Surface reactions: Informing catalyst design through fundamental studies

Atomistic models

Focus on improving selectivity for selective oxidation

IMASC MISSION:
To develop a fundamental understanding of catalyst design for sustainable conversion and production of platform chemicals

Porous Catalysts: $10^{-9}$ torr-1 atm
The need for efficient catalysts for chemical production

Growing role of chemical production in industrial energy demand

**Goal:** Develop design principles for increasing selectivity and lowering operating temperatures to reduce energy expenditure.

“The Outlook for Energy: A View to 2040” (ExxonMobil, 2014)
IMASC Research is highly integrated and broad

**Focus Area 1**
Tim Kaxiras & Robert Madix, Leads
*Reaction Mechanisms and Modeling of Active Sites*
*Other PIs:*
  - J. Biener, Friend, Hoffman
  - Tkatchenko, Sykes

**TPRS, XPS, STM, DFT**

**Focus Area 2**
Maria Flytzani-Stephanopoulos. Lead
*Catalytic performance under realistic reaction conditions*
*Other PIs:*
  - J. Biener, Friend, Madix, Tao
  - Collaborators:
    - Succi, Falcucci, Fushimi

**TAP, Reactors, TPR, flow modeling**

**Focus Area 3**
Juergen Biener, Lead
*Structure, composition and electronic properties*
*Other PIs:*
  - J. Biener, Flytzani-Stephanopoulos, Friend, Kaxiras, Salmeron, Tao

**eTEM, SEM, AP-XPS, XAS**

**TPRS, XPS, STM, DFT**
Translating understanding of selective oxidation on Au single crystals to nanoporous Au catalysts

Identification of Reactivity

Fundamentals From Model Studies: Au(111)

UHV

Adding Materials Complexity: npAu (AgAu alloy)

Computing: O$_2$ dissociation, surface interactions, reactant flow

Mapping to Catalytic Conditions: continuous flow, 1 atm.

Feedback to Model Studies: new alloy compositions, mechanistic studies

Optimization of Geometry: shells and foils

1 atm
Selective oxidation of alcohols by O adsorbed on Au(111)

O Adsorbed on metallic Au promotes selective oxidation processes—Acid/base paradigm

Local bonding of O

DFT & Vibrational Spectroscopy
Propene oxidation on Au(111)-O

O insertion to allylic C-H bond: Path to acrolein & acrylate

Allyloxy

Allylic C-H scission: Path to combustion

Allyl species

Guiding principles for scaling from UHV single crystal studies to reactor conditions

- Dominant reaction pathways must translate from $\Theta_1, T_1$ to $P_2, T_2$; reactions that govern reactions in model systems must also govern them under reactor conditions.
- Local structures of models should reflect working catalyst; ideally, reactions structure insensitive.

Adsorbed O is \textit{required} for bond activation on metallic Au

DFT: Adsorbed O required for methoxy formation

- Transfer of H to Au is unfavorable (+1.33 eV) and has a high barrier (1.58 eV)

Transitions states comparing H transfer to Au vs. to O

DFT: No C-H bond breaking on clean Au

<table>
<thead>
<tr>
<th>Surface Reaction</th>
<th>Barrier Height (eV)</th>
<th>ΔE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$O + O → H$_2$C=O + OH</td>
<td>0.49</td>
<td>-0.98</td>
</tr>
<tr>
<td>CH$_3$O + OH → H$_2$C=O + H$_2$O</td>
<td>0.63</td>
<td>-1.23</td>
</tr>
<tr>
<td>2 CH$_3$O → H$_2$C=O + CH$_3$OH</td>
<td>0.66</td>
<td>-1.20</td>
</tr>
<tr>
<td>CH$_3$O → H$_2$C=O + H</td>
<td>0.64</td>
<td>+0.15</td>
</tr>
</tbody>
</table>

- All barriers are similar
- Transfer of H to Au unfavorable

O in 3-fold site; VASP, GGA-PW91, 3 or 4 Au layers

DFT: Attack of H$_2$C=O by CH$_3$O is spontaneous—no barrier

Xu, Haubrich, Baker, Kaxiras, Friend, JPCC (2011) 115 3703-3708
Key factors in oxidative coupling of methanol

- Au itself is unreactive—$O_{ads}$ is active site
- Loss of H from CH$_3$O determines rate—adsorbed O, OH and CH$_3$O all promote formaldehyde formation
- Ordered O phase leads to over-oxidation; combustion
- Weak interaction of key reactants with surface facilitates coupling—unique to Au

Catalyst design: Activation of O$_2$ is required
Demonstration of reaction principles for complex systems: coupling of dissimilar alcohols on O/Au

\[ C_2H_5OH \quad + \quad CH_3OH \]

