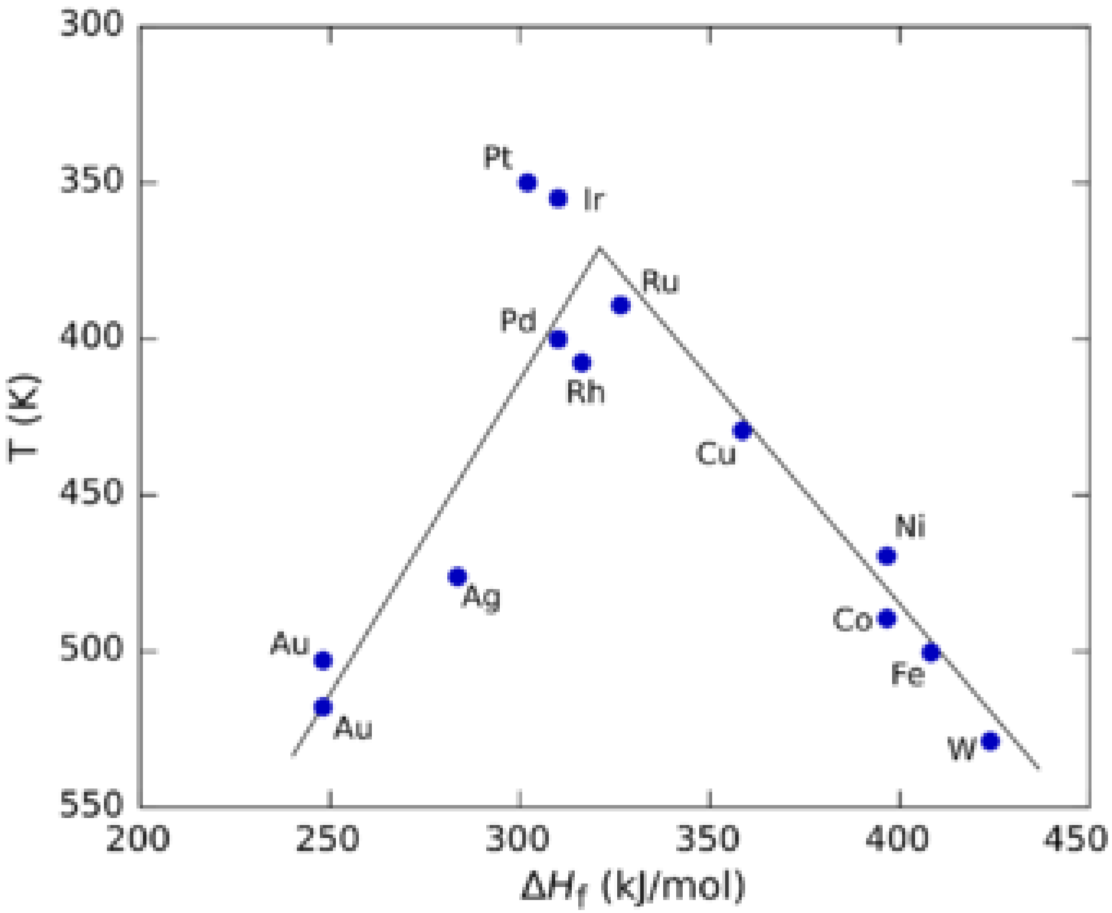
Núria López

Volcanos, cliffs and ways around

Volcanos: Our current understanding of Catalysis from theory



Sabatier principle

Volcanos: Our current understanding of Catalysis

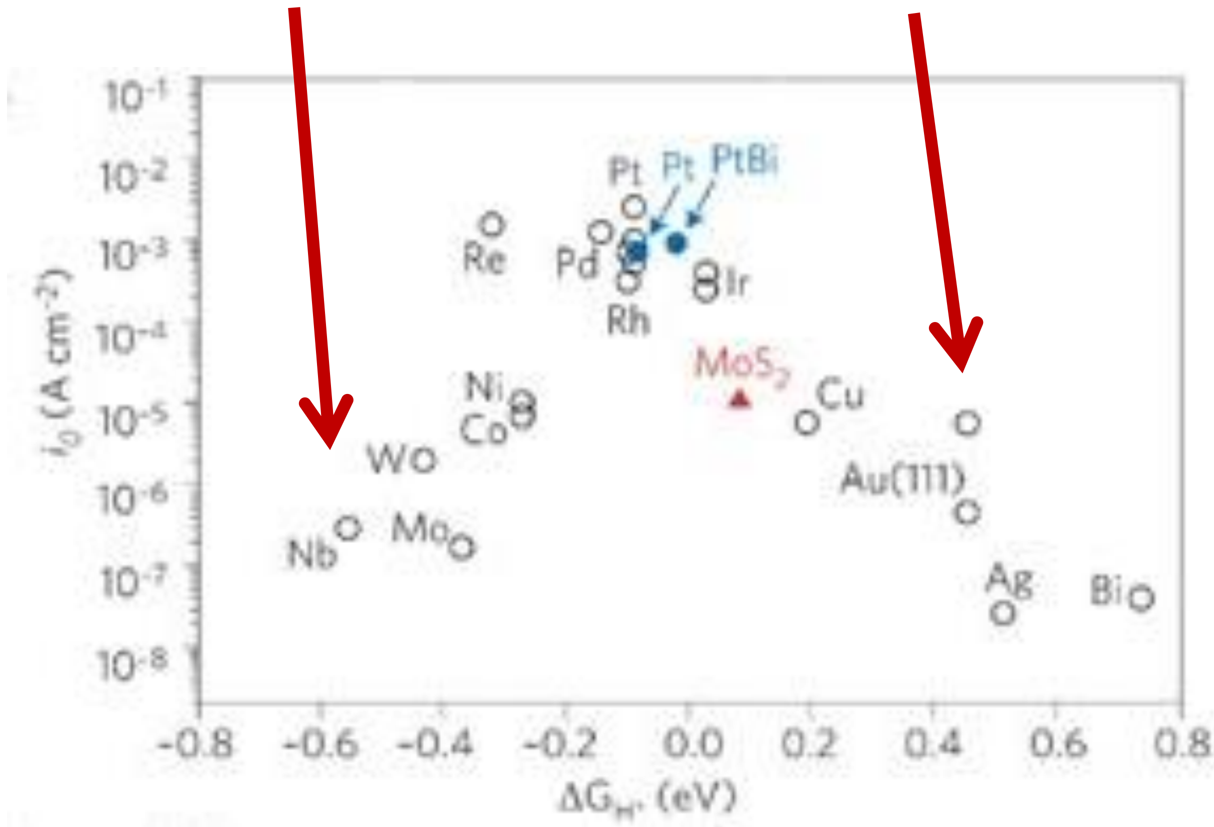
Sabatier principle

Can be reproduced

- DFT
  - Mechanism
  - Elementary steps
- Microkinetics

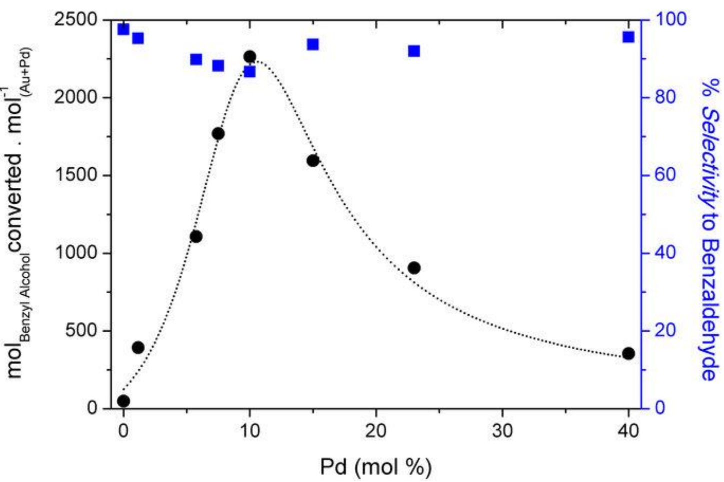
Too strong

Too weak

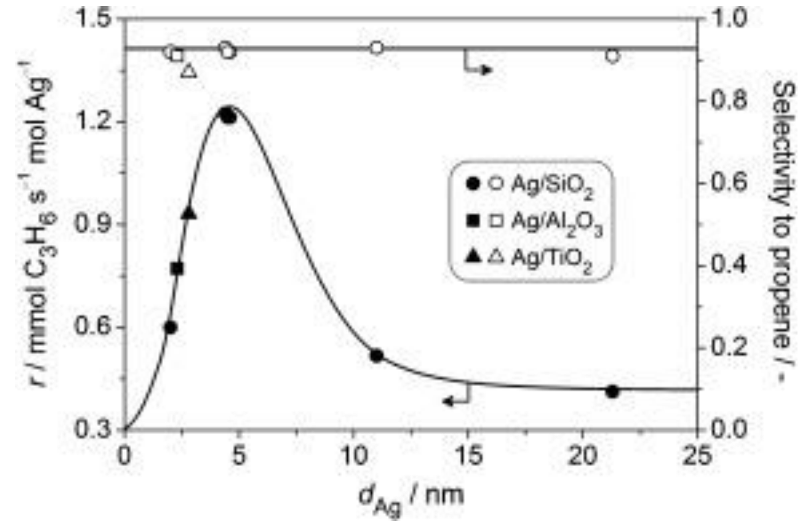


Nature Chem. (2009)

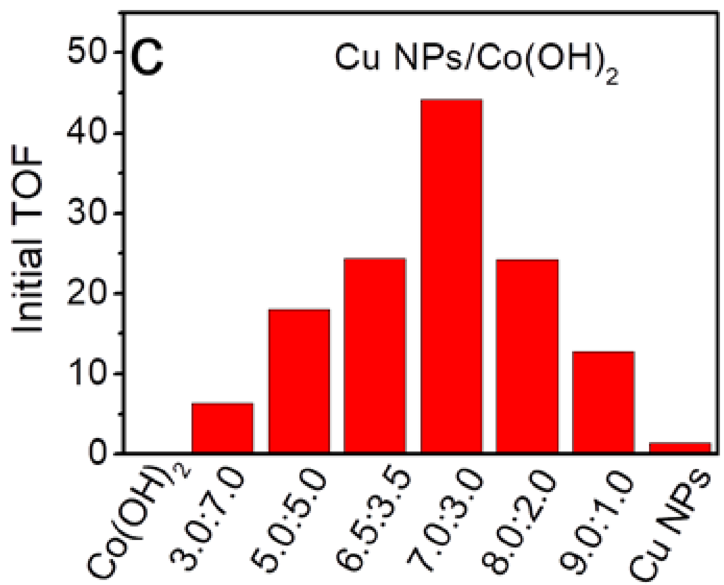
Volcanos are taken as standard for activity



With Pd content in PdAu alloys
Sci. Rep. (2014)

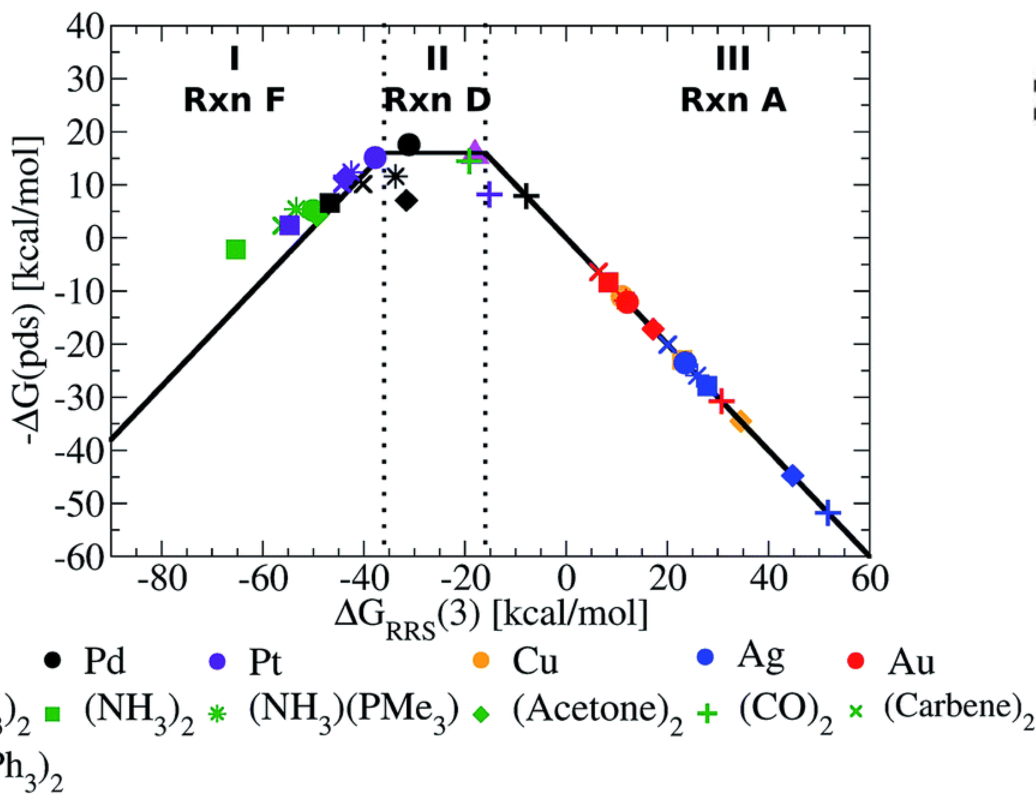


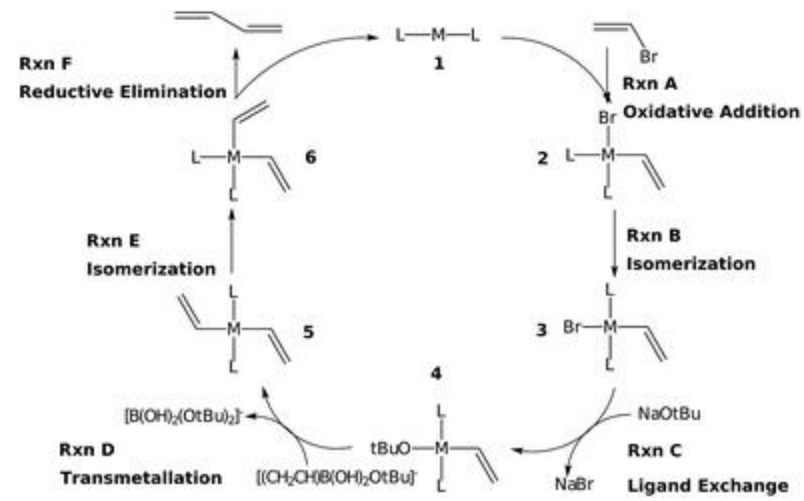
With NP Ag size
ChemCatChem (2013)

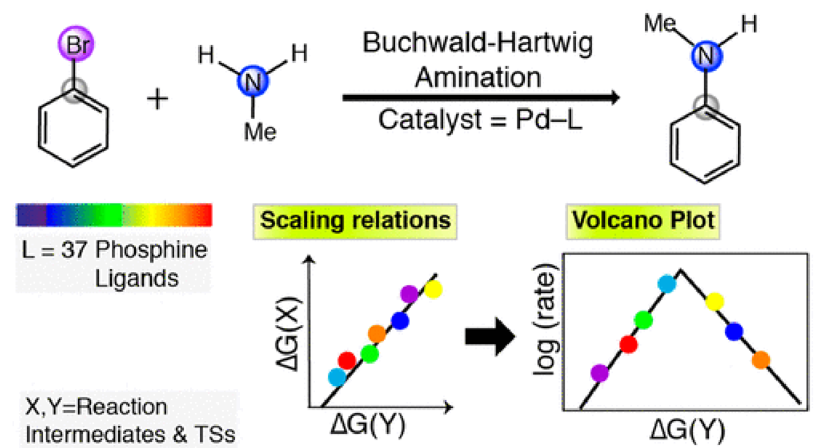


Metal/Oxide interfaces (2019)

Even in homogeneous catalysis







Corminbeuf Chem Sci. (2015); Kulik ACS Catal (2018); Norskov (2019)

Volcanos

Provide systematic way for optimization

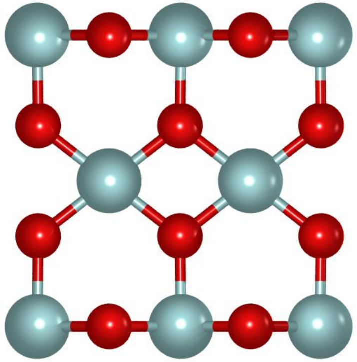
Why volcanos appear?

Symmetries between energies of different species

Example: Step 1 DFT

$HCl + \frac{1}{4} O_2 \rightarrow \frac{1}{2} Cl_2 + \frac{1}{2} H_2O$

	E_a / eV	ΔE / eV
$HCl + * \leftrightarrow HCl*$	0	-0.48
$HCl* + O_b* \leftrightarrow Cl_c* + O_bH*$	0.05	-0.98
$HCl* + O_c* \leftrightarrow Cl_c* + O_cH*$	0.11	-0.75
$O_cH* + O_bH* \leftrightarrow H_2O_c* + O_b*$	0.38	0.27
$O_cH* + O_cH* \leftrightarrow H_2O_c* + O_c*$	0.24	-0.11
$O_c* + O_bH* \leftrightarrow O_cH* + O_b*$	0.55	-0.01
$H_2O_c* \leftrightarrow H_2O + *$	0.90	0.90
$Cl_c* + Cl_c* \leftrightarrow Cl_2 + 2 *$	1.56	1.56
$O_2 + 2 * \leftrightarrow 2 O_c*$	0.38	-0.76



$RuO_2(110)$

Example: Step 2 Microkinetics

$HCl + \frac{1}{4} O_2 \rightarrow \frac{1}{2} Cl_2 + \frac{1}{2} H_2O$

$$\frac{d}{dt} HCl(t) = k1\, PHCl(t)\, Rucus(t) - k2\, HCl(t) - k3\, HCl(t)\, Ob(t) + k4\, Cl(t)\, ObH(t) - k5\, HCl(t)\, Oc(t) + k6\, Cl(t)\, OcH(t)$$

$$\frac{d}{dt} Cl(t) = k3\, HCl(t)\, Ob(t) - k4\, Cl(t)\, ObH(t) + k5\, HCl(t)\, Oc(t) - k6\, Cl(t)\, OcH(t) - 2\, k7\, Cl(t)^2 + 2\, k8\, PCl2(t)\, Rucus(t)^2$$

$$\frac{d}{dt} Oc(t) = -k5\, HCl(t)\, Oc(t) + k6\, Cl(t)\, OcH(t) - k9\, ObH(t)\, Oc(t) + k10\, Ob(t)\, OcH(t) + k15\, OcH(t)^2 - k16\, Oc(t)\, H2Oc(t) + 2\, k19\, O2(t$$

$$- 2\, k20\, Oc(t)^2$$

$$\frac{d}{dt} H2Oc(t) = k11\, ObH(t)\, OcH(t) - k12\, Ob(t)\, H2Oc(t) + k15\, OcH(t)^2 - k16\, Oc(t)\, H2Oc(t) - k13\, H2Oc(t) + k14\, PH2O(t)\, Rucus(t)$$

$$\frac{d}{dt} Ob(t) = -k3\, HCl(t)\, Ob(t) + k4\, Cl(t)\, ObH(t) + k9\, ObH(t)\, Oc(t) - k10\, Ob(t)\, OcH(t) + k11\, ObH(t)\, OcH(t) - k12\, Ob(t)\, H2Oc(t)$$

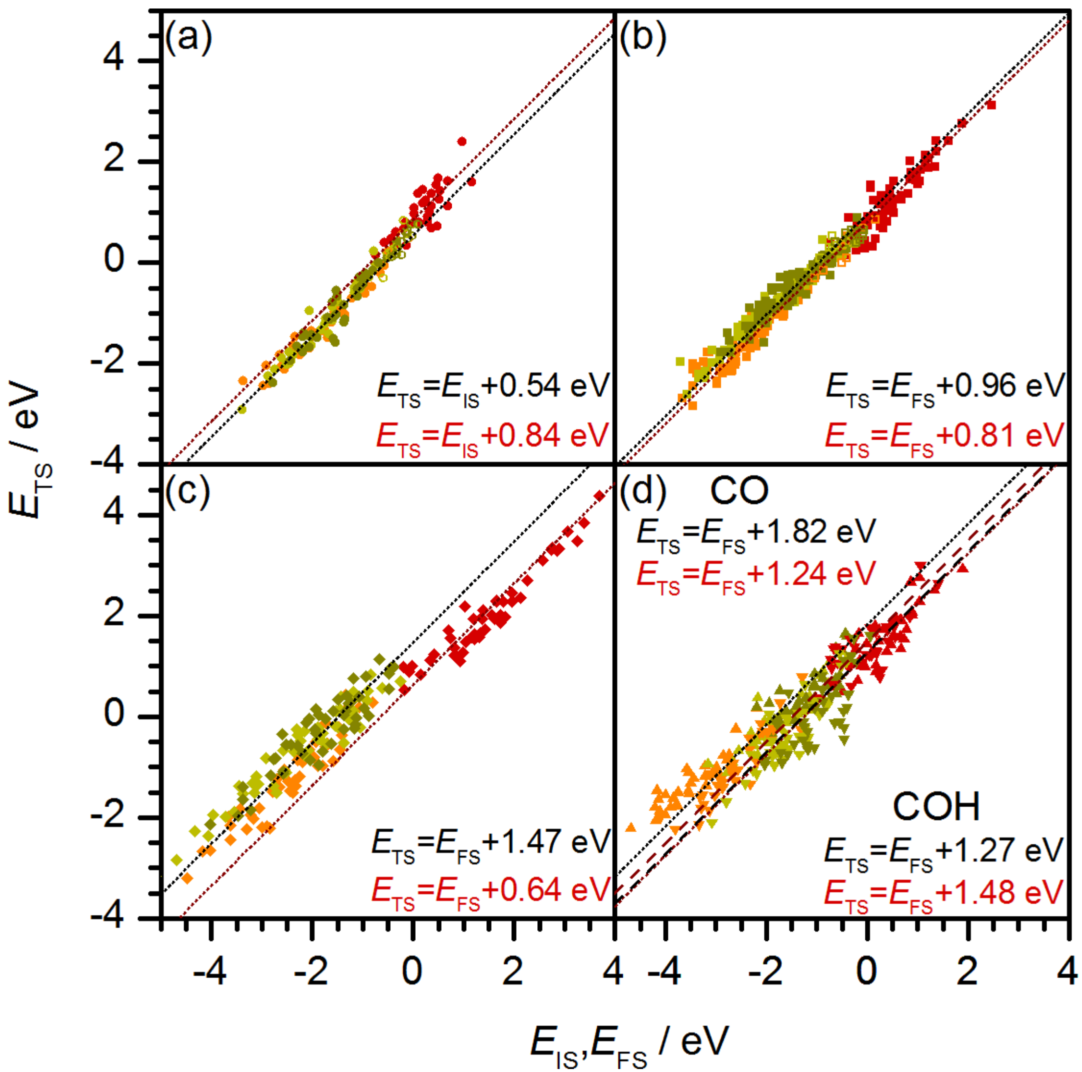
$$\frac{d}{dt} O2(t) = k17\, PO2(t)\, Rucus(t) - k18\, O2(t) - k19\, O2(t)\, Rucus(t) + k20\, Oc(t)^2$$

$$\frac{d}{dt} ObH(t) = k3\, HCl(t)\, Ob(t) - k4\, Cl(t)\, ObH(t) - k9\, ObH(t)\, Oc(t) + k10\, Ob(t)\, OcH(t) - k11\, ObH(t)\, OcH(t) + k12\, Ob(t)\, H2Oc(t)$$

$$\frac{d}{dt} OcH(t) = k5\, HCl(t)\, Oc(t) - k6\, Cl(t)\, OcH(t) + k9\, ObH(t)\, Oc(t) - k10\, Ob(t)\, OcH(t) - k11\, ObH(t)\, OcH(t)$$

$$+ k12\, Ob(t)\, H2Oc(t) - 2\, k15\, OcH(t)^2 + 2\, k16\, Oc(t)\, H2Oc(t)$$

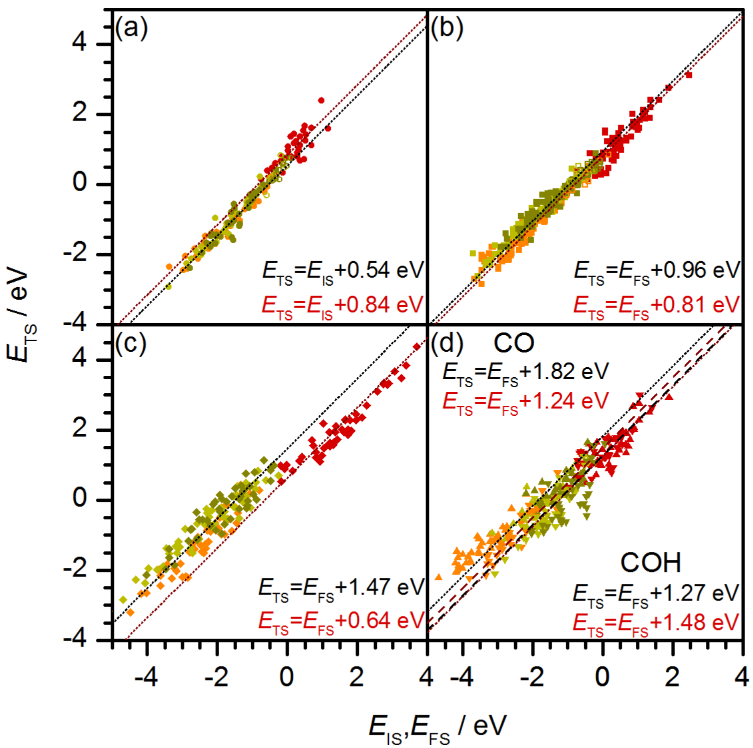
Example: Step 3 Linear-Scaling Relationships

