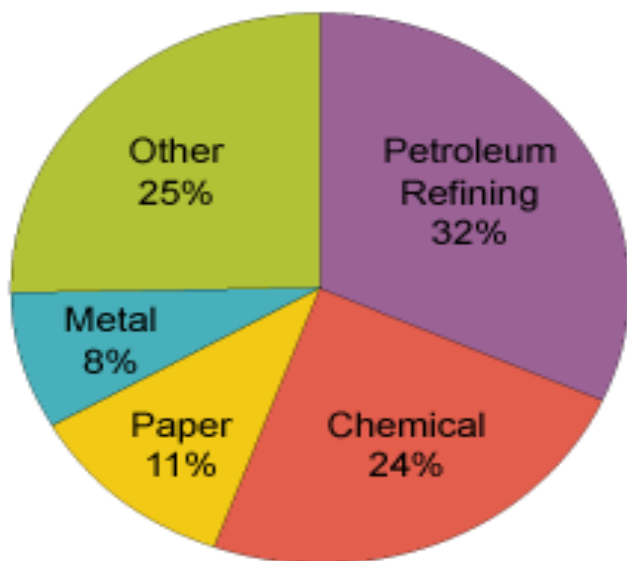
2. Hot topic: Defects and thermal oxidation/photo-oxidation on  $\text{TiO}_2$





# Opportunity for reduced energy usage in chemical industry: Catalysis is Key

*Chemical Production is energy intensive*



*Manufacturing Energy Consumption Survey 2006, Table 1.2*

- ~1 M people directly employed by US chemical industry
- Most processes rely on heterogeneous catalysis

How can reduced energy usage through improved catalysis be achieved?

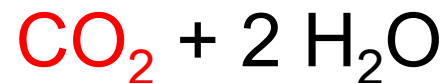
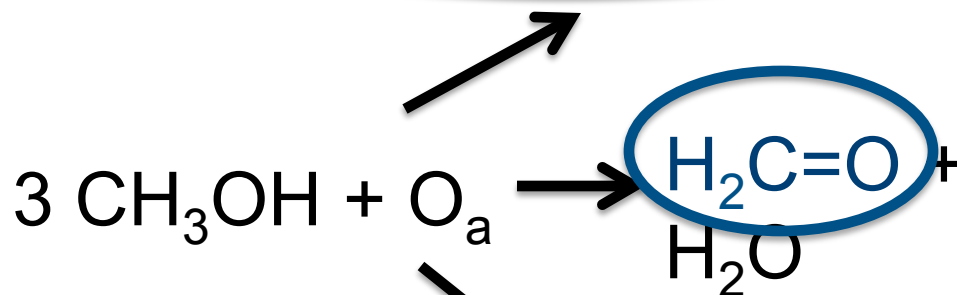
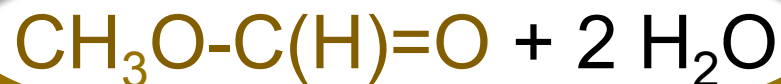


# Reduction in energy cost using catalysis

- Increase *rate*
- **Lower** operating *temperature* (save energy)
- **Increase selectivity**  
—get the product you want with little or no waste

Its all about  
***kinetics!***

Example: Methanol oxidation on **Ag** or **Au**







# Key principles in catalysis

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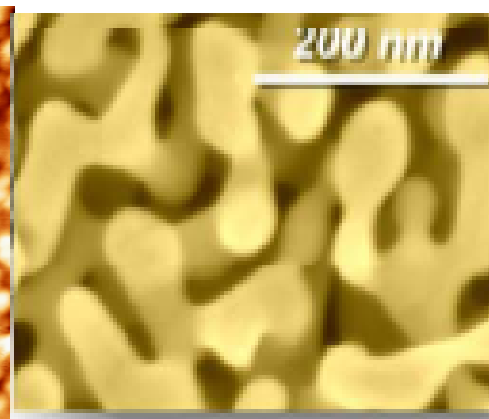
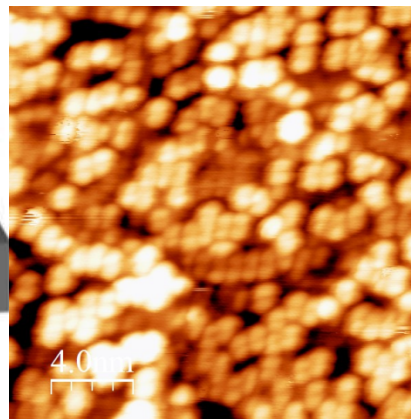
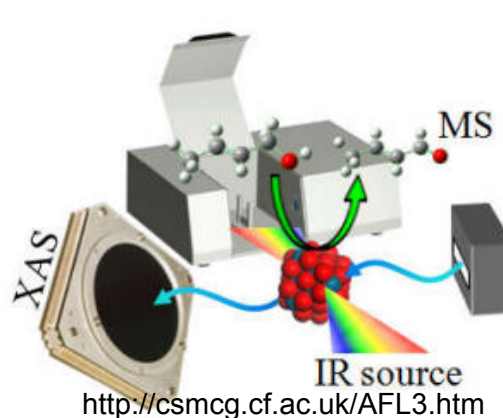
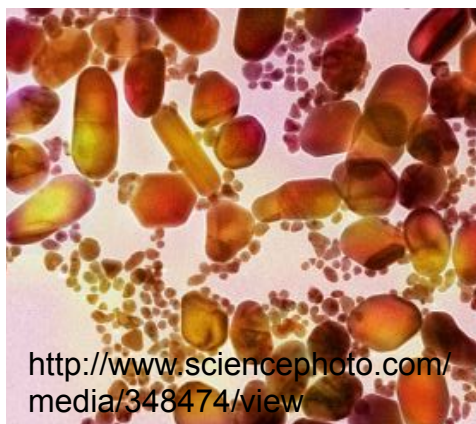
- Catalysis is controlled by ***kinetics***—
  - *dynamic metasable surface structures;*
  - *competitive binding of reactants;*
  - *small energy differences lead to large changes*
- What is a good ***catalyst***? Depends on ***reactive process!***
- ***Complexity***—most catalysis involves transformations of organic molecules
- Requires cyclic process/self renewal



# Major advances position catalysis for a major renaissance

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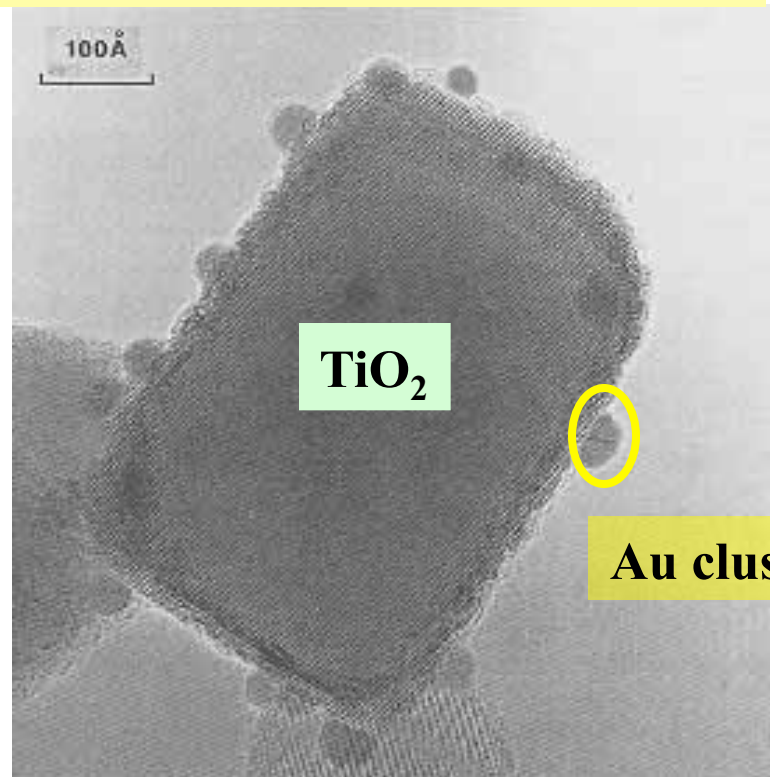
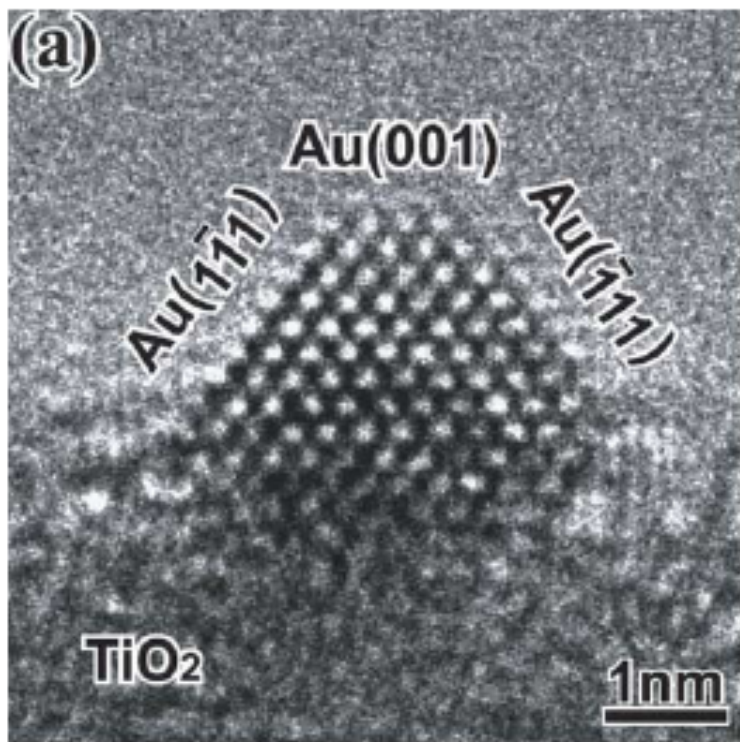
- Powerful experimental tools for understanding bonding and ***reactivity***
- Advanced understanding of surface and interfacial phenomena
- Synthesis of new nanomaterials and architectures





# Potential for low-T/highly selective chemistry using Au Nanoparticle catalysts

Complex material, not readily amenable to detailed mechanistic study



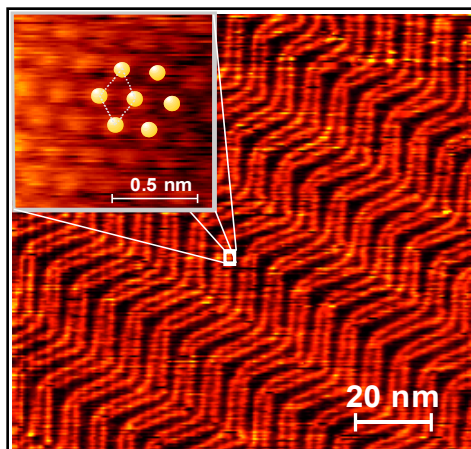
K. Okazaki, S. Ichikawa, Y. Maeda, M. Haruta and M. Kohyama, APPLIED CATALYSIS A-GENERAL, 2005, 291, 45-54.

[http://unit.aist.go.jp/isc/english\\_ver/each\\_groups\\_e/nano-cat\\_e/nano-cat\\_e.htm](http://unit.aist.go.jp/isc/english_ver/each_groups_e/nano-cat_e/nano-cat_e.htm)

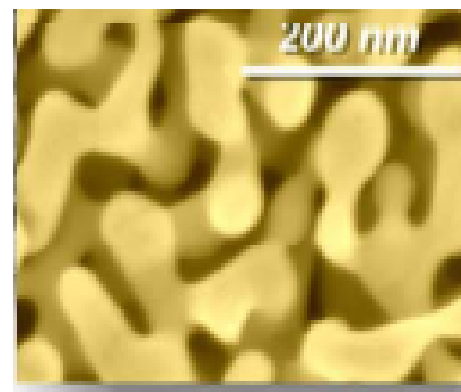


# Model systems: insight into roles of components in determining activity

Au(111)

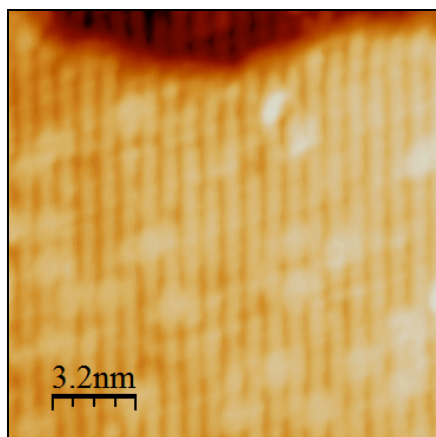


Nanoporous Au

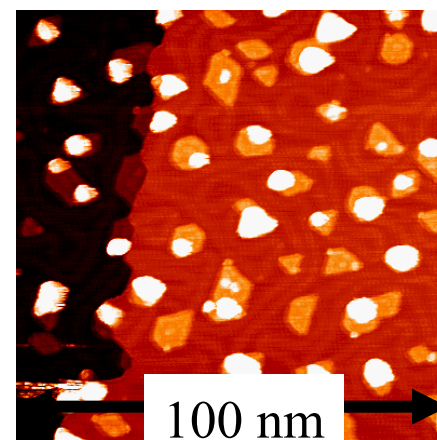


Goal:  
Deconvolute  
reactivity of  
catalyst  
components

TiO<sub>2</sub>



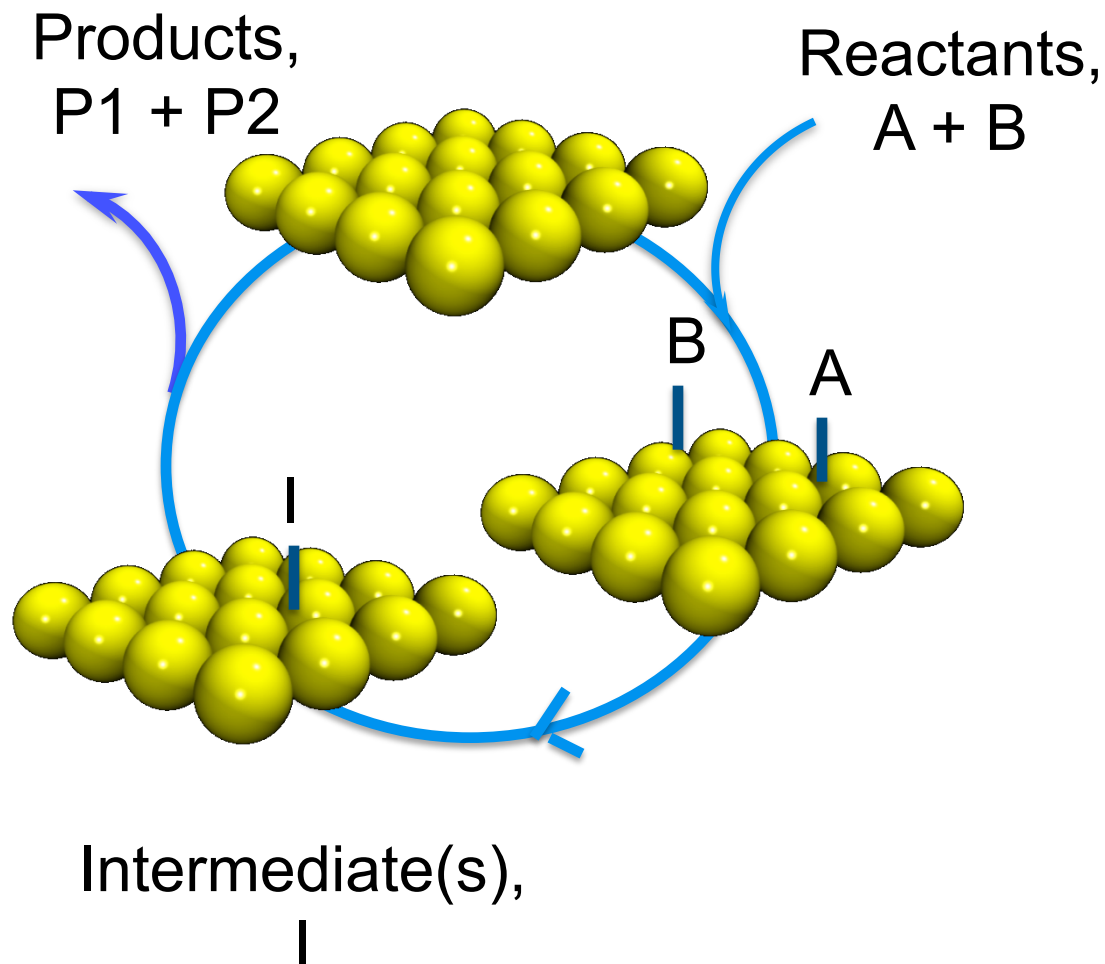
Nano-TiO<sub>2</sub>/ Au(111)





