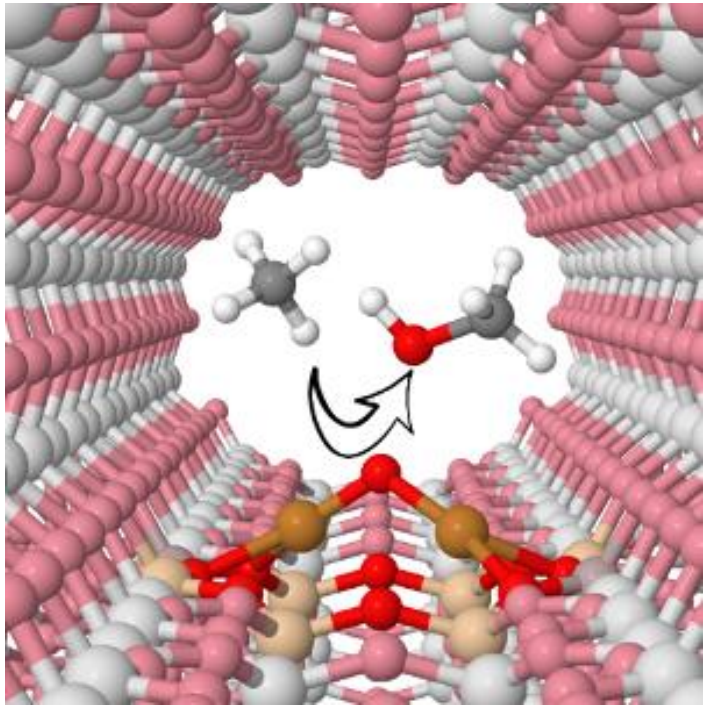
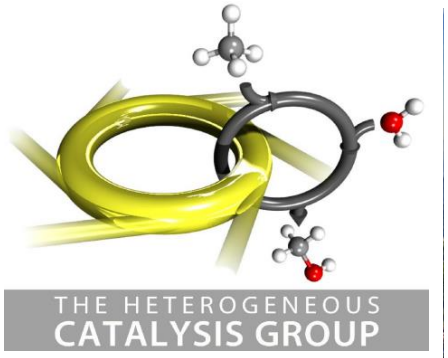
PAUL SCHERRER INSTITUT

PSI





ETH zürich

Dr. Dennis Palagin :: Paul Scherrer Institut / ETH Zürich

Introduction to first-principles modelling of catalysis at surfaces: Lecture 2

ETH Zurich, 20.10.2020

Molecular dynamics (MD)

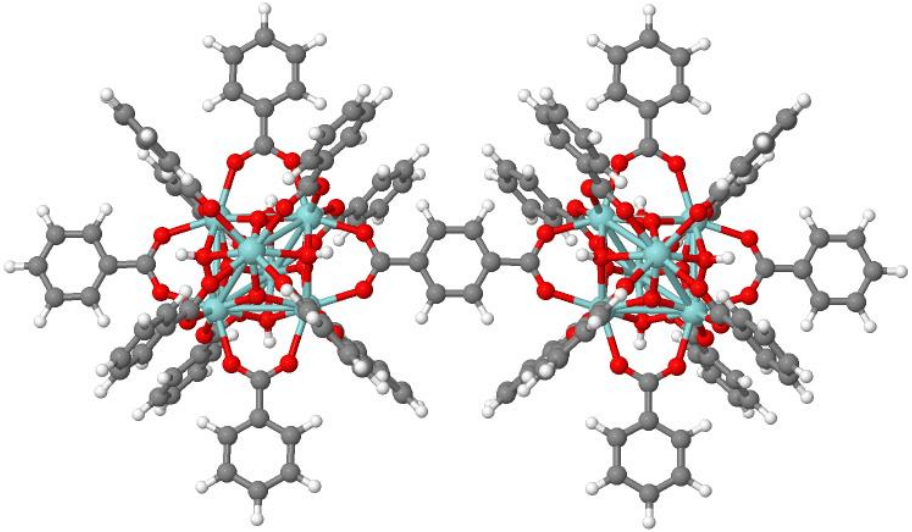
- Molecular dynamics simulations are a method for computing the equilibrium and transport properties of a classical many-body system.
- Classical: the nuclear motion of the constituent particles obeys the laws of classical mechanics, i.e. Newton's laws.
- Classical mechanics is a good approximation for many materials. Fundamentally quantum effects most relevant for light atoms and low temperatures.
- We need a potential $V(\mathbf{r}^N)$ which describes the system.
- We solve Newton's (equivalently Lagrange's or Hamilton's) equations by integrating them forward in time to generate a trajectory.

Molecular dynamics (MD)

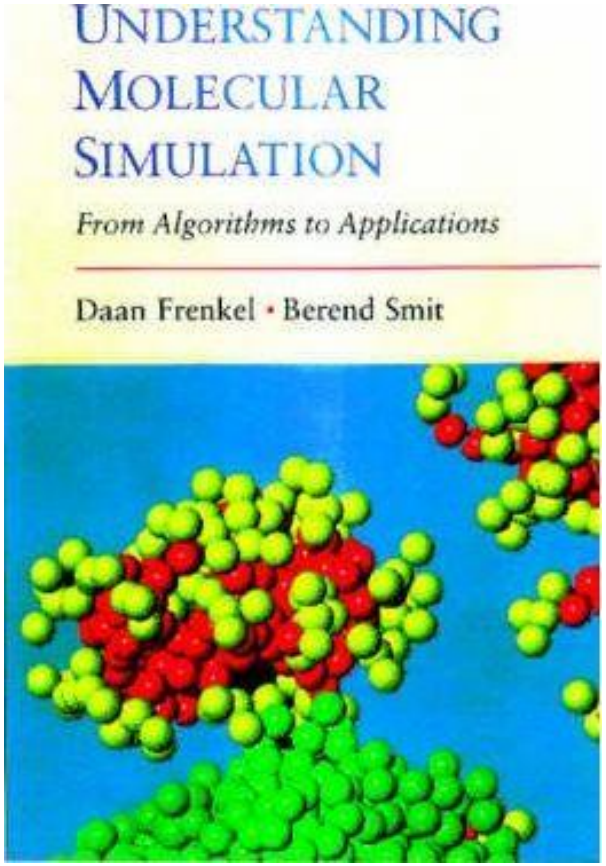
Basic scheme:

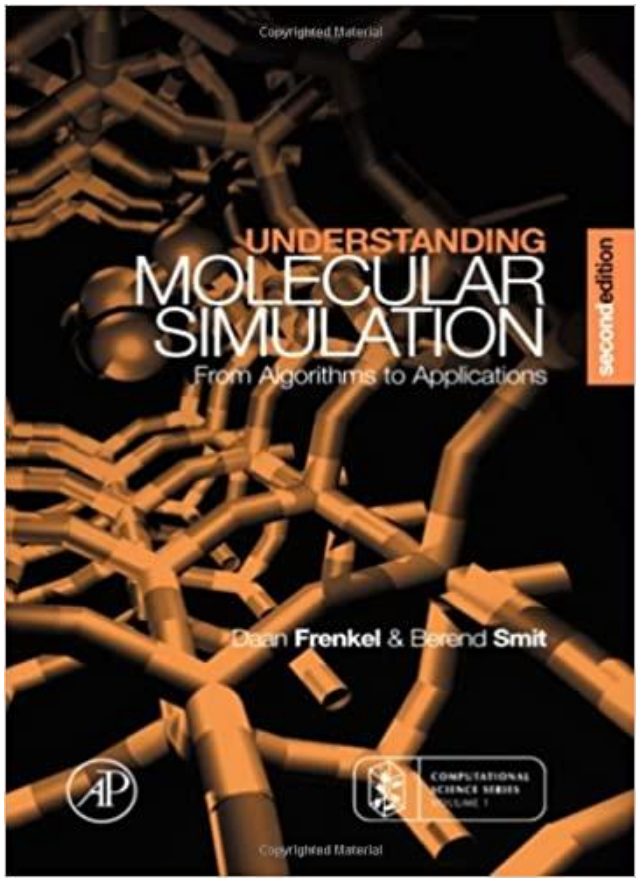
- Initialize the system: choose coordinates and momenta of all atoms: $\mathbf{r}^N(t = 0)$ and $\mathbf{p}^N(t = 0)$
- Compute forces.
- Integrate equations of motion from $t \rightarrow t + \delta t$.
- Repeat 3 and 4 until trajectory of desired length.