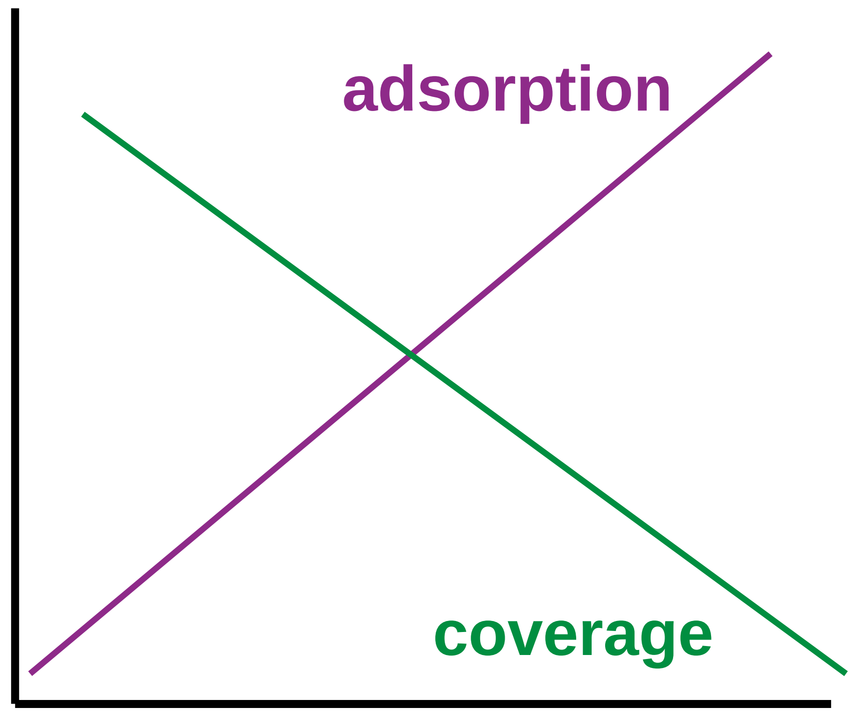


Q. Li, R. Garcia-Muelas, NL Nature Comm. (2018)

Why volcanos appear?

Linear-Scaling Relationships





Q. Li, R. Garcia-Muelas, NL Nature Comm. (2018)

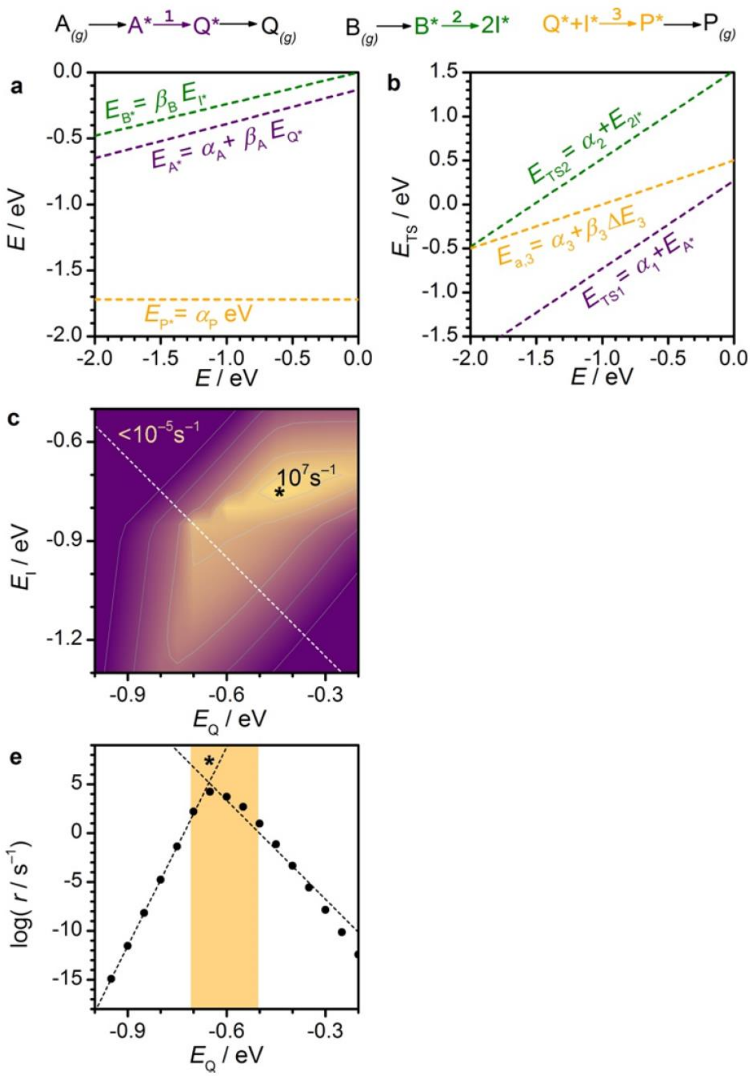
How many types of Linear-Scalings are there?

$$r=r\{E_{ads}, E_{TS}, NC\}$$

- Thermodynamic vs. Thermodynamic $E_{ads}(NH_x) \alpha E_{ads}(N)$
- Kinetic vs. Thermodynamic $E_{TS} \alpha E_{ads}(N)$
- Coordination dependence $E_{ads}(N) \alpha E_{ads}(N\text{-}111)$

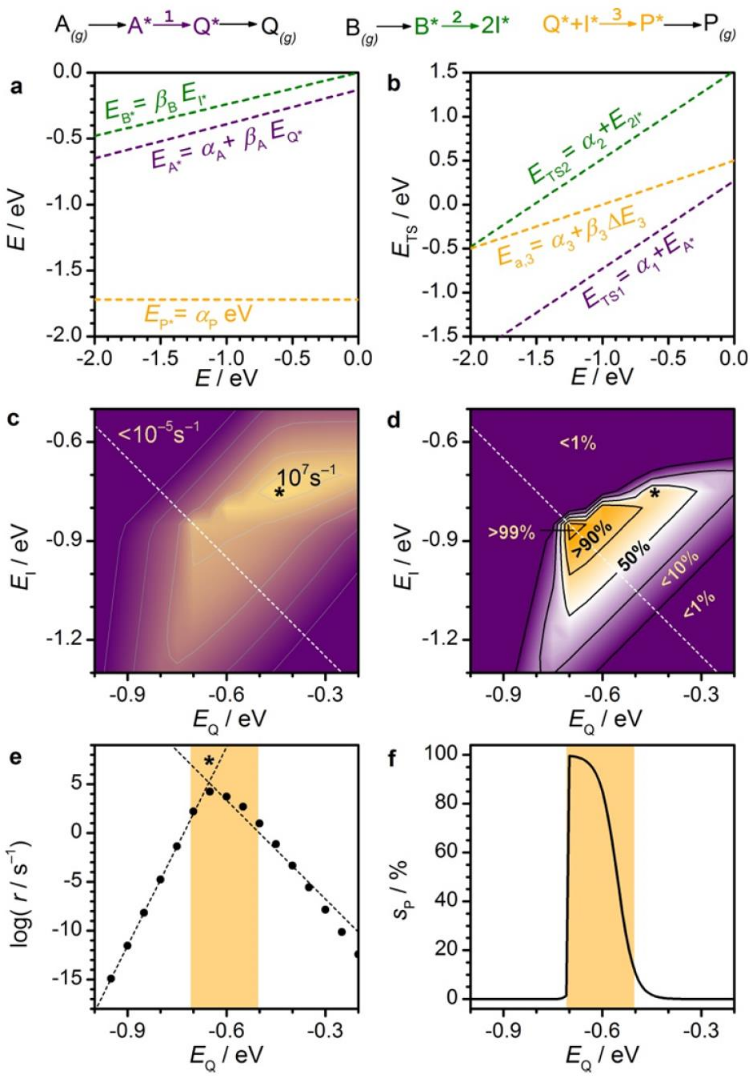
Abild-Pedersen, Norskov, Sautet, Calle-Vallejo

Volcano appears



$$r = r(E_{ads})$$

Selectivity: Cliffs



Selectivity much more demanding

0.1 eV

LSR at their limit of accuracy

Volcanos

•Provide systematic way for optimization

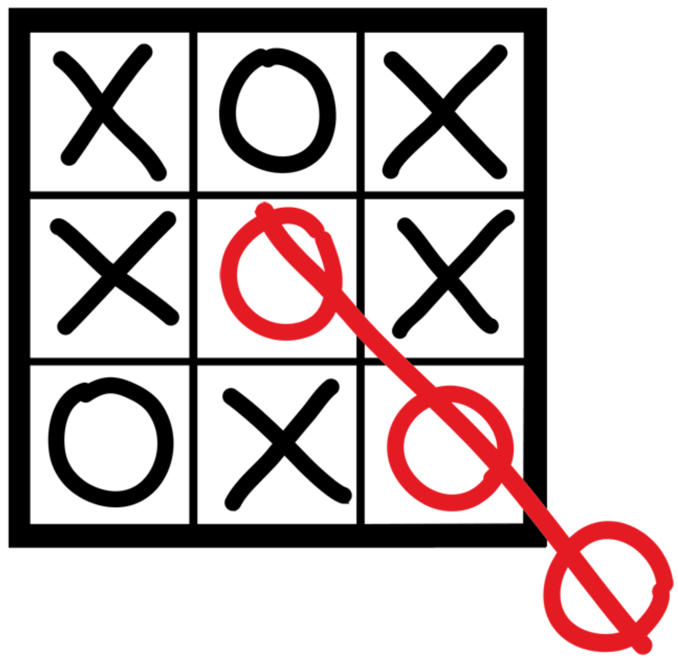
BUT:

•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

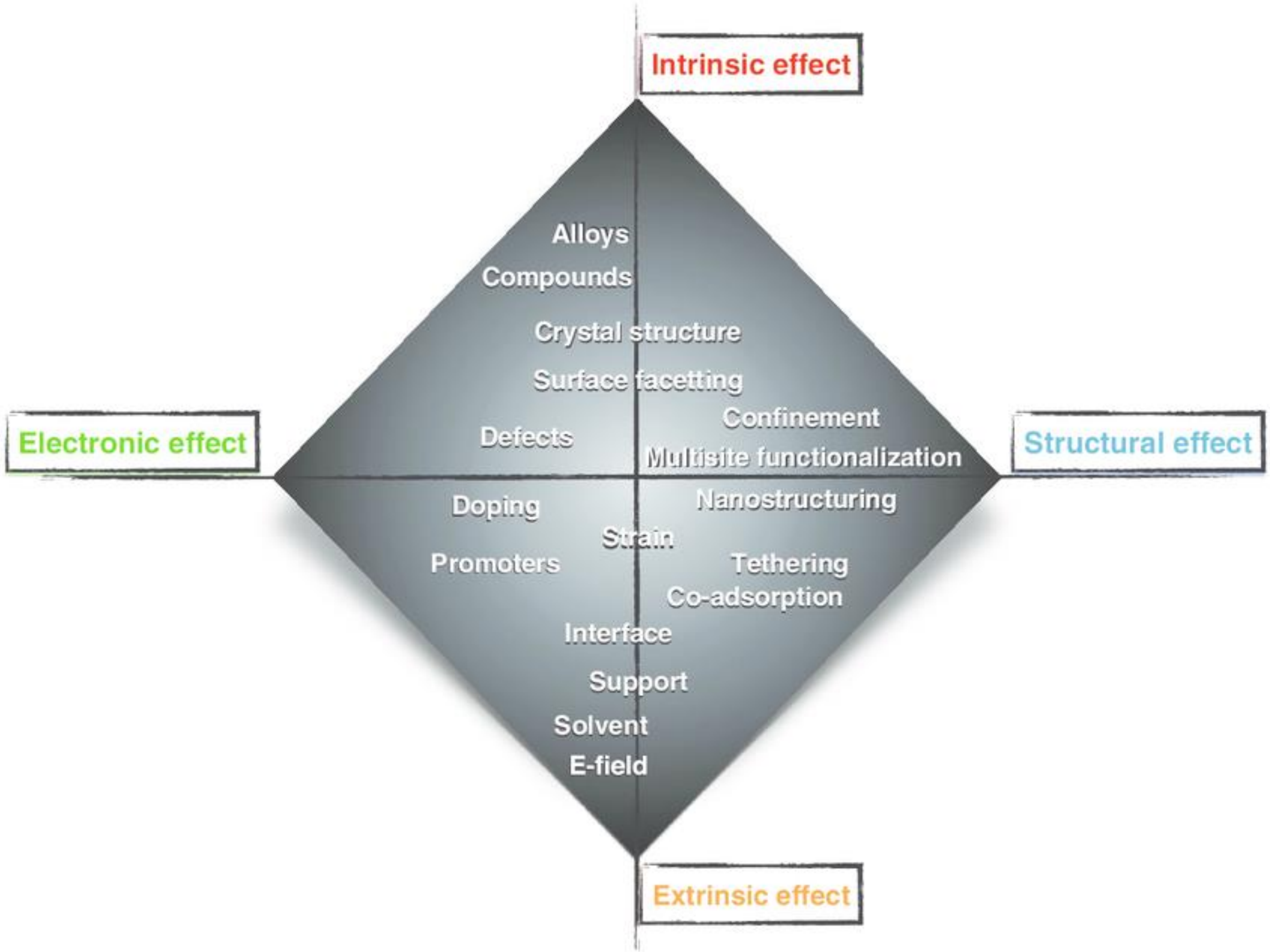
•Can we be **more active than top volcano?**

Linear-Scalings Volcanos = Thinking in the box

THINK OUTSIDE THE BOX



Linear-Scalings are constraints
are there any strategies to avoid them?



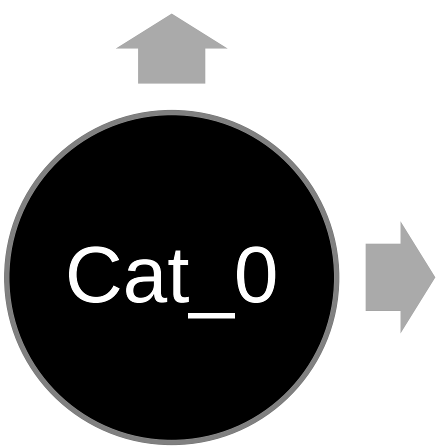
Vojvodic,Norskov (2015)

Linear-Scalings are constraints are there any strategies to avoid them?

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

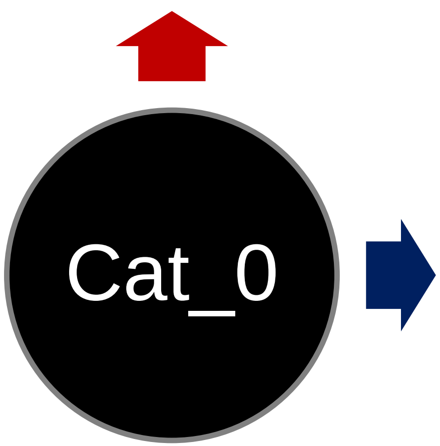
- Catalyst complexity
- Alternative energy forms

