Núria López

Volcanos, cliffs and ways around
Volcanos: Our current understanding of Catalysis from theory

![Graph showing the Sabatier principle](image)

Sabatier principle
Volcanos: Our current understanding of Catalysis

Sabatier principle
Can be reproduced

- DFT
  - Mechanism
  - Elementary steps
- Microkinetics

Volcanos are taken as standard for activity.

With Pd content in PdAu alloys

With NP Ag size
ChemCatChem (2013)

Metal/Oxide interfaces (2019)
Even in homogeneous catalysis

[Diagram with reactions and chemical structures]

Volcanos

Provide systematic way for optimization
Why volcanos appear?

Symmetries between energies of different species
Example: Step 1 DFT

\[
\text{HCl} + \frac{1}{4} \text{O}_2 \rightarrow \frac{1}{2} \text{Cl}_2 + \frac{1}{2} \text{H}_2\text{O}
\]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( E_a / \text{eV} )</th>
<th>( \Delta E / \text{eV} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl + * ( \leftrightarrow ) HCl*</td>
<td>0</td>
<td>-0.48</td>
</tr>
<tr>
<td>HCl* + O(_b)* ( \leftrightarrow ) Cl(_c) + O(_b)H*</td>
<td>0.05</td>
<td>-0.98</td>
</tr>
<tr>
<td>HCl* + O(_c)* ( \leftrightarrow ) Cl(_c) + O(_c)H*</td>
<td>0.11</td>
<td>-0.75</td>
</tr>
<tr>
<td>O(_c)H* + O(_b)H* ( \leftrightarrow ) H(_2)O(_c) + O(_b)*</td>
<td>0.38</td>
<td>0.27</td>
</tr>
<tr>
<td>O(_c)H* + O(_c)H* ( \leftrightarrow ) H(_2)O(_c) + O(_c)*</td>
<td>0.24</td>
<td>-0.11</td>
</tr>
<tr>
<td>O(_c)* + O(_b)H* ( \leftrightarrow ) O(_c)H* + O(_b)*</td>
<td>0.55</td>
<td>-0.01</td>
</tr>
<tr>
<td>H(_2)O(_c)* ( \leftrightarrow ) H(_2)O + *</td>
<td>0.90</td>
<td>0.90</td>
</tr>
<tr>
<td>Cl(_c)* + Cl(_c)* ( \leftrightarrow ) Cl(_2) + 2 *</td>
<td>1.56</td>
<td>1.56</td>
</tr>
<tr>
<td>O(_2) + 2 * ( \leftrightarrow ) 2 O(_c)*</td>
<td>0.38</td>
<td>-0.76</td>
</tr>
</tbody>
</table>
Example: Step 2 Microkinetics

\[ \text{HCl} + \frac{1}{4} \text{O}_2 \rightarrow \frac{1}{2} \text{Cl}_2 + \frac{1}{2} \text{H}_2\text{O} \]

\[
\frac{d}{dt} \text{HCl}(t) = k_1 \text{PHCl}(t) \text{Rucus}(t) - k_2 \text{HCl}(t) - k_3 \text{HCl}(t) \text{Ob}(t) + k_4 \text{Cl}(t) \text{ObH}(t) - k_5 \text{HCl}(t) \text{Oc}(t) + k_6 \text{Cl}(t) \text{OcH}(t)
\]

\[
\frac{d}{dt} \text{Cl}(t) = k_3 \text{HCl}(t) \text{Ob}(t) - k_4 \text{Cl}(t) \text{ObH}(t) + k_5 \text{HCl}(t) \text{Oc}(t) - k_6 \text{Cl}(t) \text{OcH}(t) - 2 k_7 \text{Cl}(t)^2 + 2 k_8 \text{PCl}_2(t) \text{Rucus}(t)^2
\]