Molecular dynamics (MD)



Molecular dynamics (MD)



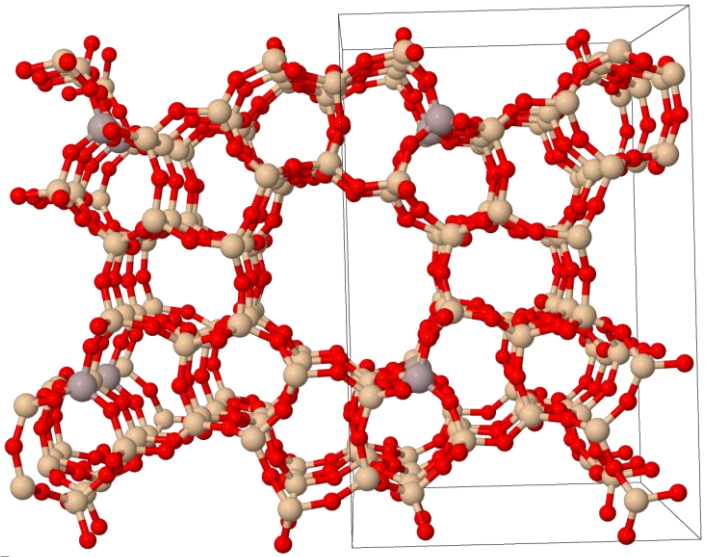


Daan Frenkel and Berend Smit

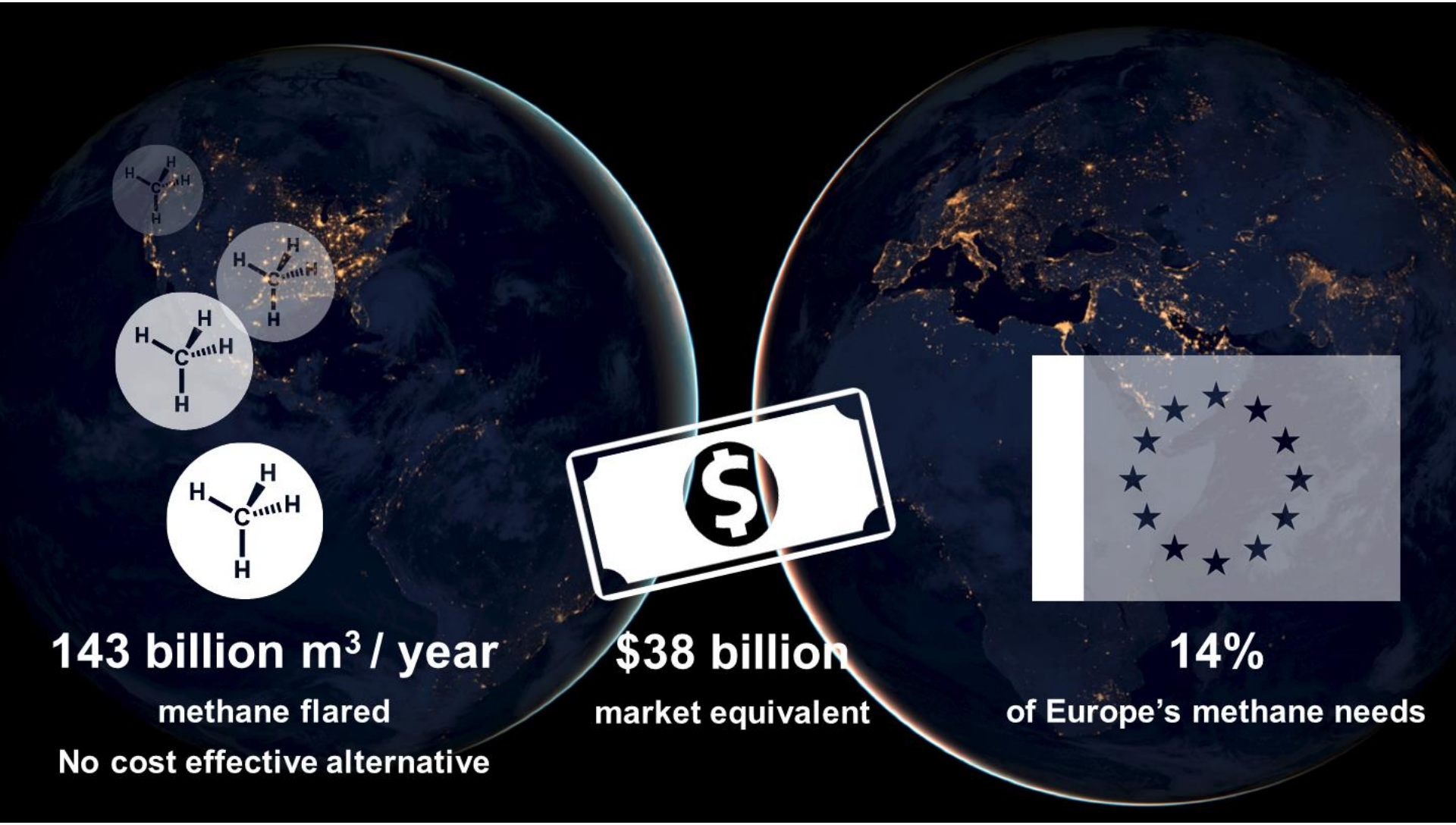
“Understanding Molecular Simulation”

TheoCat@LSK highlights:

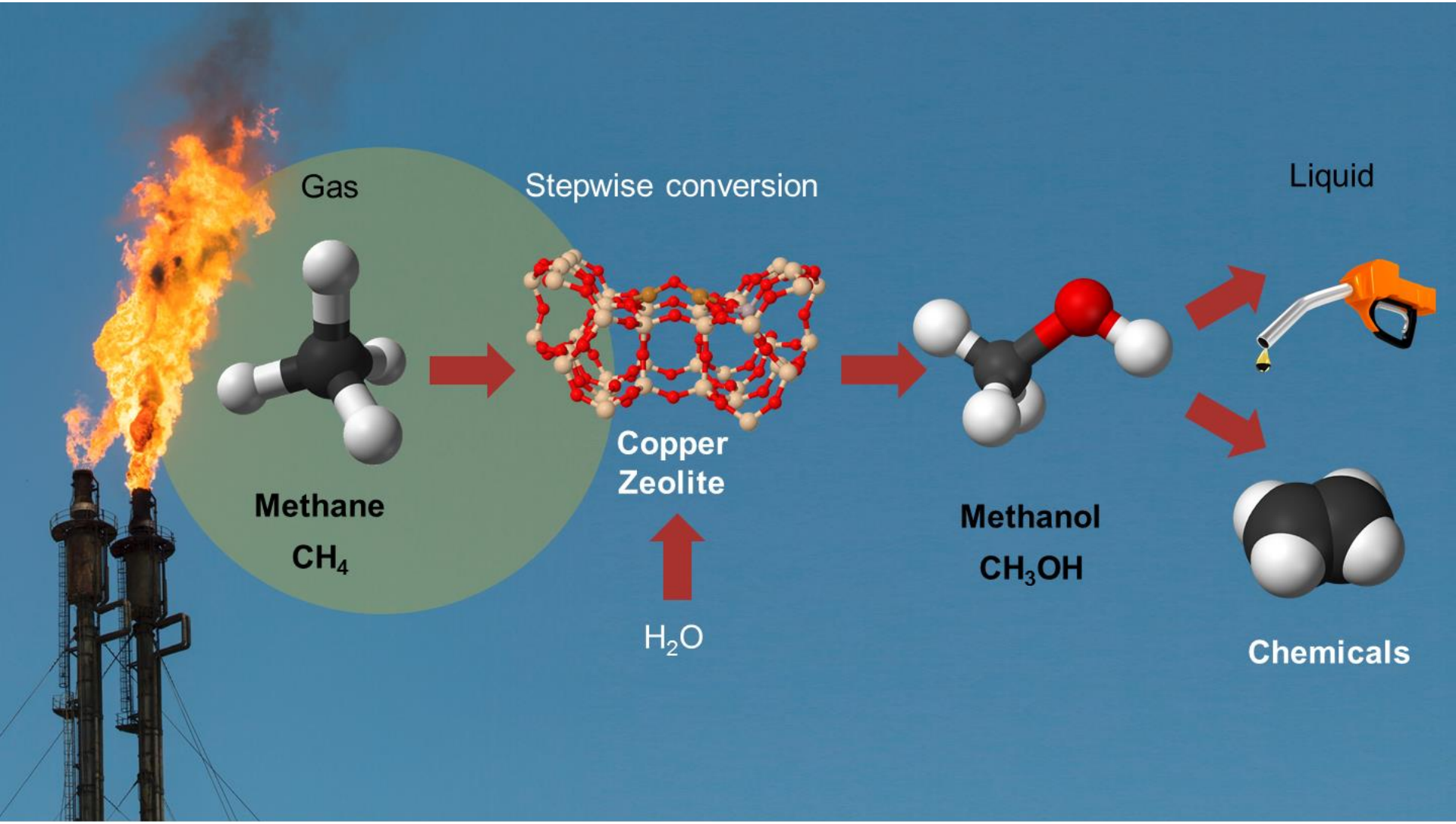
1) Methane to Methanol
   a) active sites
   b) mechanism
2) Water gas shift
3) Supported nanoparticles
4) Theory development



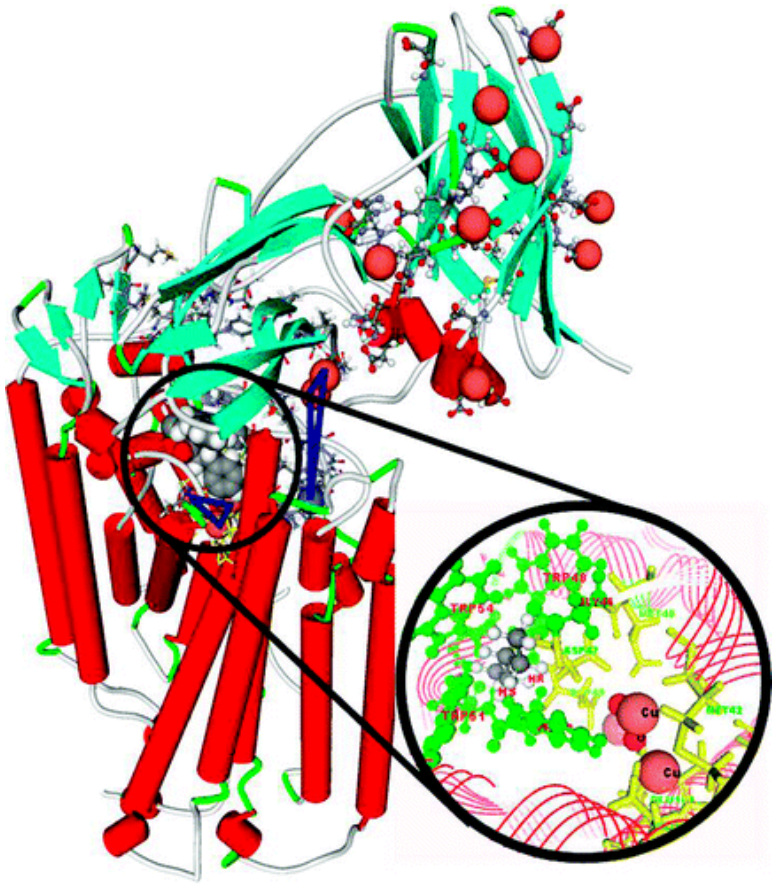
Let's burn some money, shall we?