Breaking the rules



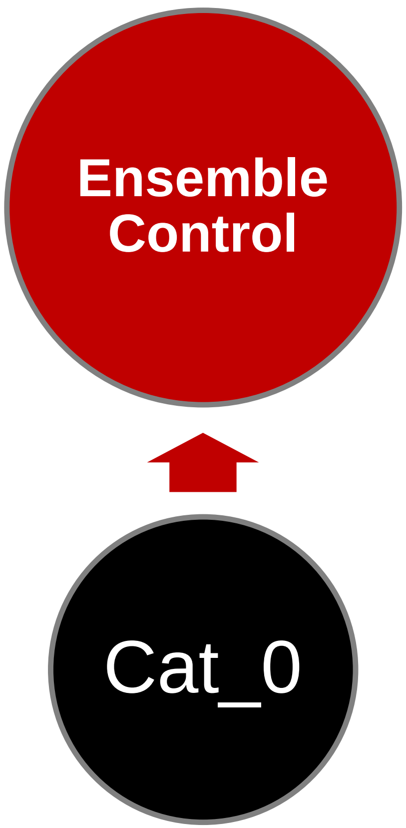
Breaking the rules

Geometric Structural Effects

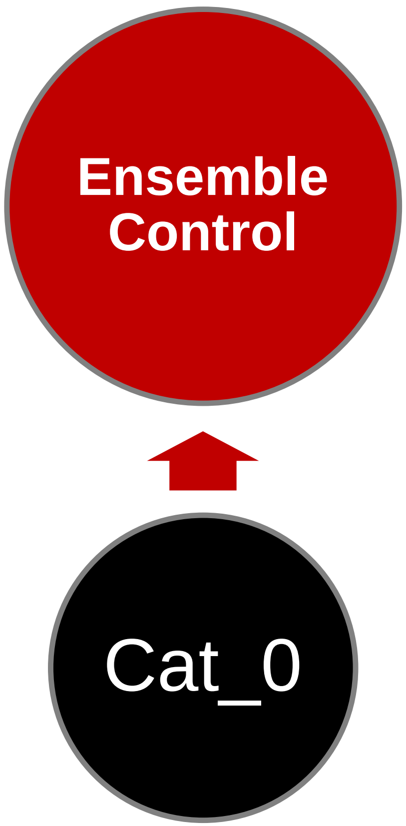


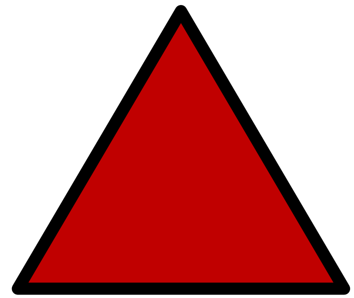
Electronic Effects

Breaking the rules

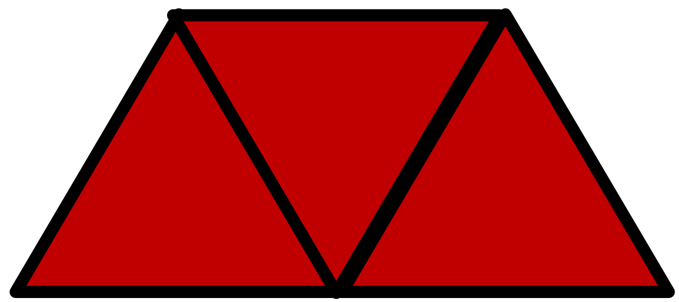


Breaking the rules



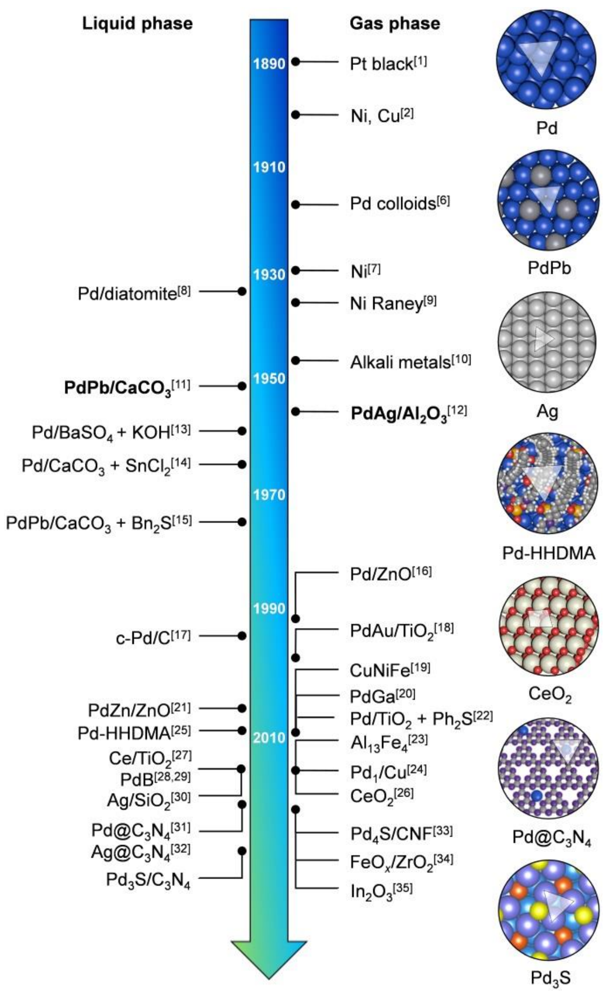


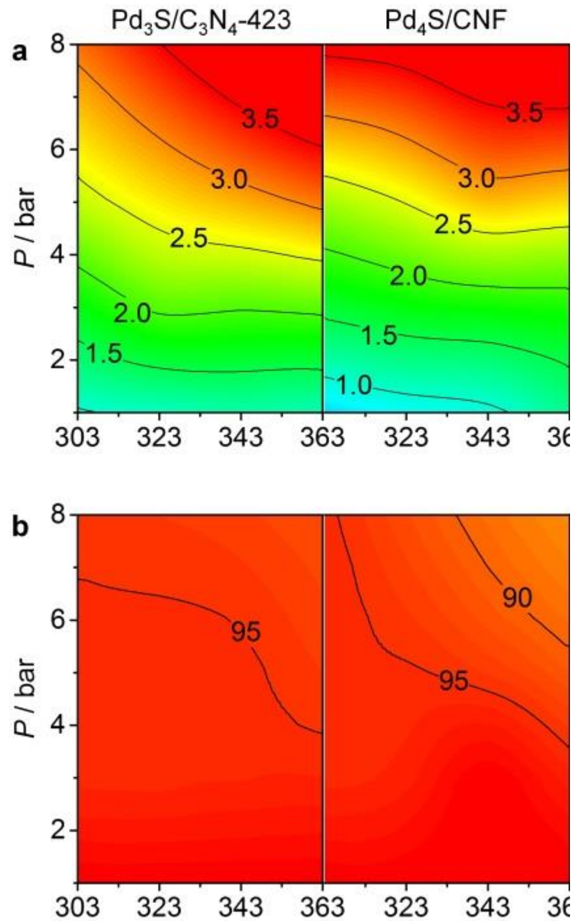
Selective Ensemble

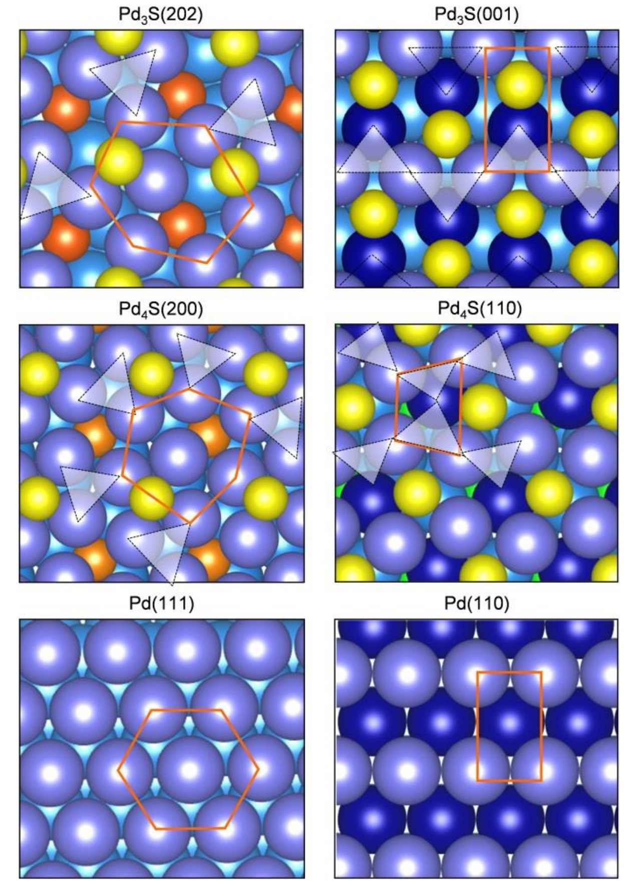


Unselective Ensemble

Ensemble control by mixed phases

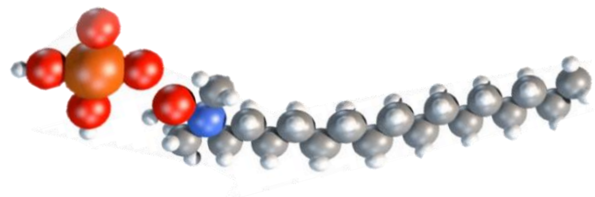


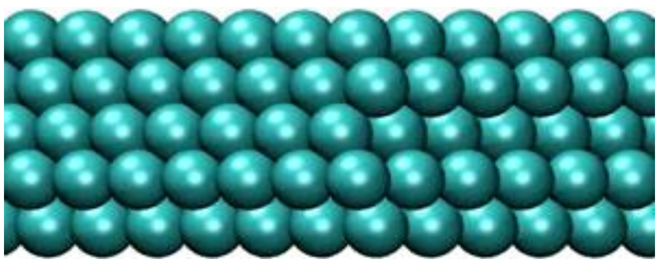




Nature Comm. (2018)

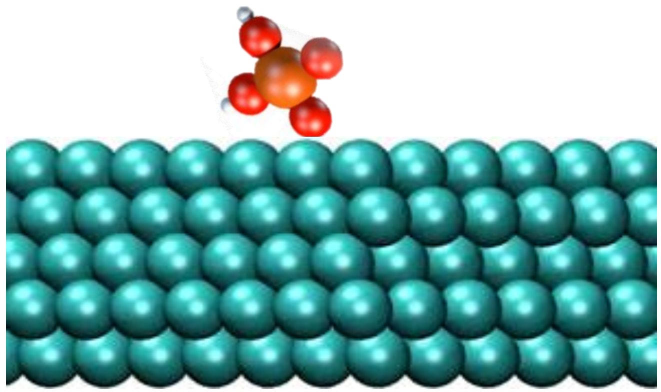
Ensemble control by ligands





Nano Lett. (2014)

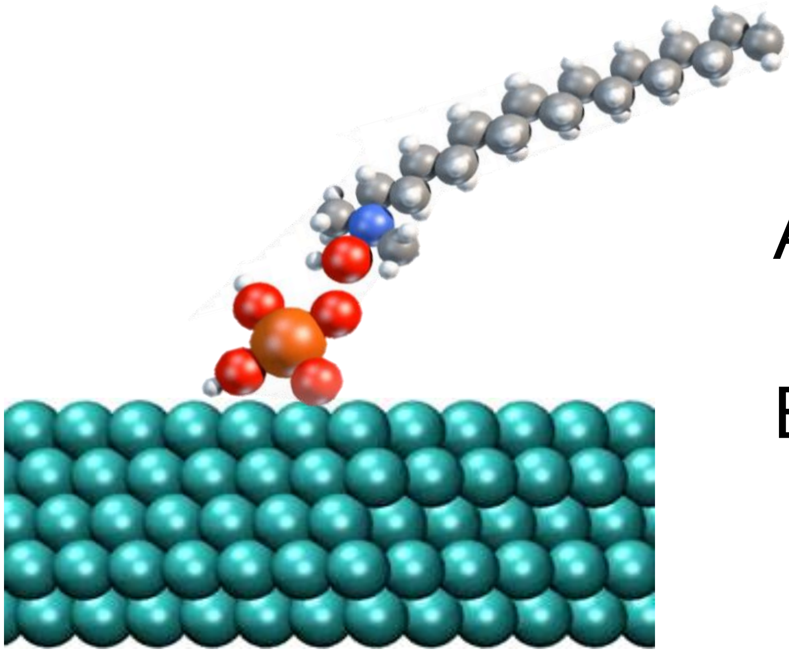
Structure of the ligand decorated particles



Anions go first on the surface

Nano Lett. (2014)

Structure of the ligand decorated particles

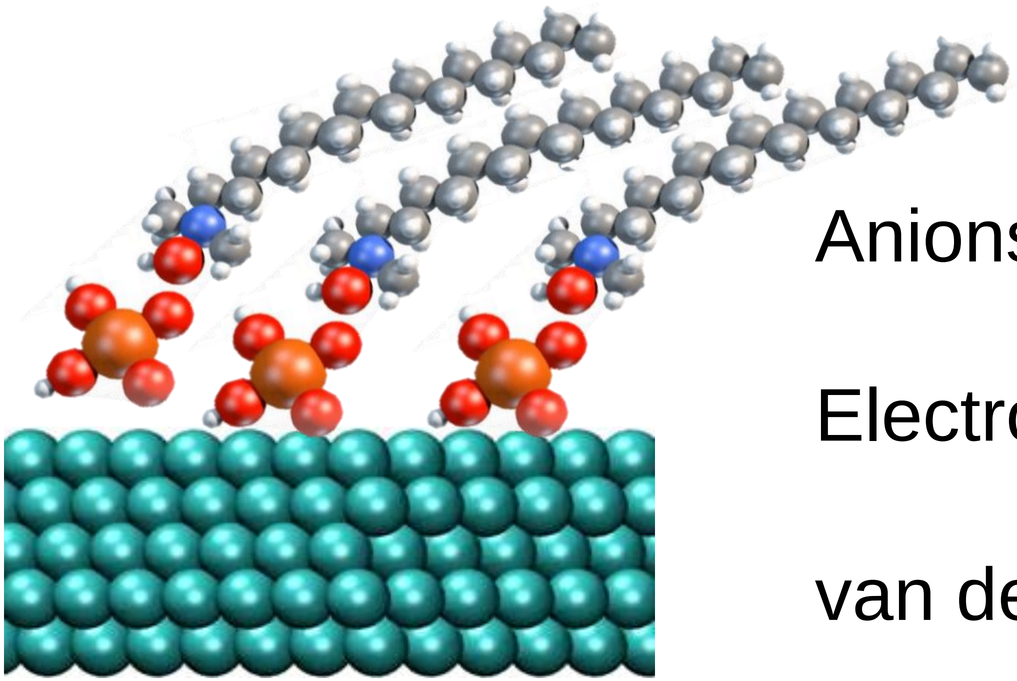


Anions go first on the surface

Electrostatics cations

Nano Lett. (2014)

Structure of the ligand decorated particles



Anions go first on the surface

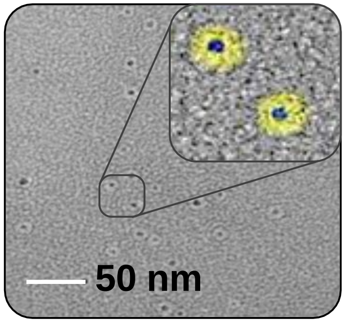
Electrostatics cations

van der Waals tails

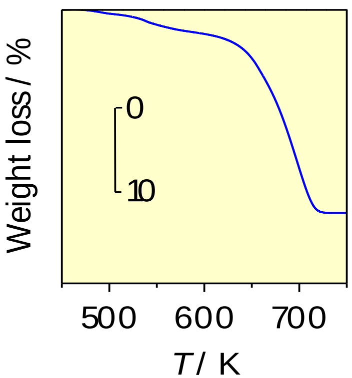
Nano Lett. (2014)

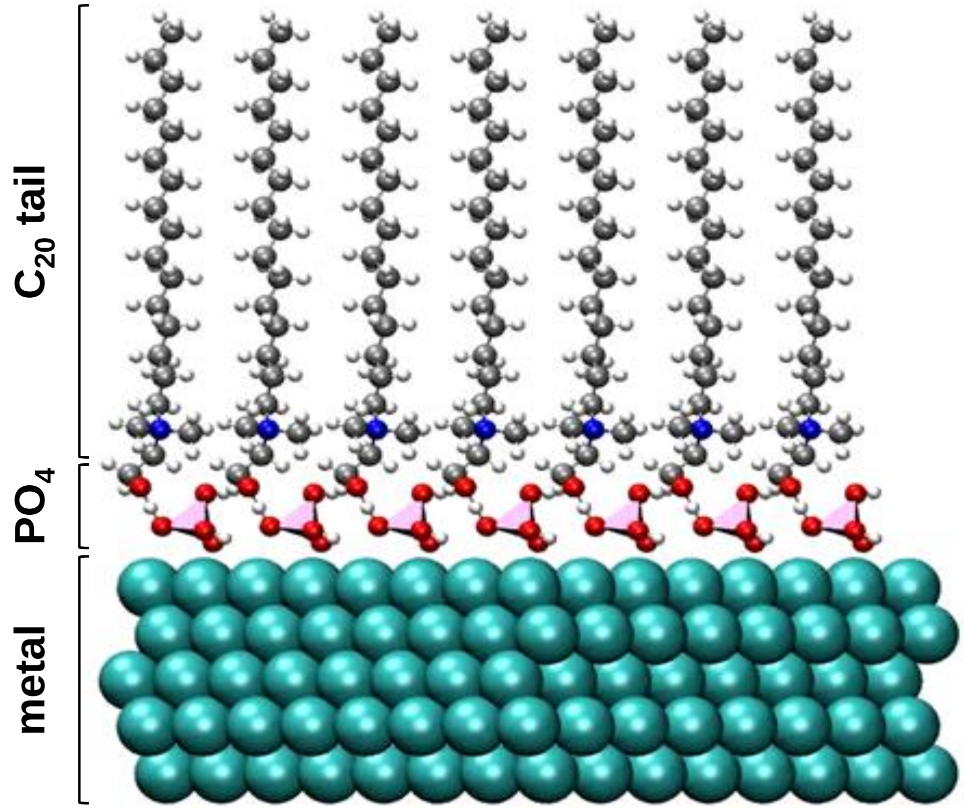
Structure of the ligand decorated particles

Cryo-TEM

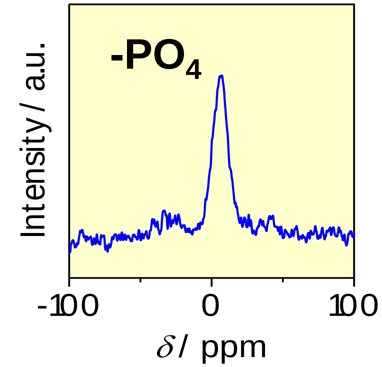


TGA

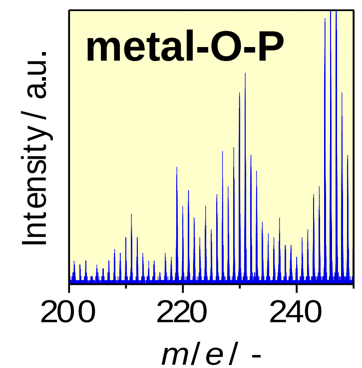




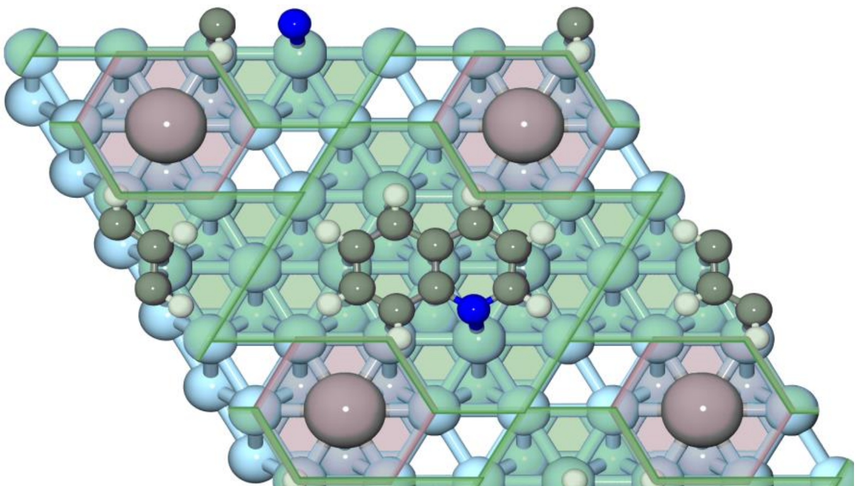
31P MAS NMR

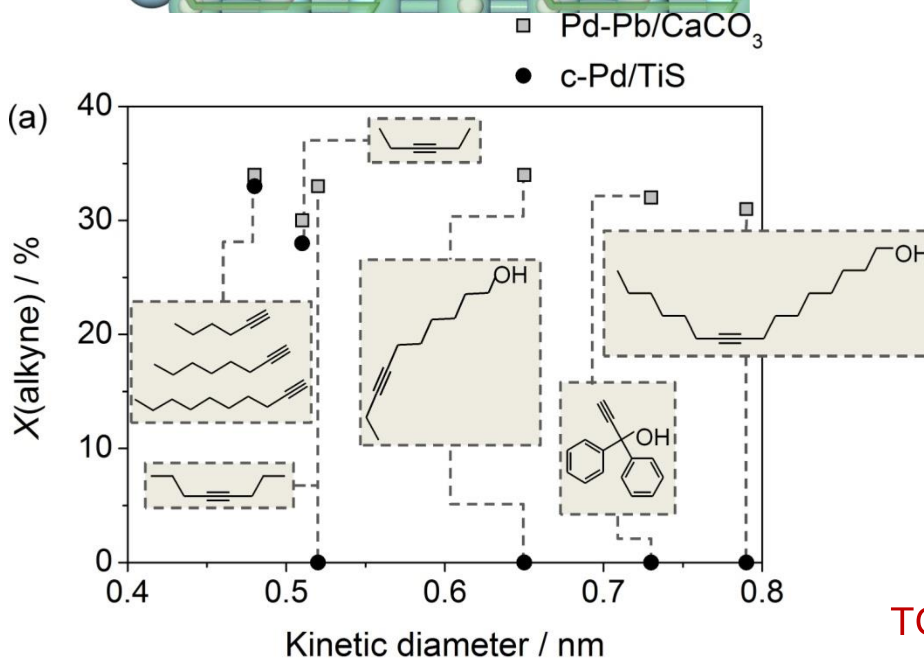


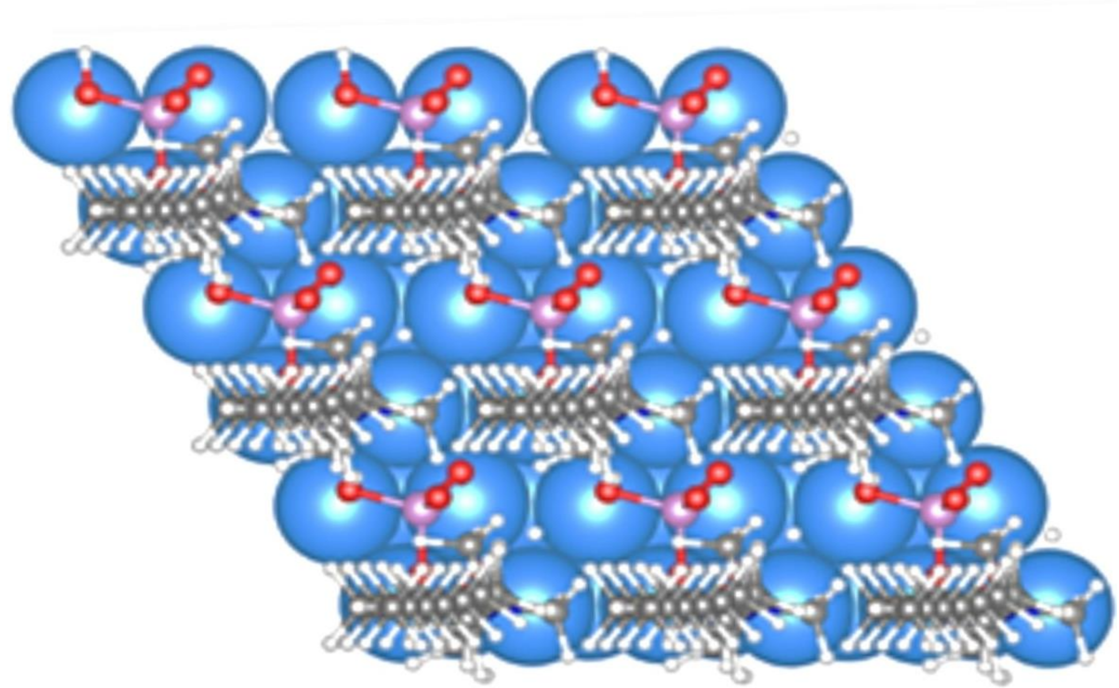
ToF-SIMS



Lindar vs ligand decorated nanoparticles

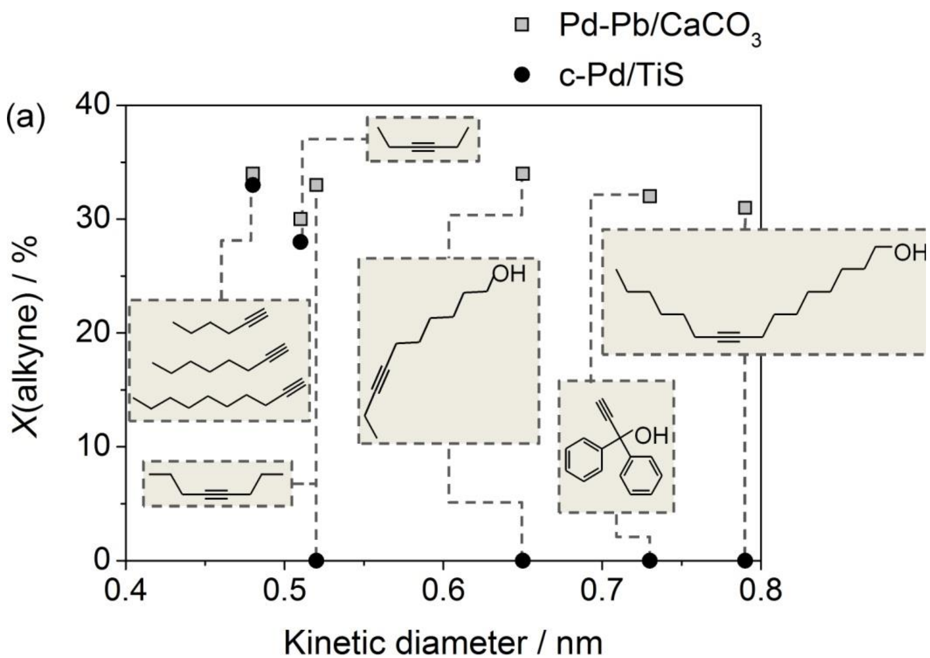






TCA (2011); Chem. Eur. J. (2014)

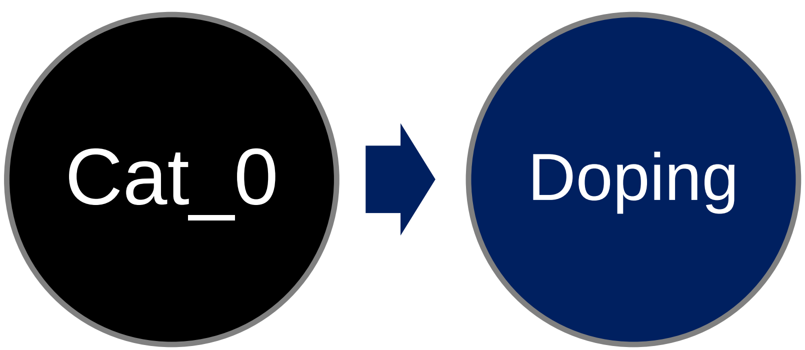
Geometric / Ensemble control



- Ensemble control
- Difficult reorganization

- Adsorption configurations change (coverage effects)

