Probing catalyst-support interactions with experiment and theory

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CFN Workshop on Theory and Computation for Interface Science and Catalysis
Controlling Size & Composition: Deposition of Mass-Selected Clusters

- Precise control over particle “size”, chemical composition (metal to non-metal ratio)
- Any support possible - not limited by surface growth and nucleation mechanisms
- Amenable to computational description – in many cases exact expt. system can be modeled

“soft-landing”<0.2eV/atom
Cluster Deposition

Cluster coverage
$10^{13}$ clusters/mm²
0.05-0.1 ML

Experimental characterization
• X-ray photoemision (XPS)
  - metal oxidation state
  - stoichiometry
• Thermal desorption/reaction
  - adsorbate binding energies
  - reaction products & mechanism
  - thermal stability/coalescence
• Laser two-photon photoemission (2PPE)
  - coverage dependent work functions & valence band
  - excited states/time evolution
Computational Considerations: Experimentalist’s Perspective

- **Unit cell size** ⇒ 1 cluster per unit cell ⇒ \( \theta \approx 0.1\text{-}0.4 \text{ ML} \)
  - experiments typically < 0.2 ML
  - small unit cells (3x3) – can lead to cluster “crowding”
  - some supports require larger (more costly) unit cells: oxides, vacancies, thin films...

- **Cluster structure** – metal compounds (C, O, S)
  - start with optimized gas-phase cluster ⇒ can be done at same or higher level of theory
  - *many* isomers and alternative surface binding arrangements for asymmetric clusters with 15-20 atoms
  - geometry optimization on surface *unlikely* to explore large departures from starting structure

- **Accuracy for adsorbate binding energies and barriers**
  - depends on functional used
  - working with TM oxides ⇒ hybrid DFT+U ; U may not be optimized for property to be measured
  - best used as comparisons among related systems

<table>
<thead>
<tr>
<th>surface</th>
<th>CO binding energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT/PBE CO/Au(111)</td>
<td>0.4 eV</td>
</tr>
<tr>
<td>DFT/PBE CO/Mo(_4)S(_6)/Au(111)</td>
<td>0.9-1.0 eV</td>
</tr>
<tr>
<td>Expt CO/Mo(_4)S(_6)/Au(111)</td>
<td>0.7 eV</td>
</tr>
</tbody>
</table>
Metal-metal oxide support interactions

Metal-oxide support interactions strongly influence catalytic activity, especially metals on reducible oxides, e.g., TiO₂ & CeO₂

- Metal ↔ metal oxide charge transfer
- Participant in reaction ⇒ bi-functional catalyst, interface sites

Cu-based water-gas-shift catalysts (CO + H₂O→ CO₂ + H₂)

- Water dissociation on oxide
- CO oxidation at interface site

Correlations with interfacial charge transfer

In many cases, activity can be correlated with charge transfer from metal to oxide
- Stabilizes reduced oxide
- Presence of O-vacancies enhances water dissociation

"Inverse" WGS catalyst
\( \text{Ce}_6\text{O}_{13}/\text{Cu}(111) \)

\[
\begin{align*}
\text{Cu} & \rightarrow \text{Ce}_6\text{O}_{13} \\
3.96 \text{e}^- & \rightarrow 2\text{Ce}^{4+} \rightarrow 2\text{Ce}^{3+}
\end{align*}
\]

\[
\begin{align*}
\text{Pt} & \rightarrow \text{Pt}^{2+} \\
\text{2Ce}^{4+} & \rightarrow \text{2Ce}^{3+}
\end{align*}
\]


Charge transfer and water dissociation: Descriptors for WGS activity

**Cu ⇌ oxide charge transfer:**
1-D structures

**Water dissociation energy:**
3-D clusters


Factors influencing activity
- Cluster structure and size
- Cu ⇌ oxide cluster charge transfer
- Cation oxidation state – reducibility
- Water dissociation energy

Currently, detailed information about interfacial charge transfer is derived mostly from theory.
Experimentally Probing Charge Transfer

- Charge transfer $\Rightarrow$ surface dipoles
- Work function ($\Phi$) sensitive to surface dipole due to changes in surface electrostatic potential ($\phi$)
  