Any alternatives to flaring?



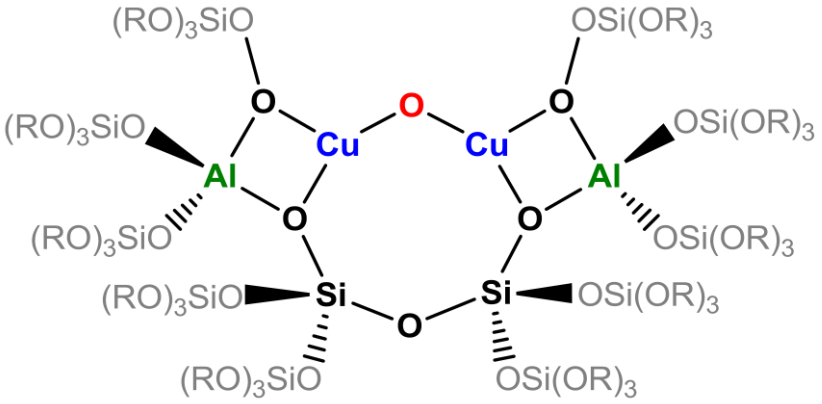
Copper oxide sites: di-copper…



Cu centers inspired by enzymes…

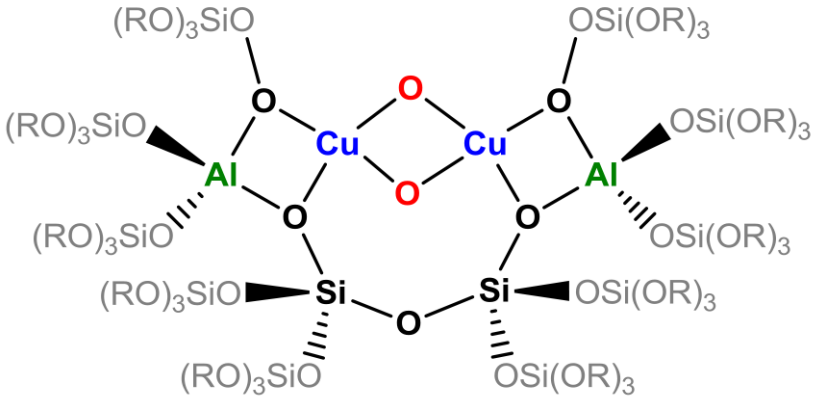
S. I. Chan, S. S. F. Yu, *Acc. Chem. Res.* **41**, 969 (2008)

mono(μ-oxo)dicopper:



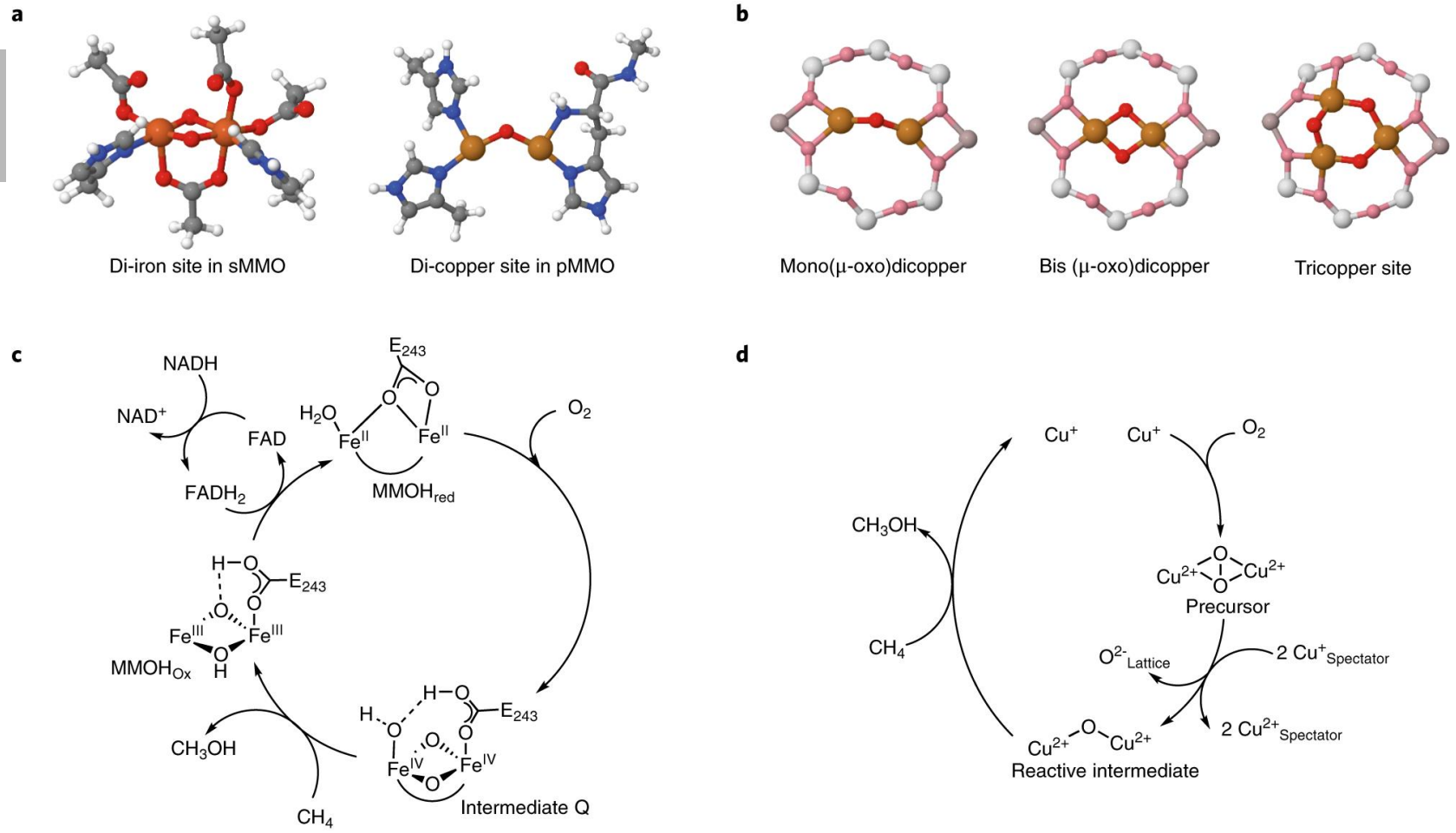
G. T. Palomino et al.,
J. Phys. Chem. B **104**, 4064 (2000)

bis(μ-oxo)dicopper:



M. H. Groothaert et al.,
J. Am. Chem. Soc. **127**, 1394 (2005)

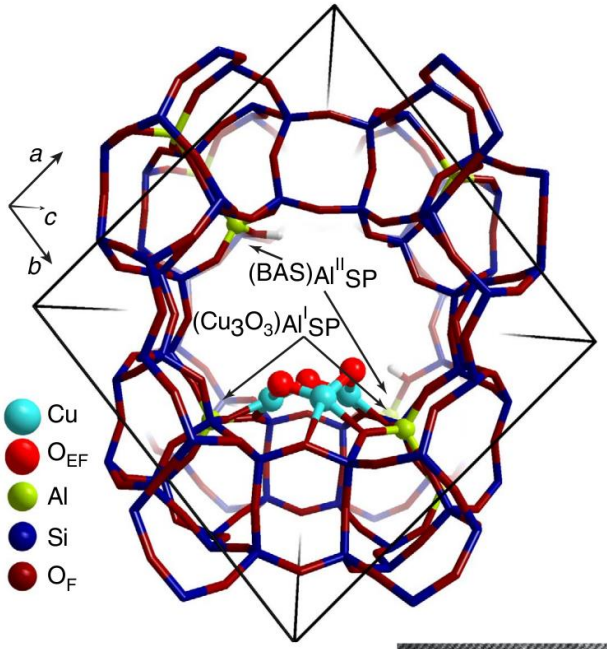
"Biomimetic"?