# Schematic of catalytic process

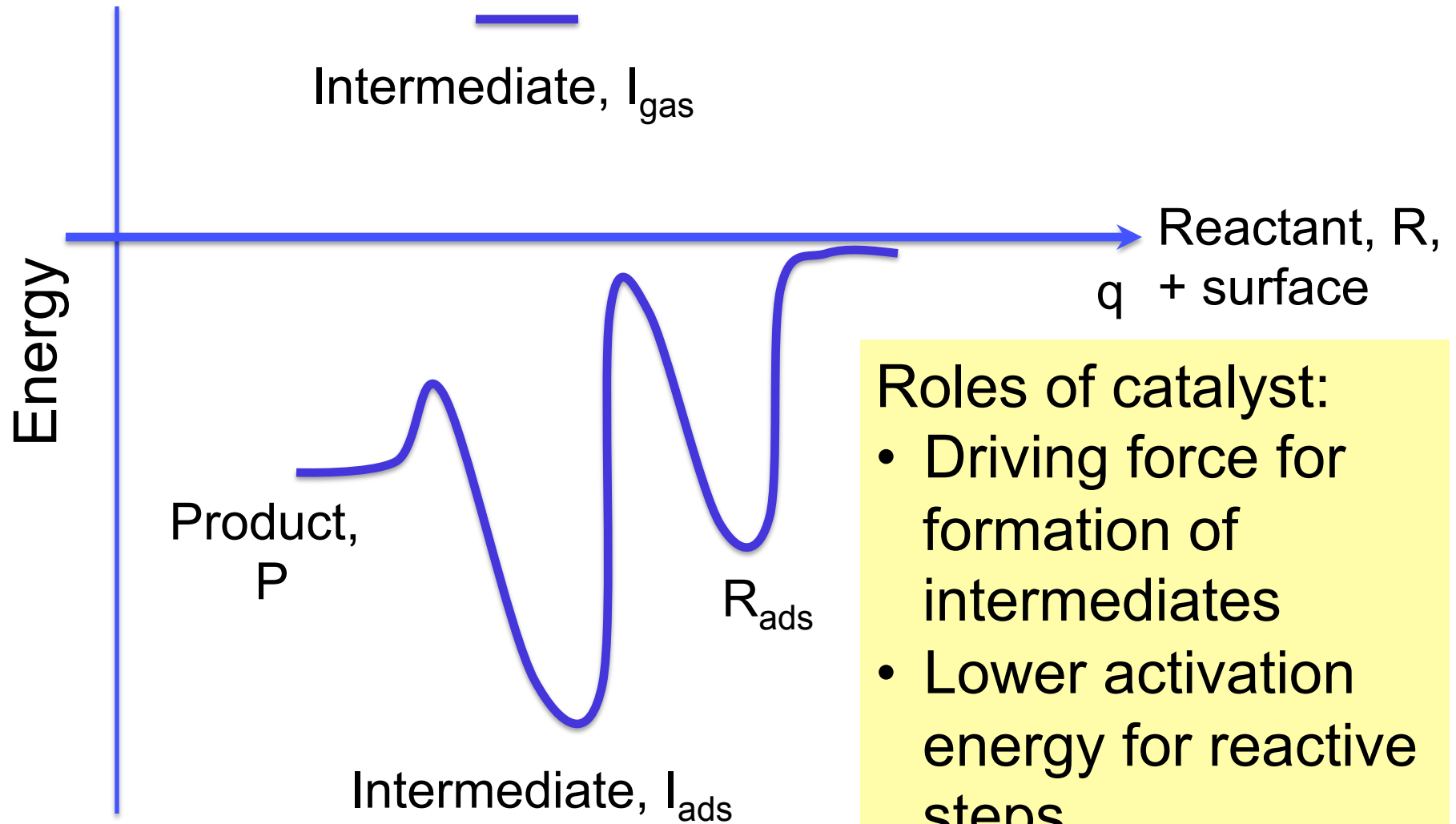
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# Schematic PE surface







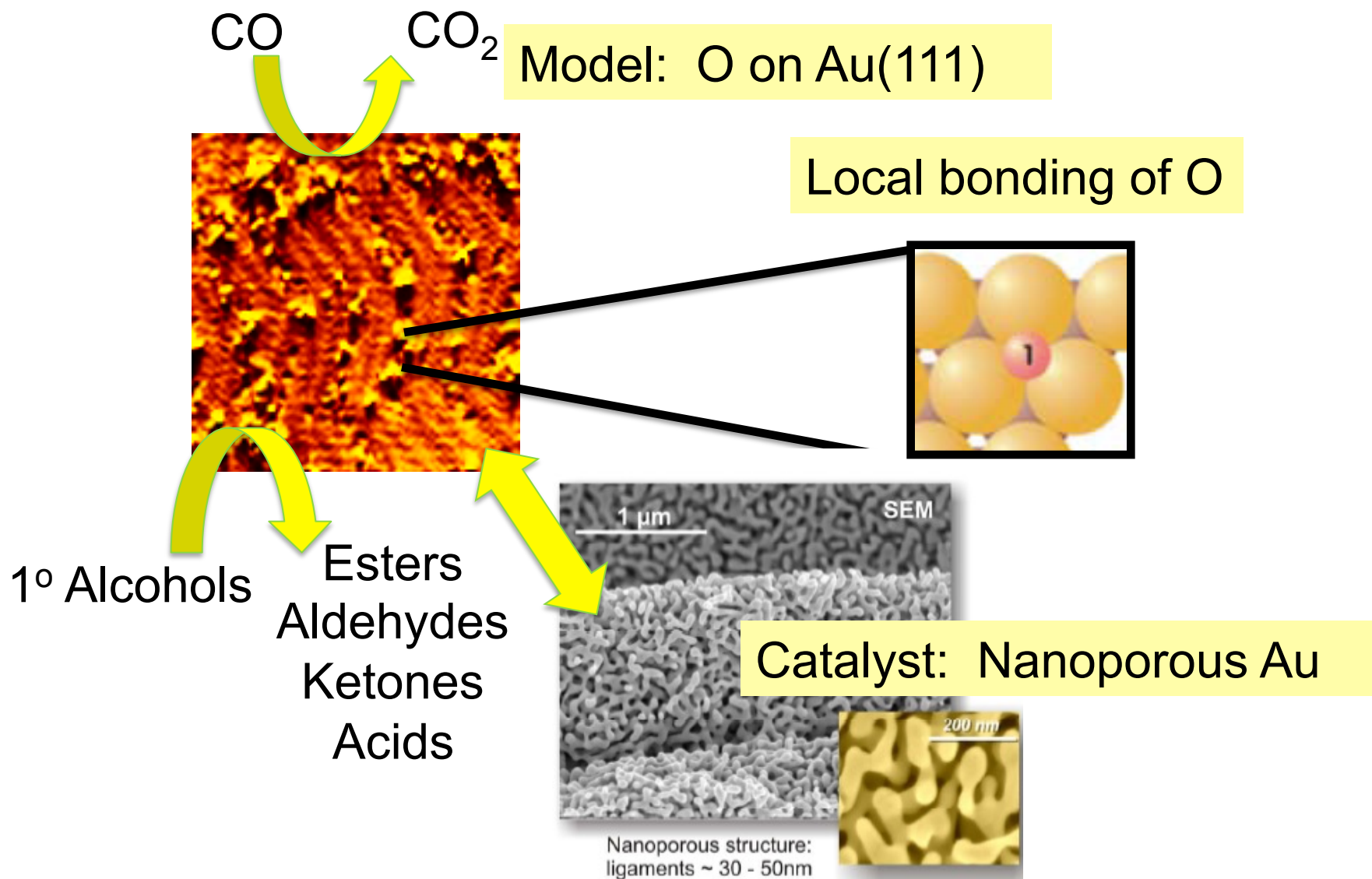
# What can theory provide?

---

- Information on ***bonding*** of surface species, including binding energy; structure; charge distribution
- Insight into ***reactivity***, including TS, barrier heights, branching
- ***Generalization*** is desirable—must include chemical complexity
- Kinetic modeling—should include surface heterogeneity and be “chemically accurate”



# Model system informs catalysis





# Challenges in Au-based catalysis

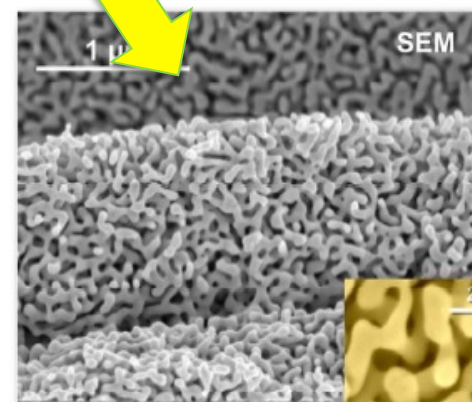
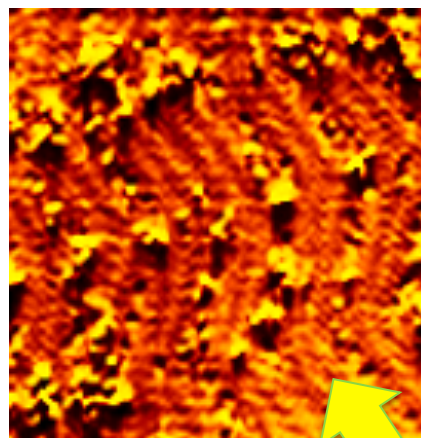
---

- $O_{ads}$  is reactive site: low rate of  $O_2$  dissociation on Au limits the production of key intermediates
- High reaction selectivity for alcohol functionalization is critical for viable chemical processes.
- Supported Au catalysts rapidly sinter, leading to short catalyst lifetime; a consequence of atom mobility



# Bridging the pressure gap in Au catalysis

- Reaction only occurs when O is present
- Spectators, including H<sub>2</sub>O, do not accumulate on the surface due to weak bonding
- Low SS coverage of reactants and products

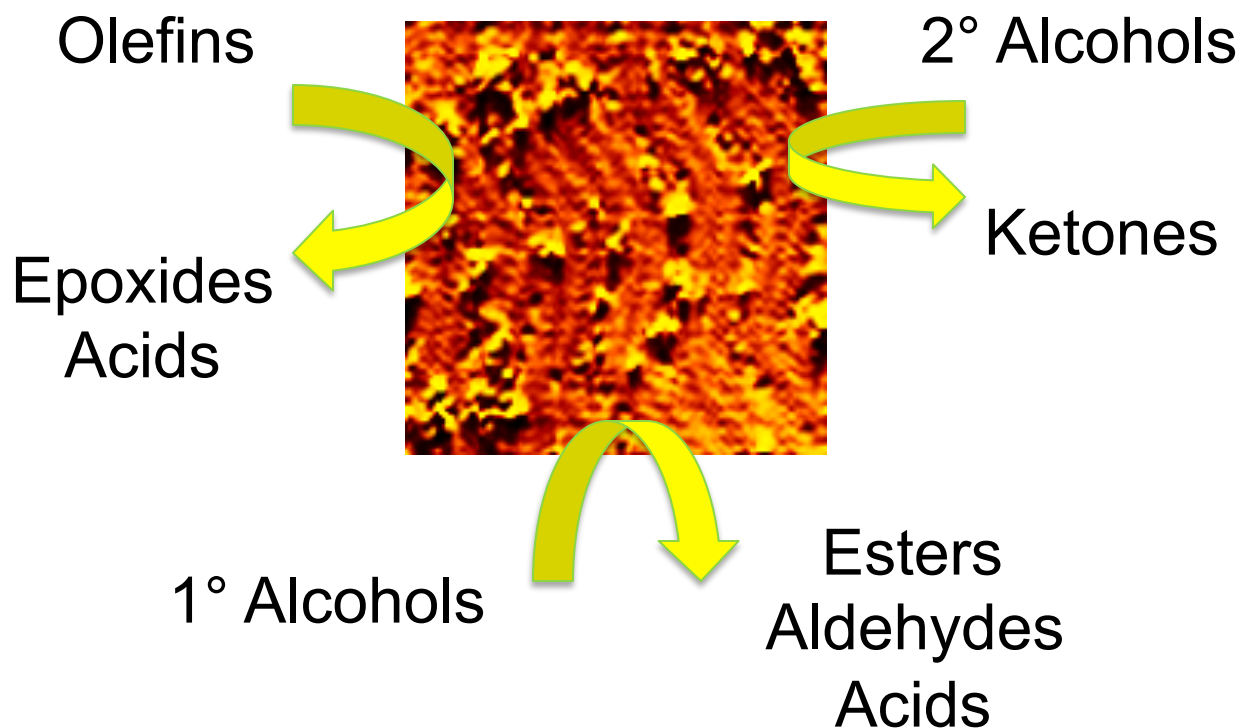


Nanoporous structure:  
ligaments ~ 30 - 50nm



## Model system: O adsorbed on Au(111)

O Adsorbed on metallic Au promotes a wide range of selective oxidation processes





# *Extended, crystalline Au surfaces do **not** dissociate O<sub>2</sub> at low pressure*

---



Au(111)-"herringbone"

No detectable dissociation at 400 K and pressures of  $\sim 10^{-6}$  torr for up to 10 minutes

**Upper** bound of dissociation probability  $\sim 10^{-7}$

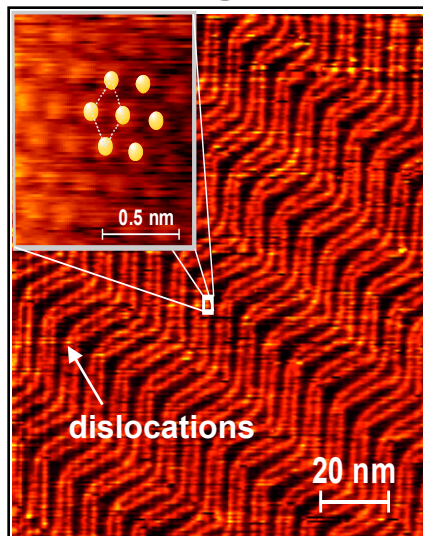




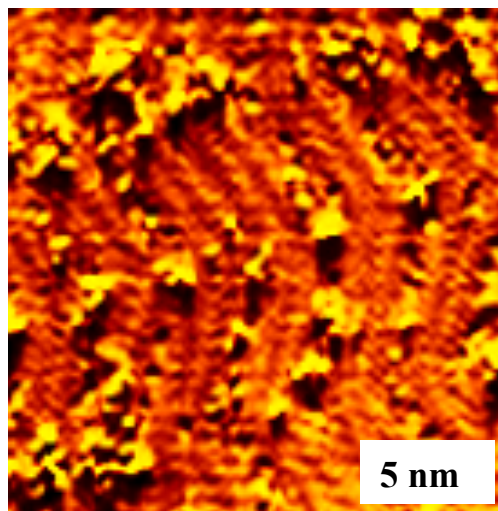
# Au is incorporated into metal complexes when O atoms are adsorbed

Au is oxidized by other methods in UHV:  $O_3$ , electron-induced  $NO_2$  dissociation,  $O_2^+$  sputtering

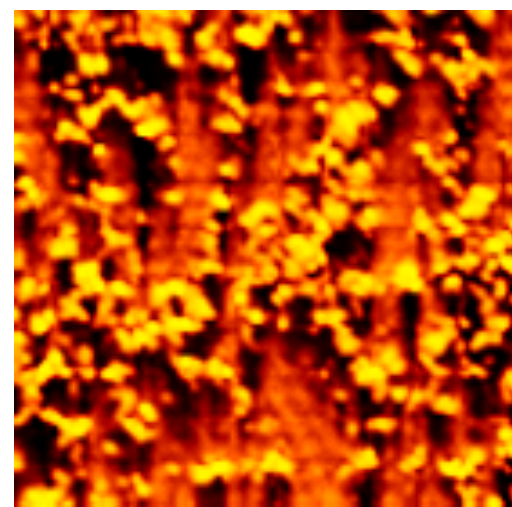
Increasing concentration of O atoms on the surface of Au



No Oxygen—  
clean Au



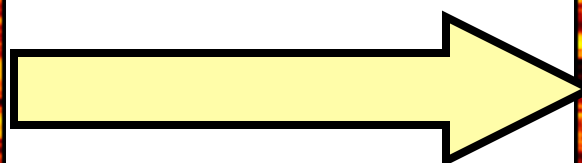
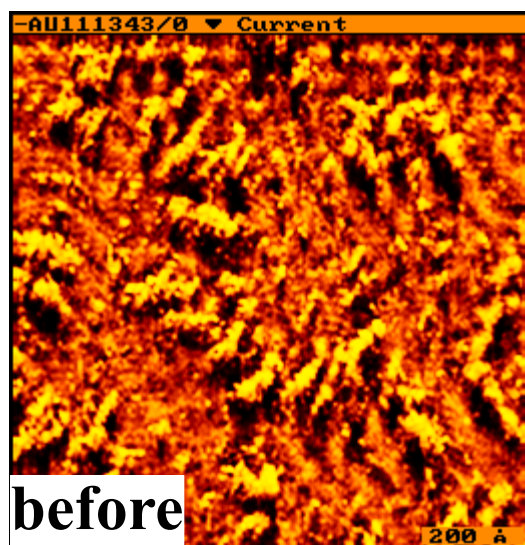
0.2 ML