Breaking the rules



Doping in Semiconductors: HBr oxidation

$HX + * \leftrightarrow HX*$

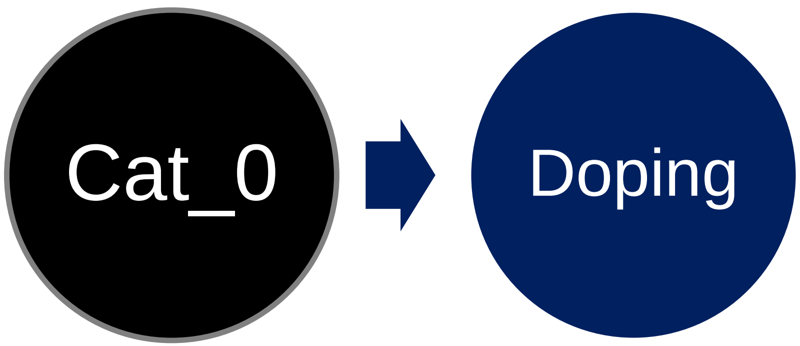
$HX* + O* \leftrightarrow X* + OH*$

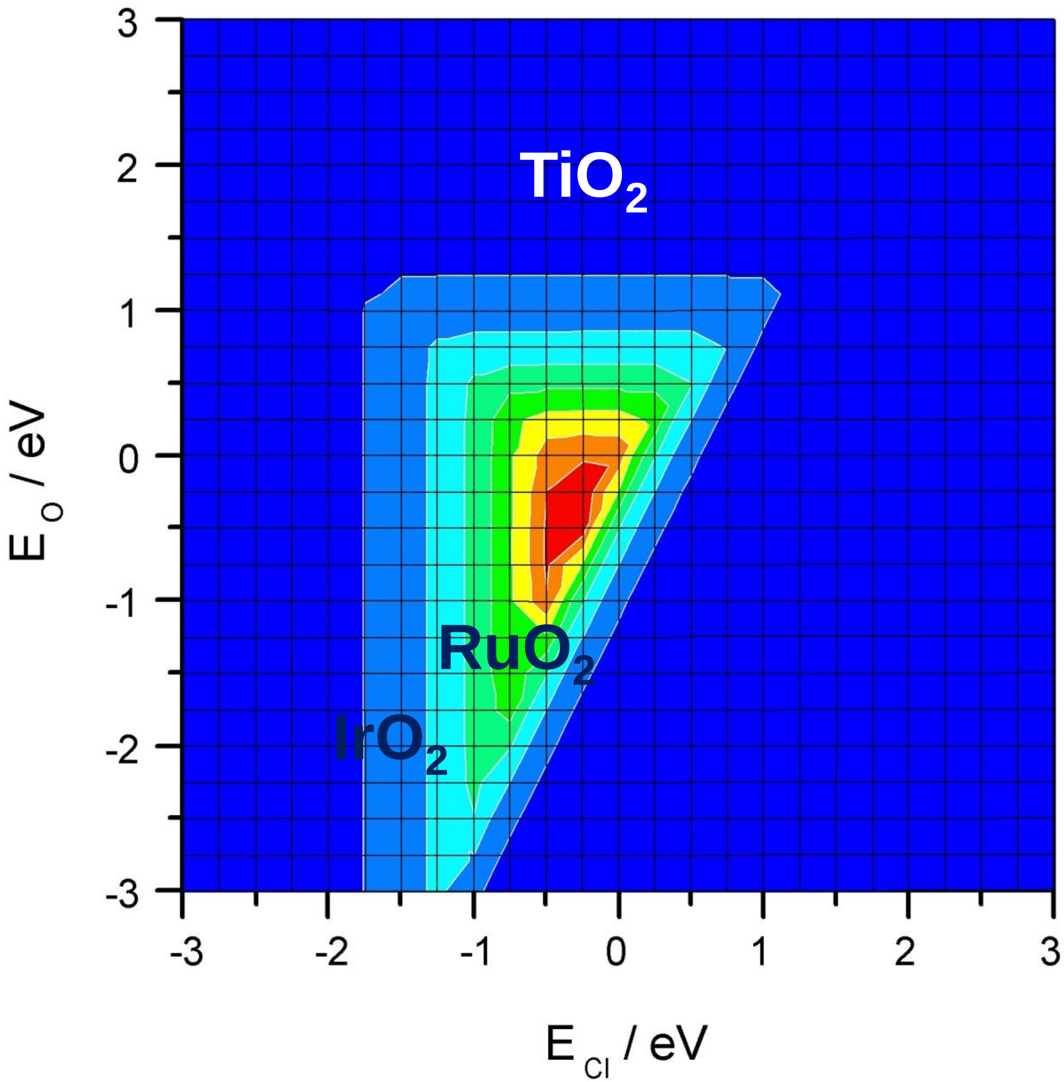
$OH* + OH* \leftrightarrow H_2O* + O*$

$H_2O* \leftrightarrow H_2O + *$

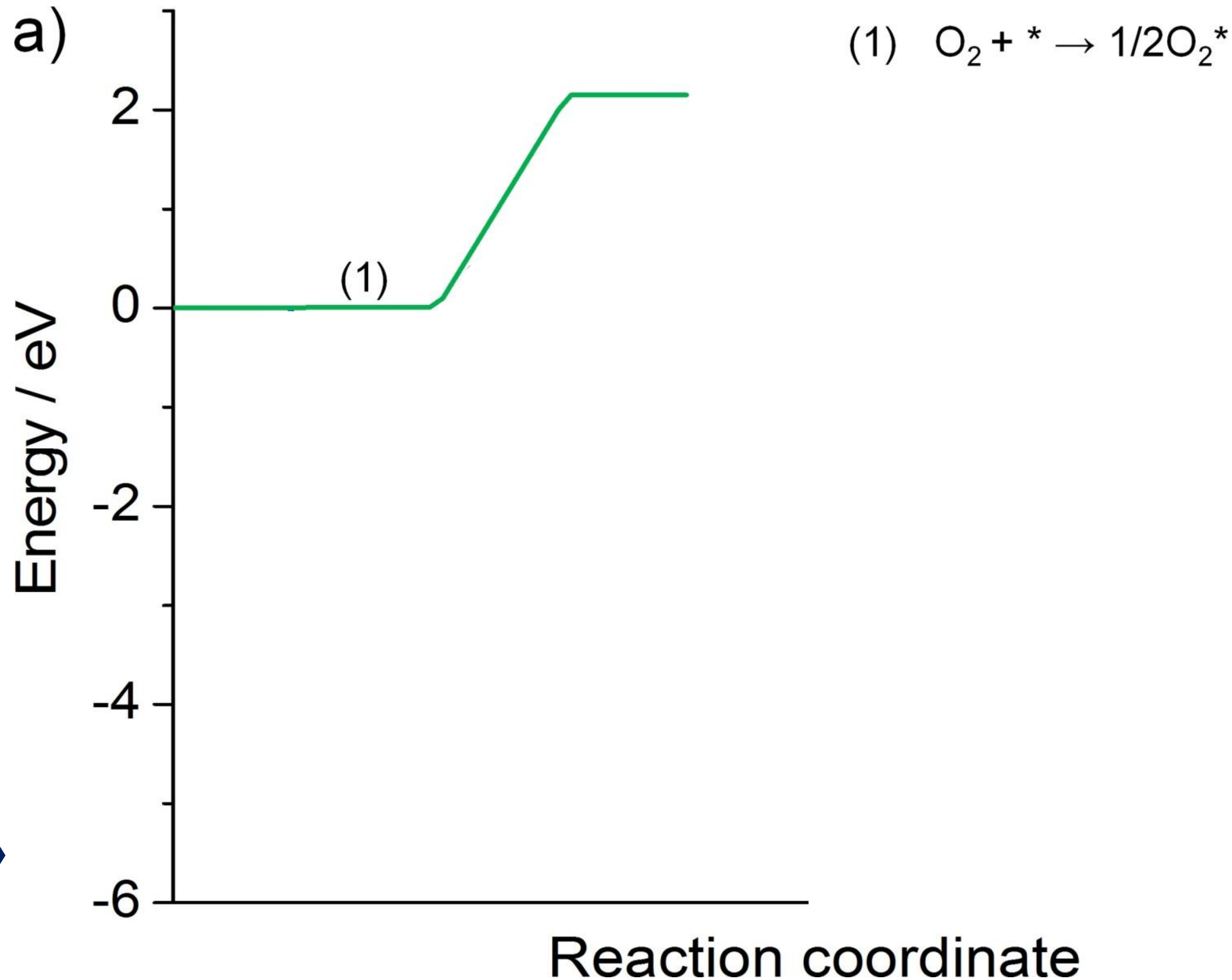
$X* + X* \leftrightarrow X_2 + 2*$

$O_2 + 2* \leftrightarrow 2O*$





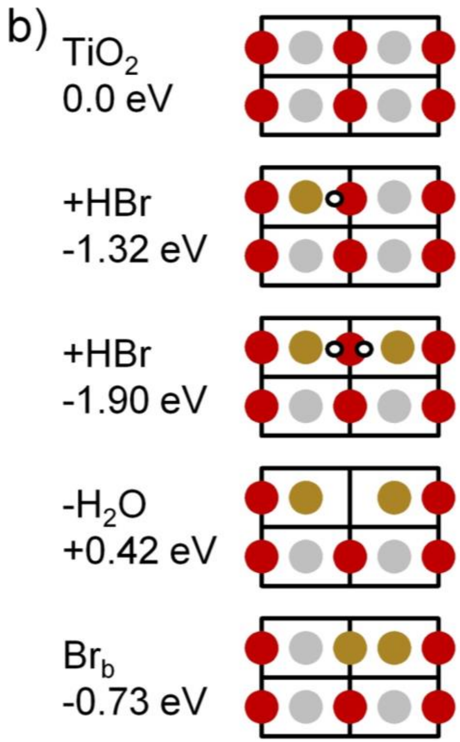
Doping in Semiconductors: HBr oxidation



Cat_0

Angew. Chem. Int. Ed. (2014)

Doping in Semiconductors: HBr oxidation



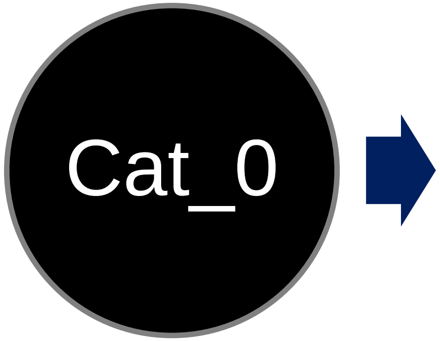
Acid-Base

$HBr + * \leftrightarrow HBr^*$

$HBr^* + O^* \leftrightarrow Br^* + OH^*$

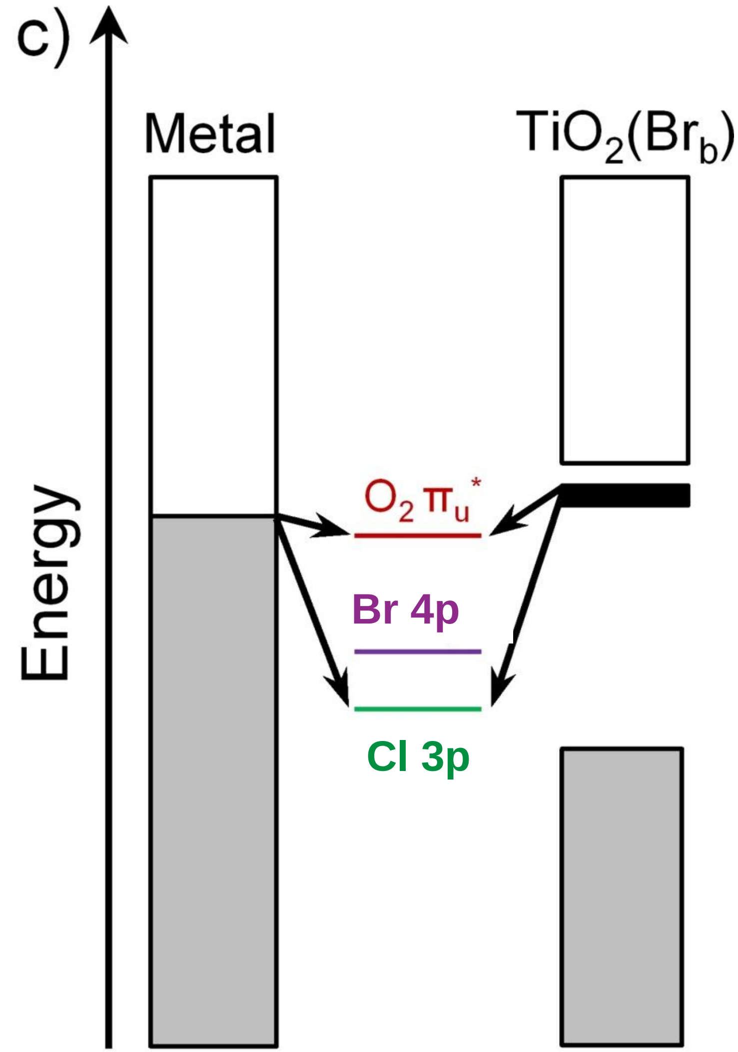
$OH^* + OH^* \leftrightarrow H_2O^* + O^*$

$H_2O^* \leftrightarrow H_2O + *$



Angew. Chem. Int. Ed. (2014)

Doping in Semiconductors: HBr oxidation

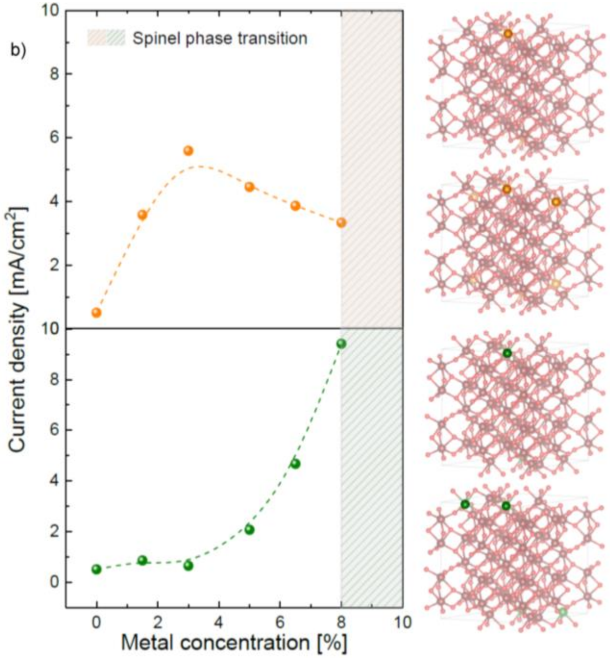


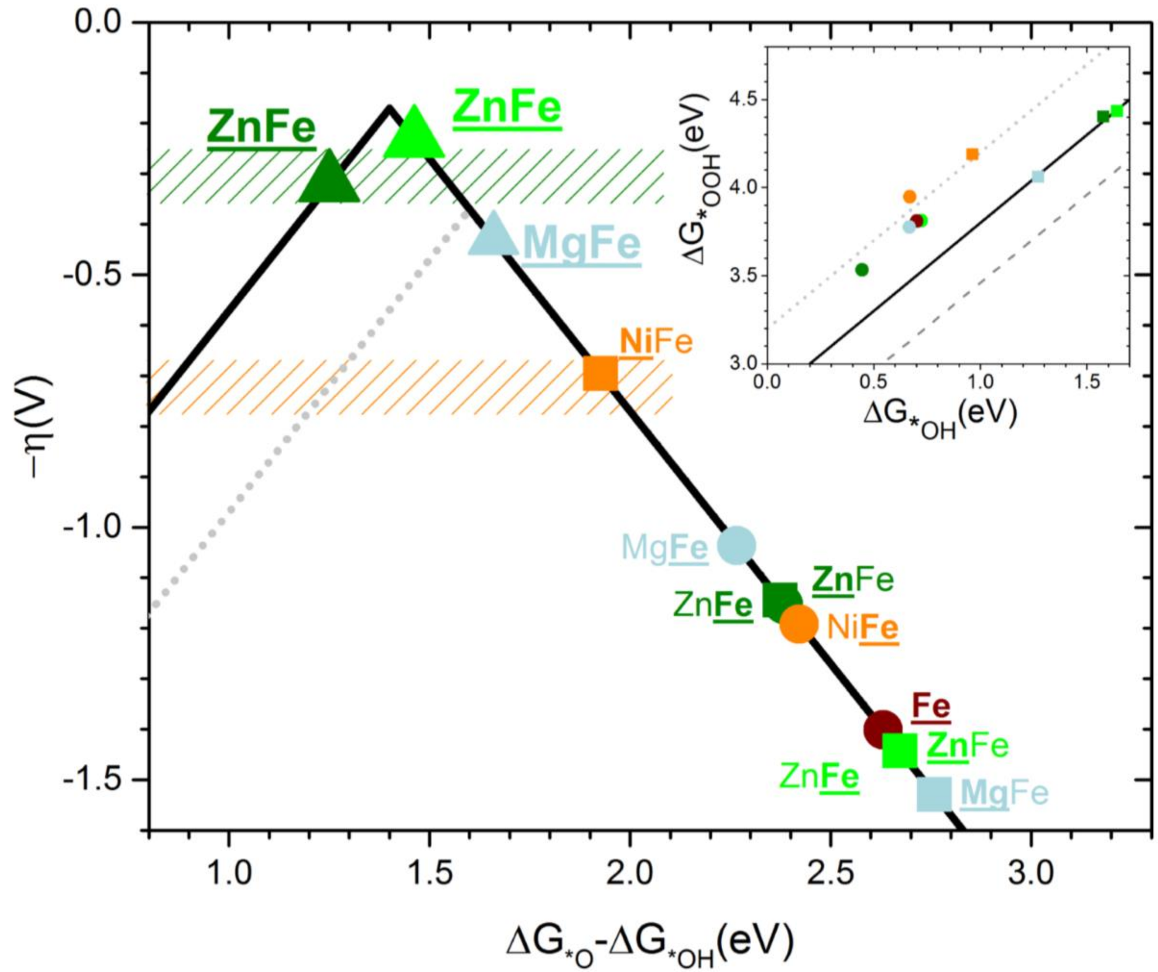
Cat_0

Electronic Effects

Angew. Chem. Int. Ed. (2014)

Extrinsic Doping Fe_2O_3 for OER

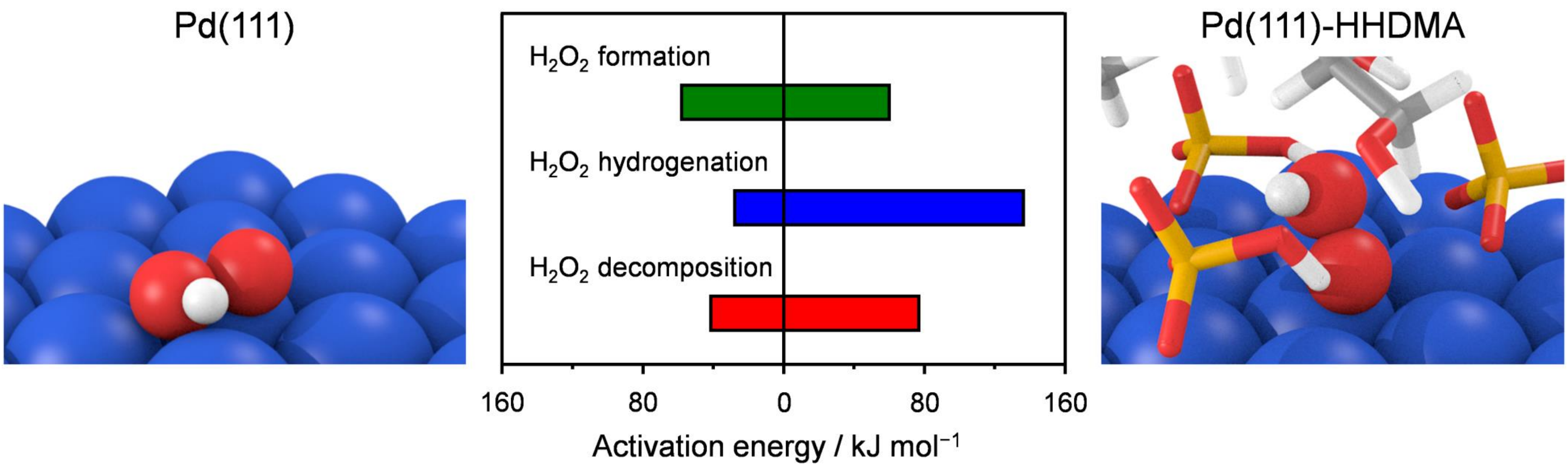




Cat_0

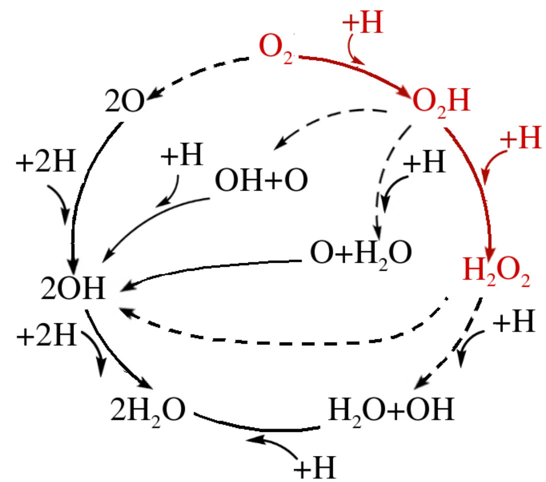
Chem. Sci. (2020)

Electrostatics / Hydrogen bond



Cat_0

E field

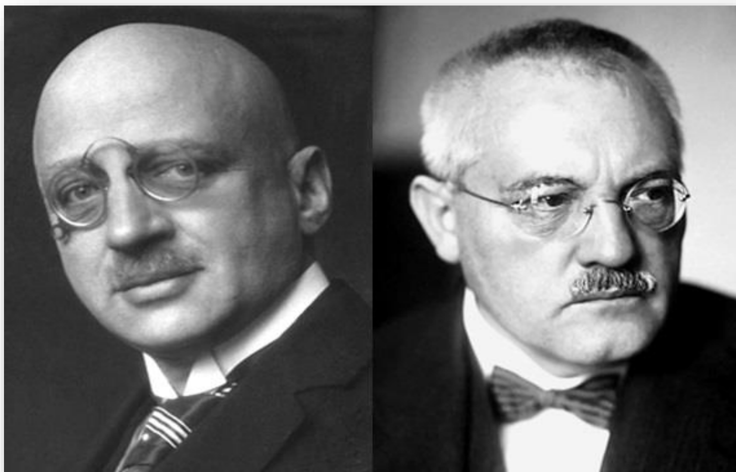


ACIE (2017)