\[
\frac{d}{dt} \text{Oc}(t) = -k_5 \text{HCl}(t) \text{Oc}(t) + k_6 \text{Cl}(t) \text{OcH}(t) - k_9 \text{ObH}(t) \text{Oc}(t) + k_{10} \text{Ob}(t) \text{OcH}(t) + k_{15} \text{OcH}(t)^2 - k_{16} \text{Oc}(t) \text{H}_2\text{Oc}(t) + 2 k_{19} \text{O}_2(t)^2
\]

\[
- 2 k_{20} \text{Oc}(t)^2
\]

\[
\frac{d}{dt} \text{H}_2\text{Oc}(t) = k_{11} \text{ObH}(t) \text{OcH}(t) - k_{12} \text{Ob}(t) \text{H}_2\text{Oc}(t) + k_{15} \text{OcH}(t)^2 - k_{16} \text{Oc}(t) \text{H}_2\text{Oc}(t) - k_{13} \text{H}_2\text{Oc}(t) + k_{14} \text{PH}_2\text{O}(t) \text{Rucus}(t)
\]

\[
\frac{d}{dt} \text{Ob}(t) = -k_3 \text{HCl}(t) \text{Ob}(t) + k_4 \text{Cl}(t) \text{ObH}(t) + k_9 \text{ObH}(t) \text{Oc}(t) - k_{10} \text{Ob}(t) \text{OcH}(t) + k_{11} \text{ObH}(t) \text{OcH}(t) - k_{12} \text{Ob}(t) \text{H}_2\text{Oc}(t)
\]

\[
\frac{d}{dt} \text{O}_2(t) = k_{17} \text{PO}_2(t) \text{Rucus}(t) - k_{18} \text{O}_2(t) - k_{19} \text{O}_2(t) \text{Rucus}(t) + k_{20} \text{Oc}(t)^2
\]

\[
\frac{d}{dt} \text{ObH}(t) = k_3 \text{HCl}(t) \text{Ob}(t) - k_4 \text{Cl}(t) \text{ObH}(t) - k_9 \text{ObH}(t) \text{Oc}(t) - k_{10} \text{Ob}(t) \text{OcH}(t) - k_{11} \text{ObH}(t) \text{OcH}(t) + k_{12} \text{Ob}(t) \text{H}_2\text{Oc}(t)
\]

\[
\frac{d}{dt} \text{OcH}(t) = k_5 \text{HCl}(t) \text{Oc}(t) - k_6 \text{Cl}(t) \text{OcH}(t) + k_9 \text{ObH}(t) \text{Oc}(t) - k_{10} \text{Ob}(t) \text{OcH}(t) - k_{11} \text{ObH}(t) \text{OcH}(t) + k_{12} \text{Ob}(t) \text{H}_2\text{Oc}(t)
\]

\[
+ k_{12} \text{Ob}(t) \text{H}_2\text{Oc}(t) - 2 k_{15} \text{OcH}(t)^2 + 2 k_{16} \text{Oc}(t) \text{H}_2\text{Oc}(t)
\]
Example: Step 3 Linear-Scaling Relationships

Why volcanos appear?

Linear-Scaling Relationships

How many types of Linear-Scalings are there?

\[ r = r \{ \text{E}_{\text{ads}}, \text{E}_{\text{TS}}, \text{NC} \} \]

- Thermodynamic vs. Thermodynamic \[ \text{E}_{\text{ads}}(\text{NH}_x) \propto \text{E}_{\text{ads}}(\text{N}) \]
- Kinetic vs. Thermodynamic \[ \text{E}_{\text{TS}} \propto \text{E}_{\text{ads}}(\text{N}) \]
- Coordination dependence \[ \text{E}_{\text{ads}}(\text{N}) \propto \text{E}_{\text{ads}}(\text{N-111}) \]

Abild-Pedersen, Norskov, Sautet, Calle-Vallejo
Volcano appears

\[ r = r(E_{\text{ads}}) \]
Selectivity: Cliffs

Selectivity much more demanding 0.1 eV
LSR at their limit of accuracy
Volcanos

• Provide systematic way for optimization

BUT:

• Based on energies
• No synthetic route to get the active material
• Can we use less material?
• Are dead areas really non-active (outliers + false negatives)?
• What about selectivity?
• High binding regime phase change poor selectivity

• Can we be more active than top volcano?
Linear-Scalings Volcanos = Thinking in the box
Linear-Scalings are constraints are there any strategies to avoid them?