**Ester formation:**

- \( CH_3O \rightarrow H_2C=O + RO \)
- \( C_2H_5O \rightarrow (CH_3)(H)C=O + RO \)
Selectivity for coupling of methanol and ethanol on O/Au(111) (0.2 ML O)

Pre-equilibrium establishes relative concentrations of alkoxides

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Controlling selectivity in complex reaction environments: Competitive binding

2 CH₃OH → O
Gold → CH₃ O CH₃ O
Gold → H₂O
Oads determine RO_ads coverage

2 C₂H₅OH + CH₃ O CH₃ Kₑq = 5 C₂H₅ O C₂H₅
Gold ↔ C₂H₅ O C₂H₅ + 2 CH₃OH
Gold

Competitive binding determines relative concentrations in complex environments
# Gas phase acidity hierarchy as a guide of binding

<table>
<thead>
<tr>
<th>Acid</th>
<th>Conjugate Base (B)</th>
<th>ΔH_{acid} (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-butanol</td>
<td>1-butoxy</td>
<td>375.2</td>
</tr>
<tr>
<td>isopropanol</td>
<td>isopropoxy</td>
<td>375.7</td>
</tr>
<tr>
<td>1-propanol</td>
<td>1-propoxy</td>
<td>376.2</td>
</tr>
<tr>
<td>ethanol</td>
<td>ethoxy</td>
<td>378.0</td>
</tr>
<tr>
<td>methanol</td>
<td>methoxy</td>
<td>381.7</td>
</tr>
<tr>
<td>dimethylamine</td>
<td>dimethylamide</td>
<td>395.5</td>
</tr>
</tbody>
</table>

\[
\text{BH(gas)} \rightarrow \text{B}^-(\text{gas}) + \text{H}^+(\text{gas})
\]

Higher Gas Phase Acidity (More Stable $\text{B}_{ads}$)

Lower Gas Phase Acidity
van der Waal’s Interactions are important for relative binding of alkoxys on Au

Selectivity depends on weak interactions

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>$E_b$ (eV) PBE</th>
<th>$E_b$ (eV) PBE+vdW</th>
<th>Difference due to vdW (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$O</td>
<td>1.15</td>
<td>1.29</td>
<td>0.14</td>
</tr>
<tr>
<td>CF$_3$CH$_2$O</td>
<td>1.11</td>
<td>1.41</td>
<td>0.30</td>
</tr>
<tr>
<td>CH$_3$CH$_2$O</td>
<td>1.38</td>
<td>1.64</td>
<td>0.28</td>
</tr>
<tr>
<td>1-CH$_3$(CH$_2$)$_3$O</td>
<td>1.33</td>
<td>1.80</td>
<td>0.47</td>
</tr>
</tbody>
</table>

Correlation with gas phase acidity is due to polarizability of species

, Rodriguez-Reyes, Siler, Liu, Tkatchenko, Friend, Madix JACS (2014)
Generalization: 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 OCH$_3$ on O/Au—e.g. CO or NR$_2$
Surface Chemistry as a platform for reaction *discovery*—new processes

Methanol carbonylation

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

DOI: 10.1002/anie.200905642.
Excess of Methanol required to drive amide formation due to competition of CH₃O and (CH₃)₂N

Translating understanding of selective oxidation on Au single crystals to nanoporous Au catalysts

Identification of Reactivity

Fundamentals
From Model Studies: Au(111)

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Adding Materials Complexity: npAu (AgAu alloy)

Computation:
O₂ dissociation
surface interactions
reactant flow

Mapping to Catalytic Conditions:
continuous flow, 1 atm.

Optimization of Geometry:
shells and foils

Feedback to Model Studies:
new alloy compositions
mechanistic studies

1 atm
Design principle: Activate $O_2$ for reaction on Au under catalytic conditions

Example: Formation of $O_{ads}$ on Au for selective oxidation

- Minority active component creates reactive intermediates; selective reaction occurs on less reactive majority component after migration

$\text{npAu is a dilute Ag/Au alloy (~3% Ag)}$
Unsupported npAg$_{0.03}$Au$_{0.97}$ Catalysts are prepared with a variety of architectures: All are active for alcohol coupling.

Ingots used in this work were provided by Monika Biener and Juergen Biener at LLNL.
Dilute Ag/Au alloys dissociate O₂—even in UHV

Nanoporous Ag$_{0.03}$Au$_{0.97}$ Ingots/UHV

$\text{O}_2$ does not dissociate unless npAu is first cleaned using ozone doses.