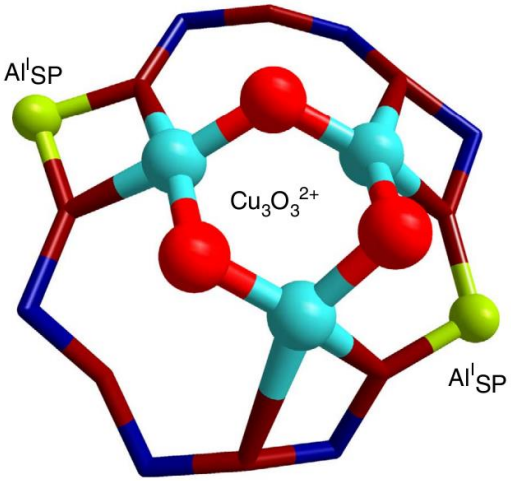


$$CH_4 + O_2 + NADH + H^+ \rightarrow CH_3OH + H_2O + NAD^+ \qquad CH_4 + \tfrac{1}{2}O_2 \rightarrow CH_3OH$$

M. Ravi *et al., Nat. Catal.* **2**, 485 (2019)

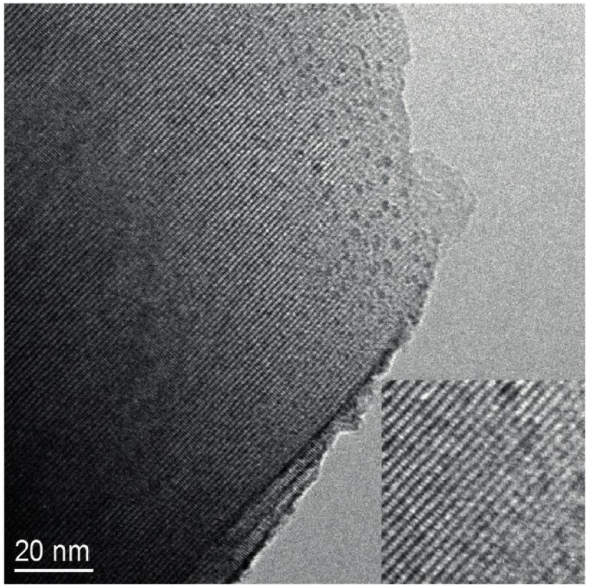
Copper oxide sites: … or larger?

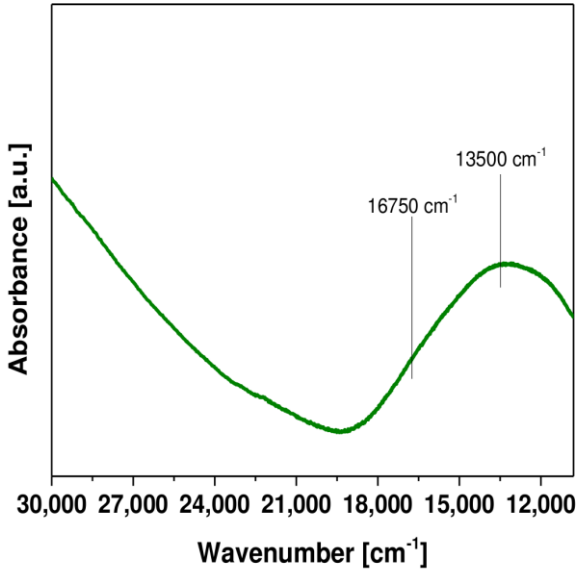




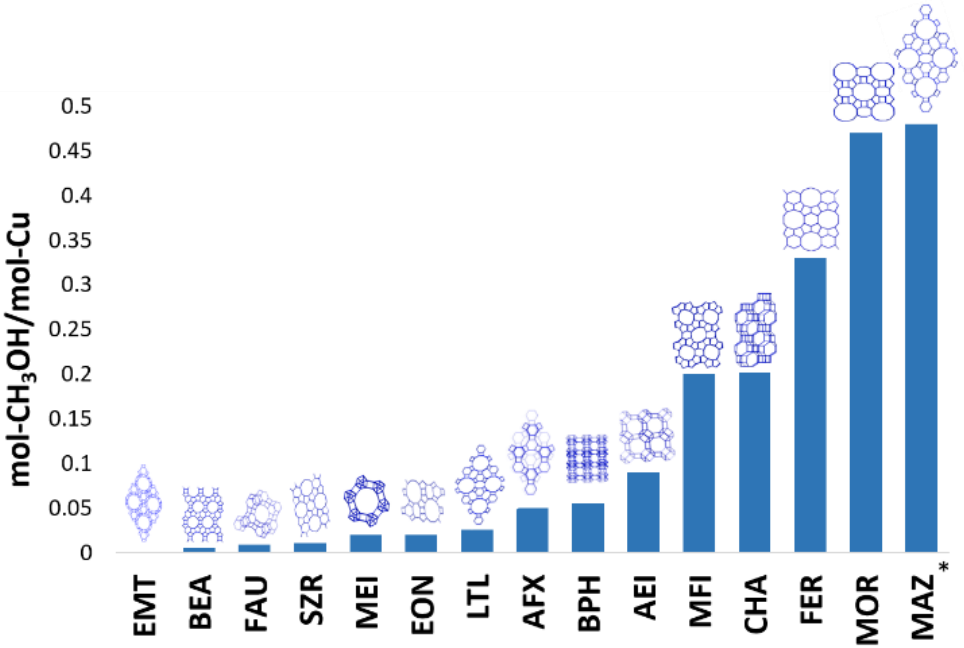
S. Grundner et al.,
Nat. Comm. **6**, 7546 (2015)

P. Tomkins et al.,
Angew. Chem. Int. Ed.
5, 5467 (2016)





Zeolite type influences structure



M. A. Newton *et al., Chem. Soc. Rev.* (2020)

Timeline of various suggested configurations of the copper oxide active species in Cu/MOR.

Any single site responsible for <u>all chemistry</u>?

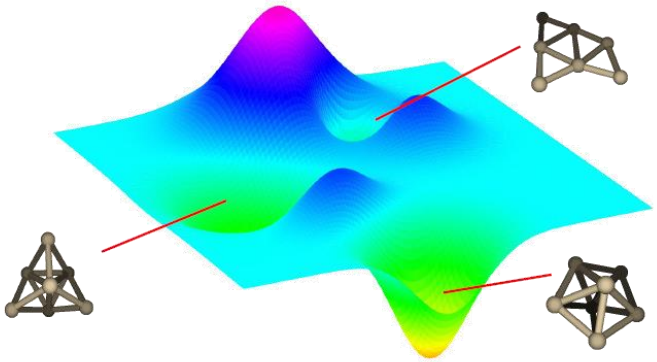
Methods: DFT + global optimization

Computational Details:

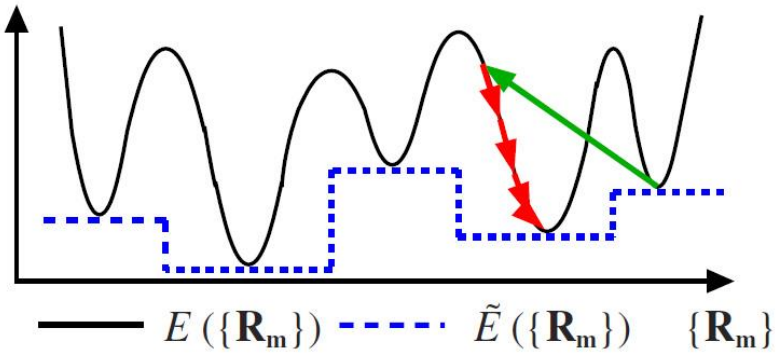
- DFT: all-electron atom-centered orbitals code FHI-aims
- Exchange-correlation: hybrid PBE0 functional
- «Tier3» set of atom-centered basis functions

V. Blum et al., *Comp. Phys. Comm.* **180**, 2175 (2009)
X. Ren et al., *New J. Phys.*, **14**, 053020 (2012)

Global structure optimization with basin hopping:



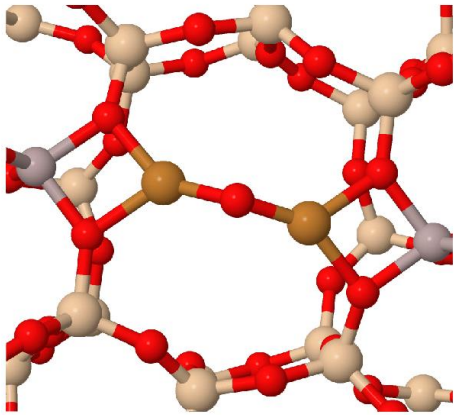
D. J. Wales et al., *Adv. Chem. Phys.* **115**, 1 (2000)



R. Gehrke, K. Reuter, *Phys. Rev. B* **79**, 085412 (2009)

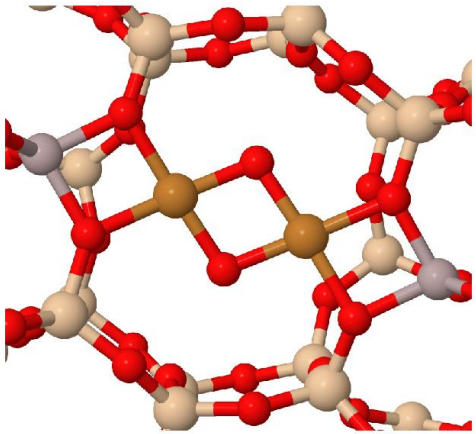
Dimers and trimers: CuMOR

Cu-MOR:



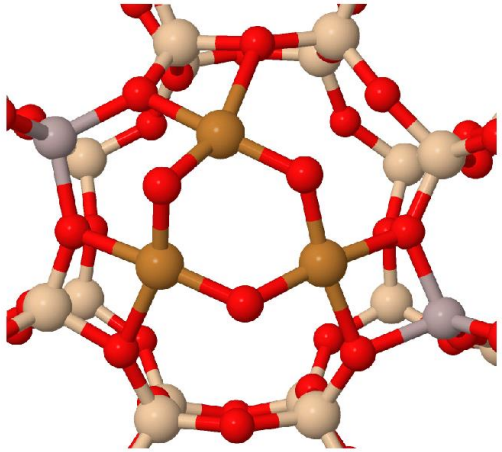
Cu_2O^{2+}

0.23 eV



$Cu_2O_2{}^{2+}$

0.00 eV



$Cu_3O_3{}^{2+}$

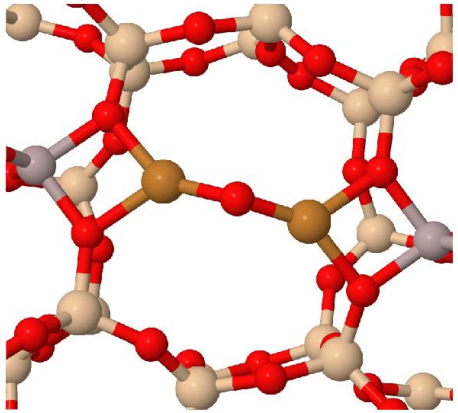
0.11 eV

Relative stability?

$$\Delta E = \frac{1}{6}[2 \times E(\mathrm{Cu_3O_3}^{2+}) + E(\text{empty zeolite}) - 3 \times E(\mathrm{Cu_2O_2}^{2+})]$$

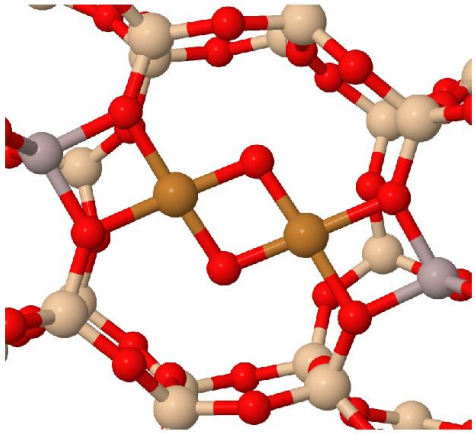
$$\Delta E = \frac{1}{2}[2 \times E(\mathrm{Cu_2O}^{2+}) + 0.5 \times E(\mathrm{O_2}) - E(\mathrm{Cu_2O_2}^{2+})]$$