  $\Phi = -e\phi - E_F$

- Measurements of $\Phi$ made by photoemission (UPS, 2PPE)
- $\Delta \Phi$ typically interpreted in terms of classical Topping model

\[
\Delta \Phi = \frac{e \times n_0 \theta \times \mu}{\varepsilon_0} \left(1 + \frac{\delta \times \alpha \times (n_0 \theta)^{3/2}}{4\pi \varepsilon_0}\right)^{-1}
\]

- $\mu \equiv$ dipole moment at interface $\Rightarrow 2dq$
- $\theta \equiv$ cluster coverage
- $\alpha \equiv$ cluster polarizability
- $\delta \equiv$ dipole-dipole interaction term
  
  $= \theta^{-1/2}$ for random distribution

\[
\Delta \Phi = \left(\frac{a\theta}{1 + b\theta}\right)\mu
\]

Examples

\[ \Delta \Phi = \left( \frac{a\theta}{1 + b\theta} \right) \mu \]

- Topping model assumes uniform spacing

\[ \Delta \Phi \triangleq \Theta \pm \Theta \mu \]

Mo\textsubscript{7}S\textsubscript{10} clusters on Al\textsubscript{2}O\textsubscript{3}/NiAl(110)

Zhou, Zhou, Camillone, White, PCCP, 2012, 14, 8105

Pivetta, Patthey, Schneider, Delley, PRB, 65 045417 (2002)
Two-Photon Photoemission (2PPE): Local Work Functions

- Ti:Sapphire laser; 80 MHz, 100 fs pulses
- 400nm & 267 nm; ≤ 30 mW avg power
- $2\hbar\nu = 6.0-9.5\text{eV}$
- focused beam spot (~200μm); raster scan surface
- Detect unoccupied states at $1\hbar\nu$
- Short pulses allow time dynamics
Work Function Measurements vs Coverage

- Map coverage using O-atom Auger intensity: focused e-beam (200-300 μm)
- Normalize to total number of ions deposited to obtain coverage vs position
- Measure spatially resolved 2PPE spectrum with focused laser

Deposited cluster distribution

Mo$_3$O$_9$/Cu(111)

2PPE vs position

\( IS_1 \)

\( Cu\ 3d \)

\( SS \)

2PPE intensity (a.u.)

final state energy (eV)

Normalized AES \( I_O/I_0 \)

Z position (mm)

X position (mm)

Normalized AES \( I_O/I_0 \)

work function shift (eV)

x-axis position with respect to deposition center (mm)
**Ti**

- Ti$_3$O$_6$
- Ti$_4$O$_8$
- Ti$_5$O$_{10}$

**Clusters**

- Ti$_x$O$_y^+$

![Graph showing mass intensity for Ti species](image)

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**Nb**

- Nb$_3$O$_7$
- r-Nb$_3$O$_5$
- r-Nb$_4$O$_7$
- Nb$_4$O$_{10}$
- r-Nb$_5$O$_{10}$
- Nb$_5$O$_{12}$

**Clusters**

- Nb$_x$O$_y^+$

![Graph showing mass intensity for Nb species](image)

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**Stoichiometric**

- Ti$_4^+$
- Nb$_5^+$

**Reduced**

- Nb$_3^+/Nb_4^+$

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**Samples**

- Ti$_3$O$_6$/Cu(111)
- Ti$_5$O$_{10}$/Cu(111)
- Nb$_3$O$_7$/Cu(111)
- Nb$_4$O$_7$/Cu(111)

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**Notes**

- "reduced": Nb$_3^+/Nb_4^+$
Work Function Shifts vs Coverage: $M_xO_y/Cu(111)$

- $\Delta \Phi > 0$ ($\mu < 0$) for all oxides: Cu → cluster charge transfer
- “Reducible” oxides $Ti_xO_y$ and $Nb_xO_y$ generally lower $\Delta \Phi$
- “Reduced” sub-stoichiometric clusters induce smaller $\Delta \Phi$
- Fits of $\Delta \Phi$ vs $\theta$ to Topping model provide intrinsic surface dipole, $\mu$

Surface dipoles and Bulk Oxide Work Functions $\Phi_{\text{bulk}}$

- Derived surface dipoles correlate with $\Phi_{\text{bulk}}$ (oxide)
- Includes bulk “reduced” samples
- $\Phi_{\text{bulk}}$ : measure of electronegativity