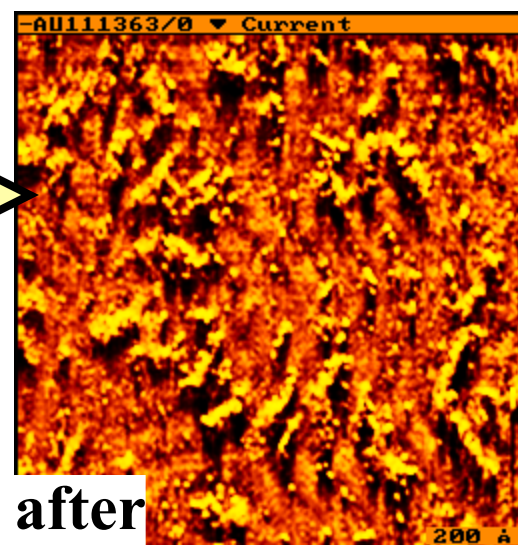
0.5 ML



# Rough Surface morphology remains after reacting away all O via CO oxidation



$5 \times 10^{-8}$  torr CO,  
5 min @ 200 K



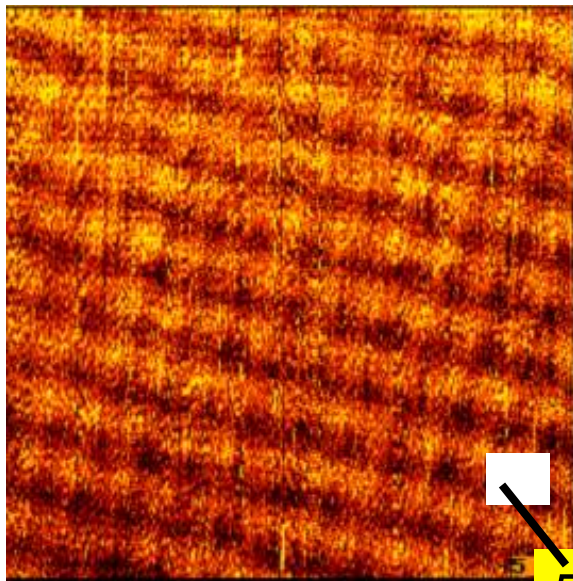
~0.3 ML O  
deposited at  
200 K

No residual O

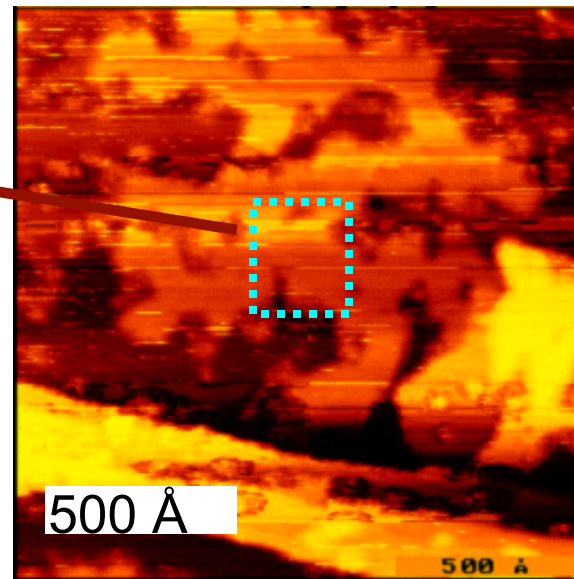
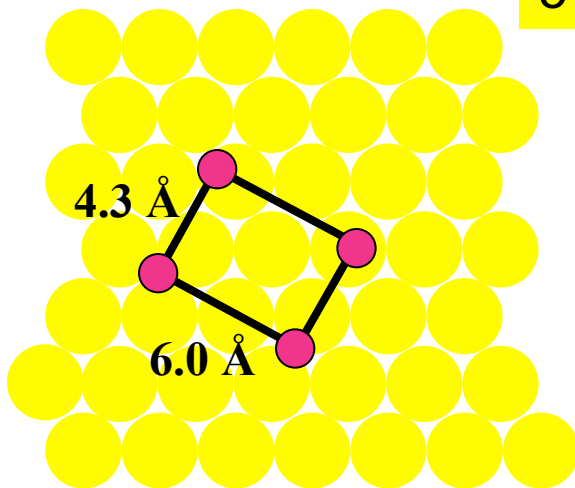
In situ scanning



Atomically resolved images of larger islands have rectangular symmetry indicating the presence of O



5 Å



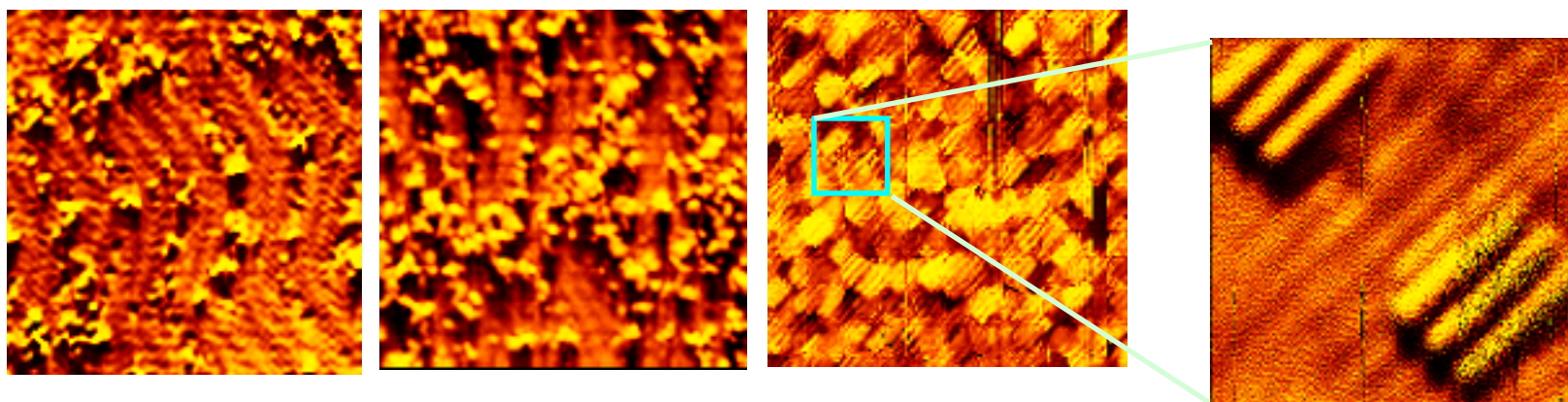
500 Å

500 Å

0.5 ML of O annealed to 400 K for 5 min to produce large islands



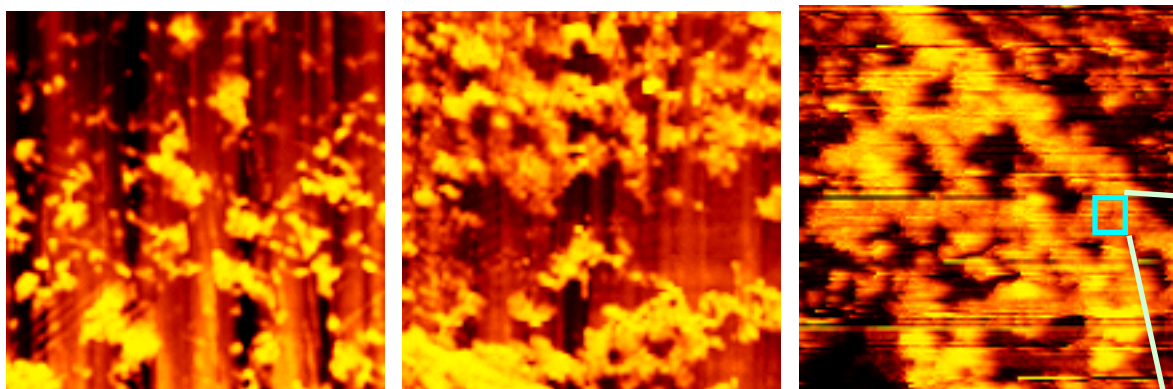
Metastable nanostructures formed at 200 K, have high reactivity & selectivity—attributed to mobile species



$T_D = 200 \text{ K}$

O-coverage

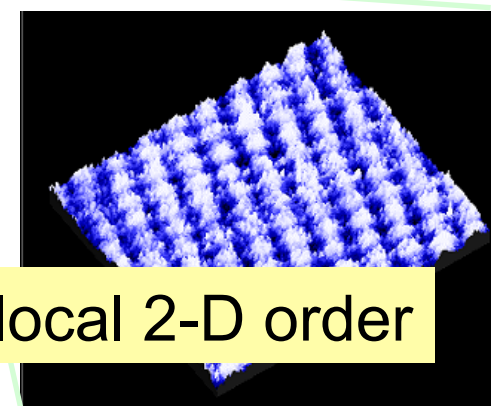
3D islands



2D islands

$T_D = 400 \text{ K}$

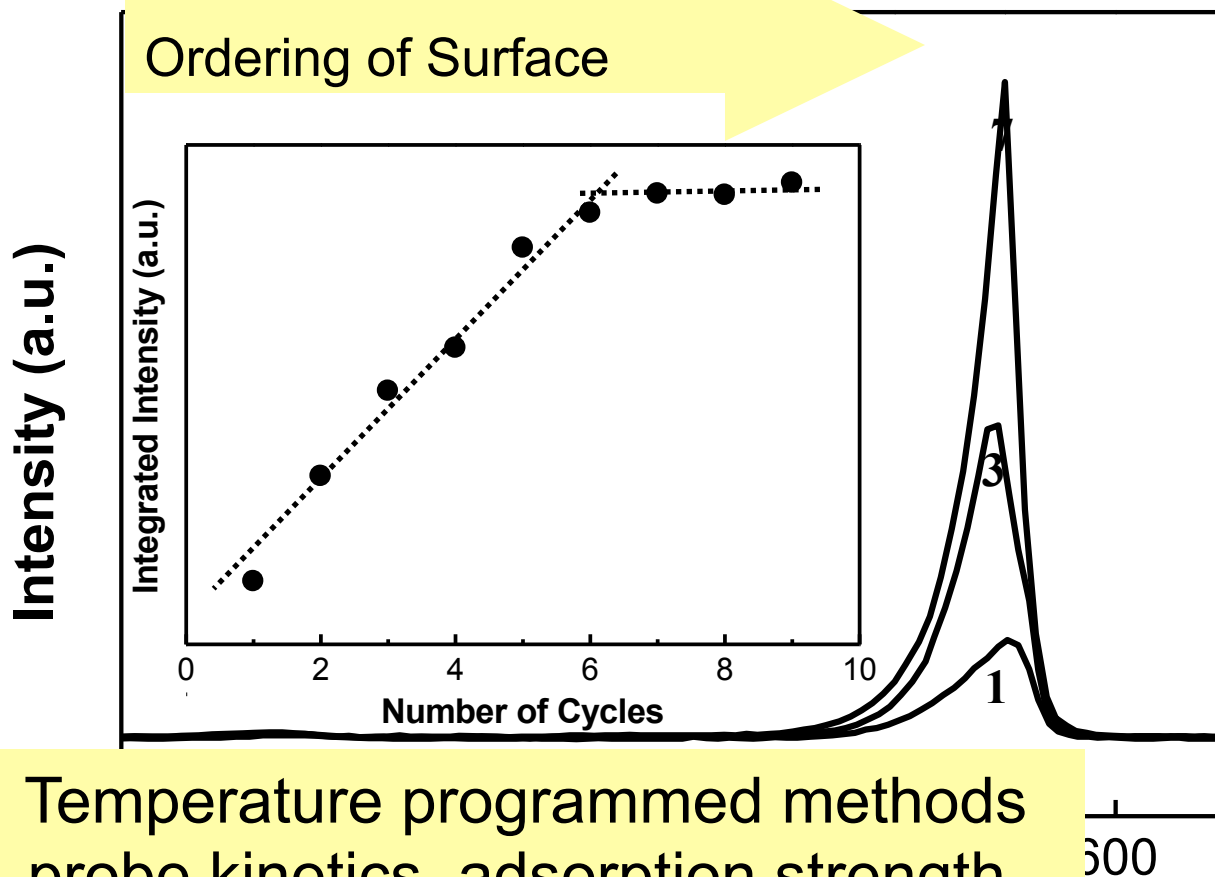
5 nm



Thermal annealing leads to larger islands with local 2-D order



# Au-O bonding is robust, Bond energy ~140 kJ/mol



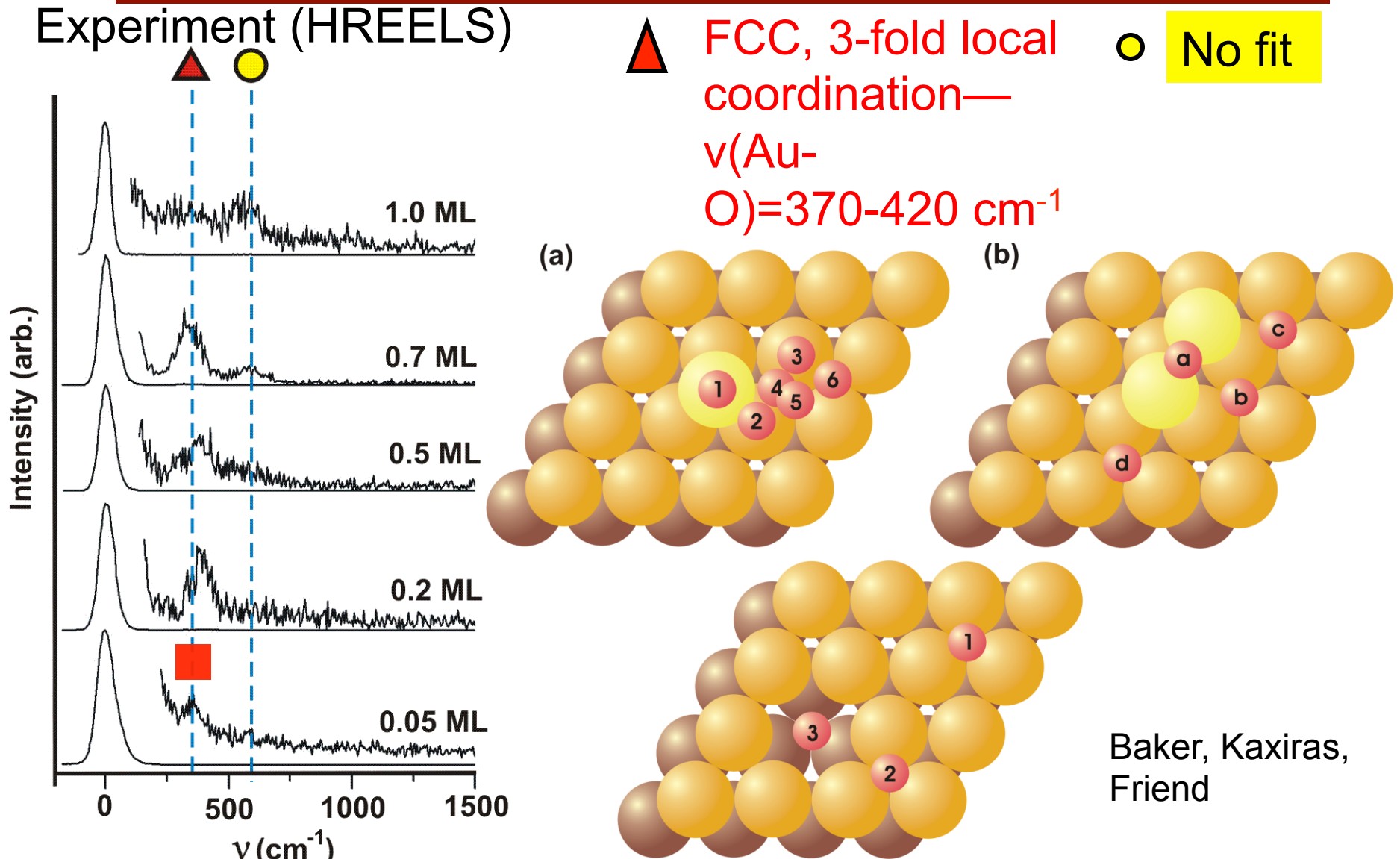
Temperature programmed methods probe kinetics, adsorption strength, and selectivity.

- Maximum O coverage of 1 ML using  $O_3$
- oxidation achieved by  $O_3$  decomposition or electron-induced dissociation of  $NO_2$

X. Deng, B.K. Min, A. Guloy and C.M. Friend, *JACS.*, **2005**, 127 (25) 9267-9270.



# Local Bonding of O depends on Coverage







# Molecular Dynamics with DFT: understand local bonding of O species at higher coverage

Chemisorbed O

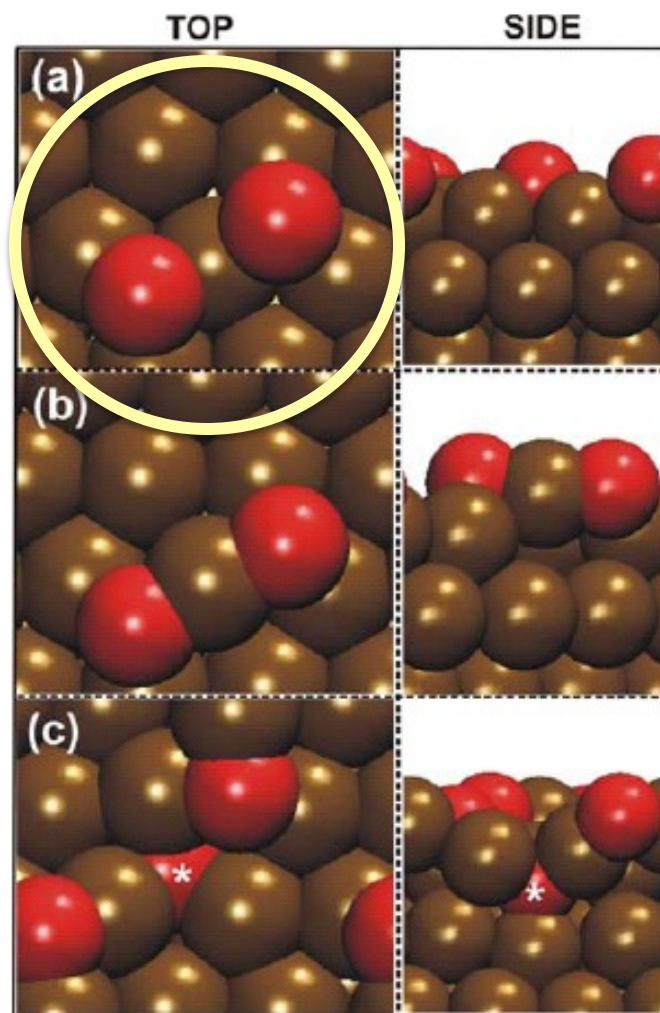
380  $\text{cm}^{-1}$  peak

2-D “oxide”

380 & 560  $\text{cm}^{-1}$  peaks

Subsurface “oxide”

380 & 560  $\text{cm}^{-1}$  peaks



Low T, Low  $\theta_{\text{O}}$

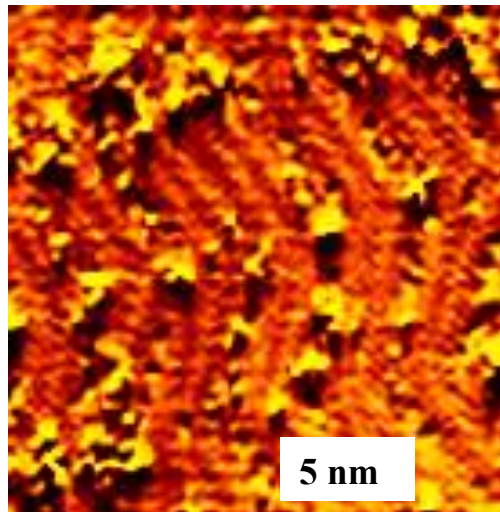
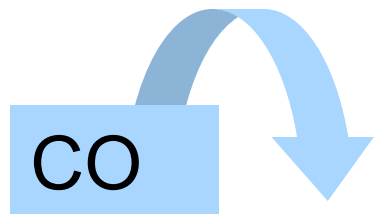
Most reactive and selective; e.g. CO oxidation faster

