Design of Catalysts and Electrocatalysts: From DFT Prediction to Experimental Verification

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Development of Novel Catalysts

• Supported catalysts:
  - More relevant to commercial catalysts and processes
  - Fast (high throughput) evaluation
  - "Heterogeneous" in electronic and catalytic properties

• Single crystal surfaces:
  - Atomic level understanding from experiments and theory
  - Materials gap: single crystal vs. polycrystalline materials
  - Pressure gap: ultrahigh vacuum (UHV: ~10^{-12} psi)

• Need to bridge "materials gap" and "pressure gap"
From DFT Prediction to Experimental Verification

- Single Crystal Model Surfaces
  - UHV studies
  - DFT modeling

- Bridging “Materials Gap”
  - Thin films
  - Supported catalyst

- Bridging “Pressure Gap”
  - Reactor studies
  - Electrochem cells

Use DFT to assist catalysts design: (activity, selectivity, stability, cost):

- Binding energy calculations (activity, stability)
- Activation barriers and reaction network (selectivity)
Outline of Presentation

Examples of DFT prediction and experimental verification:

- Correlating hydrogen binding energy (HBE) with water electrolysis activity
- Correlating hydrogen binding energy (HBE) with hydrogenation activity
- Correlating activation barrier with hydrogenation selectivity
Correlating HBE with Water Electrolysis Activity

Esposito, Hunt & Chen, 
*Angew. Chem. Int. Ed.* 
49 (2010) 9859
• Classic volcano curve observed for the HER is explained by Sabatier’s Principle

\[ H^+ + e^- + \ast \rightarrow H^* \]  
(Volmer Step)
\[ 2H^* \rightarrow H_2(g) + 2 \ast \]  
(Tafel Step)

Reduce Pt Loading with Monolayer (ML) Pt

Goal: Supporting ML Pt on Pt-like substrates, such as WC
DFT Prediction: Similar HBE Values between Monolayer Pt-WC and Bulk Pt

<table>
<thead>
<tr>
<th>Surface</th>
<th>HBE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC(001)</td>
<td>-0.99</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>-0.46</td>
</tr>
<tr>
<td>1 ML Pt-WC(001)</td>
<td>-0.43</td>
</tr>
</tbody>
</table>

DFT-calculated per-atom hydrogen binding energy (HBE) for WC, Pt, and 1 ML Pt-WC surfaces with a hydrogen coverage of 1/9 ML.
Experimental Verification of Activity and Stability

HER Activity of 1 ML Pt/WC approaches to that of Pt foil

DFT Prediction of Stability of Pt/WC and Pt/C

- Use DFT to compare adhesion of Pt atoms to WC and Pt surfaces:

### Binding Energy

<table>
<thead>
<tr>
<th>ML surface atoms</th>
<th>Substrate</th>
<th>Binding energy / eV</th>
<th>(M-X^) - (M-M) BE / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>Pt(111)</td>
<td>-5.43</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>C(0001)</td>
<td>-4.12</td>
<td>1.31</td>
</tr>
<tr>
<td></td>
<td>WC(0001)</td>
<td>-6.59</td>
<td>-1.16</td>
</tr>
<tr>
<td></td>
<td>W_2C(0001)</td>
<td>-6.51</td>
<td>-1.08</td>
</tr>
</tbody>
</table>
Experimental Verification of HER Stability

- No change in overpotential observed with time
- No change in LSV before and after CP
- XPS and SEM measurements confirmed stability

Other ML/TMC Electrocatalysts for HER in Acid

Volcano relationship provides design principles of electrocatalysts

Kimmel, Yang & Chen, J. Catalysis, 312 (2014) 216
Volcano relationship also appears to hold in alkaline electrolyte

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- DFT modeling

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- Supported catalyst

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Monolayer Bimetallic Surfaces

Surface Alloy

Surface Monolayer

Subsurface Monolayer

Modified surface chemical properties due to:
- Ligand effect – electronic configuration
- Compressive and tensile strain - lattice mismatch
Hydrogen binding energy (HBE) can be controlled by surface structures

Controlling Hydrogenation Activity: Correlating with Binding Energy

Low-Temperature Cyclohexene Hydrogenation:

Assumption for Higher Hydrogenation Activity:

• Weakly bonded H atoms
• Weakly bonded cyclohexene
DFT Calculations of Binding Energies of Hydrogen and Cyclohexene

BE values follow the same trend: Ni-Pt(111) > Ni ~ Pt > Pt-Ni-Pt(111)
Low-Temperature Hydrogenation of Cyclohexene Due to Weakly Bonded H

- Weakly bonded M-H leads to low-T hydrogenation
Binding Energies Correlate with Cyclohexene Hydrogenation Activity