Isotopic labeling establishes presence of atomic O

Transient Studies using a TAP Reactor:

- $O_2$ activation

- Single pulse $\rightarrow$ Rate constants
- Simultaneous pulsing $\rightarrow$ Reaction activity/selectivity
- Sequential/Alternate pulsing $\rightarrow$ Probe lifetime/transformation of adsorbed intermediate species (e.g., $O_{ad}$)

- Continuous flow valve
- Pulse valve
- Microreactor
- Vacuum chamber $< 10^{-8}$ Torr

- Time scale:
  - 0.01 ~ 0.1 ms
  - ~$10^{15}$ molecules/pulse
  - 0.5 ~ 10 s

- Diagram showing the experimental setup and pulse timing.
\( \text{npAg}_{0.03}\text{Au}_{0.97} \) Catalyst Material Fundamentally Changed by Activation Procedure Derived From Fundamental Studies

- Literature method for activating npAu ingots is inconsistent and irreproducible.
- Ozone pre-treatment reproducibly activates npAu catalysts (ingots, foils, and shells) for the sustained oxidation of alcohols.

**Procedure:**

1. Pre-treatment of npAu in flowing ozone at 150 °C for 1 hour, followed by cooling to room temperature in He.
2. Heating to 150 °C in a stream of 10% methanol and 20% \( \text{O}_2 \) in He.

2nd Step of Activation of npAg$_{0.03}$Au$_{0.97}$ Catalysts occurs under reaction conditions

**Conditions:** 10% methanol and 20% O$_2$ in He, 150°C, 50 mL/min, 10 mg npAu shells

- CO$_2$ is only formed during the initial activation period following ozone treatment.
- Previously active catalyst materials reactivate after exposure to air for four months without additional ozone treatment.

Activity of npAg$_{0.03}$Au$_{0.97}$ Catalysts Materials is Stable Over Time

- Stable conversion of methanol has been observed for one month after an initial 24 hour stabilization period.

**Conditions:** 10% methanol and 20% O$_2$ in He, 150°C, 50 mL/min, 50 mg npAu shell catalyst
New procedure activates all npAg$_{0.03}$Au$_{0.97}$ catalysts architectures

<table>
<thead>
<tr>
<th>Catalyst material</th>
<th>Rate of conversion of methanol</th>
<th>Selectivity to methyl formate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ingots</td>
<td>0.017 mmol s$^{-1}$ g$^{-1}$</td>
<td>100%</td>
</tr>
<tr>
<td>Foils</td>
<td>0.091 mmol s$^{-1}$ g$^{-1}$</td>
<td>100%</td>
</tr>
<tr>
<td>Shells</td>
<td>0.083 mmol s$^{-1}$ g$^{-1}$</td>
<td>100%</td>
</tr>
</tbody>
</table>

Conditions: 10% methanol and 20% O$_2$ in He, 150°C, 50 mL/min

- Higher rates of methanol conversion for the foils and shells indicate that these materials overcome some of the mass transport limitations of the ingots.
**npAg$_{0.03}$Au$_{0.97}$ Catalysts** selectively couple higher alcohols to yield esters

- Aldehyde (acetaldehyde or butyraldehyde) is the only other product.
- No CO$_2$ detected.

<table>
<thead>
<tr>
<th>Catalyst material</th>
<th>Ethanol self-coupling selectivity to ester*</th>
<th>1-Butanol self-coupling selectivity to ester*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ingots</td>
<td>36.1%</td>
<td>20.6%</td>
</tr>
<tr>
<td>Foils</td>
<td>22.1%</td>
<td>11.9%</td>
</tr>
<tr>
<td>Shells</td>
<td>20.2%</td>
<td>16.4%</td>
</tr>
</tbody>
</table>

**Conditions:** 5% alcohol and 20% O$_2$ in He, 150°C, 50 mL/min
Van der Waal’s interactions are important in determining catalytic performance of npAg$_{0.03}$Au$_{0.97}$ Catalysts

Competition for binding sites under SS conditions mirrors that on O/Au(111)—van der Waal’s interactions play an important role

Solution phase amide synthesis from (CH₃)₂NH + ROH mirrors UHV results: Weak interactions important

Key points:
• O is required for reaction
• Competitive binding predicted from displacement experiments in UHV reflect selectivity in solution

Distinct from npAu activated by previous methods, ozone pre-treated npAu catalysts:

- Activate reproducibly and recover their activity after being exposed to air for four months, without requiring a second ozone treatment.

- Operate stably at or above 150 °C, and are inactive in the 20-80 °C temperature range previously reported.

- Do not catalyze the oxidation of CO to CO$_2$ at 150 °C or at lower temperatures.

- Catalyze the self-coupling of 1-butanol to form butyl butyrate and stably catalyze the self-coupling of ethanol to yield ethyl acetate.

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Key messages: Guided Catalyst Design

- Mechanism used to *predict* new reactions
- Van der Waal’s interactions partly determine competitive binding and reactivity
- Minority component (Ag) activates O₂
- Catalyst material is dynamic, yet robust

Next Challenge: Generalization to other reaction and materials systems
Thanks to great collaborators and to DOE

- David Bell
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- Branko Zugic

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