Ammonia the chemical that feeds the World

Global supply of fertilizers

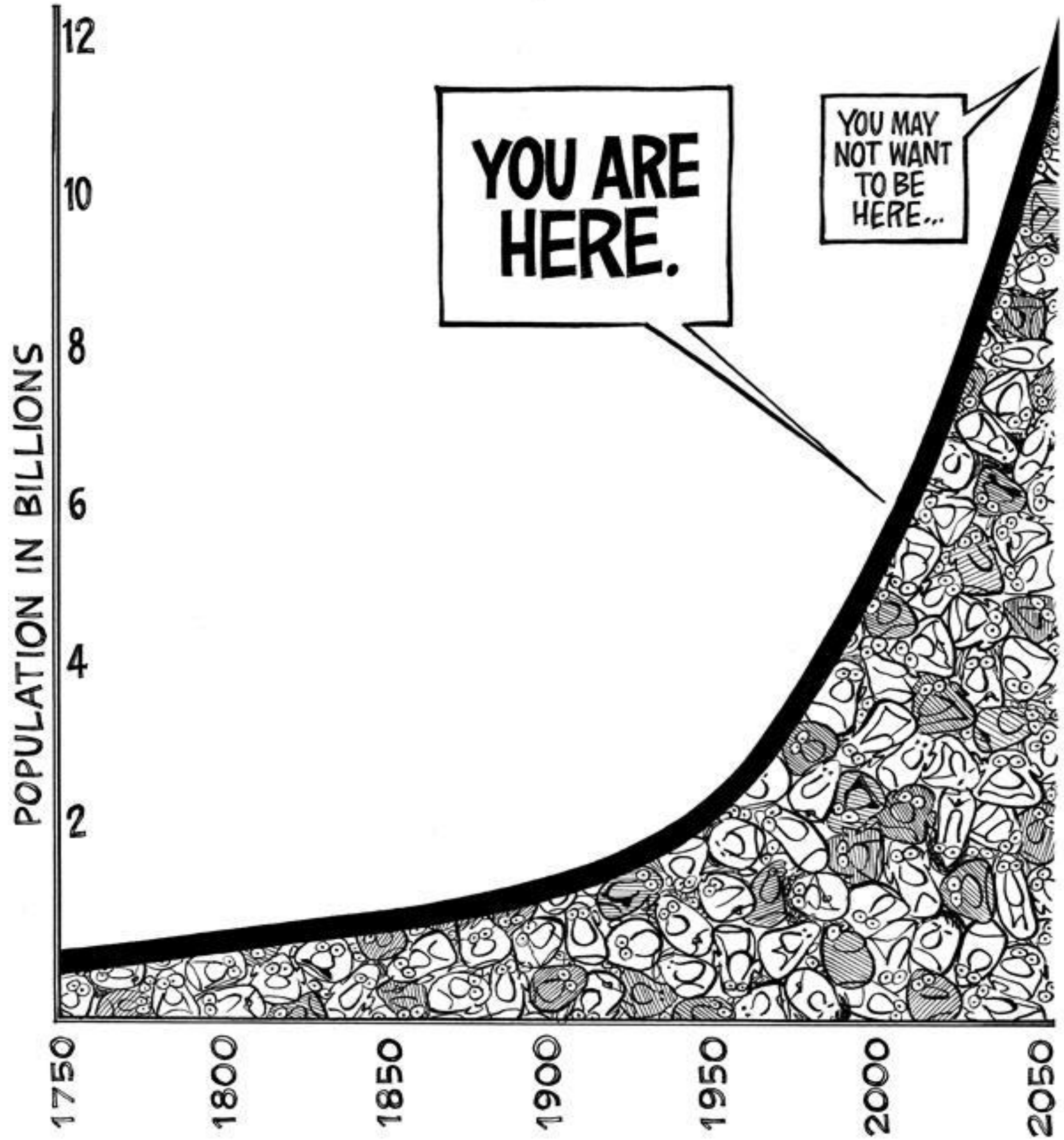
500 millions tons of NH_3



$N_2 + H_2$ + harsh conditions (T, P)

1% of global energy

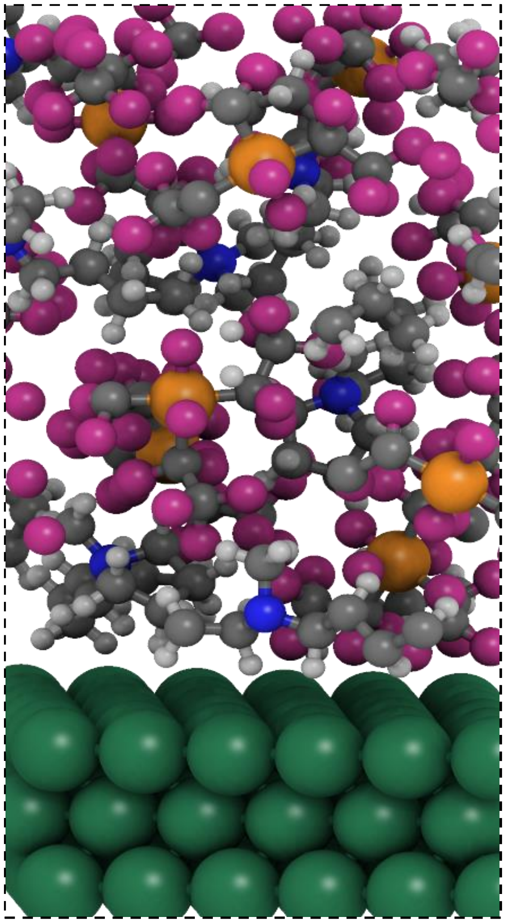
1.6% of global CO_2 emissions

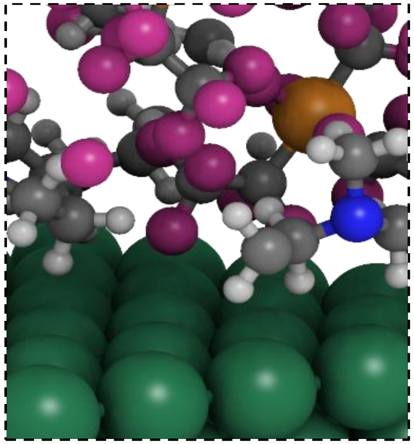


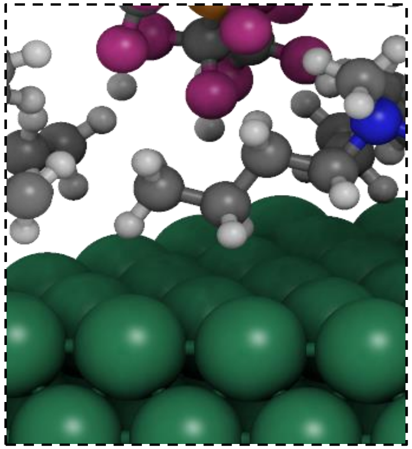
Ionic liquids for eN_2RR

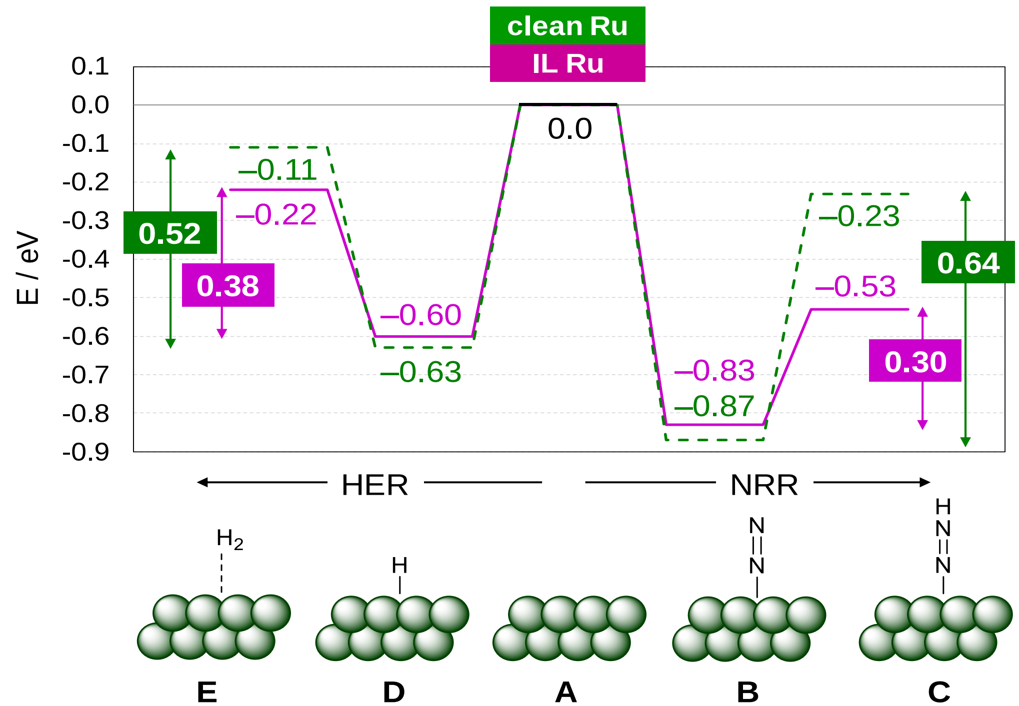
Interface: Ru(6×6) and 8 IL pairs

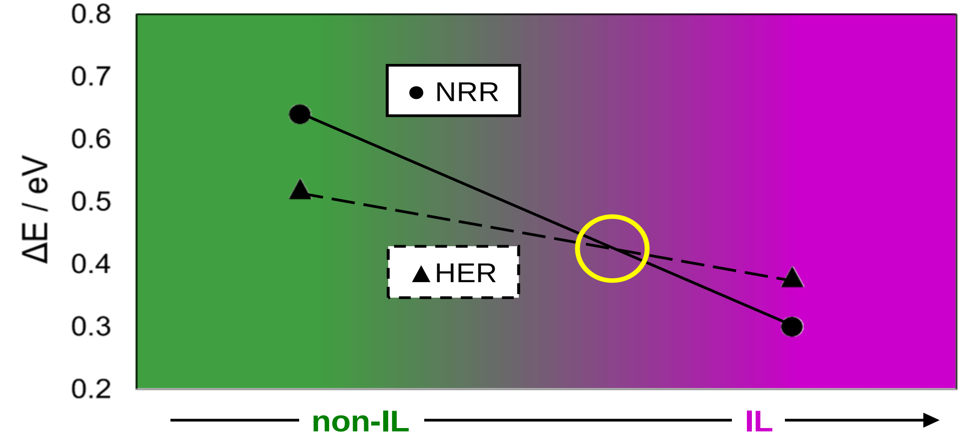
Protocol: CMD + AIMD + DFT







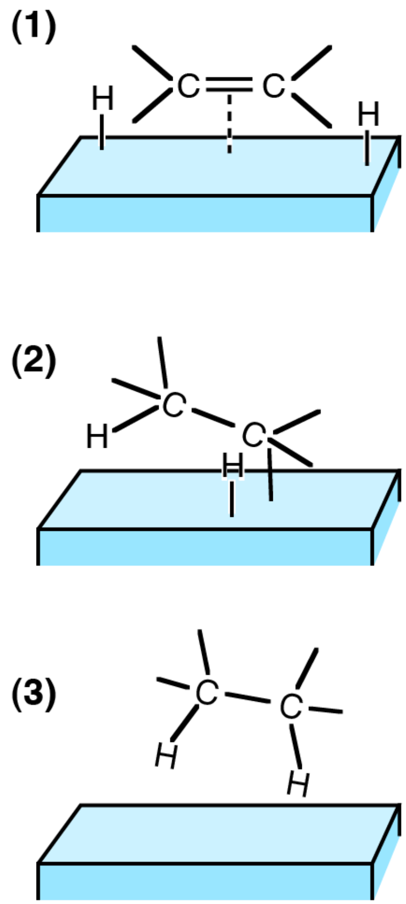




J. Phys. Chem. Lett. (2019)

Hydrogenations: Simplest H_2 activation

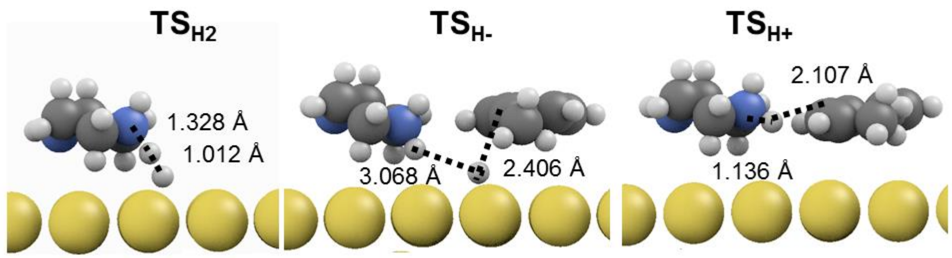
$H_2 \rightarrow 2H^\bullet$ Horiuti-Polanyi Metals

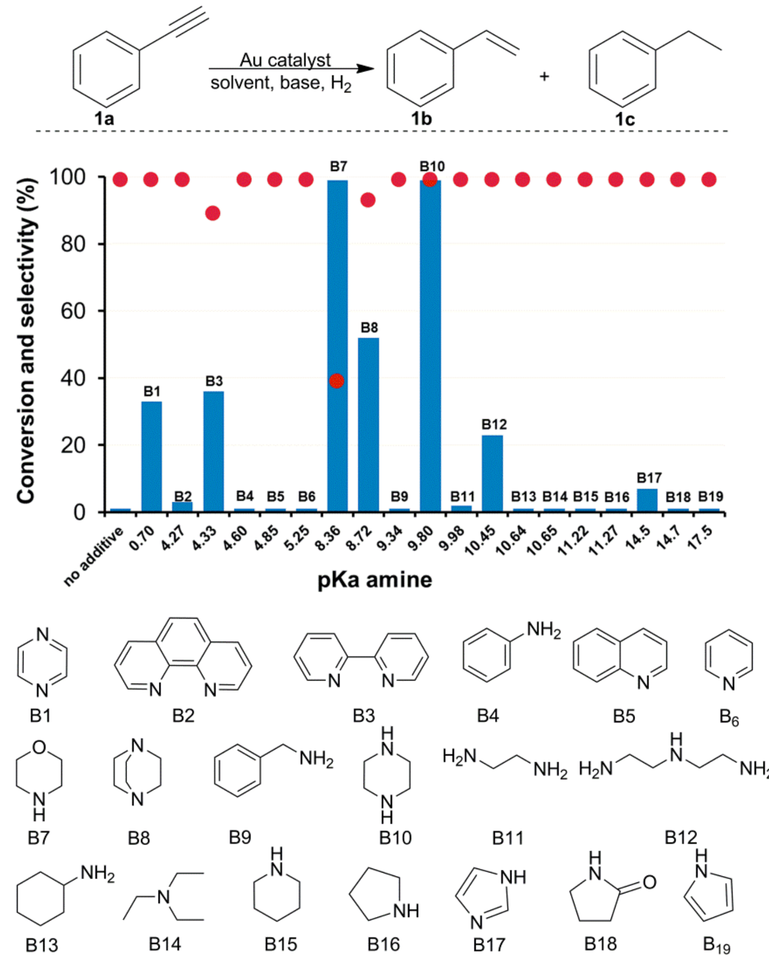


Breaking Scalings by reaction mechanisms

$H_2 \rightarrow 2H^{\bullet}$	Horiuti-Polanyi	Metals
$H_2 \rightarrow H^+ + H^-$	Hydride-Proton	
$H_2 \rightarrow H^+ \cdots H^-$	Proton-Hydride Pair	

Ligand assisted reactions: N-ligands
Hydride-proton activation

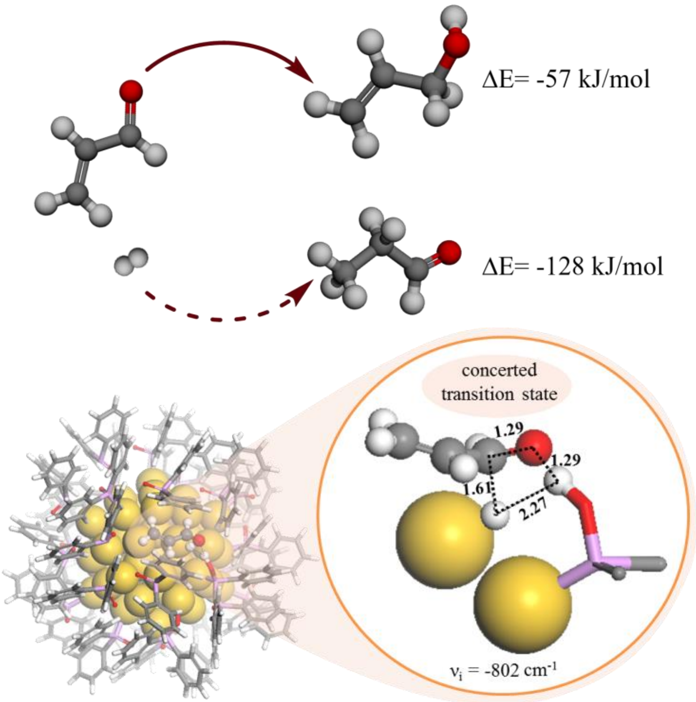


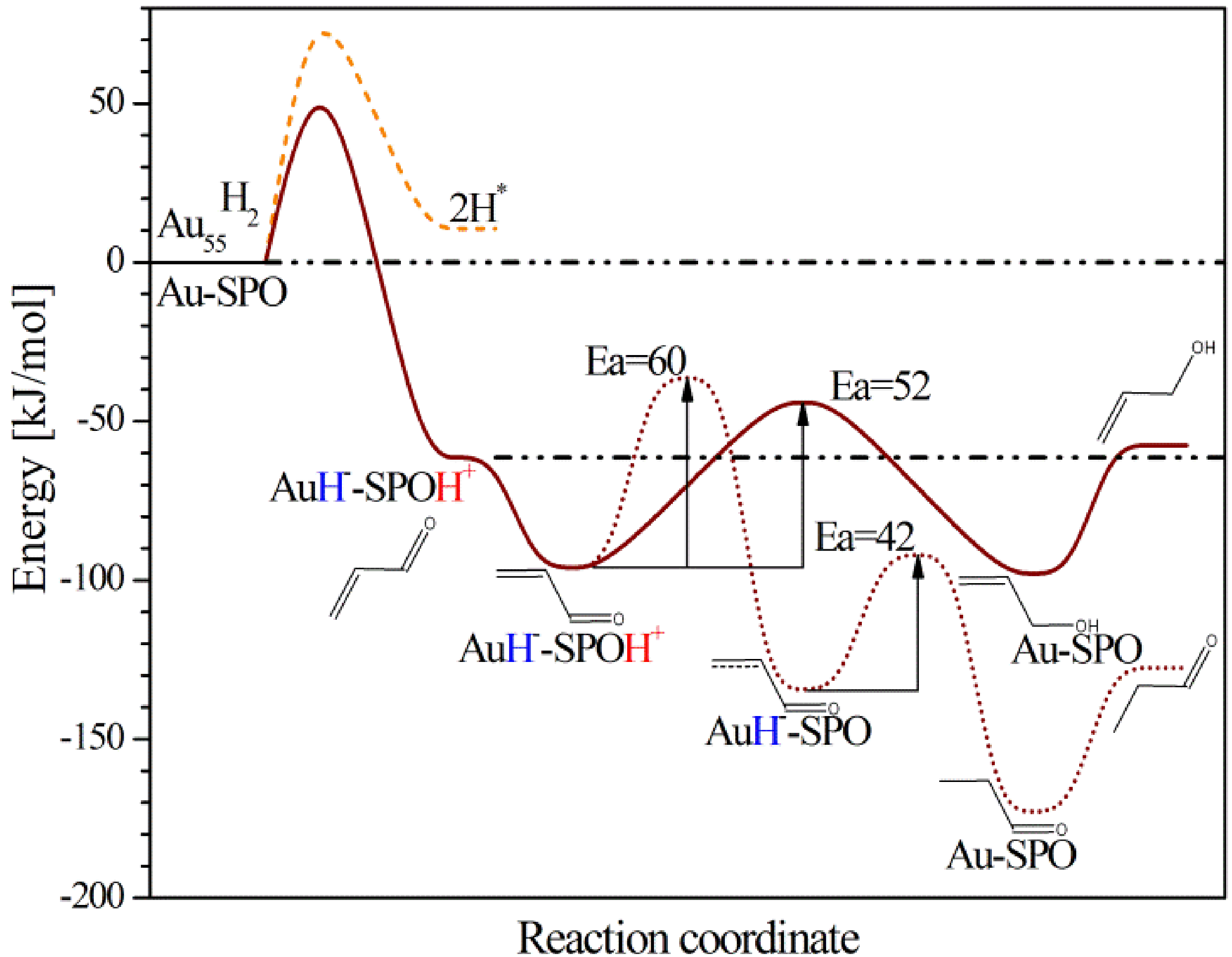


Cat_0 → Ligand

ACS Catal. (2017)

Ligand assisted reactions: H_2 transfer concerted steps

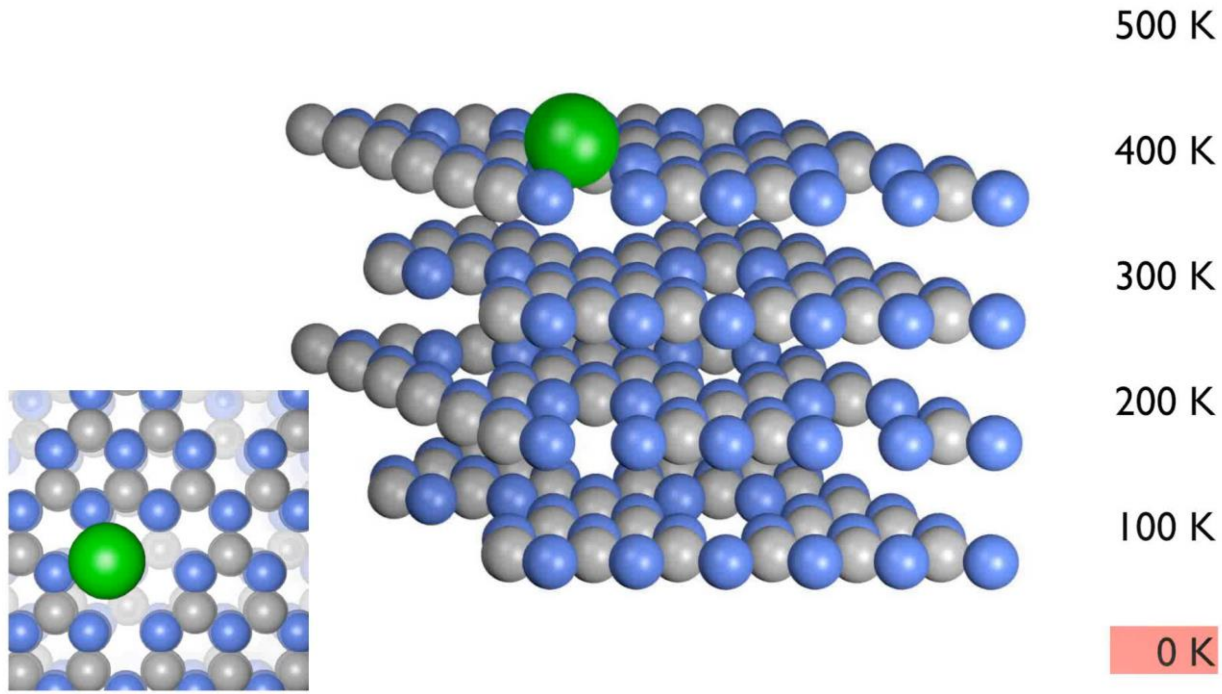




Cat_0 → Ligand

ACS Catal. (2017)