Sabatier’s principle: not too strong, not too weak!
Volcano relationship allows prediction of hydrogenation activity
DFT Prediction of Stable Bimetallic Structures

General Stability includes:
- Admetals – 3d, 4d, 5d
- Host metals – Ni, Pd, Pt

Menning & Chen,
### Experimental Verification of Bimetallic Structures

<table>
<thead>
<tr>
<th>Coordination Number</th>
<th>10% H₂ at 50 °C—NiPt/C</th>
<th>10% H₂ at 225 °C—NiPt/C</th>
<th>APR at 225 °C—NiPt/C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
<td>Simulation</td>
<td>Experimental</td>
</tr>
<tr>
<td>Pt-Pt</td>
<td>1.9 ± 0.8</td>
<td>2.696 ± 0.003</td>
<td>2.0 ± 0.7</td>
</tr>
<tr>
<td>Pt-Ni</td>
<td>3.5 ± 0.4</td>
<td>3.904 ± 0.007</td>
<td>3.8 ± 0.3</td>
</tr>
</tbody>
</table>

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**Examples of DFT prediction and experimental verification:**

- Correlating hydrogen binding energy (HBE) with water electrolysis activity
- Correlating hydrogen binding energy (HBE) with hydrogenation activity
- Correlating activation barrier with hydrogenation selectivity
Selective Hydrogenation Requires More Complicated DFT Calculations

Activation barriers on Pd(111) surface (eV):

\[ \text{C}_4\text{H}_6 \xleftrightarrow{+H 1.04} \xrightarrow{-H 0.64} \text{C}_4\text{H}_7 \xleftrightarrow{+H 0.92} \xrightarrow{-H 0.49} \text{C}_4\text{H}_8 \xleftrightarrow{+H 1.01} \xrightarrow{-H 0.49} \text{C}_4\text{H}_9 \xleftrightarrow{+H 0.87} \xrightarrow{-H 1.05} \text{C}_4\text{H}_{10} \]

Activation barriers on PdNiPd(111) surface (eV):

\[ \text{C}_4\text{H}_6 \xleftrightarrow{+H 0.68} \xrightarrow{-H 0.60} \text{C}_4\text{H}_7 \xleftrightarrow{+H 0.88} \xrightarrow{-H 1.03} \text{C}_4\text{H}_8 \xleftrightarrow{+H 0.88} \xrightarrow{-H 0.81} \text{C}_4\text{H}_9 \xleftrightarrow{+H 0.80} \xrightarrow{-H 1.52} \text{C}_4\text{H}_{10} \]

The activation barriers are generally lower on PdNiPd(111) than on Pd(111), leading to higher hydrogenation activity on PdNiPd(111)
# Predicting Selectivity Requires DFT Calculations of Reaction Network

<table>
<thead>
<tr>
<th>Surface</th>
<th>Pd(111)</th>
<th>PdNiPd(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>d-band center (eV)</strong></td>
<td>-1.90</td>
<td>-2.25</td>
</tr>
<tr>
<td>C₄H₆</td>
<td>-34.47</td>
<td>-19.19</td>
</tr>
<tr>
<td>C₄H₇</td>
<td>-37.27</td>
<td>-13.48</td>
</tr>
<tr>
<td>C₄H₈</td>
<td>-12.68</td>
<td>-2.90</td>
</tr>
<tr>
<td>C₄H₉</td>
<td>-36.54</td>
<td>-29.67</td>
</tr>
<tr>
<td>C₄H₁₀</td>
<td>-2.61</td>
<td>-2.54</td>
</tr>
</tbody>
</table>

Binding energy of butene is weaker on PdNiPd(111), leading to higher selectivity for butene production on PdNiPd(111)
Experimental Verification on Model Surfaces

UHV-TPD: Ultra-High Vacuum Temperature Programmed Desorption

PdNiPd bimetallic structure is very active for 1,3-butadiene hydrogenation, and may also be selective for 1-butene production.
Batch Reactor: Hydrogenation Activity

Activity trend: PdNi > Pd >> Ni
Flow Reactor: Hydrogenation Selectivity

Selectivities in flow reactor at conversions of (a) 10% (b) 60%

$H_2:CH_4 = 2.2:1$  Total Flow Rate: 9.6 ml/min

PdNi shows higher 1-butene selectivity than Pd, and higher yield in producing 1-butene

Hou, Porosoff, Chen & Wang, *J. Catalysis*, 316 (2014) 1
Conclusions

• Bimetallic and carbide catalysts offer the advantages of reduced cost and enhanced activity, selectivity and stability

• Combined theory, surface science, and catalytic studies are critical in design of novel catalytic materials