High T, High  $\theta_{\text{O}}$



# CO oxidation: simple prototype

---

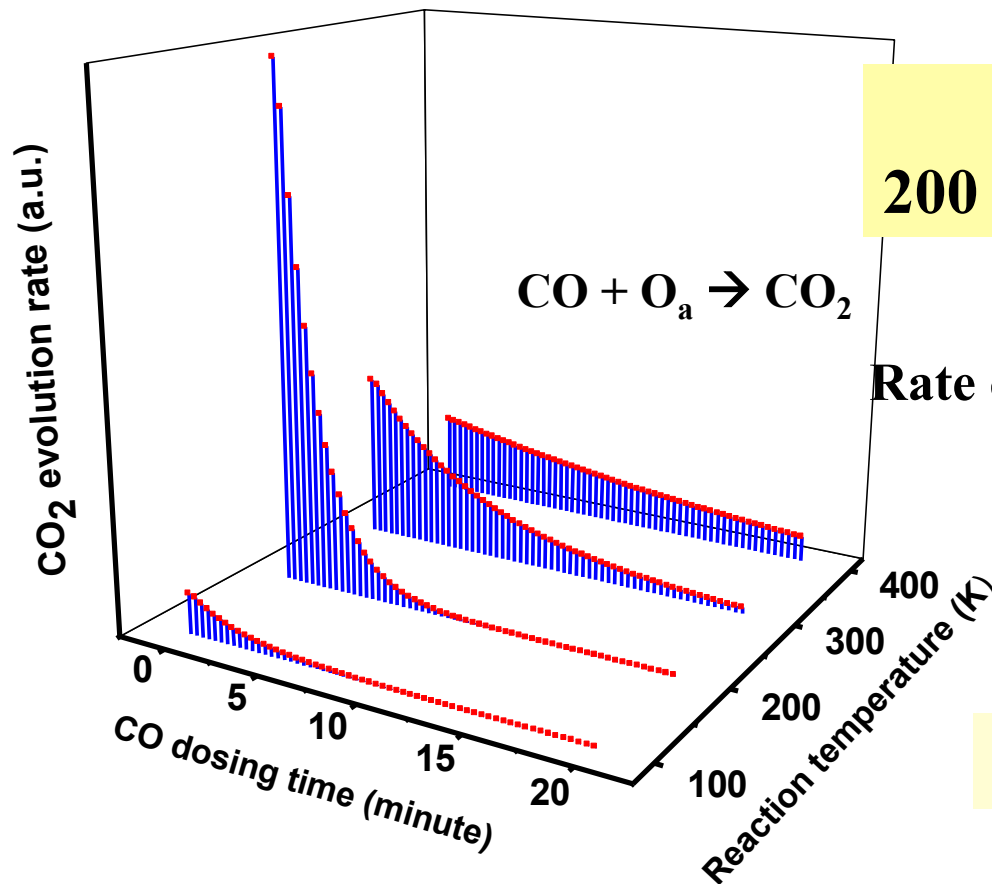


Rate of CO oxidation depends on temperature:

- Local bonding and morphology of surface
- Surface lifetime of reactants



# CO Oxidation on Au(111): Unusual T dependence



Reaction rate:  
**200 K > 300 K > 400 K > 100 K**

Rate constant vs equilibrium CO coverage

$$R_{\text{CO}_2} = k(T) \theta_{\text{CO}} \theta_{\text{O}}$$

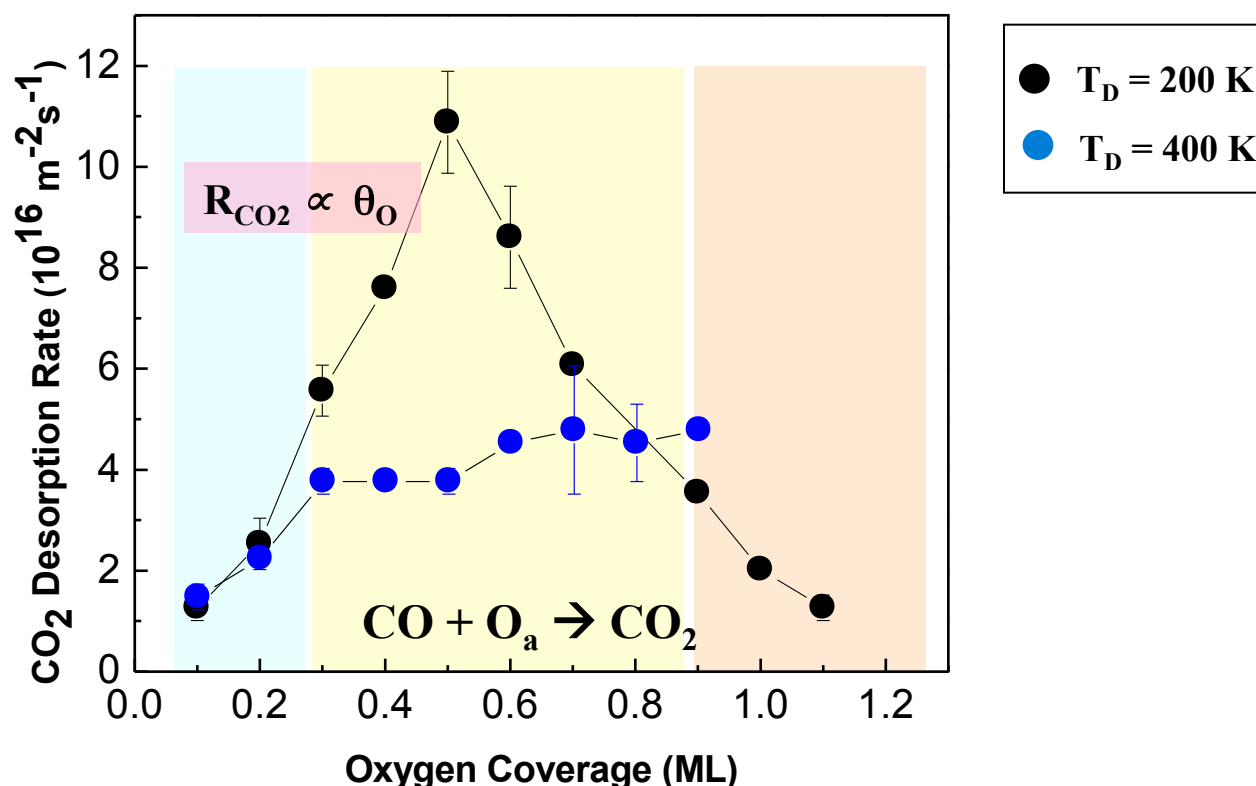
$$k(T) = A \exp(-E_a/RT)$$

$$\theta_{\text{CO}} \propto \tau = k_d (T)^{-1} = [A \exp(-E_d/RT)]^{-1}$$

**The surface lifetime of CO decreases with increasing T;  
However the lifetime does not account for the rate...**



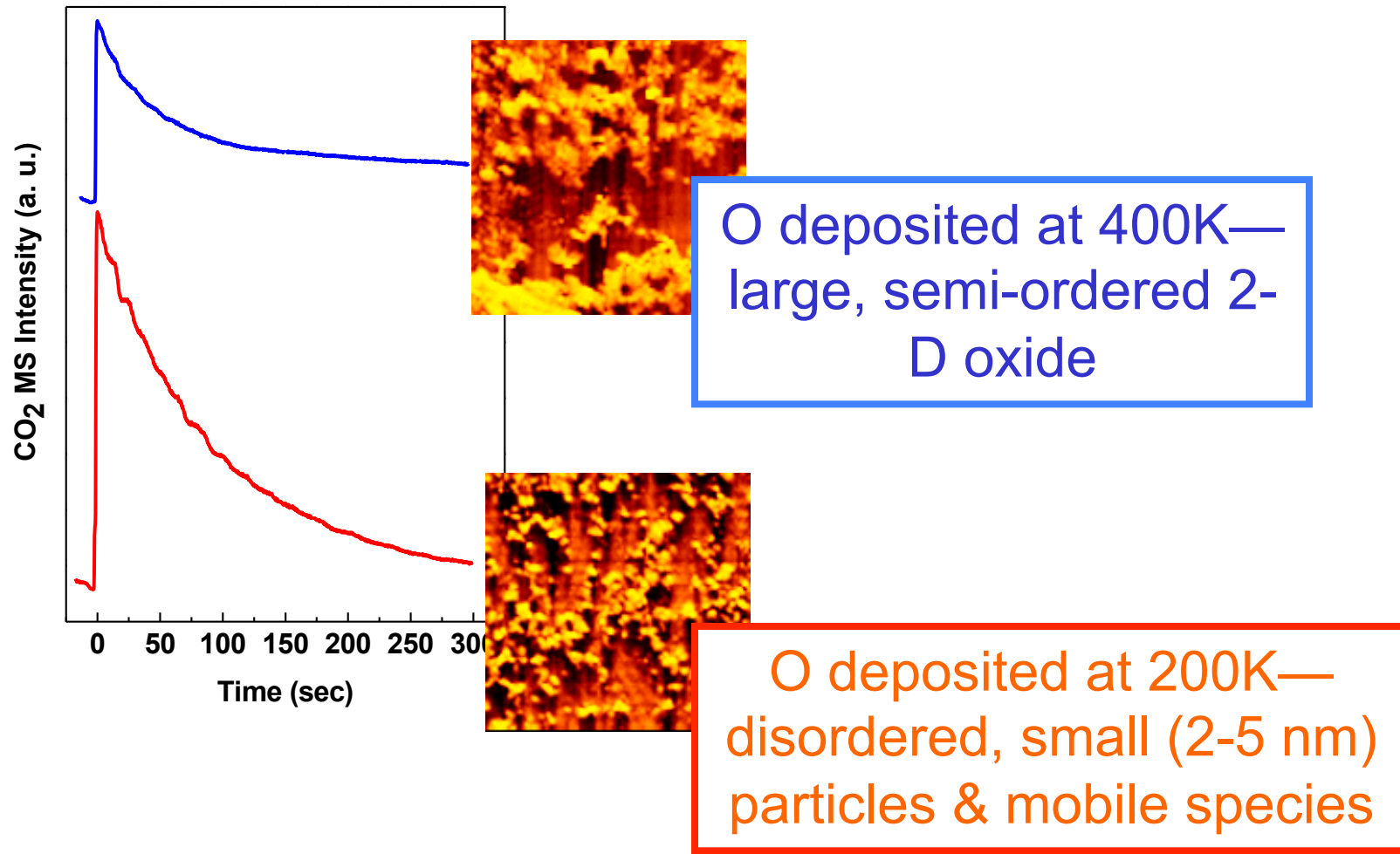
# CO oxidation rate measured isothermally at 200K—dependence on O coverage



Different dependence on O coverage is related to overlayer structure



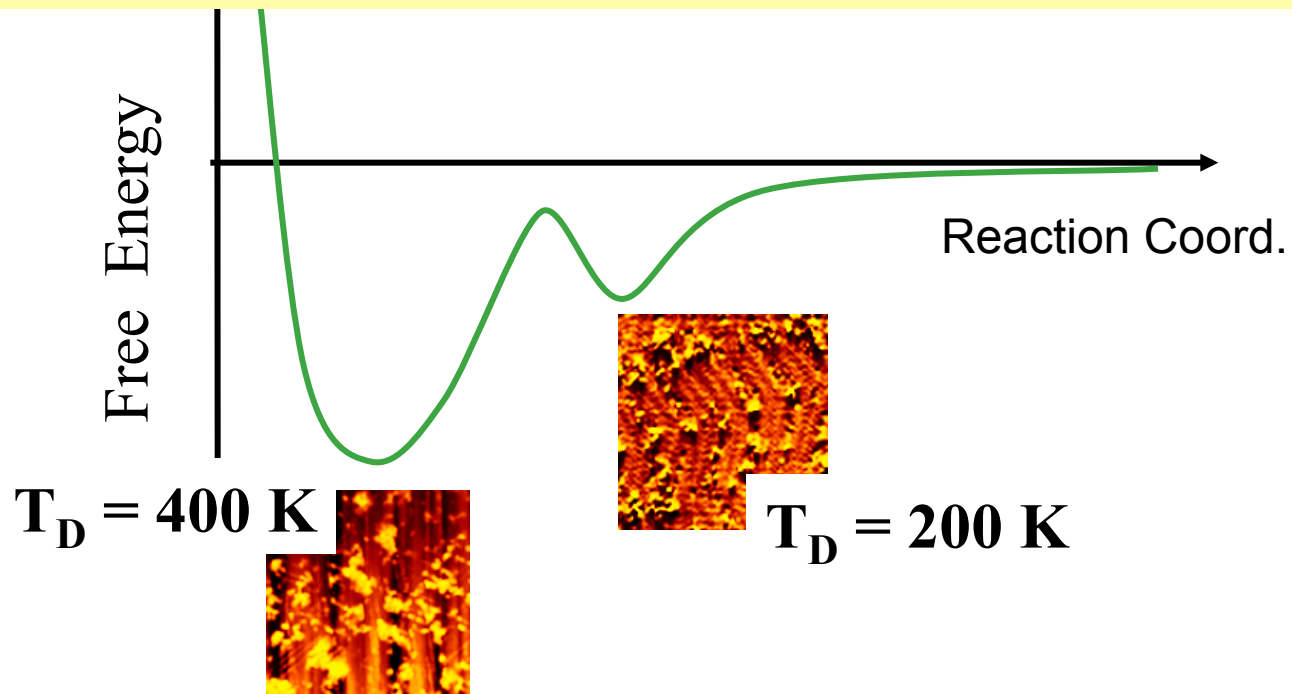
# CO Oxidation Rate higher for metastable O phase





# Metastable state has a higher free energy, increasing reactivity

most active for oxidation, are more readily released from metastable phases

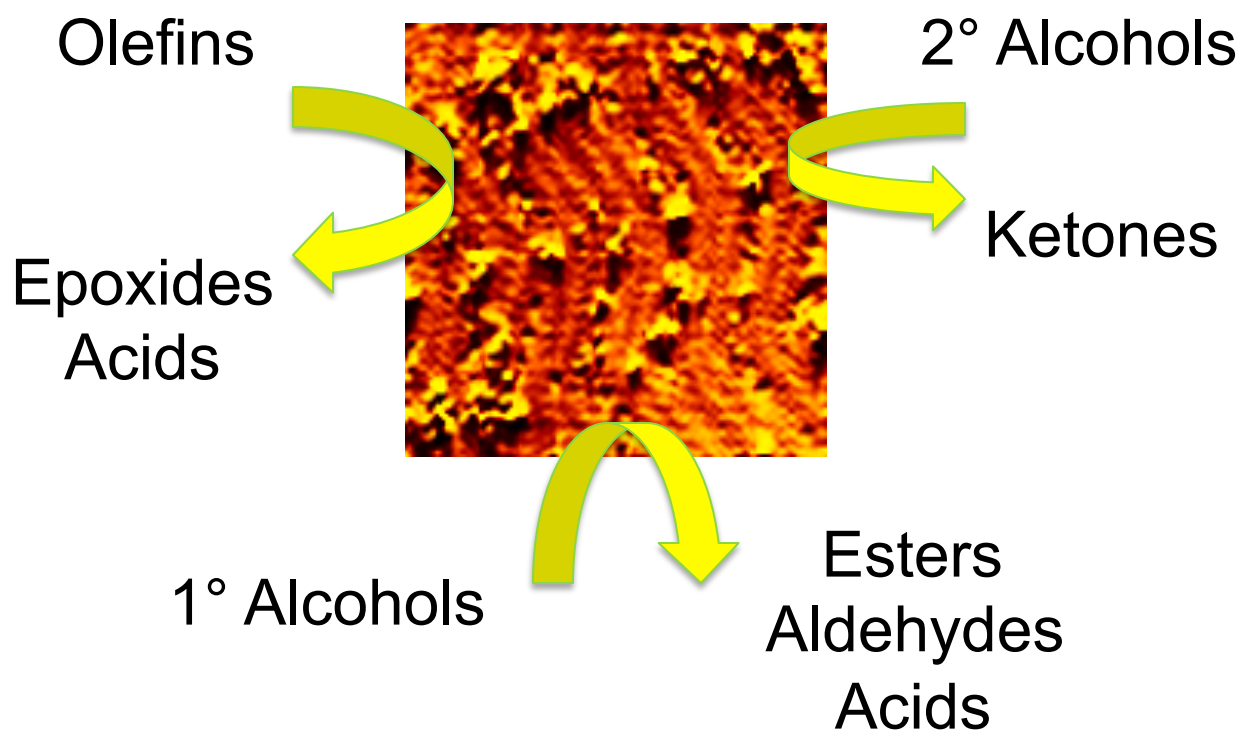






# Extension to more complex reactions

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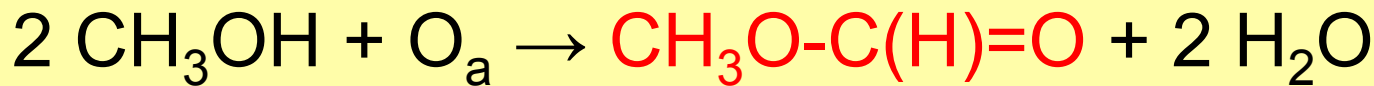
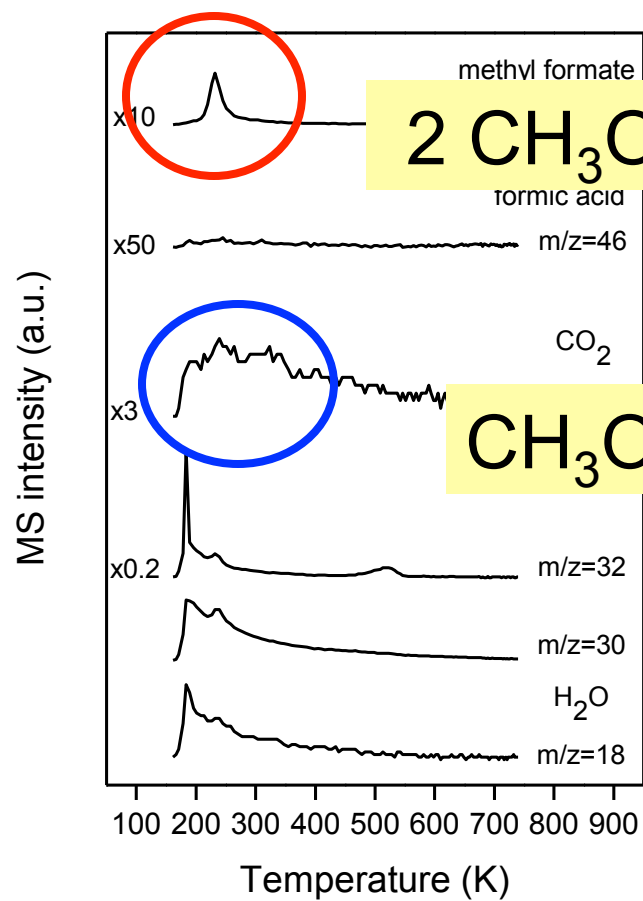
O Adsorbed on metallic Au is required for bond activation