Relative stability: CuMOR



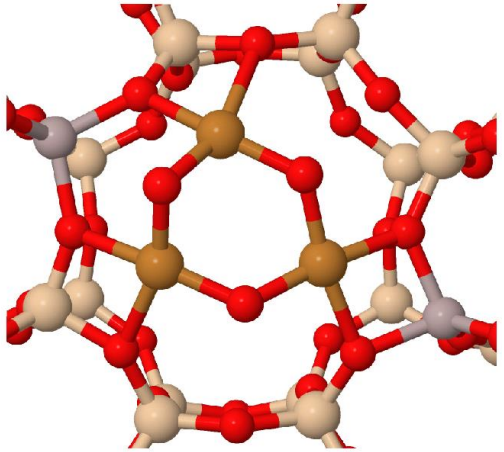
Cu_2O^{2+}

0.23 eV



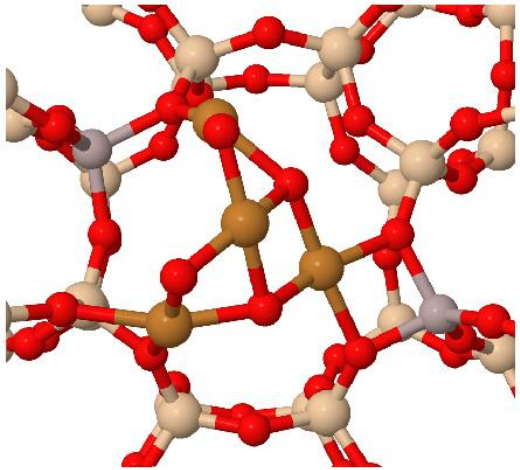
$Cu_2O_2^{2+}$

0.00 eV



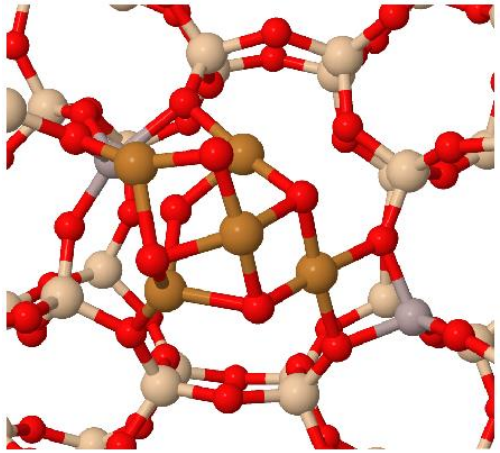
$Cu_3O_3^{2+}$

0.11 eV



$Cu_4O_4^{2+}$

– 0.26 eV

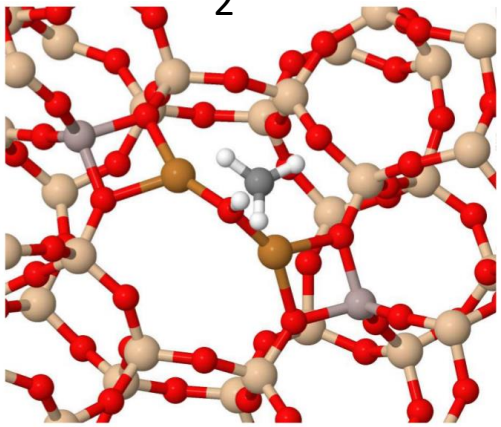


$Cu_5O_5^{2+}$

– 0.48 eV

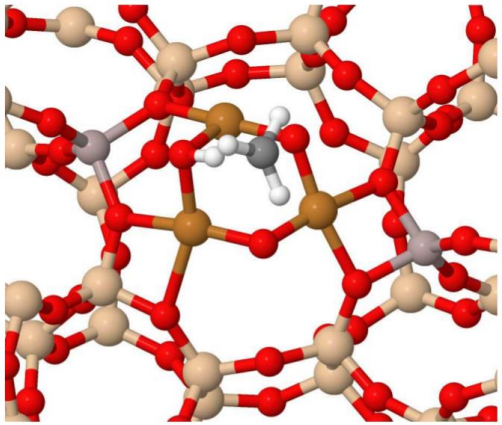
Methane reactivity

Cu_2O^{2+}



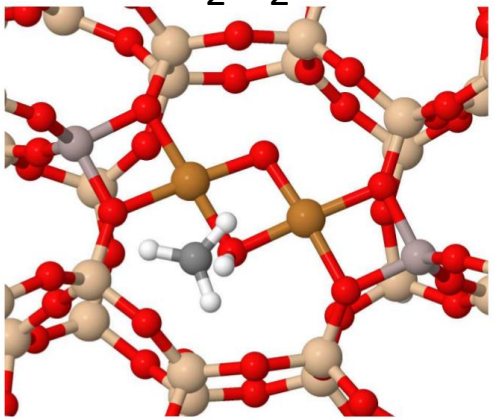
0.87 eV

$Cu_3O_3^{2+}$



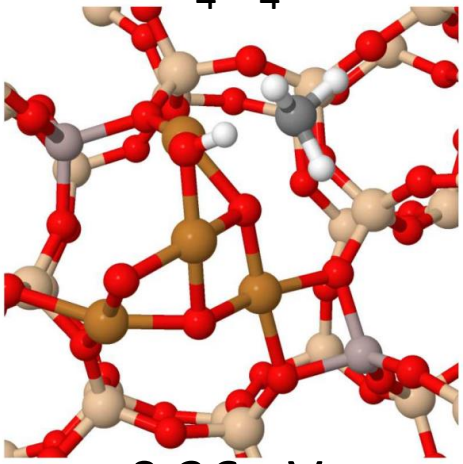
0.43 eV

$Cu_2O_2^{2+}$



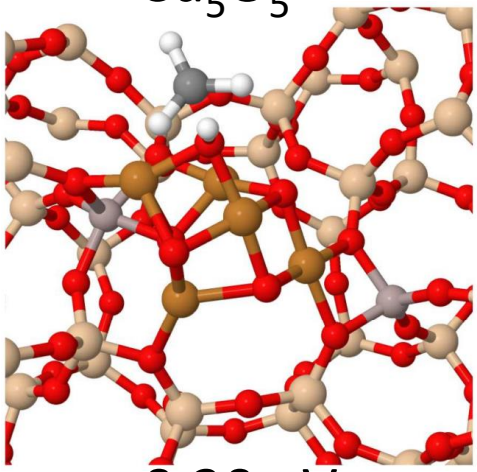
1.12 eV

$Cu_4O_4^{2+}$



0.36 eV

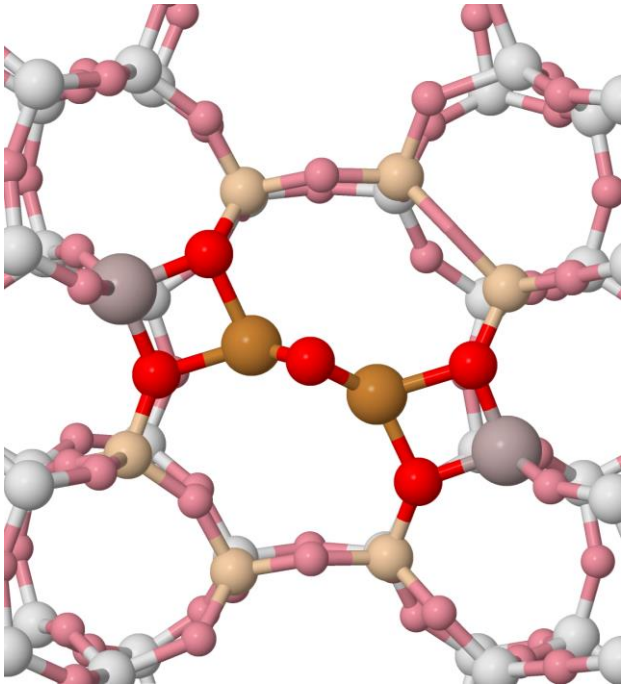
$Cu_5O_5^{2+}$



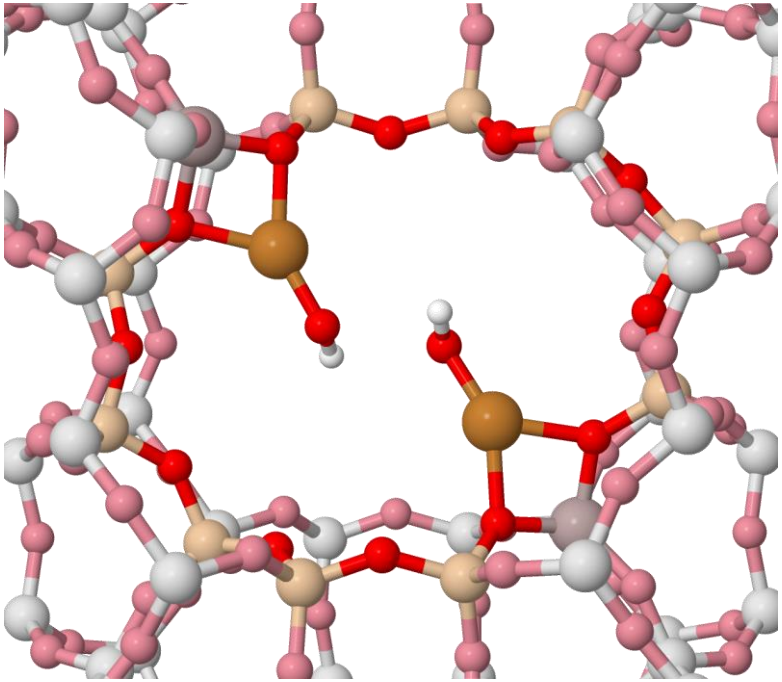
0.30 eV

Monomers vs. monomer pairs

"Aggregates" in 8MR channels



"Monomers" In 12MR channels



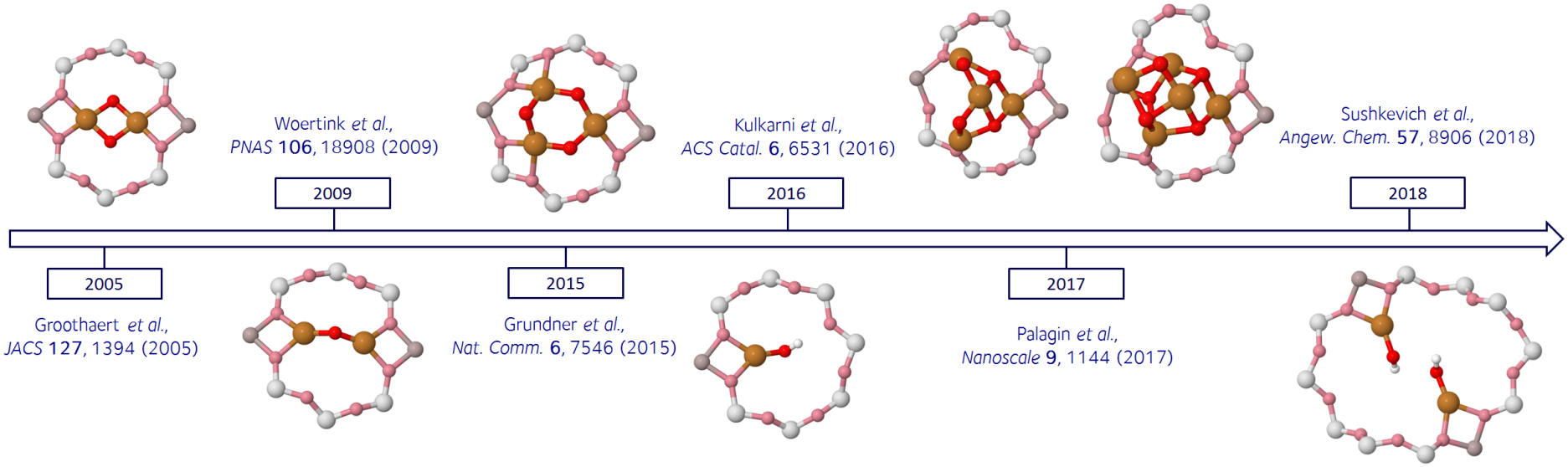
Sushkevich, Palagin, *et al.*, *Angew. Chem. Int. Ed.* **57**, 8906 (2018)

Active centers conclusions

- Stability increases with cluster size
- Larger clusters better stabilize the OH and CH_3 fragments in the process of methane activation
- Interaction of two monomers is possible

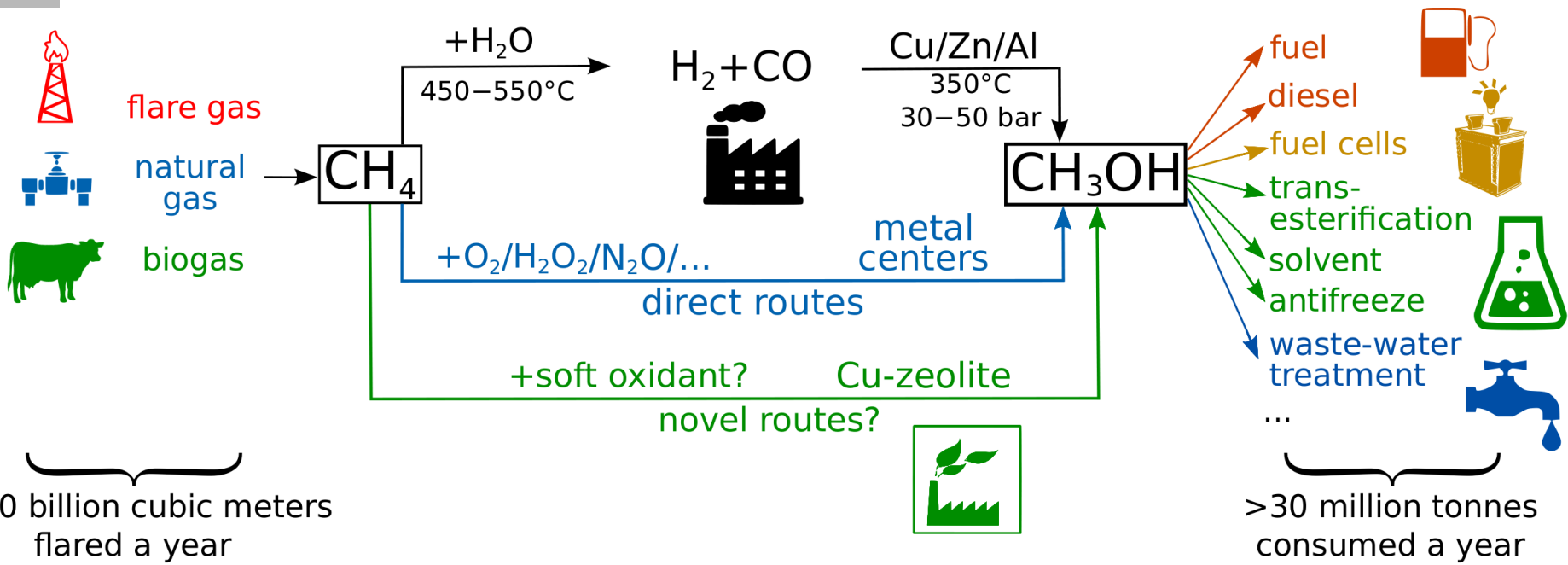
chemical bonding → geometry → properties! ← theory

Multiple active centers are possible!