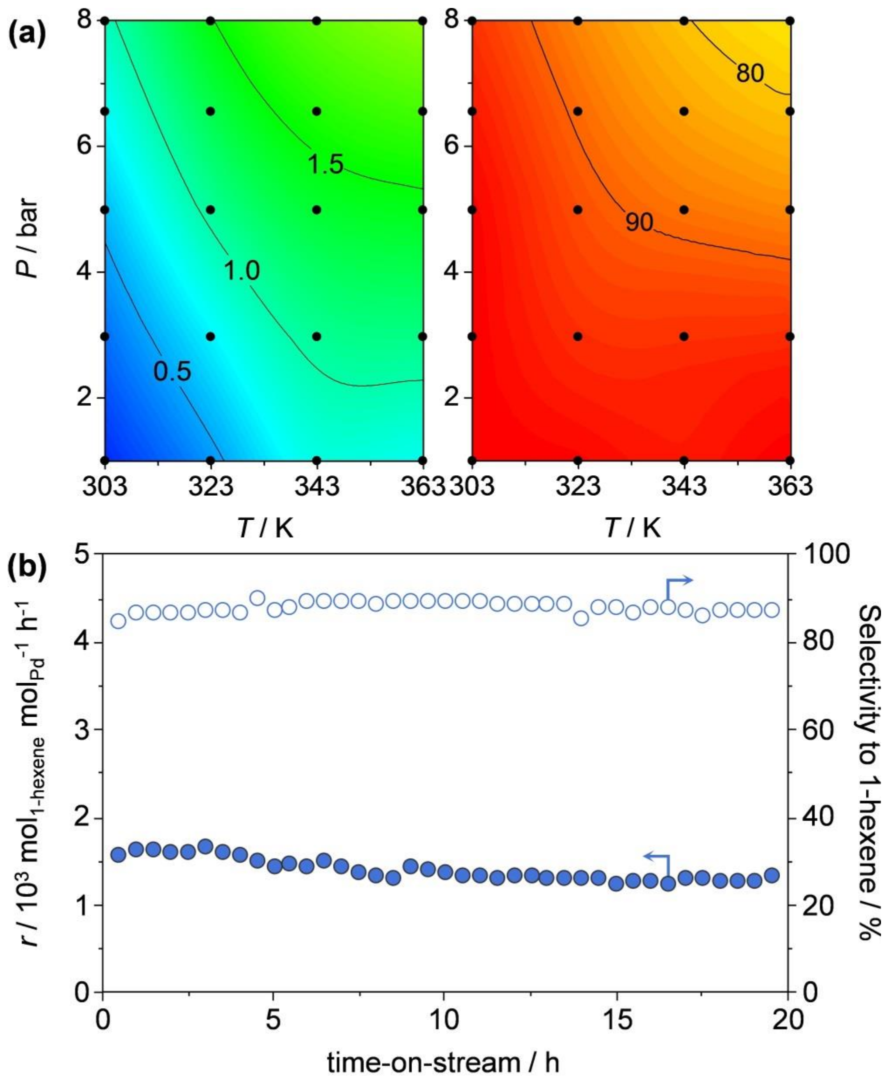
Single atoms: Pd-C_3N_4

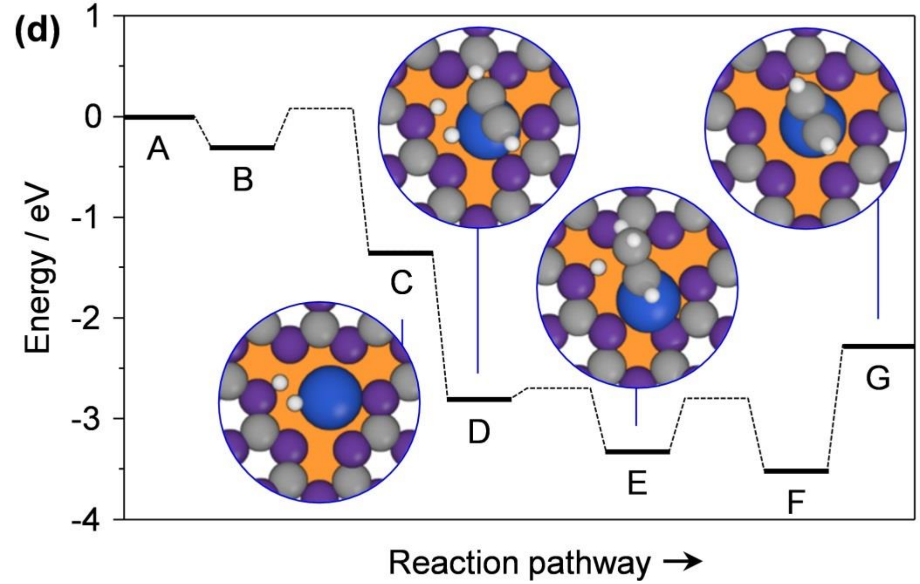


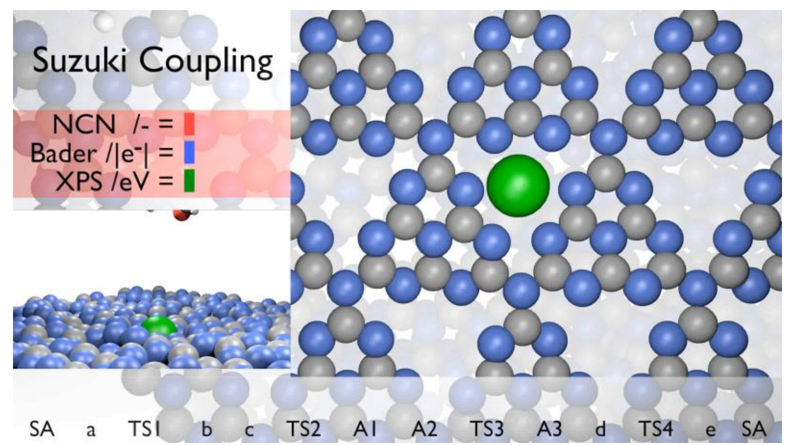
Cat_0

Ligand

Single atoms: Pd-C_3N_4 Hydrogenation / Suzuki







ACIE (2015)
Nature Nano (2018)

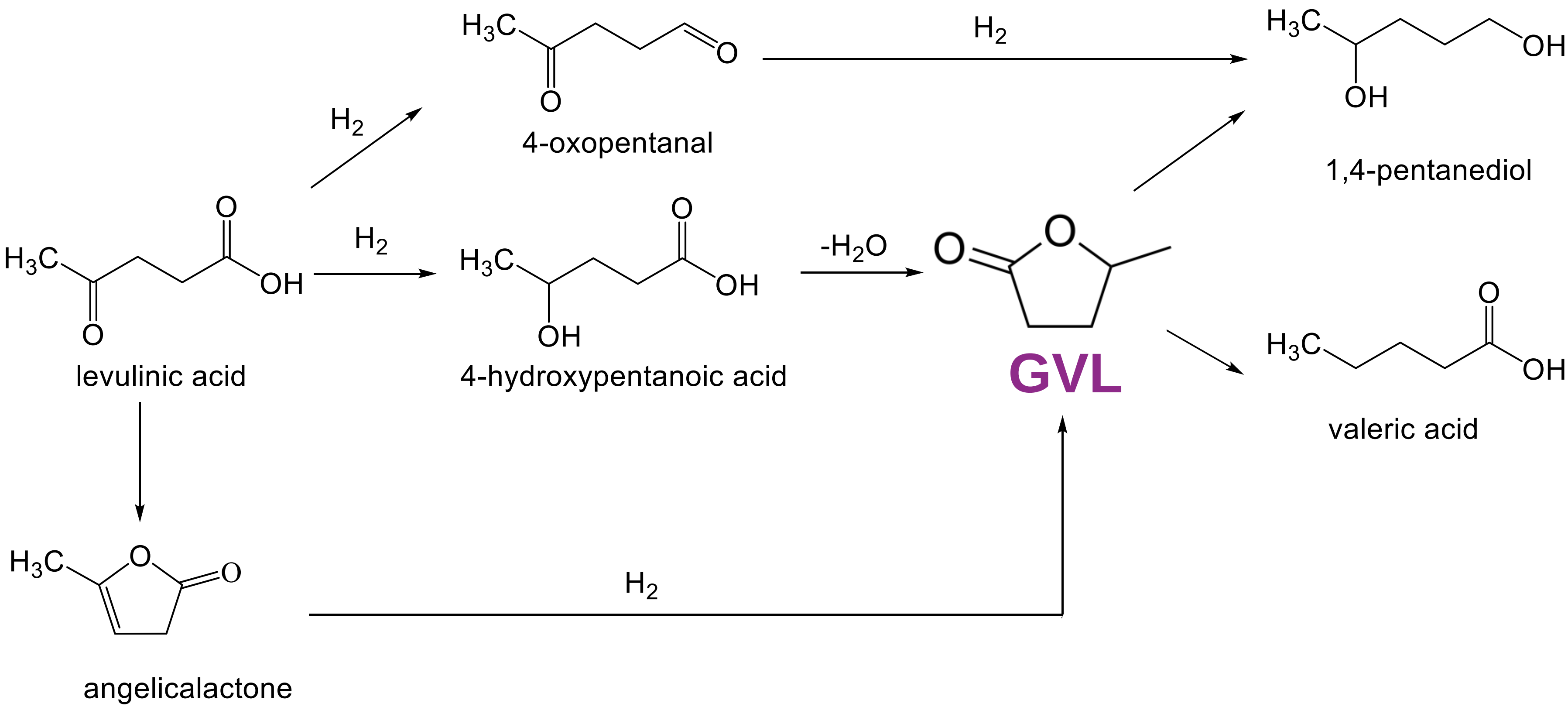
Single atoms

- In Metal Alloys
- In Oxides
- In Polymers
- In MOFs
- In Molecular Crystals
  - Double Metal Cyanides
  - Prussian Blue

Breaking Scalings by reaction mechanisms

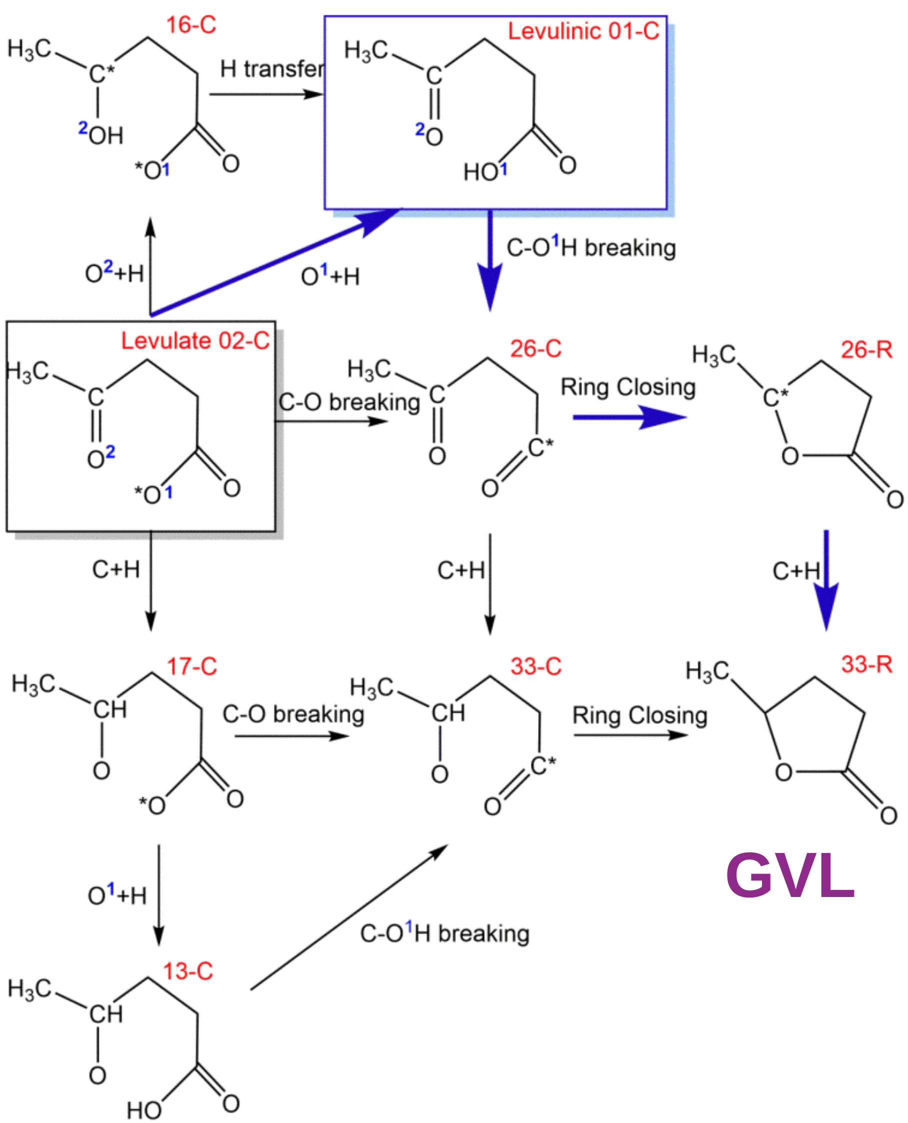
$H_2 \rightarrow 2H^{\bullet}$	Horiuti-Polanyi	Metals
$H_2 \rightarrow H^+ + H^-$	Hydride-Proton	
$H_2 \rightarrow H^+ \cdots H^-$	Proton-Hydride Pair	
$H_2 \rightarrow 2H^+ + 2e^-$	Acidity Electron potential	

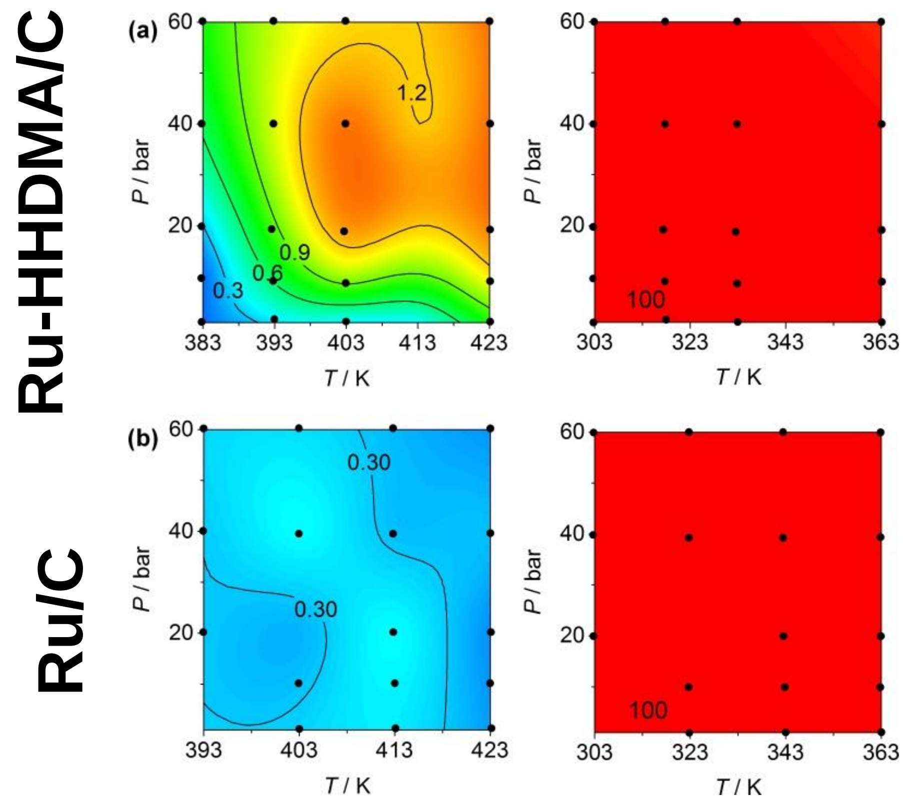
Interface acidity (pH control)



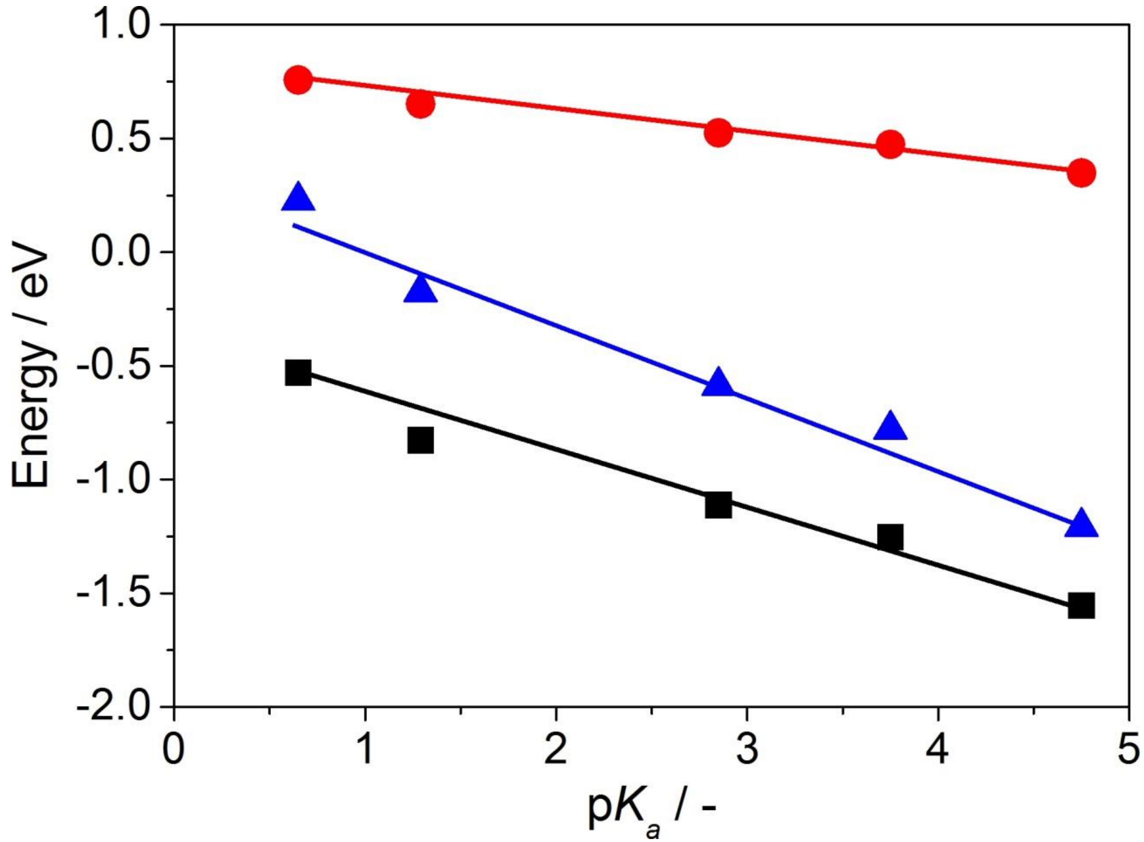
Green Chem. (2017)

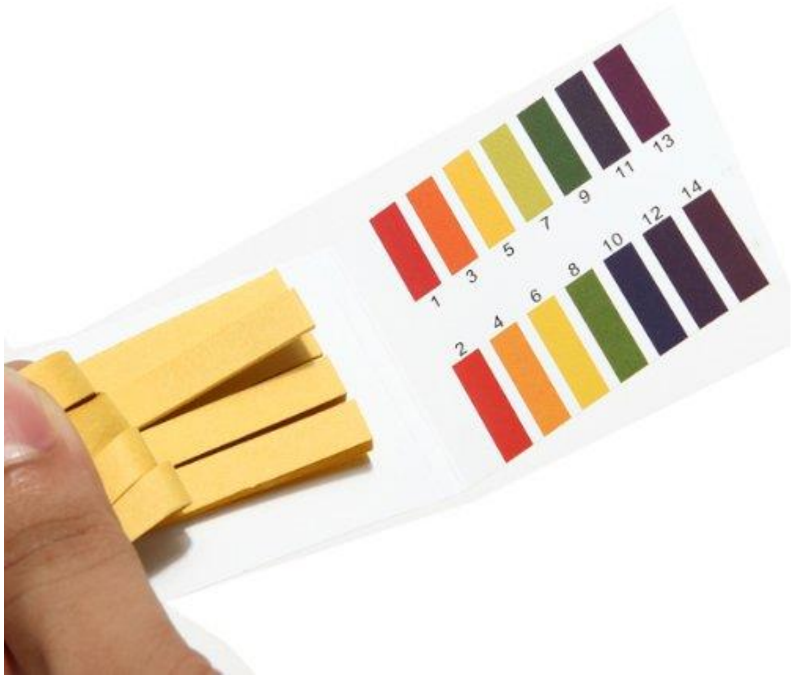
Interface acidity (pH control)





Interface acidity (pH control)

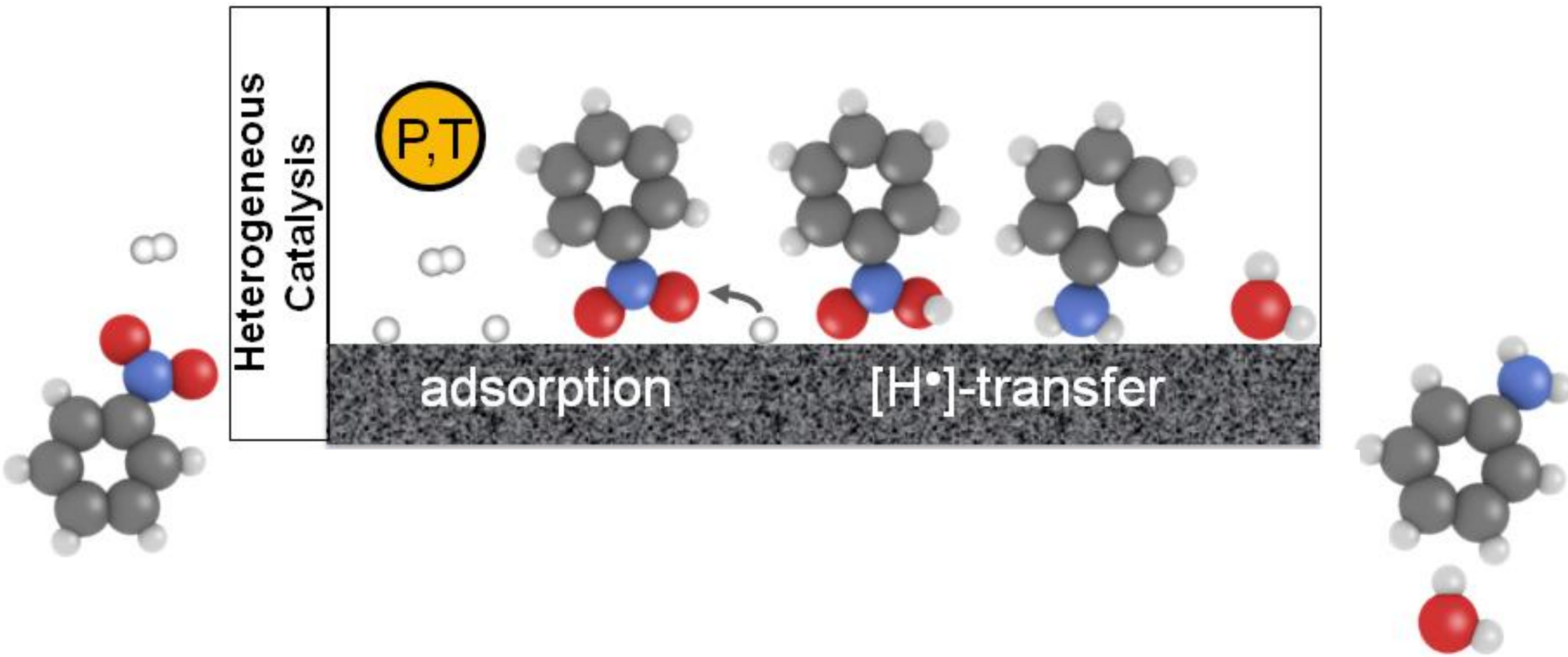




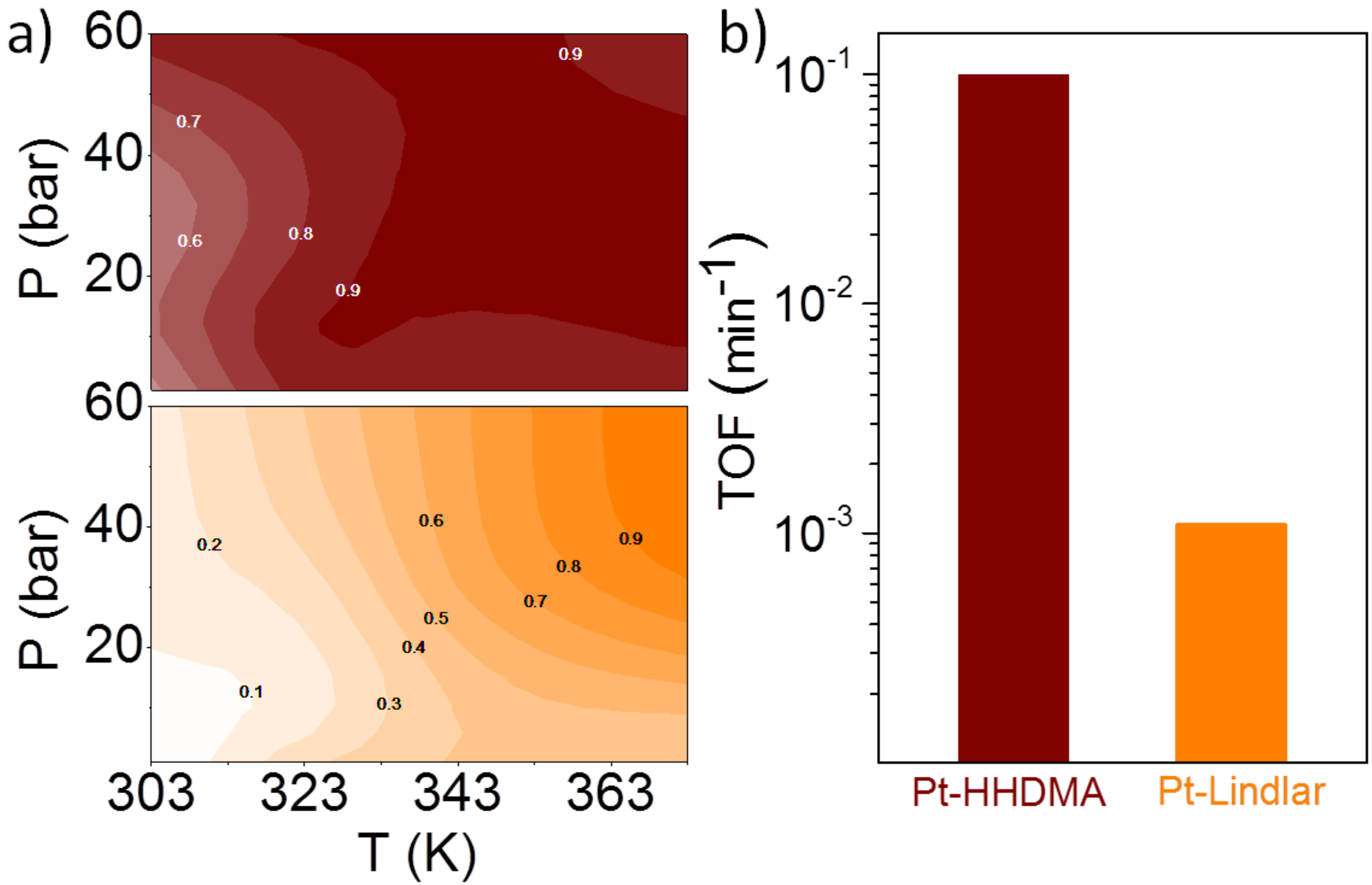
Our artificial pH-meter

Green Chem. (2017)