- $\Delta \Phi$ at ~1ML significantly below bulk values (relative to Cu(111))
- Thicker oxide layers required to reach bulk properties
Surface dipoles: DFT Bader Charge Transfer

Bader charge transferred to cluster: Cu→MₓOᵧ

- Surface dipoles roughly correlate with Bader charge transfer
- “Reduced” clusters accept less charge (lower oxid state)
- Larger clusters, more cations – more charge transfer

Level of agreement due to accuracy of DFT, unrealistic cluster structure, or ?
Comparison with charge transfer from DFT

- DFT gives electronic density \( n(r) = |\psi(r)|^2 \)
- continuous function without boundaries for atoms, so defining charge on each atom somewhat artificial, but nonetheless useful!

- If using atomic orbital expansions for wavefunctions, easy to define Mulliken populations (R. S. Mulliken, JCP, 23, 1833, 1955; Nobel Prize 1966)

\[
n_{\alpha}(r) = |\psi_{\alpha}|^2 \text{ and define charge on atom as } q_{\alpha} = Z_{\alpha} - \int n_{\alpha}(r)d^3r
\]
basis set dependent – not connected to observable charge density

- DFT codes provide Bader Charges – uses real space density with sharp boundaries for atoms (Richard Bader, McMaster Univ)

\[
q_{\alpha} = Z_{\alpha} - \int_{v_{\alpha}} n_{\alpha}(r)d^3r \quad v_{\alpha} \equiv \text{defines “volume” of atom } \alpha
\]

- Uses “zero flux surfaces” to define boundaries between atoms (\( \nabla n_{\perp} = 0 \))

- maxima typically at nuclei and minima between atoms
- charge within dividing surface defines atomic charge
- based on “observable” \( n(r) \)

http://theory.cm.utexas.edu/henkelman/research/bader/
Comparison with Bader Charges from DFT

- All systems show negative dipole moments, suggest Cu→cluster charge transfer in every case
- Dipoles less for reducible Nb clusters and “reduced” clusters with O-atoms removed
- Bader charge roughly correlates with surface dipole, but not always, i.e., r-W\textsubscript{3}O\textsubscript{6} and r-Nb\textsubscript{3}O\textsubscript{5} which transfer charge transfer to Cu(111) surface

Dipole has two contributions: from charge transfer and intrinsic cluster dipole
DFT surface electrostatic potentials: work functions

- calculated electrostatic potential energy normal to the surface
- \( \Delta \Phi^{\text{(DFT)}} = +0.07 \text{eV} \) with cluster on surface at 0.13 ML
- \( \Delta \Phi^{\text{(expt)}} = +0.06 \text{eV} \) @ 0.13 ML

\[ \text{Electrostatic Potential Energy (eV)} \]

- Z(Å)
- \( \text{Nb}_3\text{O}_7/\text{Cu}(111) \)
- \( \text{Cu}(111) \)

W. An and P. Liu, unpublished
DFT electrostatic potentials: cluster dipole and charge transfer

Calculate electrostatic potential along surface normal

\[ V_{\text{cluster/Cu}(111)} = V_{\text{Cu}(111)} + V_{\text{cluster}} + V_{\text{charge}} \]

The change from below and above the surface gives contribution to \( \Delta \Phi \)

\[ \Delta \Phi = \Delta V_{\text{cluster}} + \Delta V_{\text{charge}} \]

Mo\(_3\)O\(_9\): Highly symmetric cluster has no dipole along surface normal

\[ \Delta \Phi \approx \Delta V_{\text{charge}} \]

W\(_3\)O\(_6\): Oxygen atoms pointed away from surface leads to larger cluster dipole

\[ \Delta \Phi \approx \Delta V_{\text{cluster}} \]

Charge transfer: Charge density difference maps (isosurfaces)

Charge density difference is alternative approach to “visualizing” charge transfer defined as $\Delta \rho = \rho_{(\text{slab+cluster})} - \rho_{\text{slab}} - \rho_{\text{cluster}}$

- Charge accumulation at interface- consistent with surface dipole, $\mu_{\text{exp}} = -0.84 \text{ D}$
- Suggests Nb$_3$O$_7$ on Cu(111) is partially reduced,
- Consistent with Bader charge on cluster -0.18e