Vojvodic, Norskov (2015)
Linear-Scalings are constraints are there any strategies to avoid them?

To break the **symmetry** we need **more ingredients** in the catalyst

- Catalyst complexity
- Alternative energy forms
Breaking the rules

Geometric Structural Effects

Cat_0 ➔ Electronic Effects
Breaking the rules

Ensemble Control

Cat_0
Breaking the rules

Ensemble Control

Selective Ensemble

Unselective Ensemble

Cat_0
Ensemble control by mixed phases

Ensemble control by ligands
Structure of the ligand decorated particles

Anions go first on the surface

Nano Lett. (2014)
Structure of the ligand decorated particles

Anions go first on the surface

Electrostatics cations

Nano Lett. (2014)
Structure of the ligand decorated particles

- Anions go first on the surface
- Electrostatics cations
- van der Waals tails
Structure of the ligand decorated particles

Cryo-TEM

TGA

31P MAS NMR

ToF-SIMS

C20 tail

PO4

metal

Weight loss / %

Intensity / a.u.

Intensity / a.u.

50 nm
Lindar vs ligand decorated nanoparticles

- Ensemble control
- Difficult reorganization
- Adsorption configurations change (coverage effects)
Breaking the rules

Cat_0 → Doping
Doping in Semiconductors: HBr oxidation

\[ \text{HX}^+ \leftrightarrow \text{HX}^* \]
\[ \text{HX}^* + \text{O}^* \leftrightarrow \text{X}^* + \text{OH}^* \]
\[ \text{OH}^* + \text{OH}^* \leftrightarrow \text{H}_2\text{O}^* + \text{O}^* \]
\[ \text{H}_2\text{O}^* \leftrightarrow \text{H}_2\text{O}^* + \text{e}^* \]
\[ \text{X}^* + \text{X}^* \leftrightarrow \text{X}_2 + 2^* \]
\[ \text{O}_2 + 2^* \leftrightarrow 2\text{O}^* \]
Doping in Semiconductors: HBr oxidation

\[ \text{Cat}_0 \]

Graph showing energy vs. reaction coordinate:

1. \[ \text{O}_2 + {} \rightarrow 1/2\text{O}_2^* \]
Doping in Semiconductors: HBr oxidation

Acid-Base
HBr⁺ ↔ HBr*
HBr⁺ + O* ↔ Br⁺ + OH*
OH⁺ + OH⁺ ↔ H₂O⁺ + O*
H₂O⁺ ↔ H₂O + *
Doping in Semiconductors: HBr oxidation

Cat_0

Electronic Effects

Extrinsic Doping Fe$_2$O$_3$ for OER

Cat_0

Electrostatics / Hydrogen bond

Pd(111)

Activation energy / kJ mol\(^{-1}\)

- H\(_2\)O\(_2\) formation
- H\(_2\)O\(_2\) hydrogenation
- H\(_2\)O\(_2\) decomposition

Pd(111)-HHDMA

Cat_0 → E field

ACIE (2017)
Ammonia the chemical that feeds the World

Global supply of fertilizers
500 millions tons of NH$_3$

N$_2$ + H$_2$ + harsh conditions (T, P)

1% of global energy
1.6% of global CO$_2$ emissions
Ionic liquids for eN$_2$RR

Interface: Ru(6×6) and 8 IL pairs
Protocol: CMD + AIMD + DFT

Hydrogenations: Simplest $H_2$ activation

$H_2 \rightarrow 2H^\bullet$

Horiuti-Polanyi

Metals

(1)

(2)