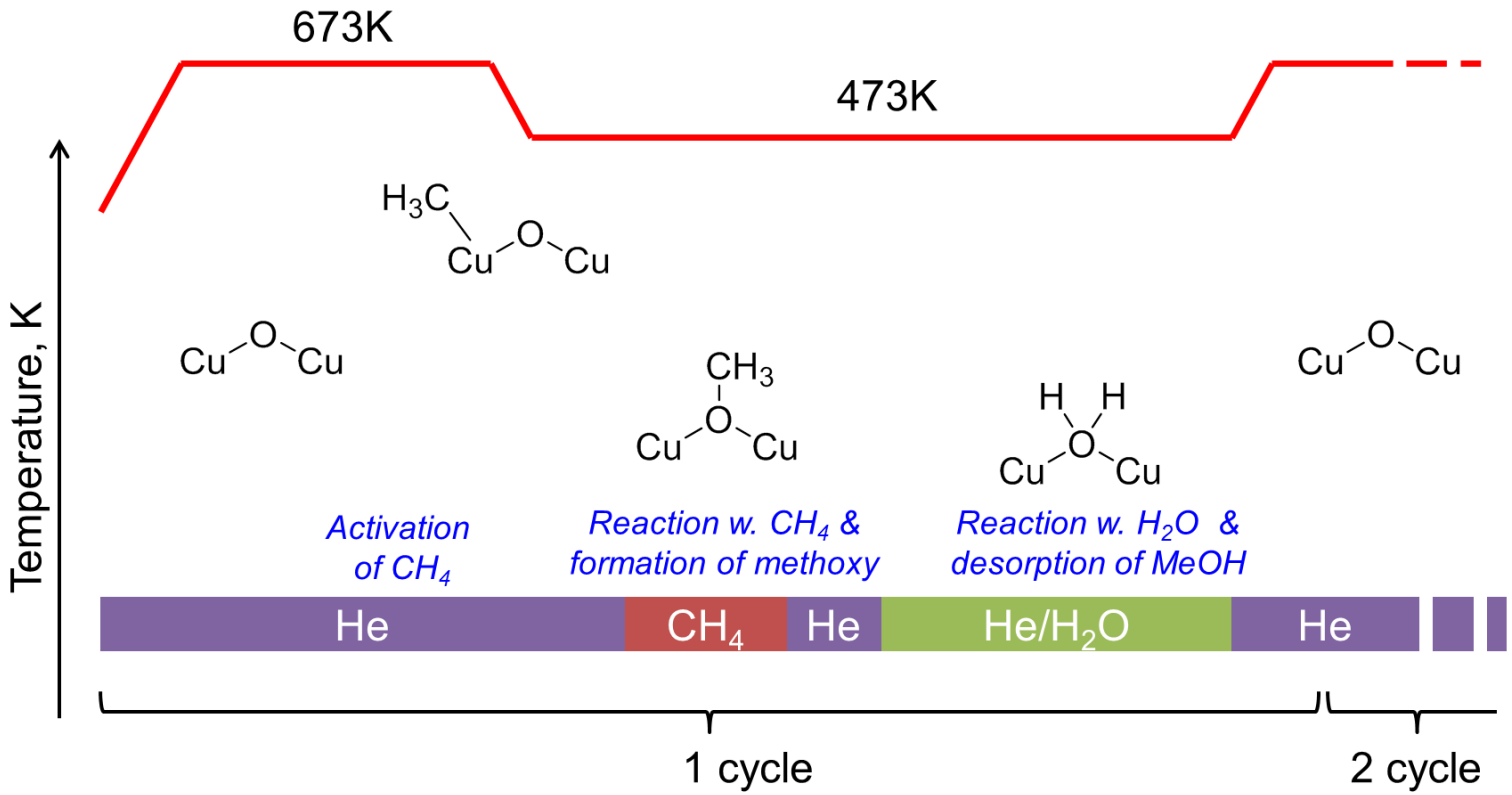
Palagin *et al.*, *Nanoscale* **9**, 1144 (2017)

Reaction mechanism

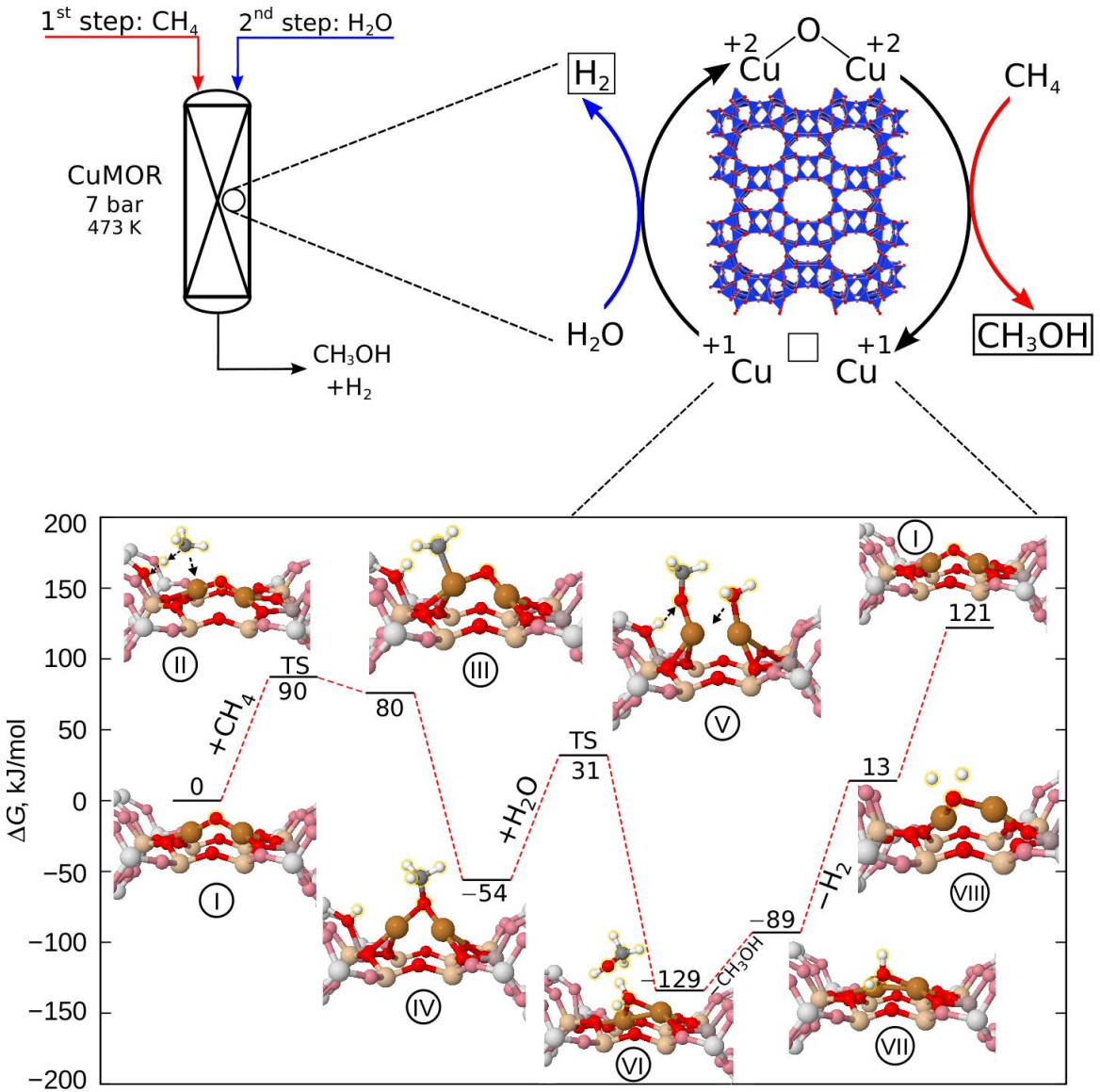


Reaction mechanism

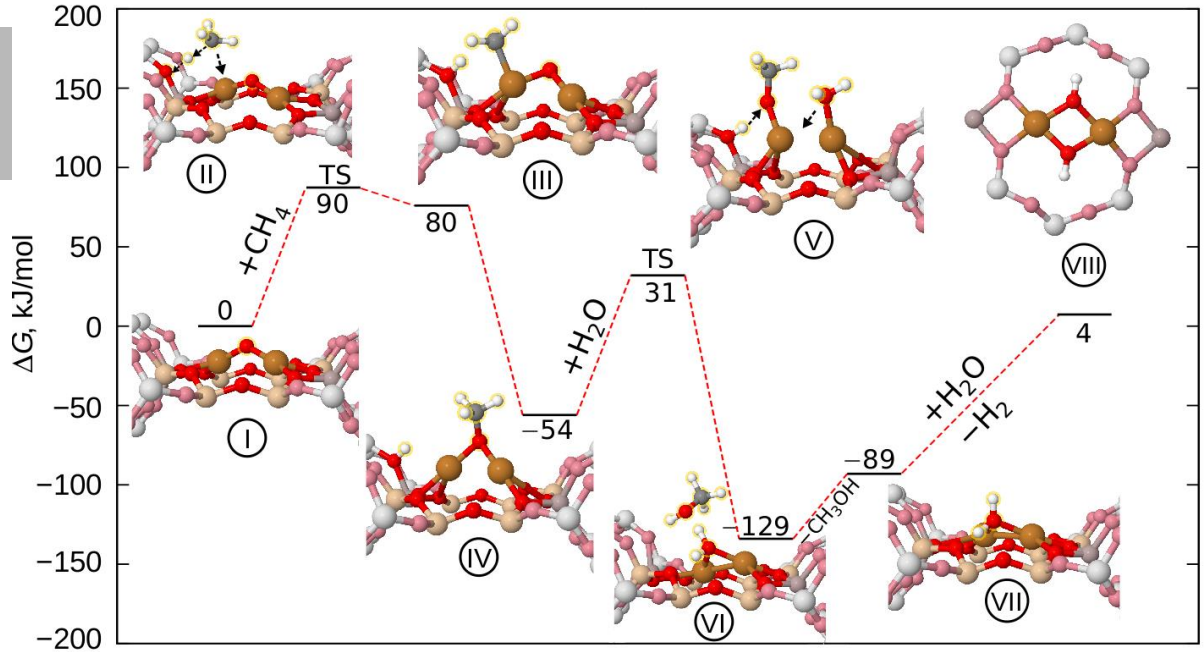
Dr. Vitaly Sushkevich

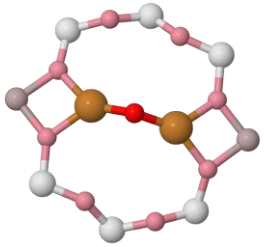


Oxidation with water!