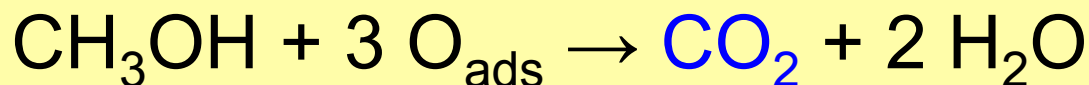
# Methanol partial oxidation on Au(111): Partial oxidation at low O coverage

Low oxygen coverage (0.05 ML):

No reaction on clean surface: flat or defective



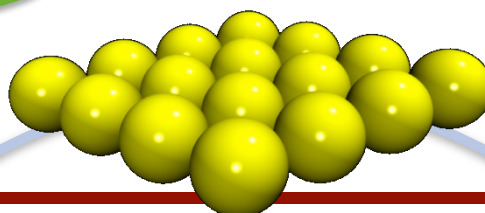
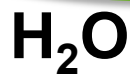
Competing combustion:



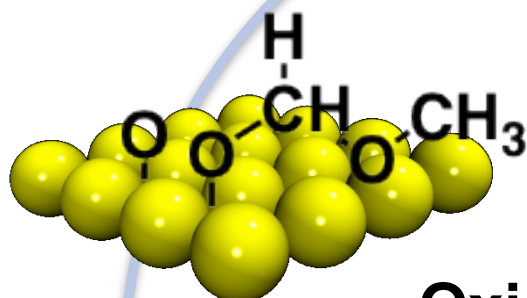
Liu, Xu, Haubrich, Friend, Madix, Ang. Chemie, (2009)



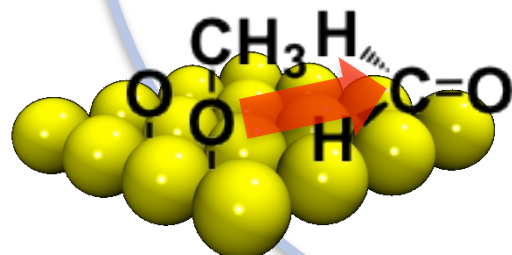
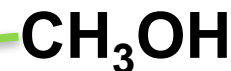
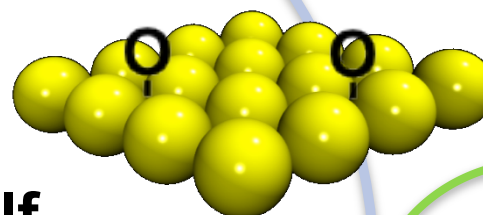
*Ester: Methyl Formate*



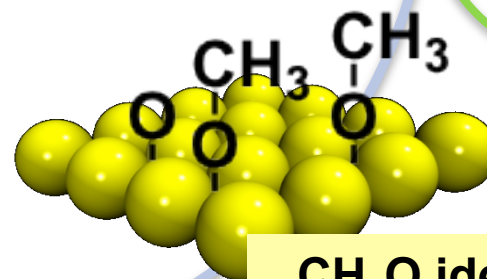
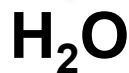
Au(111)



Oxidative self-coupling of methanol



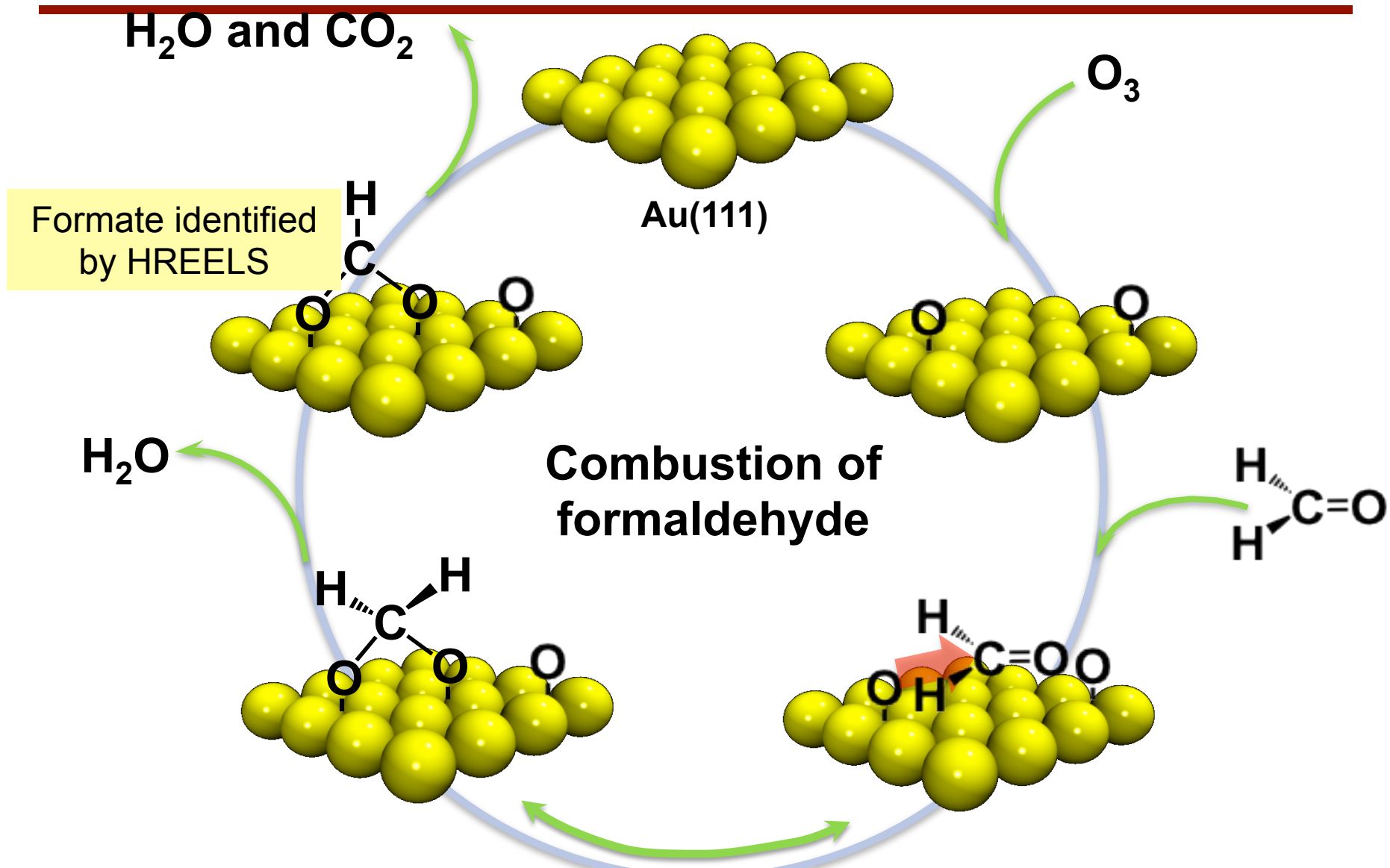
Rate-limiting step:  
H elimination from  
 $\text{CH}_3\text{O}$



$\text{CH}_3\text{O}$  identified using  
vibrational  
spectroscopy &  
isotopic labeling



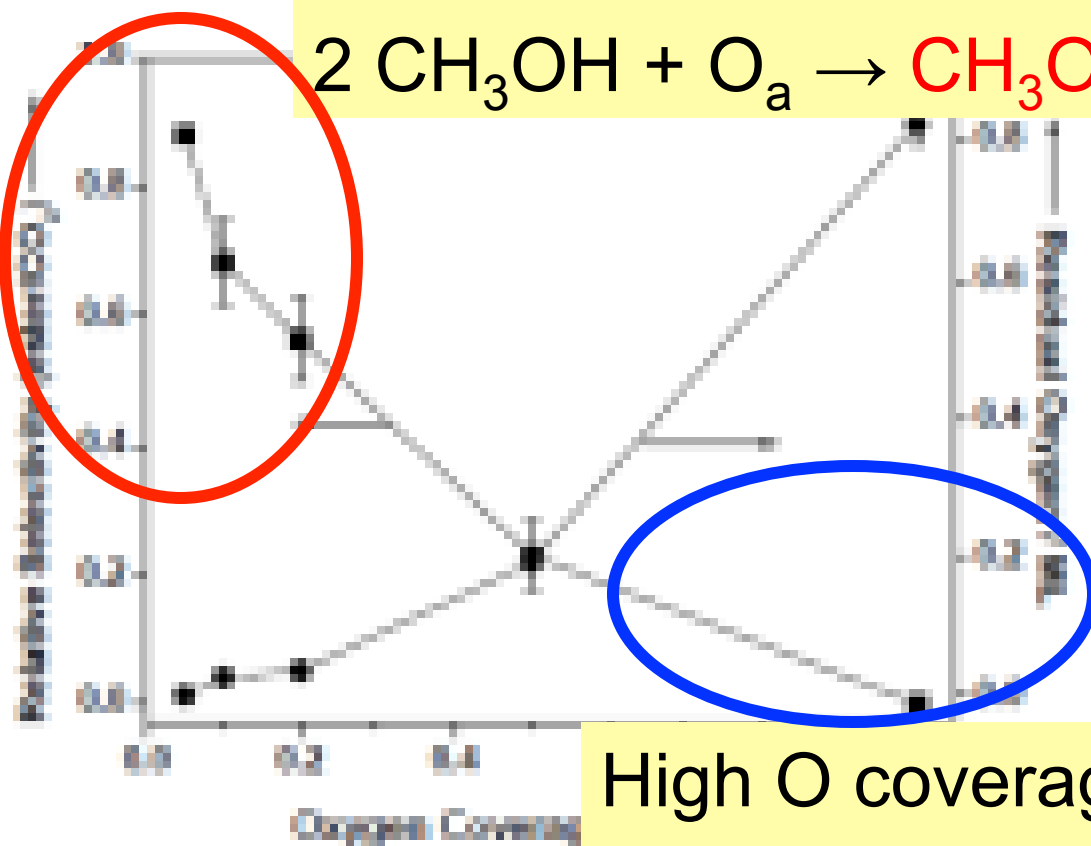
# Formaldehyde Oxidation: Pathway for combustion/Reservoir of Formaldehyde



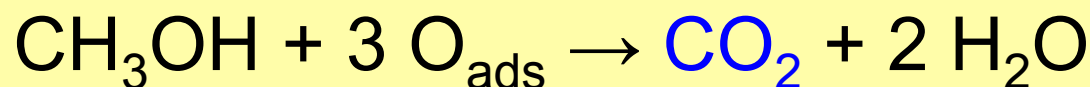


# Selectivity for methanol esterification: O coverage dependence

Low O coverage: **esterification** dominates



High O coverage: **combustion**





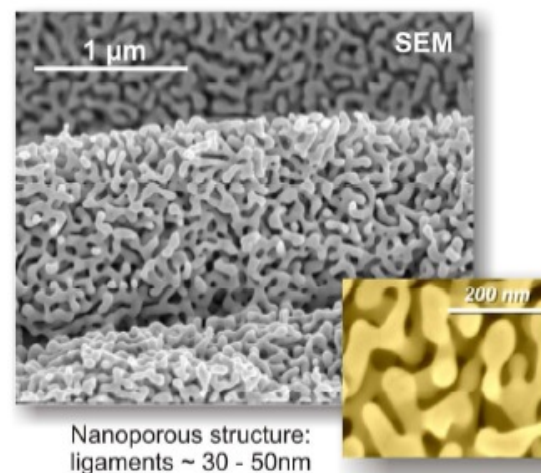


# Bridge to Catalytic System

## ***Predictions from molecular mechanism:***

- High  $\text{CH}_3\text{OH}$ :  $\text{O}_2$  favors esterification
- Low temperature reaction anticipated
- Rate limitation: supply of O

Predictions born out  
@atmospheric pressure  
using nanoporous Au

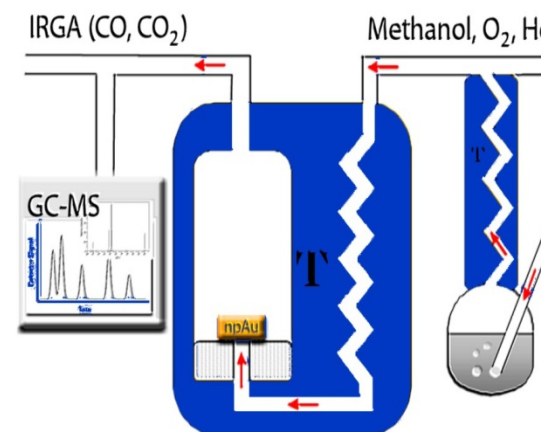
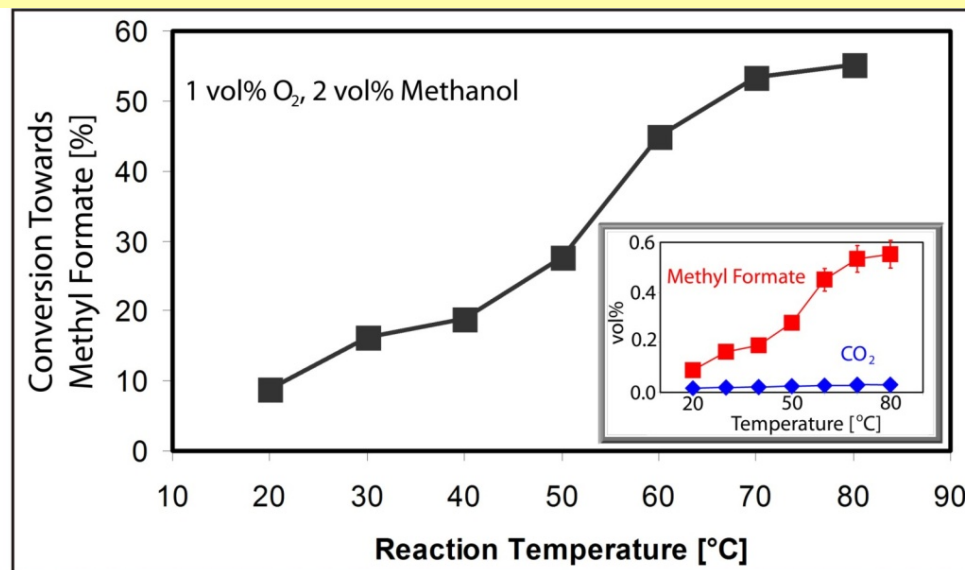


*Wittstock & Bäumer, Science, 2010, 327, 319-322*

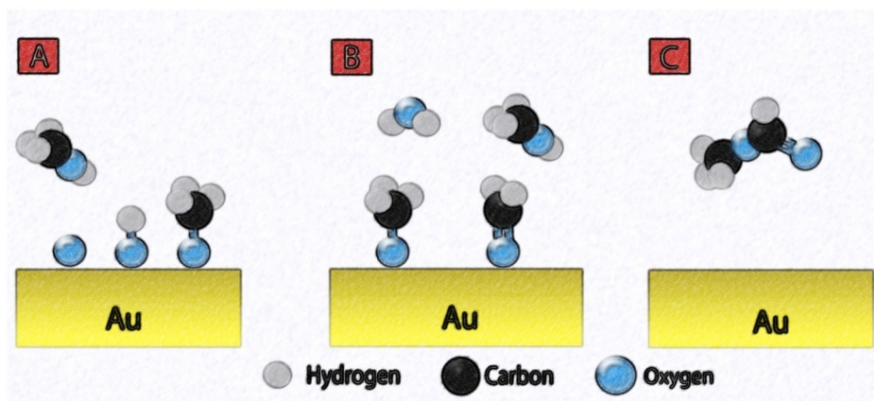


# Methanol Esterification over NP Au

Mechanism at low pressure *is* predictive of catalytic reactivity and selectivity