Electron potential

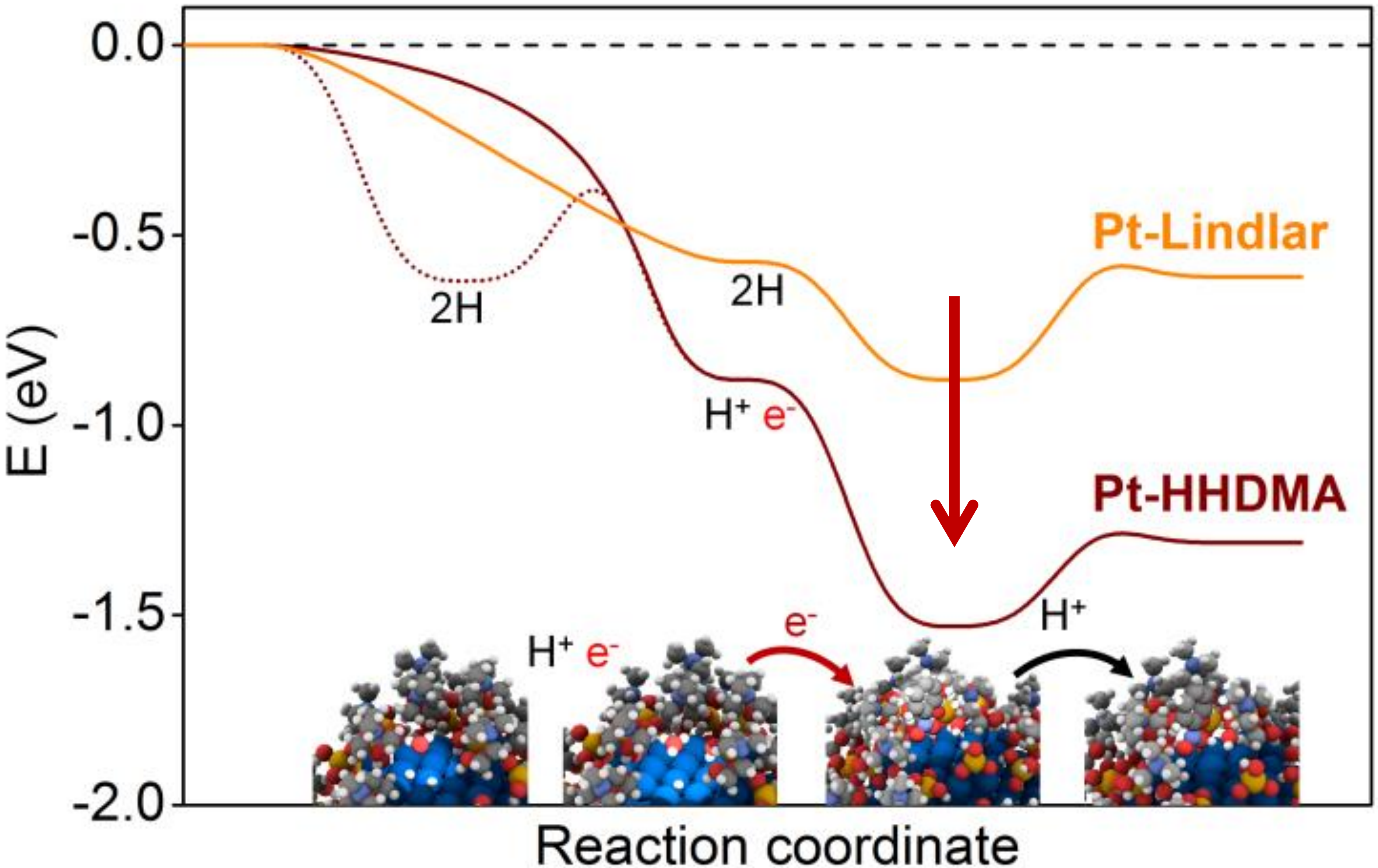


Decorated nanoparticles 100 times more active



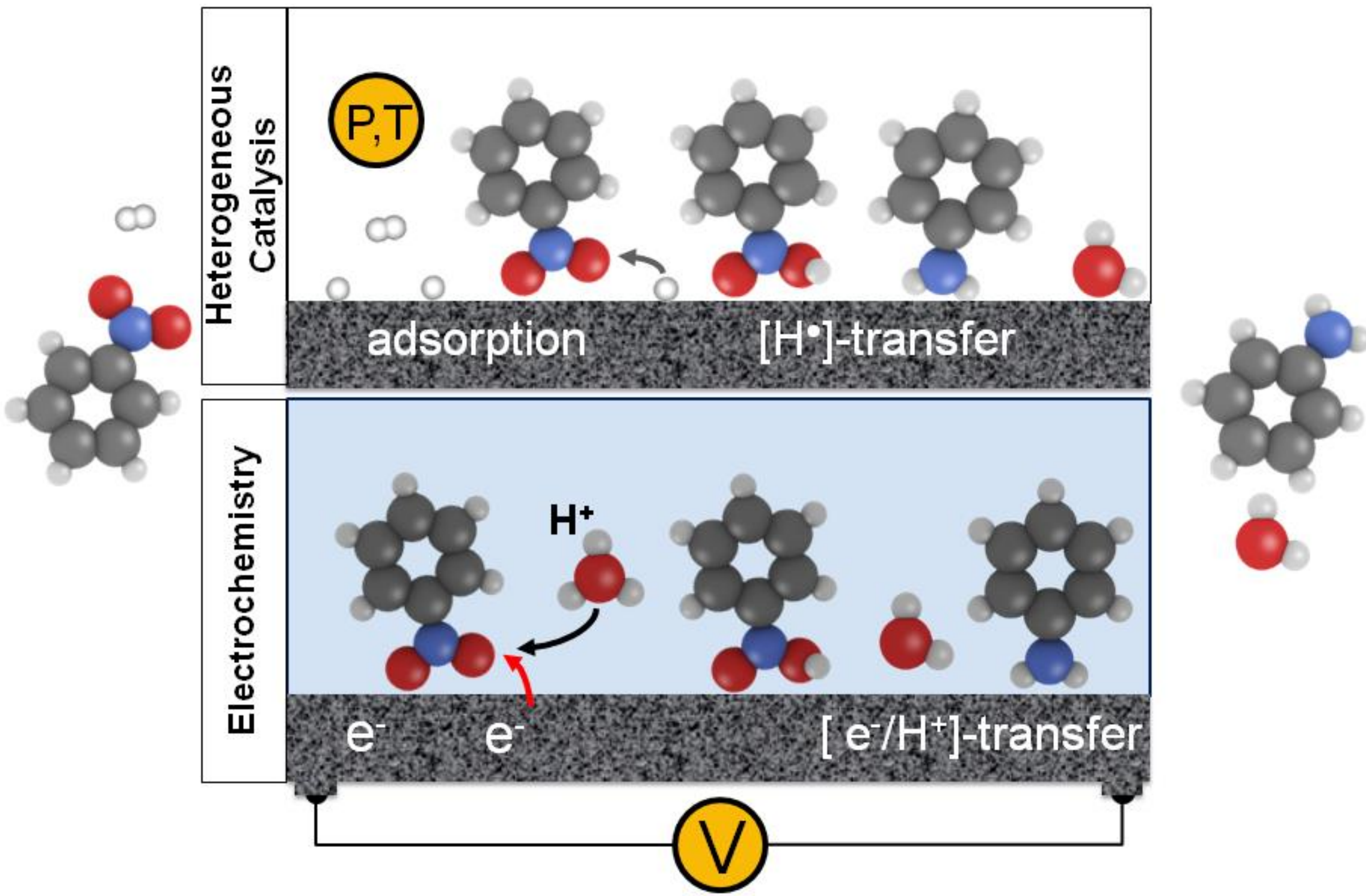
ACS Catal. 5, 3767 (2015); ChemCatChem (2017)