The isosurfaces are 0.005 e/Å$^3$

$W. \, \text{An and P. Liu, unpublished}$
Water dissociation on $M_xO_y/Cu(111)$ surfaces

Water dissociation key step for water-gas-shift (WGS)

$$H_2O(g) + O_{(cluster)} \rightarrow 2OH_{(cluster)} \rightarrow O_{(cluster)} + H_2$$

Different metal oxides

$Cu(111)$

- $Mo_3O_6$
- $Ti_3O_6$
- $Nb_3O_7$

Changes cluster stoichiometry

$Cu(111)$

- $Ti_3O_5$
- $Ti_3O_6$

Changes in support

$Cu_2O/Cu(111)$

- $Nb_3O_5$
- $Nb_3O_7$

Reducible oxides more active:
$NbO_x >> TiO_x > MoO_x, WO_x$

Clusters with “O-vacancies” very active: $Ti_3O_5 >> Ti_3O_6$

Only reducible clusters with O-vacancies active on $Cu_2O$
Water dissociation on $\text{M}_x\text{O}_y$/Cu(111) surfaces

<table>
<thead>
<tr>
<th>Cluster</th>
<th>$\mu$(D) expt</th>
<th>Bader charge (e)</th>
<th>DFT water dissociation energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{W}_3\text{O}_9$</td>
<td>-3.96</td>
<td>-1.37</td>
<td>+0.68 eV $^a$</td>
</tr>
<tr>
<td>$\text{Mo}_3\text{O}_9$</td>
<td>-4.52</td>
<td>-1.37</td>
<td>+0.74 eV $^a$</td>
</tr>
<tr>
<td>$\text{Ti}_3\text{O}_6$</td>
<td>-0.48</td>
<td>-0.33</td>
<td>-0.75 eV $^a$</td>
</tr>
<tr>
<td>$\text{Nb}_3\text{O}_7$</td>
<td>-0.84</td>
<td>-0.18</td>
<td>-0.82 eV</td>
</tr>
</tbody>
</table>

$^a$ Vidal, Liu, PCCP, 14, 16626 (2012)

- DFT results consistent with experiment
- Rxn takes place on cluster and not interface to form $2\text{OH}_{\text{ad}}$
- Reactivity correlated with small charge transfer?

W. An and P. Liu, unpublished
Water dissociation of Nb$_3$O$_7$ on Cu(111) and Cu$_2$O surfaces

H$_2$O@Nb$_3$O$_7$/Cu(111)

- $E_a =$ 0.32 eV
- IS(-0.72 eV) → TS(-0.40 eV) → FS(-1.43 eV)
- $\Delta E_{\text{rxn}} =$ -0.71 eV

H$_2$O@Nb$_3$O$_7$/Cu$_2$O(111)

- $E_a =$ 2.27 eV
- IS(-0.97 eV) → TS(1.30 eV) → IS(-1.12 eV)
- $\Delta E_{\text{rxn}} =$ -0.14 eV

• Very high barrier to dissociation on oxide surface
• Consistent with experiments

W. An and P. Liu, unpublished
Summary

- Size-selected cluster experiments are well suited to computational modeling with DFT
  - Computer and experiments work on exactly the same system (or nearly so)
  - Adsorption structures, interfacial charge transfer, reactions
- DFT is ideally suited for unraveling experimental data
  - e.g., the microscopic origins of surface work function shifts deposition and water dissociation on different supports
- Challenges for computation
  - Need more robust methods for obtaining cluster structures – rapid sampling, annealing, ...
  - Electronic properties still too dependent on functional and empirical fixes like DFT+U for oxides
  - Need to incorporate dynamic motions of clusters and surface atoms, e.g., most calculations based on 0 K minimum energy paths
- DFT is an incredibly powerful ally of experimentalists in surface chemistry
Collaborative Theory Interactions at BNL

**Ping Liu, Chemistry**  
transition metal compound clusters on surfaces; alcohol synthesis on modified Cu surfaces (DFT and KMC)

**Jim Muckerman, Chemistry**  
First studies of transition metal clusters for catalysis (high level QC)

**Yan Li, Computational Science Center**  
Self-assembled molecular wires (DFT, GW)

**Hua-Gen Yu, Chemistry**  
Reaction Dynamics on cluster models of surfaces (DFT/TDDFT, TDWP)
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Dr. Jing Zhou

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Wei An

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