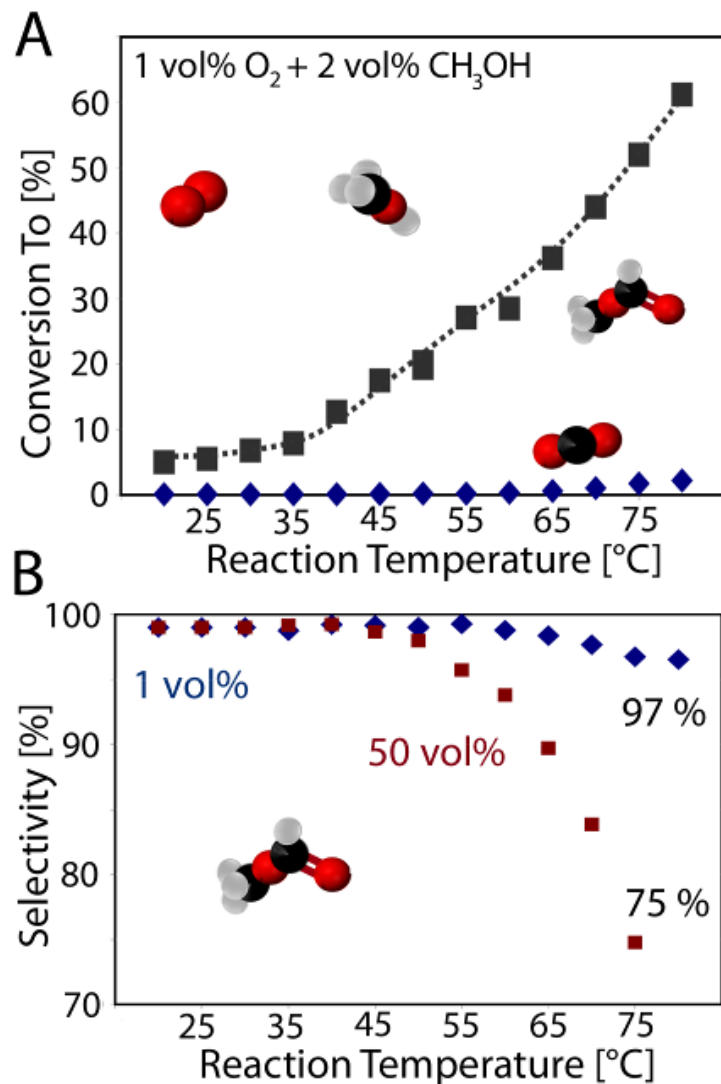


Atmospheric pressure, ***catalytic*** transformation





# Methanol oxidation on NP Au



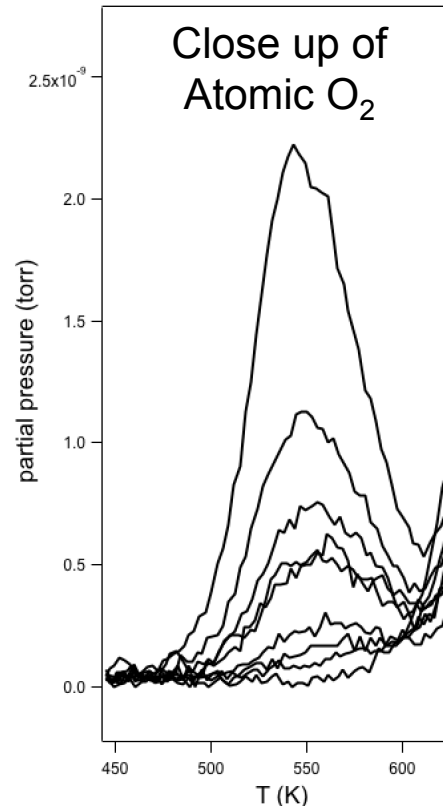
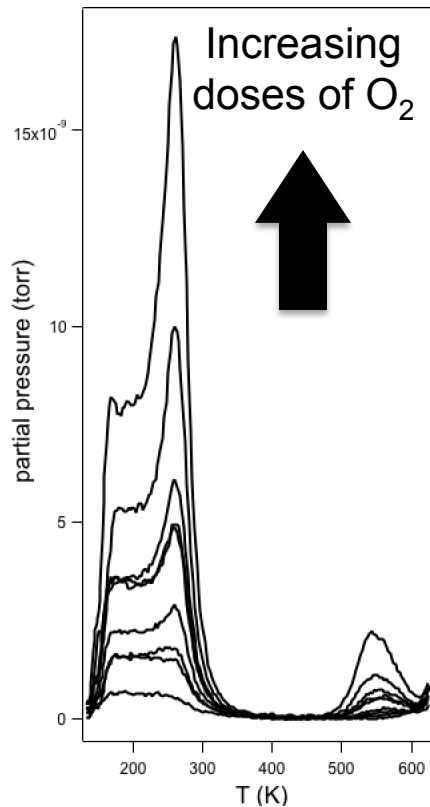
As predicted: **esterification** dominates at low O<sub>2</sub> partial pressures

*NP Au is stable: activity maintained after 14 days of operation, TON~687,000*

As predicted:  
Selectivity=**ester**:CO<sub>2</sub> decreases with T and O<sub>2</sub> partial pressure



# Confirmation that NP Au dissociates O<sub>2</sub>--Ag key



O<sub>2</sub> dosed at 130 K,  
varying the  
pressure from  
1x10<sup>-9</sup> to 1x10<sup>-7</sup> torr

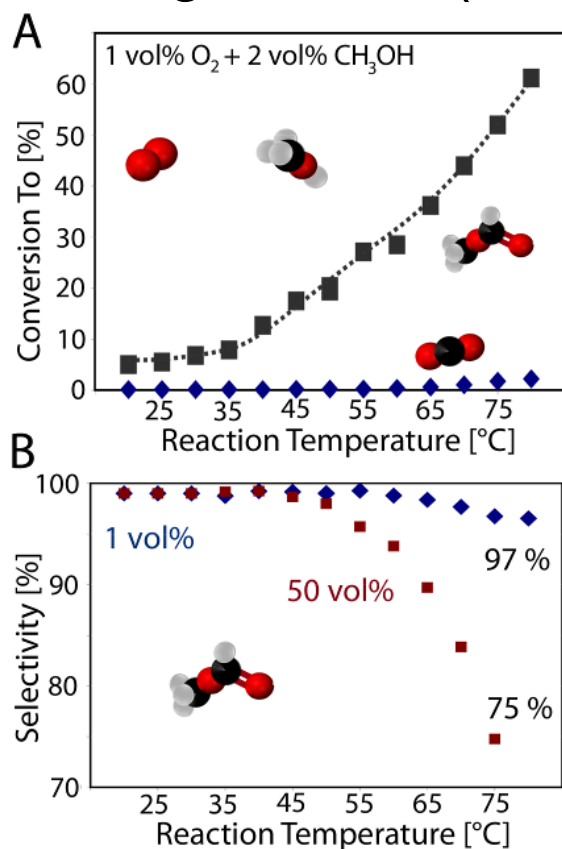
The atomic O<sub>2</sub> stays  
relatively the same  
with each dose

*Molecular oxygen is adsorbed onto the Ag/Au alloy  
at a temperature of 130 K*

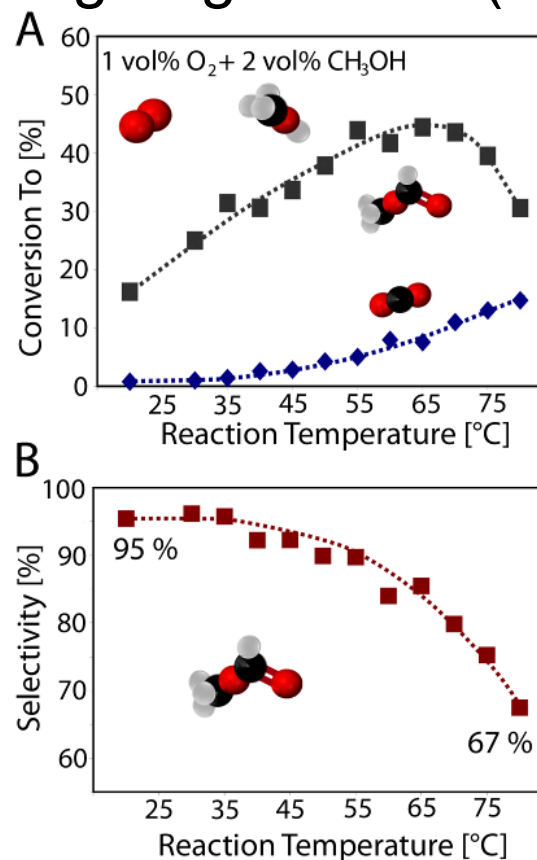


# Increase in Ag content lowers selectivity: Suggests increase in $\theta_{\text{O}}$

## Low Ag content (<1%)



## High Ag content (~5%)



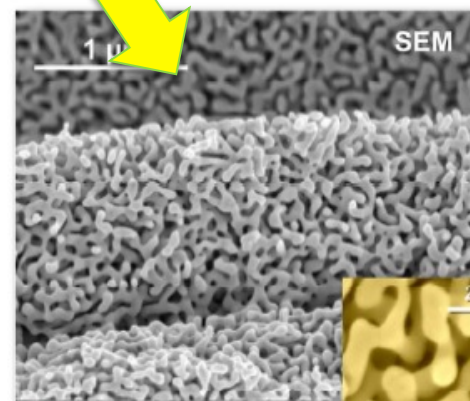
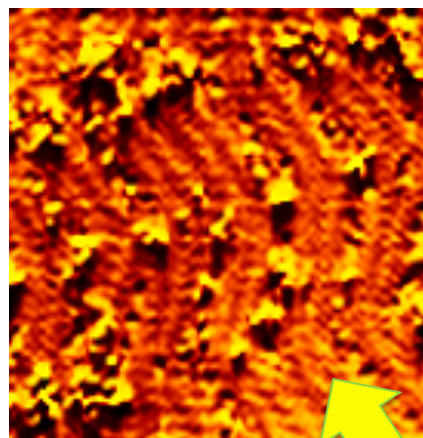
Note similarity in low Ag content/high O<sub>2</sub> pressure and high Ag content/low O<sub>2</sub> pressure



# Bridging the pressure and materials gap

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Clear  
correspondence  
between NP Au  
and single  
crystal Au



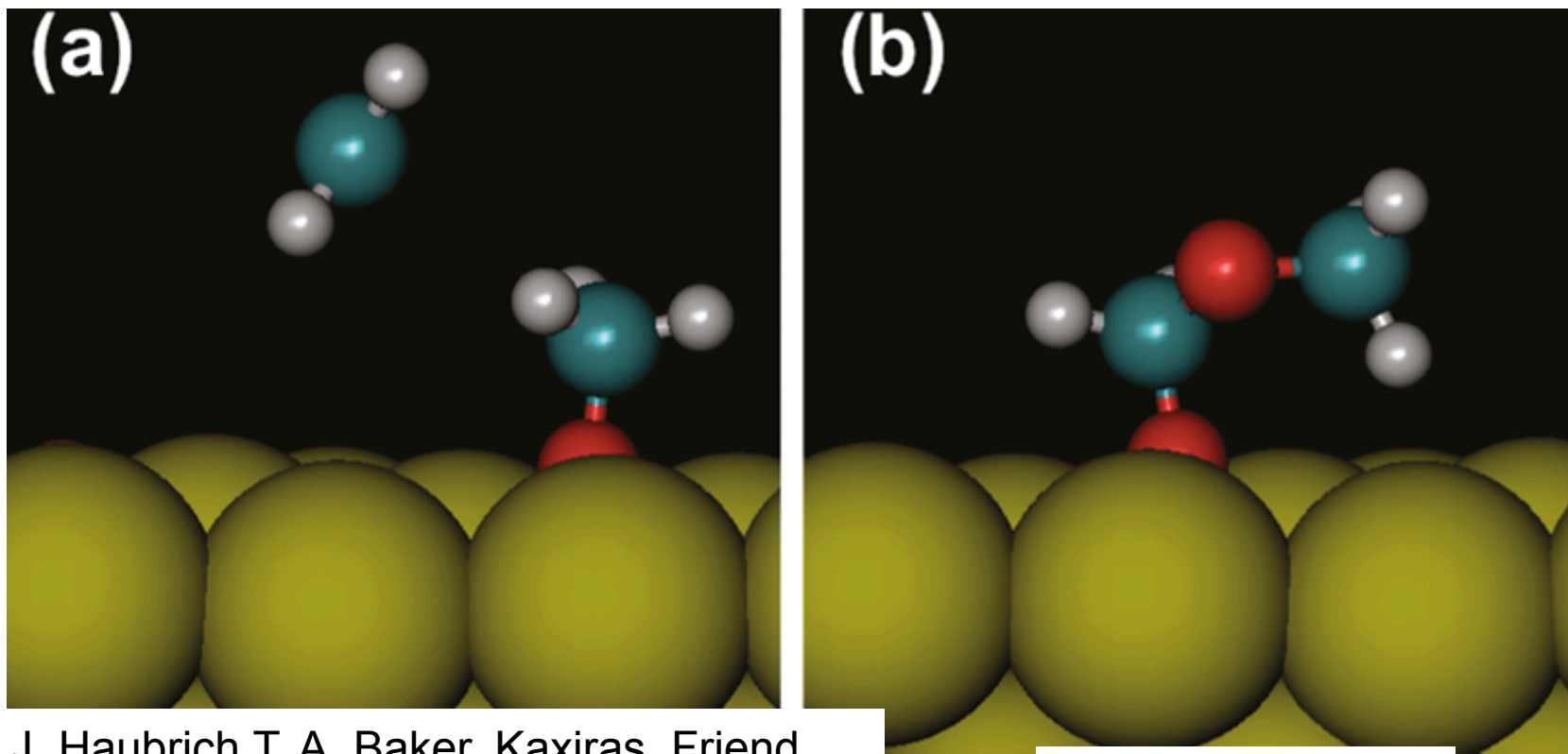
Nanoporous structure:  
ligaments ~ 30 - 50nm





# DFT: Attack of $\text{H}_2\text{C}=\text{O}$ by $\text{CH}_3\text{O}$ is spontaneous—no barrier

Adsorbed O facilitates last  $\beta$ -H elimination step;  
low barrier for transfer to Au (0.22 eV)



B. Xu, J. Haubrich, T. A. Baker, Kaxiras. Friend,  
JPC C (2011) doi.org/10.1021/jp110835w

VASP, GGA-PW91



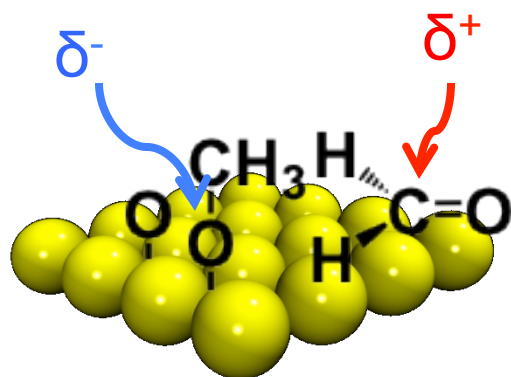
# Insights from DFT studies

---

- Loss of H from  $\text{CH}_3\text{O}$  is ***determines rate***—adsorbed O, OH and  $\text{CH}_3\text{O}$  all promote formaldehyde formation
- Weak binding of reactants, e.g.  $\text{H}_2\text{C}=\text{O}$ , OH, &  $\text{H}_2\text{O}$ , facilitates rearrangement to preferred reaction geometry for coupling—key aspect of Au reactivity



# Guiding principle for designing new reactions



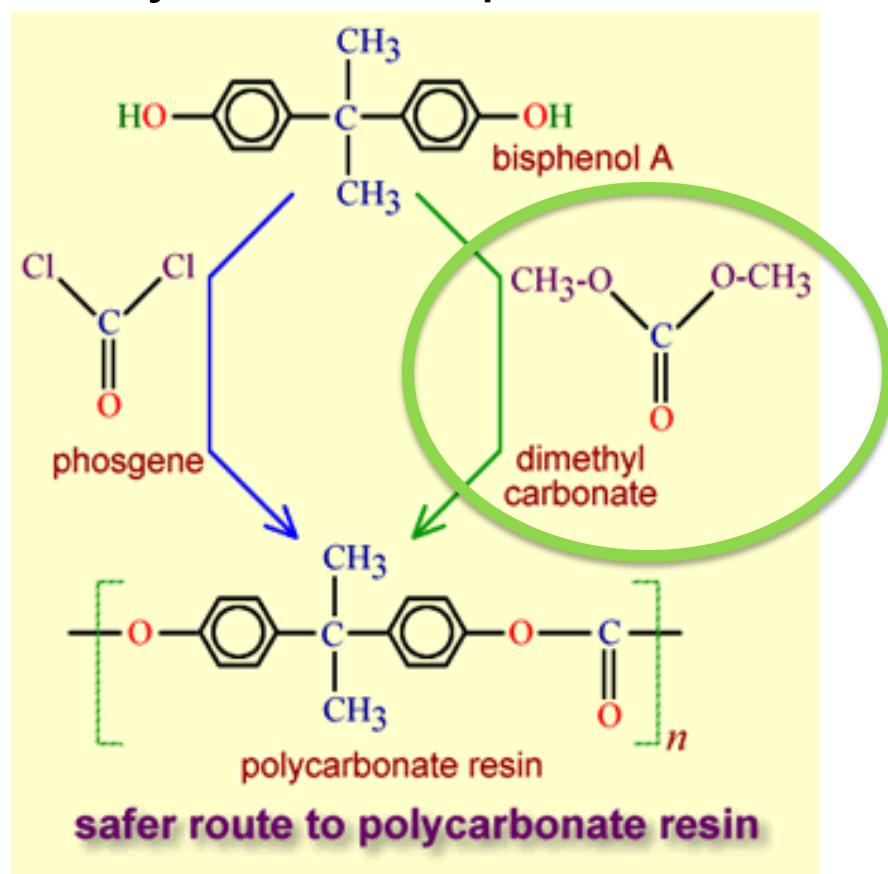
Electron distribution leads to reaction of negatively polarized species with positively charged one

**Prediction:** Any molecule with electron-deficient carbon should react with  $\text{OCH}_3$  on  $\text{O}/\text{Au}$ —e.g.  $\text{CO}$