(3)
Breaking Scalings by reaction mechanisms

\[ \text{H}_2 \rightarrow 2\text{H}^\bullet \quad \text{Horiuti-Polanyi} \quad \text{Metals} \]

\[ \text{H}_2 \rightarrow \text{H}^+ + \text{H}^- \quad \text{Hydride-Proton} \]

\[ \text{H}_2 \rightarrow \text{H}^+ \cdots \text{H}^- \quad \text{Proton-Hydride Pair} \]
Ligand assisted reactions: N-ligands
Hydride-proton activation

Cat_0 → Ligand

Ligand assisted reactions: H₂ transfer concerted steps

\[ \Delta E = -57 \text{ kJ/mol} \]

\[ \Delta E = -128 \text{ kJ/mol} \]

\[ \text{concerted transition state} \]

\[ v_l = -802 \text{ cm}^{-1} \]

\[ \text{Energy [kJ/mol]} \]

\[ \text{Reaction coordinate} \]

Single atoms: Pd-C$_3$N$_4$
Single atoms: Pd-C$_3$N$_4$ Hydrogenation / Suzuki

ACIE (2015)
Single atoms

- In Metal Alloys
- In Oxides
- In Polymers
- In MOFs
- In Molecular Crystals
  - Double Metal Cyanides
  - Prussian Blue
Breaking Scalings by reaction mechanisms

\[ \text{H}_2 \rightarrow 2\text{H}^\bullet \quad \text{Horiuti-Polanyi} \quad \text{Metals} \]

\[ \text{H}_2 \rightarrow \text{H}^+ + \text{H}^- \quad \text{Hydride-Proton} \]

\[ \text{H}_2 \rightarrow \text{H}^+ \cdots \text{H}^- \quad \text{Proton-Hydride Pair} \]

\[ \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \quad \text{Acidity} \quad \text{Electron potential} \]
Interface acidity (pH control)

levulinic acid → 4-hydroxypentanoic acid → GVL → 1,4-pentanediol

H₂

4-oxopentanal → H₂

valeric acid

angelicalactone
Interface acidity (pH control)
Interface acidity (pH control)

Our artificial pH-meter

Electron potential

Heterogeneous Catalysis

adsorption [H⁺]-transfer

P,T
Decorated nanoparticles 100 times more active

Two different mechanisms

Nitrobenzene Adsorption Enhanced
Two different mechanisms

Heterogeneous Catalysis

- Adsorption
- $[^{[H^+]}]$-transfer

Electrochemistry

- $e^-$ to $e^-$
- $[^{[e/H^+]}]$-transfer

$P,T$
Electron confinement + electric field
Electron confinement + electric field

Confinement 1.7 nm
Electric field
Water
Proton Shuttles
Self-powered catalyst
Tethering: CO2RR

Cat_0 → bond

Basicity as a descriptor
Dynamic charge oxidation states: SAC

Cat_0 ➔ OS
Effect on reactivity: $150^\circ\text{C}$ challenge

[Diagram and text from Nature Materials (2019)]
OER: Magnetic enhancement

450 mT

Cat_0  ➔  Force

NiZnFe$_4$O$_x$
Spin control of the activity

\[ 2\text{OH}^- \rightarrow 2\text{H}^+ \]

\[ \text{Ni} \quad \text{Ni} \]

\[ \text{O} \quad \text{O} \]

\[ \text{O} \quad \text{O} \]

\[ \text{Ni} \quad \text{Ni} \]

\[ \text{current density (m} \text{A/cm}^2) \]

\[ \text{Potential (V vs RHE)} \]
Strategies to avoid LSR
Where are we in modelling
Thank you for your attention

Rodrigo Garcia-Muelas
Miquel Garcia-Rates*
Qiang Li*
Franziska Hegner
Edvin Fako
Albert Sabadell
Federico Dattila
Bob Nguyen
Paulina Prslja
Yecheng Zhou*
Manuel Ortuño
Sergio P. Garcia
Nathan Daelman
Marcos Rellan-Piñeiro
Jordi Miralles
Andrea Ruiz-Ferrando
Julian Geiger
Pavle Nicazevic
Neyvis Almora-Barrios*

J Pérez-Ramírez
JR Galán-Mascarós
L. Rossi
P. v. Leeuwen