Two different mechanisms

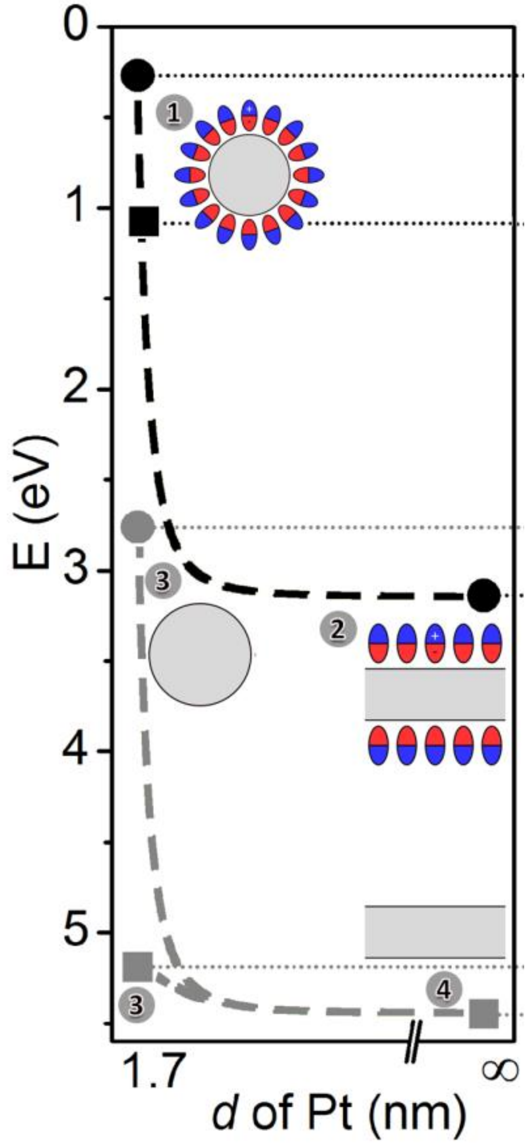


Nitrobenzene Adsorption Enhanced

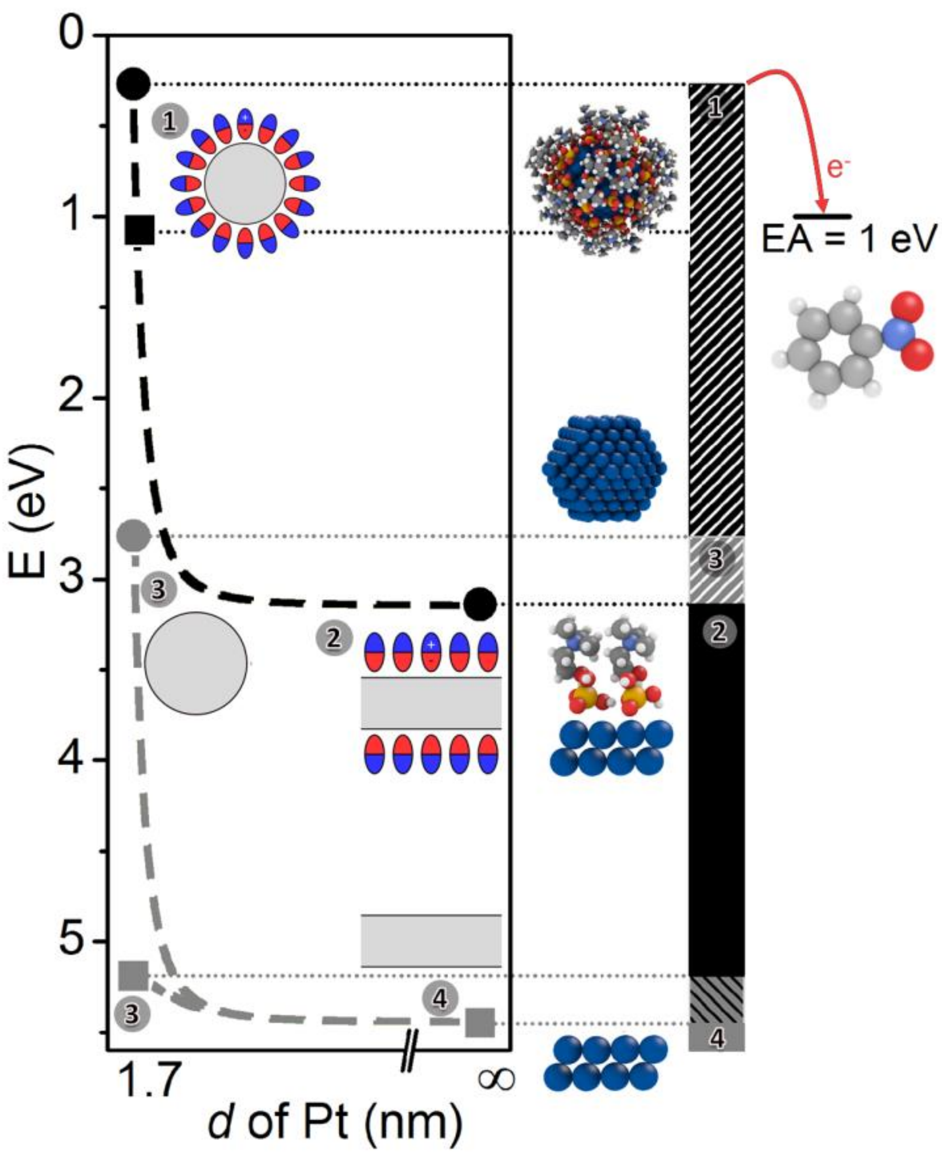
Two different mechanisms



Electron confinement+electric field



Electron confinement+electric field



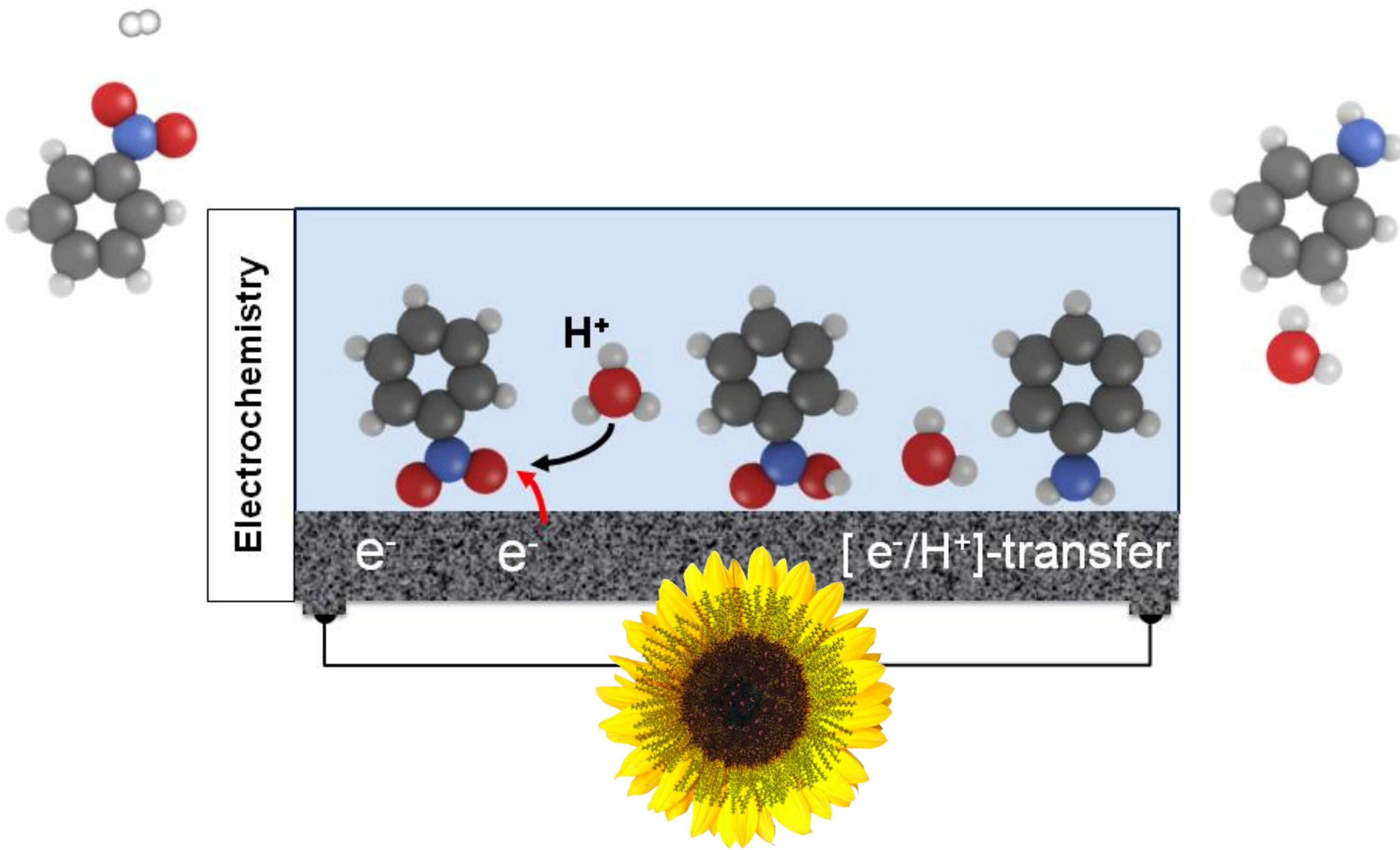
Confinement 1.7 nm

Electric field

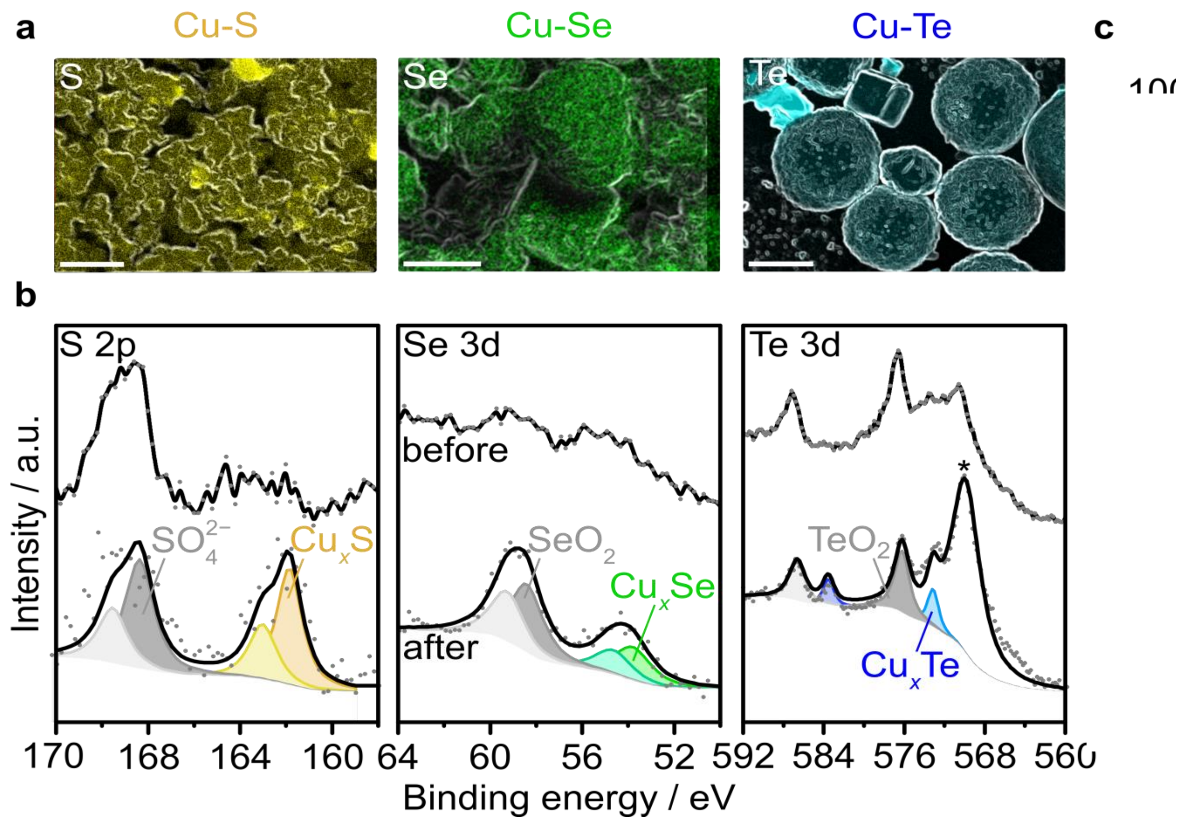
Water

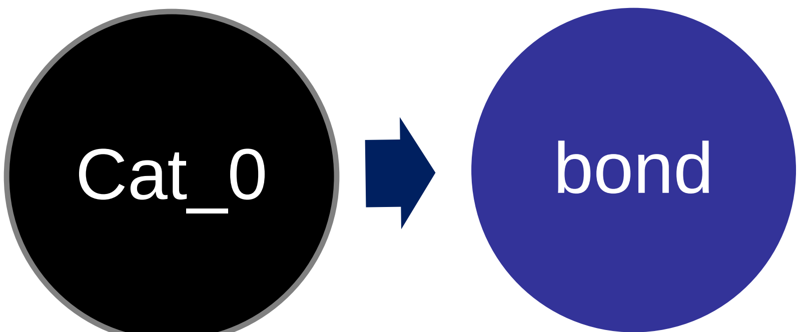
Proton Shuttles

Self-powered catalyst



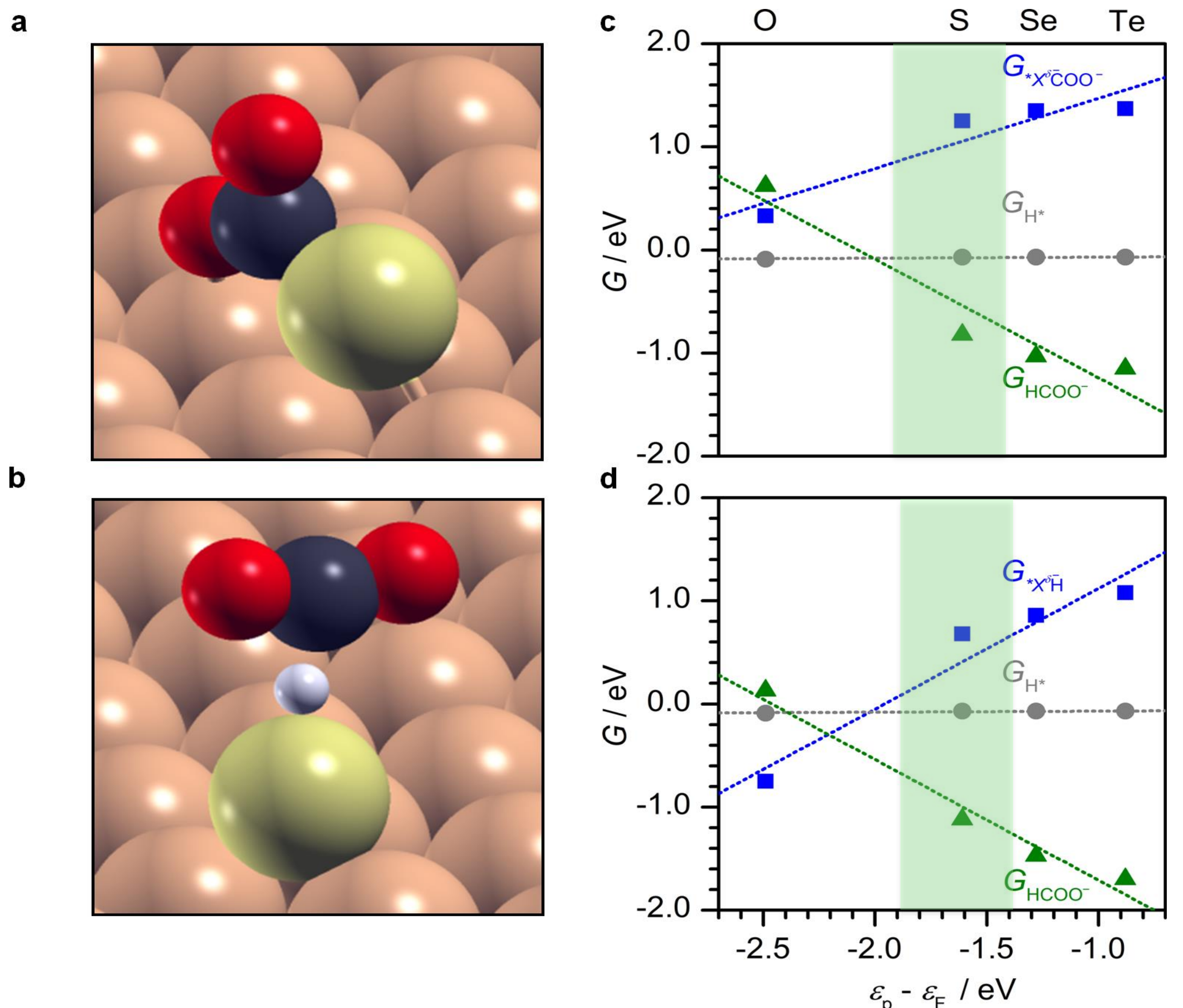
Tethering: CO_2RR



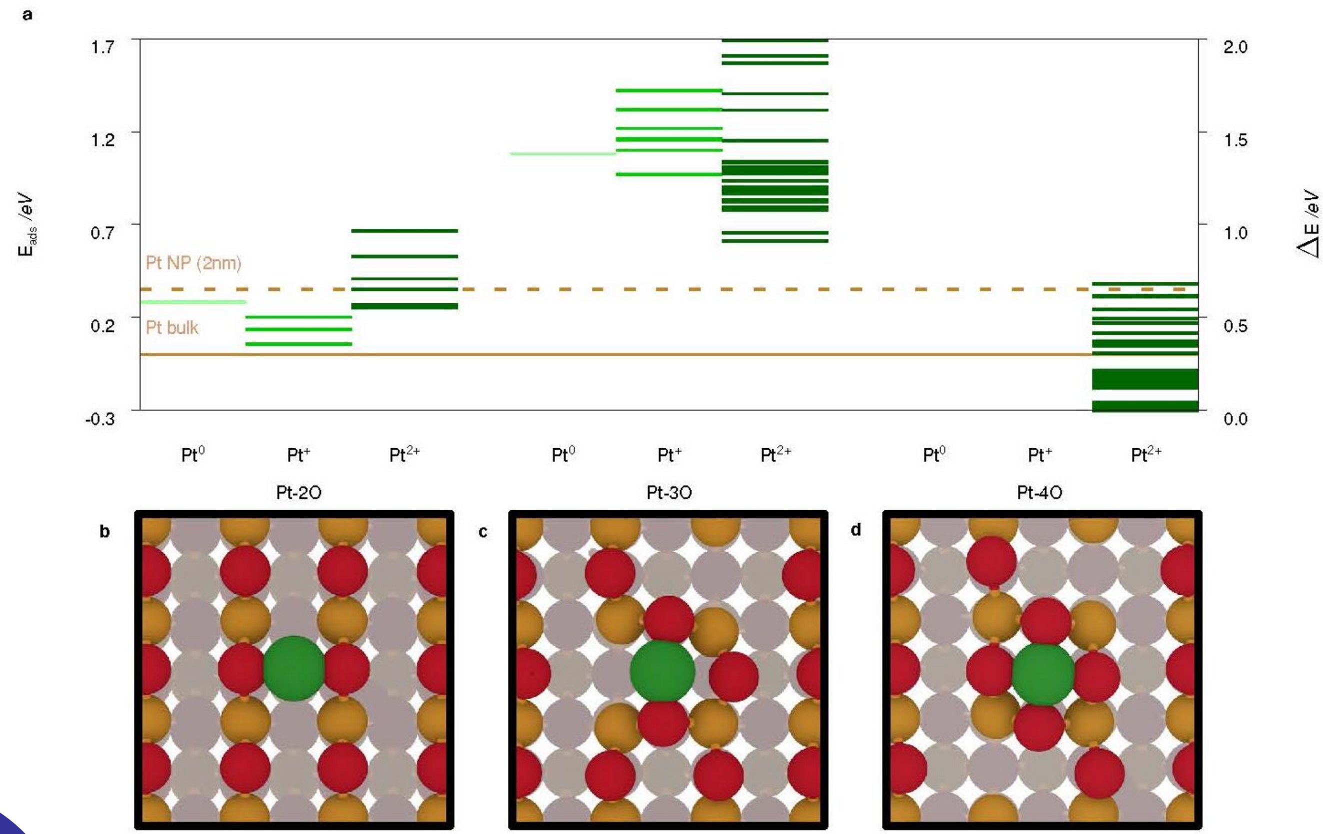


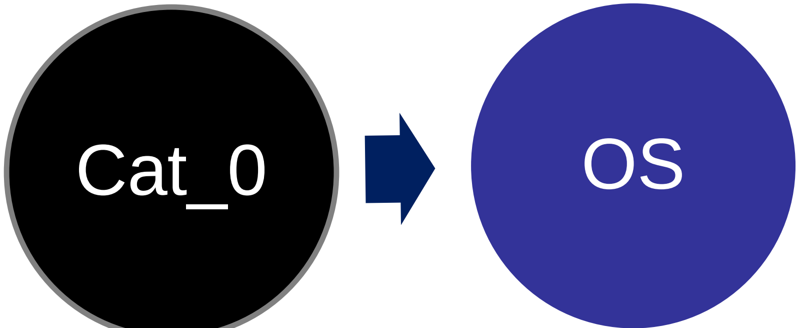
J. Phys. Chem. Lett. 2018, *9*, 7153

Basicity as a descriptor

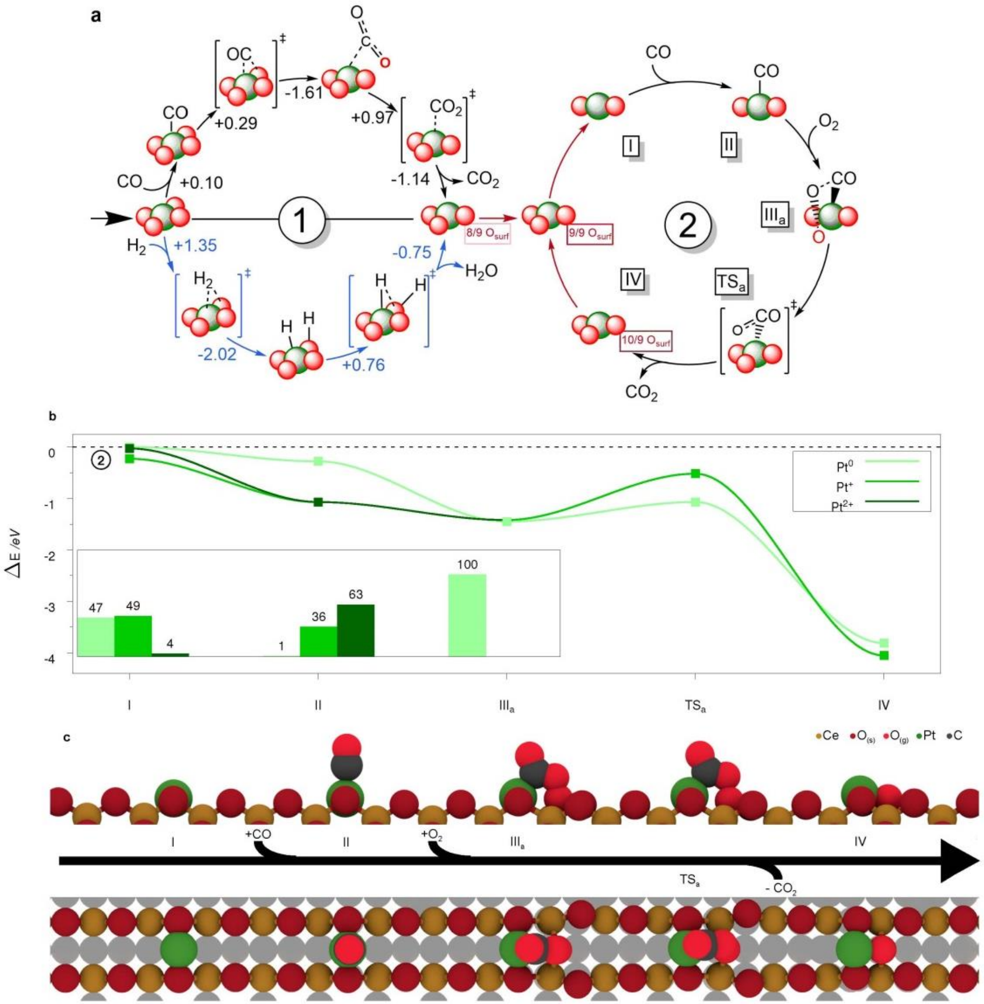


Dynamic charge oxidation states: SAC



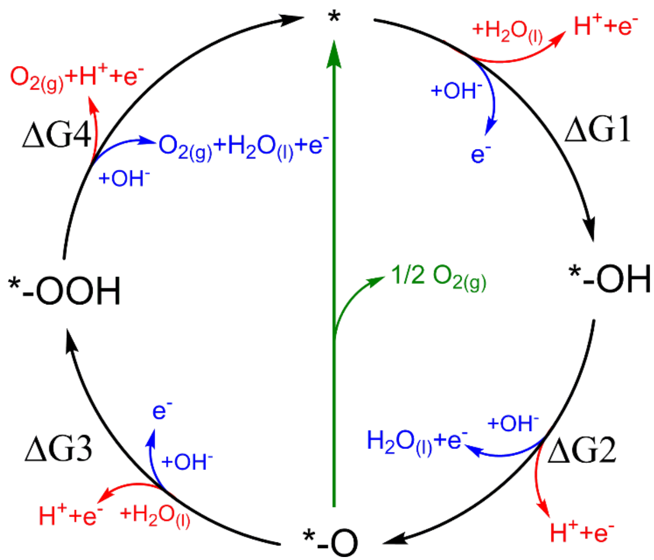


Effect on reactivity: 150ºC challenge



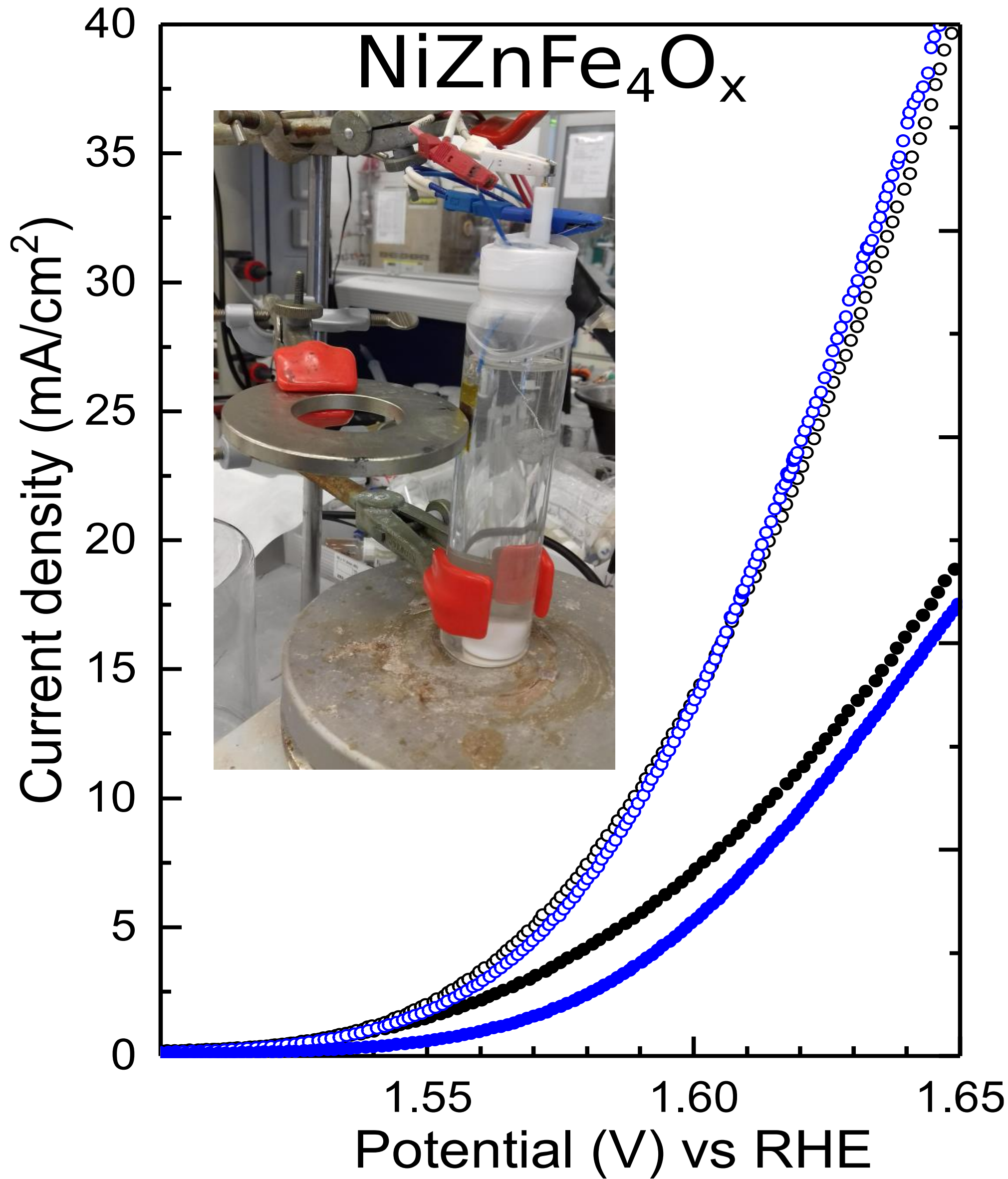
Nature Materials (2019)

OER: Magnetic enhancement

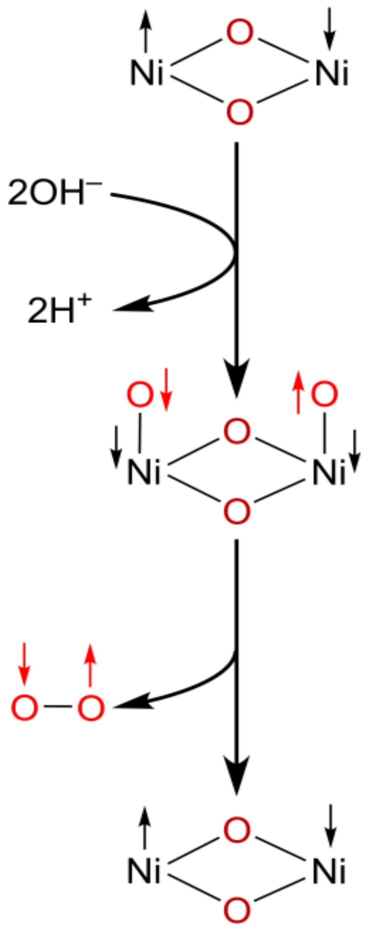


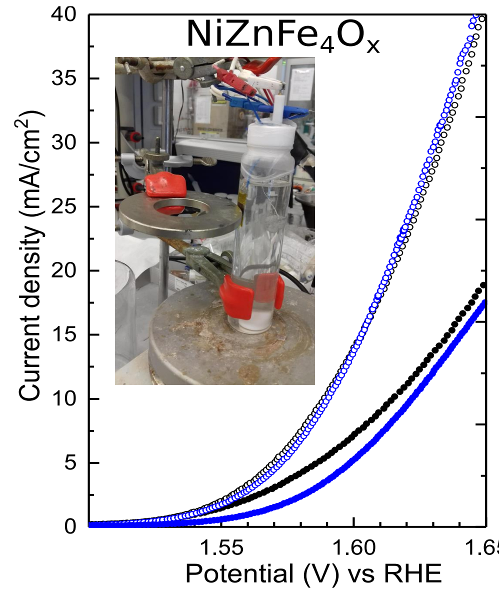
450 mT

Cat_0 → Force

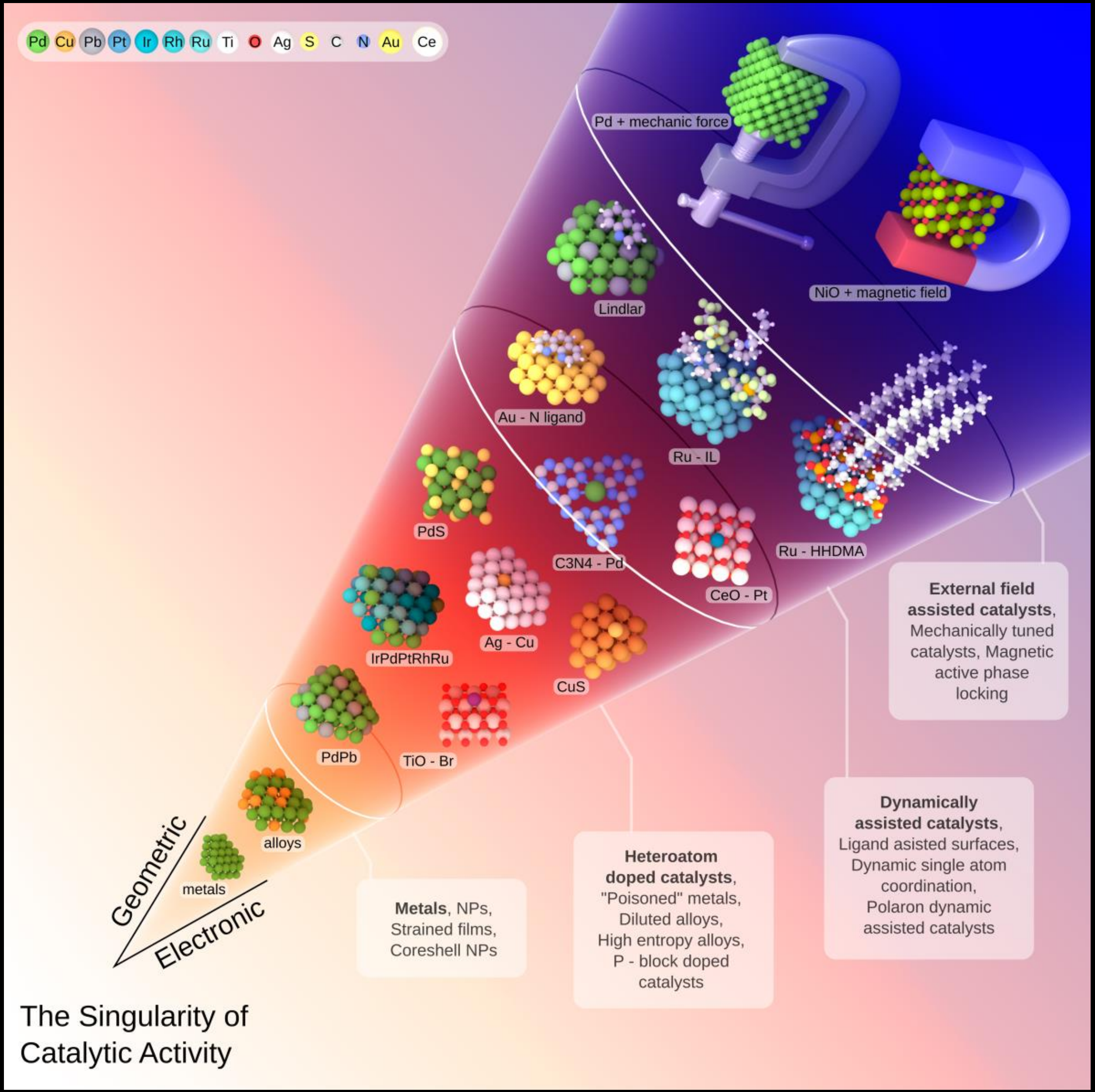


Spin control of the activity





Strategies to avoid LSR



JPR, NL Nature Catal. (2019)

Where are we in modelling

Thank you for your attention

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JR Galán-Mascarós
L. Rossi
P. v. Leeuwen

a-leaf

TOGETHER TOWARDS AN ARTIFICIAL LEAF

ELCOREL
Electrochemical Conversion of Renewable Electricity into Fuels and Chemicals

SOLAR CHEM2

FLOW PHOTO CHEM