# Design of new synthetic routes: Dimethylcarbonate production using Au

## Polycarbonate production



## Biofuel production

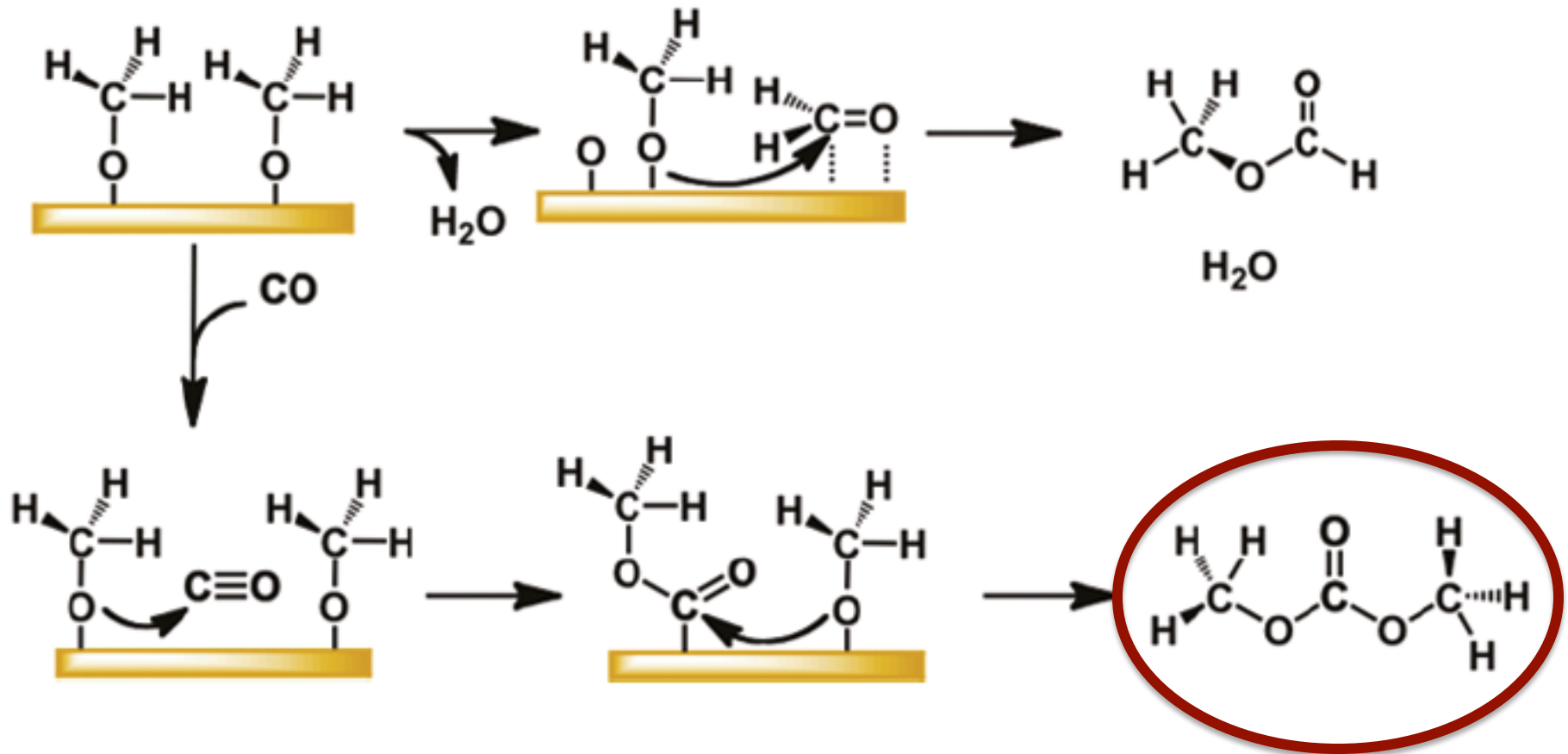


[http://www.greener-industry.org.uk/pages/safer/safer\\_4\\_reactions.htm](http://www.greener-industry.org.uk/pages/safer/safer_4_reactions.htm)

[http://blogs.rsc.org/cy/files/2011/02/biofuels\\_1.gif](http://blogs.rsc.org/cy/files/2011/02/biofuels_1.gif)

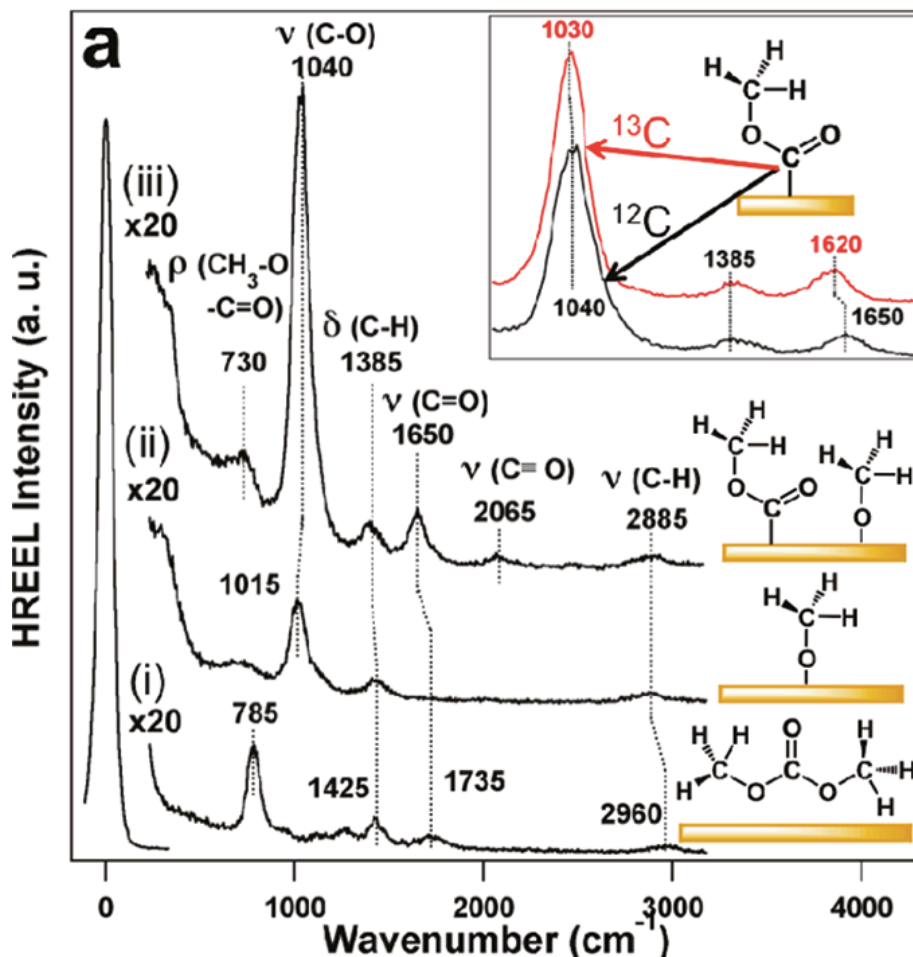


# Dimethyl carbonate production on Au(111)/O

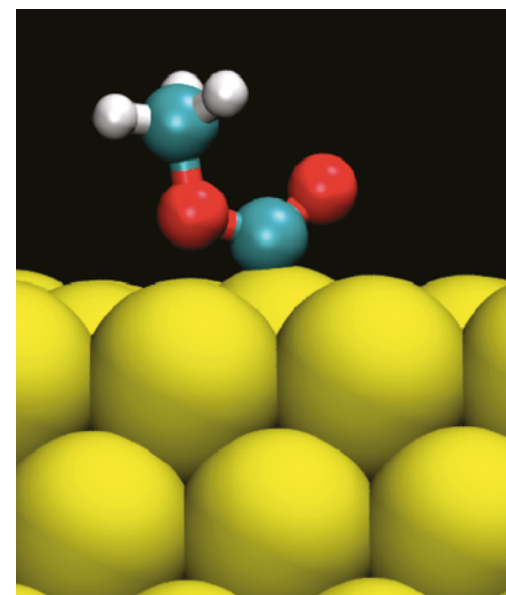




# Spectroscopic identification of $\text{CH}_3\text{OC}=\text{O}$ intermediate



DFT probes structure & used for vibrational assignments

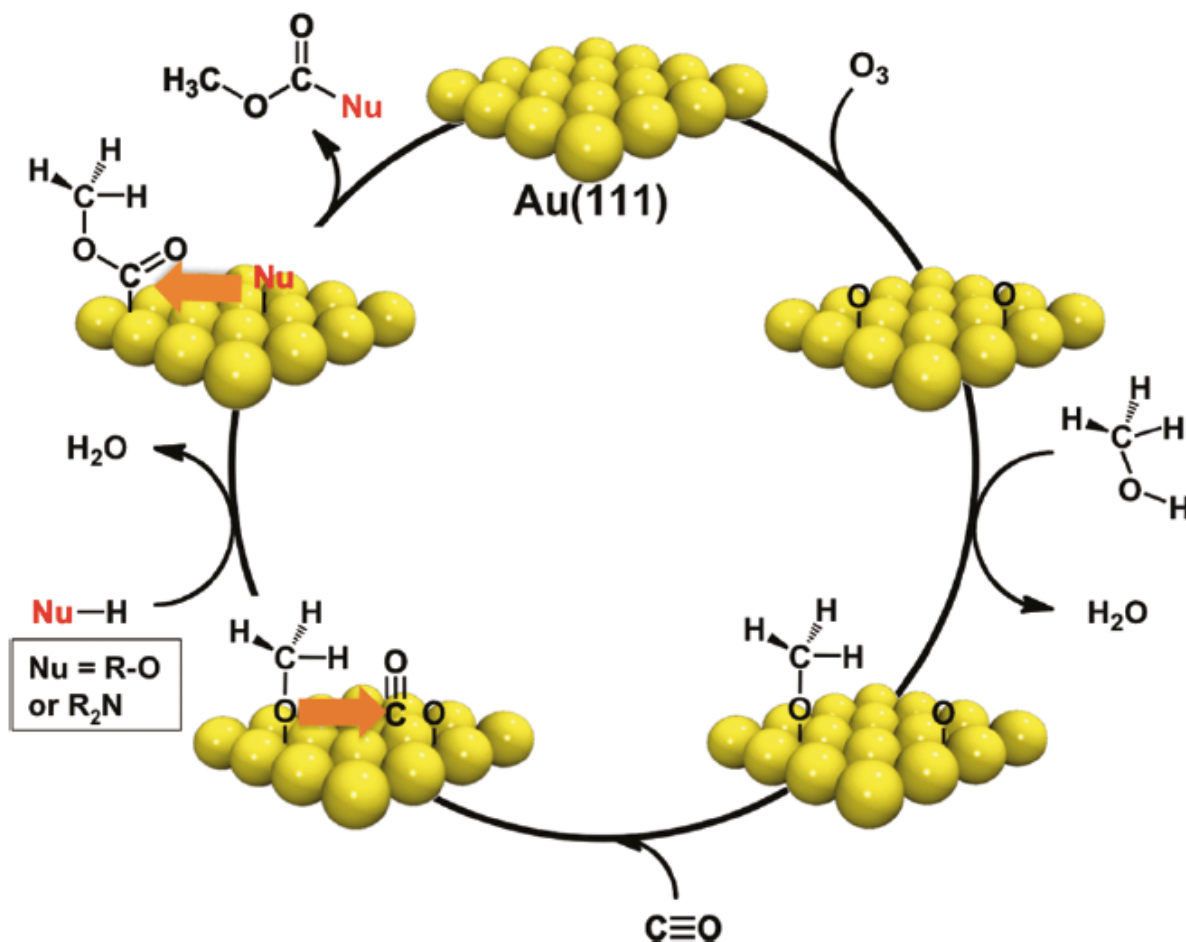


Xu, Madix, Friend, JACS(2011); [dx.doi.org/10.1021/ja207389z](https://doi.org/10.1021/ja207389z)





# Surface Chemistry as a platform for reaction *discovery*: Dimethyl carbonate production



- Low temperature process
- No noxious byproducts—existing process produces HCl



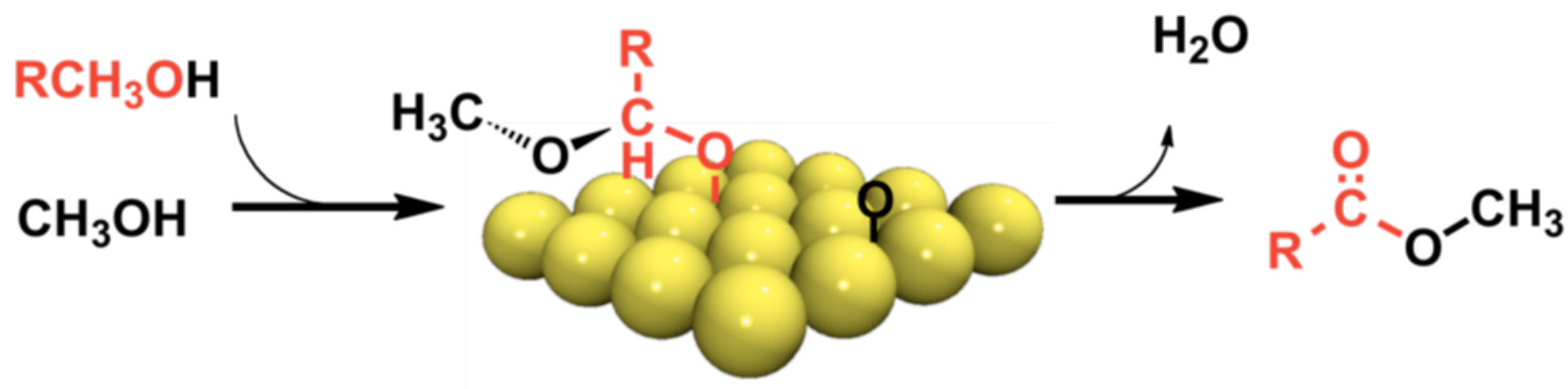
# Insights from DFT studies

---

- Loss of H from  $\text{CH}_3\text{O}$  is **determines rate**  
—adsorbed O, OH and  $\text{CH}_3\text{O}$  all promote formaldehyde formation
  - **Insight: longer chain alcohols will form aldehydes at a faster rate/lower temperature**
- Weak binding of reactants, e.g.  $\text{H}_2\text{C}=\text{O}$ , OH, &  $\text{H}_2\text{O}$ , facilitates rearrangement to preferred reaction geometry for coupling—  
key aspect of Au reactivity



# Tailoring coupling of higher alcohols

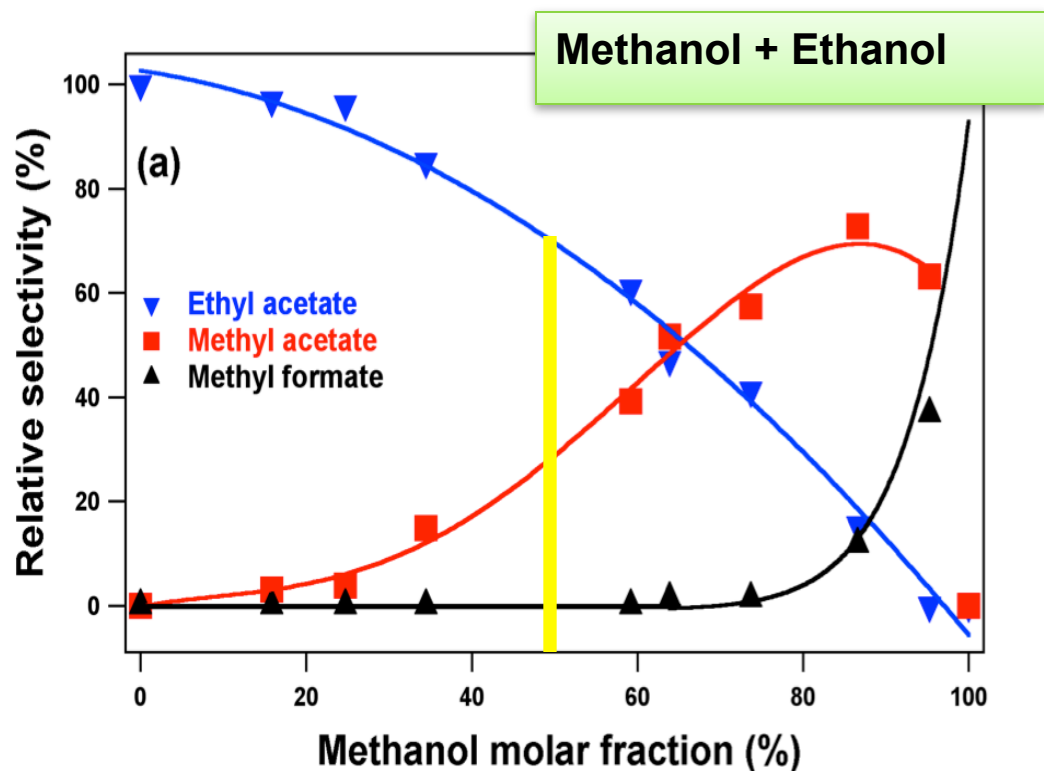


What controls selectivity for the different possible coupling pathways?

Xu, Friend, Madix, Chemical Sciences (2010) 1, 310-314, DOI: 10.1039/C0SC00214C.



# Higher Alcohols: Displacement & $\beta$ -H elimination are key factors



**Relative surface coverage determined by equilibrium**

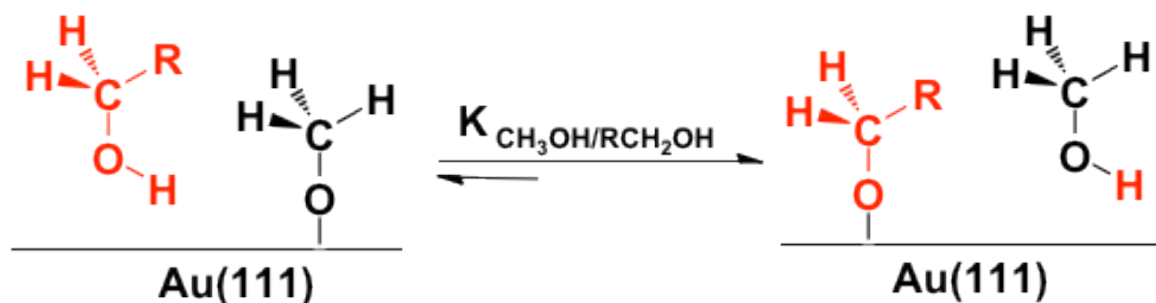
Rate of  $\beta$ -H elimination from  $RCH_2O(ads)$ :  $CH_3O$  reacts slowest

Madix, R.J. & Friend, C.M. JACS (2010).



# Reactant binding determines competition for reaction sites

Relative surface concentration of intermediates determined by equilibrium:



$$K = \frac{[\text{CH}_3\text{OH}][\text{C}_2\text{H}_5\text{O}]}{[\text{CH}_3\text{O}][\text{C}_2\text{H}_5\text{OH}]} = 8$$

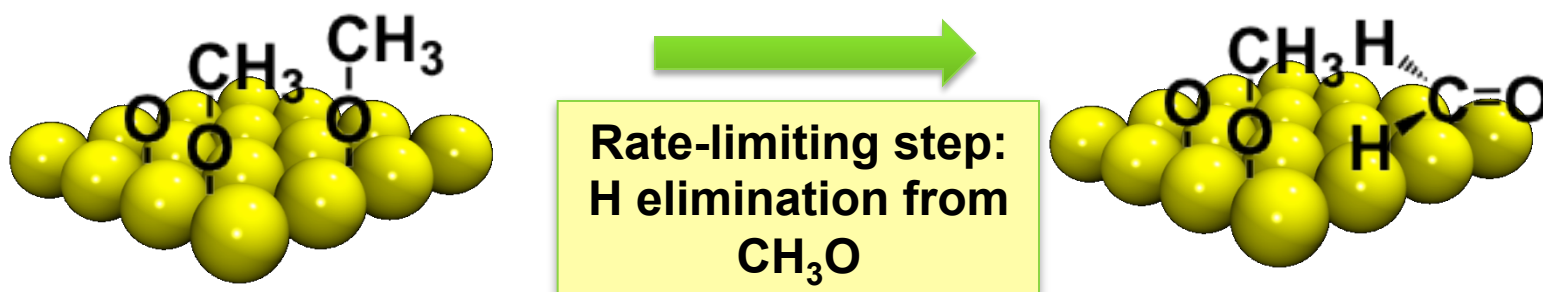
**Challenge for theory:** Can competitive binding be predicted?

Xu, B., Madix, R.J. & Friend, C.M. JACS (2010).



# Second factor: H loss from alkoxy species on O/Au(111)

Faster rate of H elimination (aldehyde formation) from  $\text{RCH}_2\text{O}(\text{ads})$  as chain grows longer:  $\text{CH}_3(\text{CH}_2)_3\text{O} > \text{CH}_3\text{CH}_2\text{O} > \text{CH}_3\text{O}$



**Methanol:** only coupling product observed; no formaldehyde

**Ethanol:** Acetaldehyde produced in significant quantities;  
also coupling

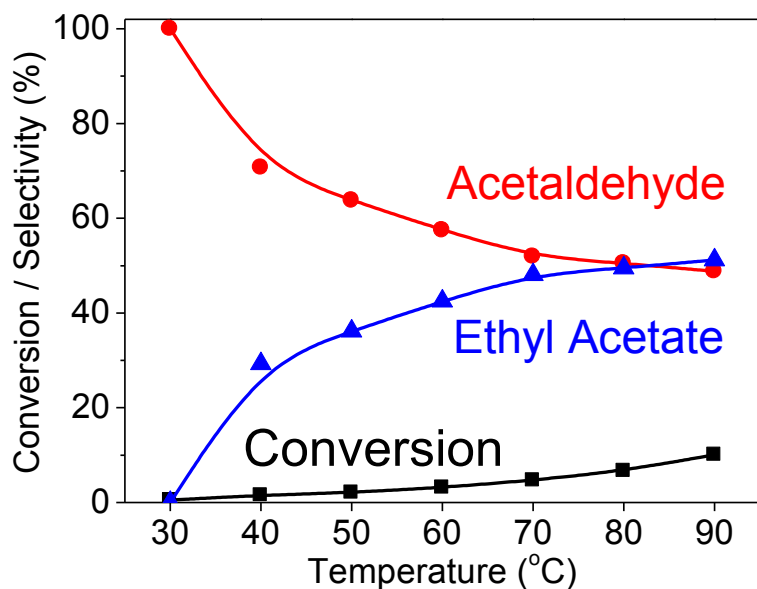
**1-Butanol:** Aldehyde primary product; formed at lower T;  
minor amount of coupling



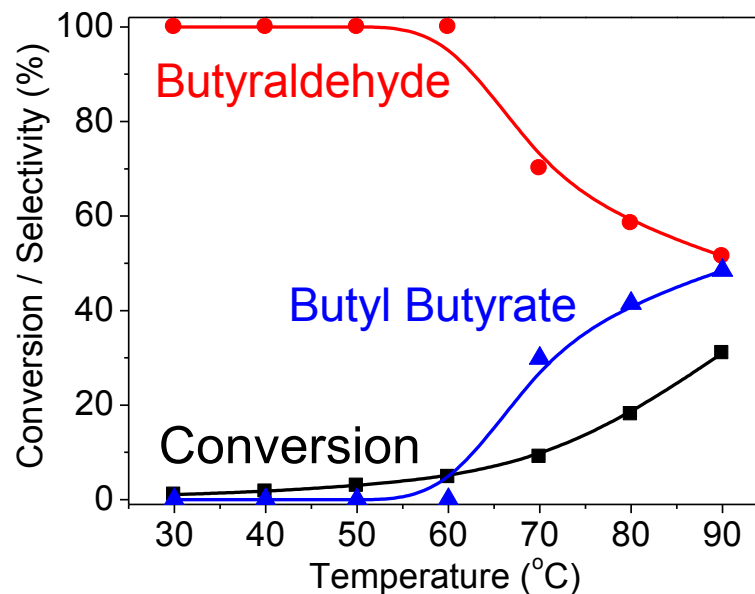


# O<sub>2</sub>-assisted **self-coupling** of alcohols on NP Au: Same trend as for O/Au(111)

## Ethanol



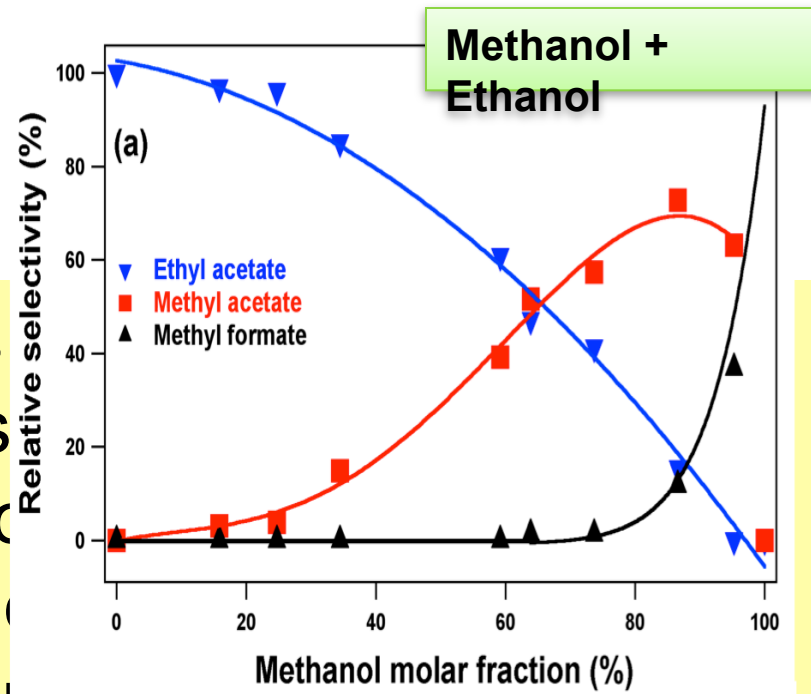
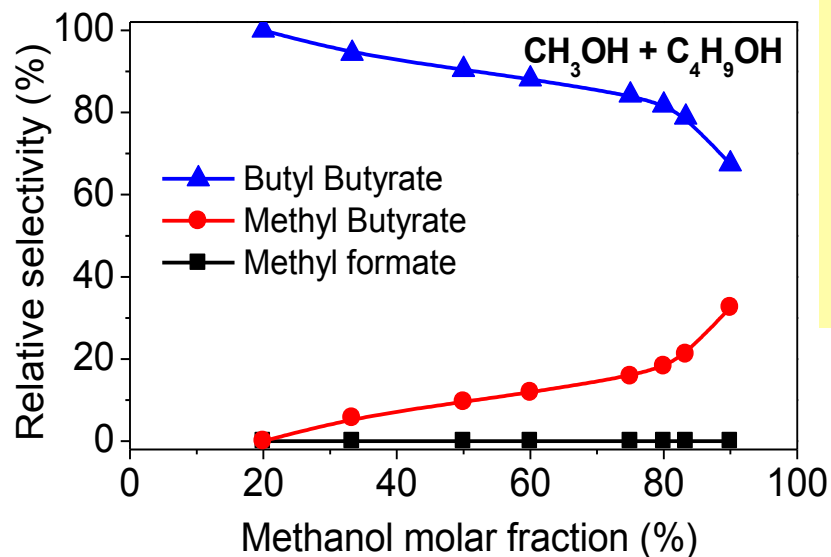
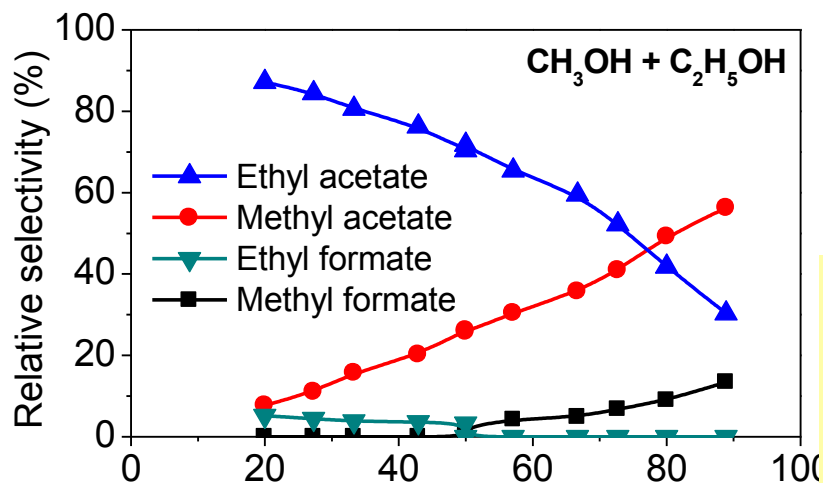
## n-Butanol



NP Au is also active in oxidative coupling of alcohols other than methanol



# O<sub>2</sub>-assisted cross-coupling of **dissimilar alcohols** on NP Au



As dis

two

1)

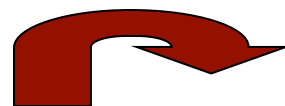
2)

relative surface concentrations of alkoxy.

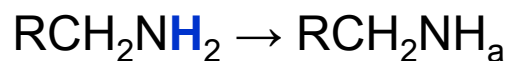
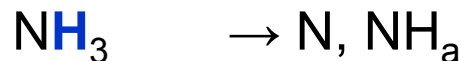
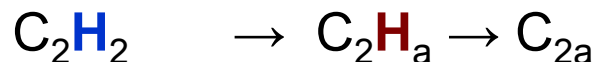
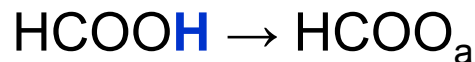
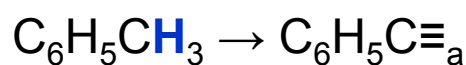
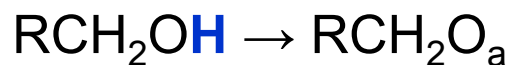


# General Reaction Patterns for Atomic Oxygen on Ag and Au

## I. Activation of Acidic Hydrogens: $O_a$ as Brønsted Base



(Reactions of BH(g) suggested by gas phase acidity)

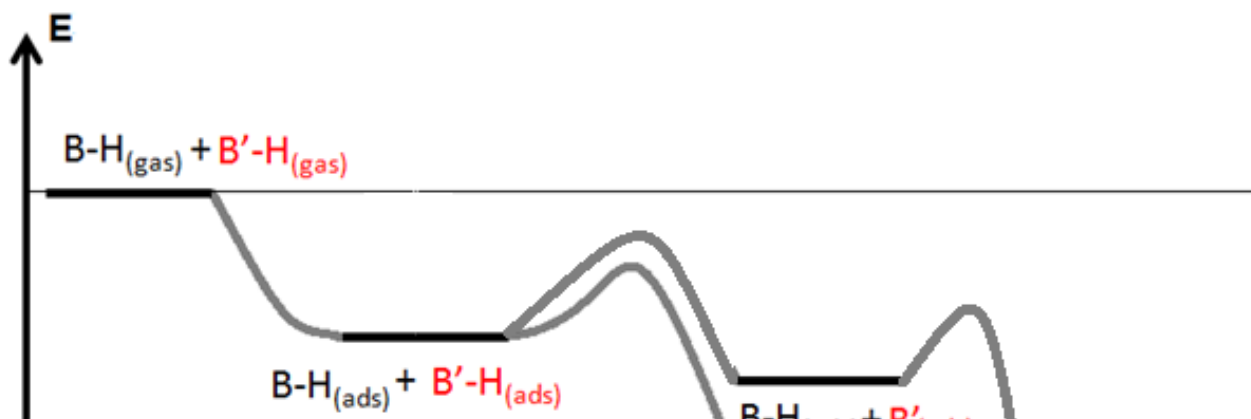
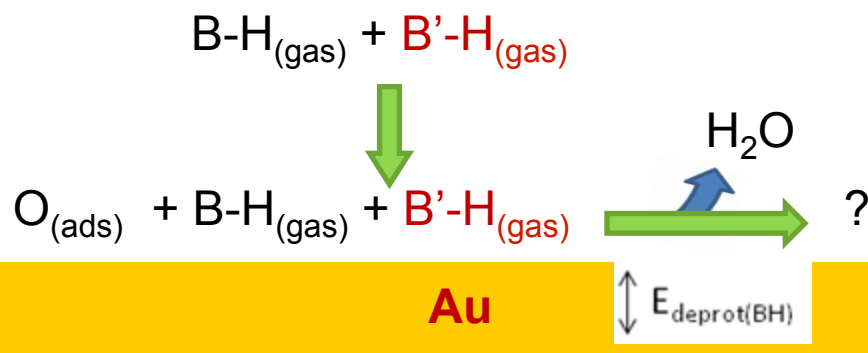


M.A. Barteau and R.J. Madix, Surf. Sci. 94 (1980) 303.

X. Liu, R.J. Madix and C.M. Friend, Chem. Soc. Rev. 137 (2008) 2243



# General concept: Acid-base reactions determine surface concentrations

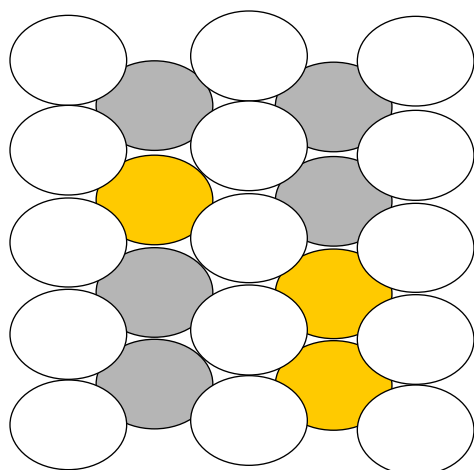


**Challenge:**  
Determination of relative binding and charge distributions for different molecules.

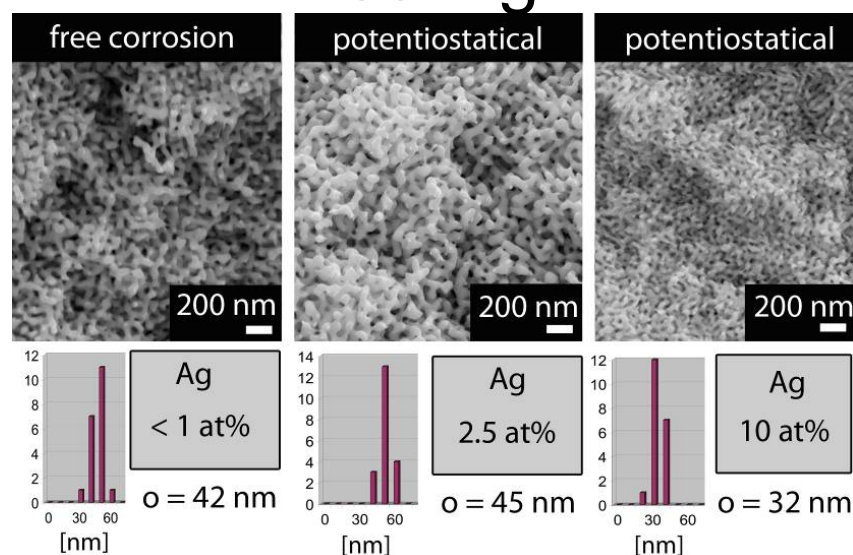


# Current outlook: Alloy catalysts

## Single crystal models



## Catalyst synthesis and testing



Challenge for theory: electronic and geometric structure under reaction conditions



# Overview

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- Fundamental mechanistic studies provide basis for predicting *new* reactions
- New nanoscale architectures, e.g. nanoporous materials, are promising materials
- Theoretical insight provides guiding principles





# “Wish list” for advancement of theory

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- Prediction/modeling of metal atom release
- Accurate description of charge distribution
- Inclusion of weak interactions; more accuracy
- Kinetic modeling over various time scales
- Treatment of complex materials—  
multicomponent and over different length scales
- Excited state dynamics (photochemistry)  
—“hot topic”



# *Friend Group*



**Funding:**  
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NSF  
Harvard/NSEC  
Humboldt Foundation

## **Co-workers:**

M. Baeumer  
T. Baker  
M. Biener  
J. Biener  
T. Cremer  
S.C. Jensen  
J. Haubrich  
E. Kaxiras  
J. Klobas  
R. Madix  
K. Phillips  
M. Schmid  
C. Siler  
K. Stowers  
L.-C. Wang  
B. Xu