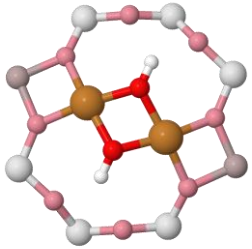


Water: additional stabilization



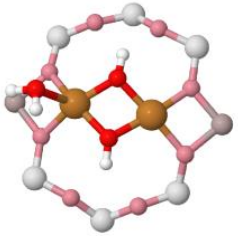


+ H_2O =

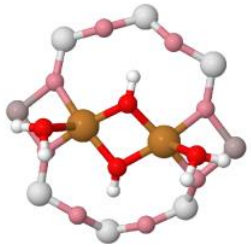


+ 117 kJ/mol

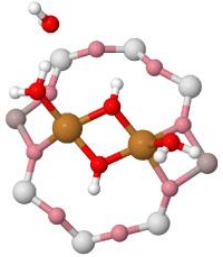
0 kJ/mol



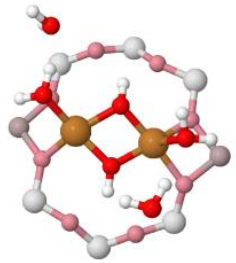
−44 kJ/mol



−85 kJ/mol

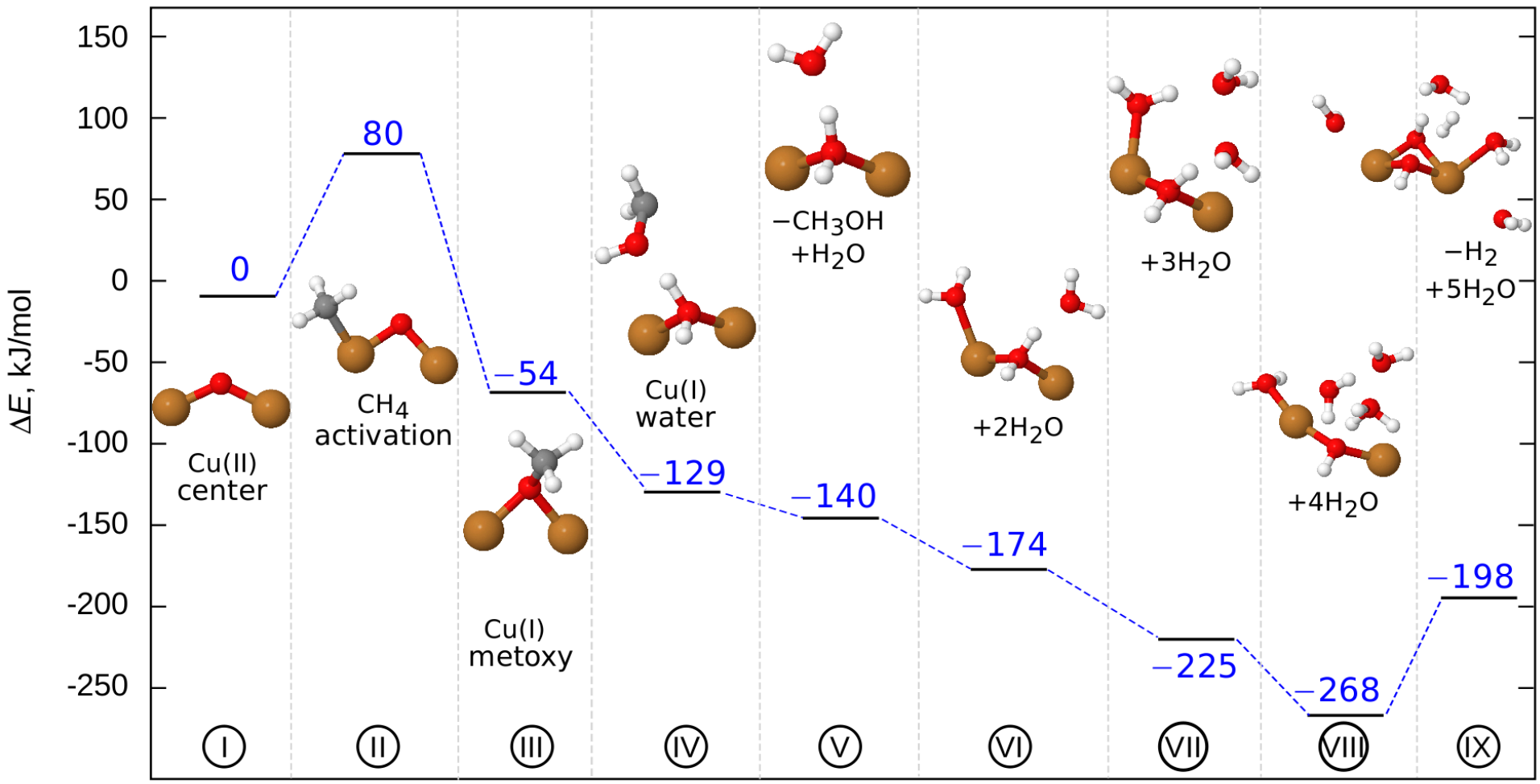


−143 kJ/mol



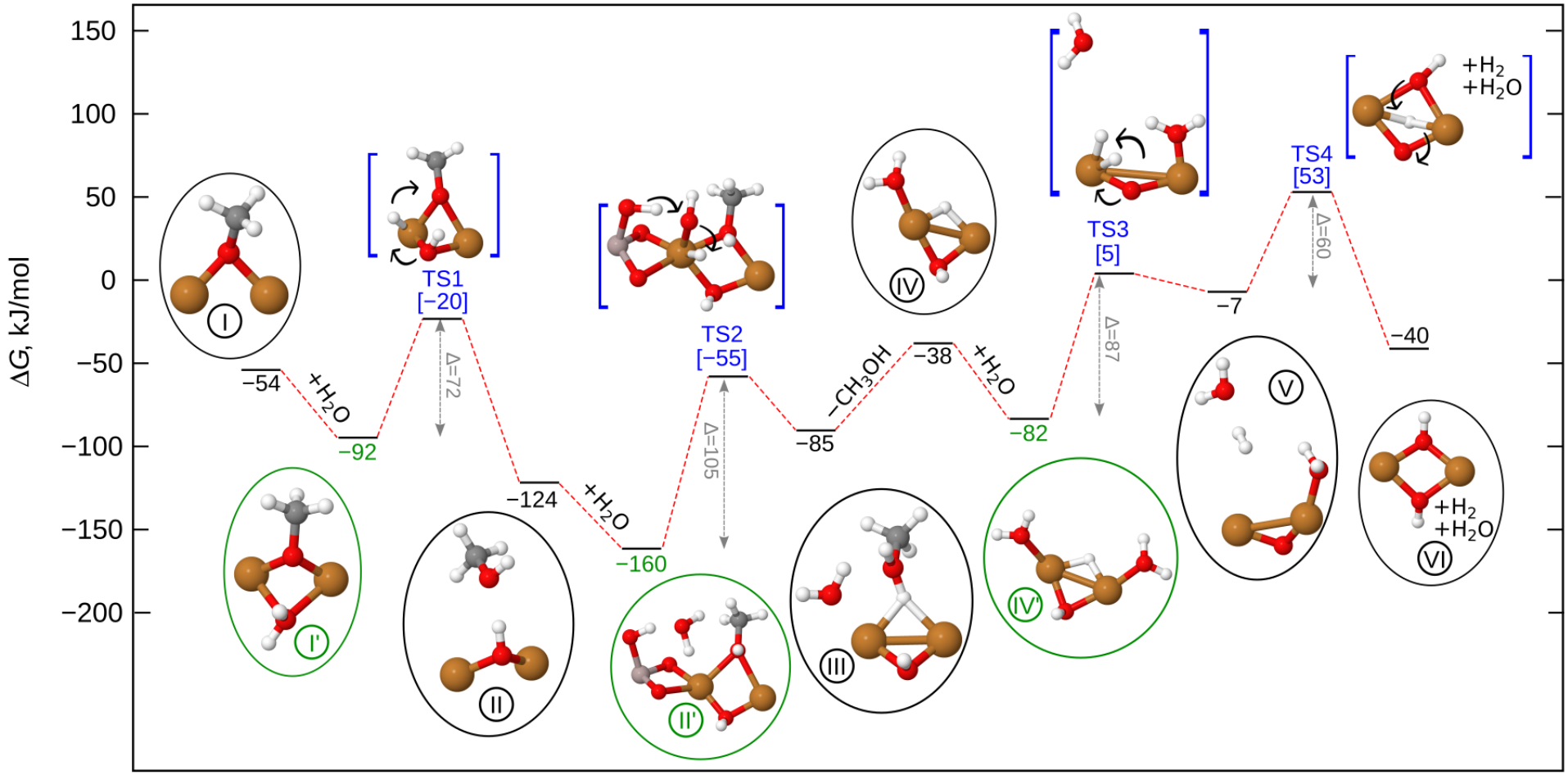
−177 kJ/mol

Simply, lots of stabilization!



Sushkevich, Palagin, *et al.*, *Science* **356**, 523 (2017)

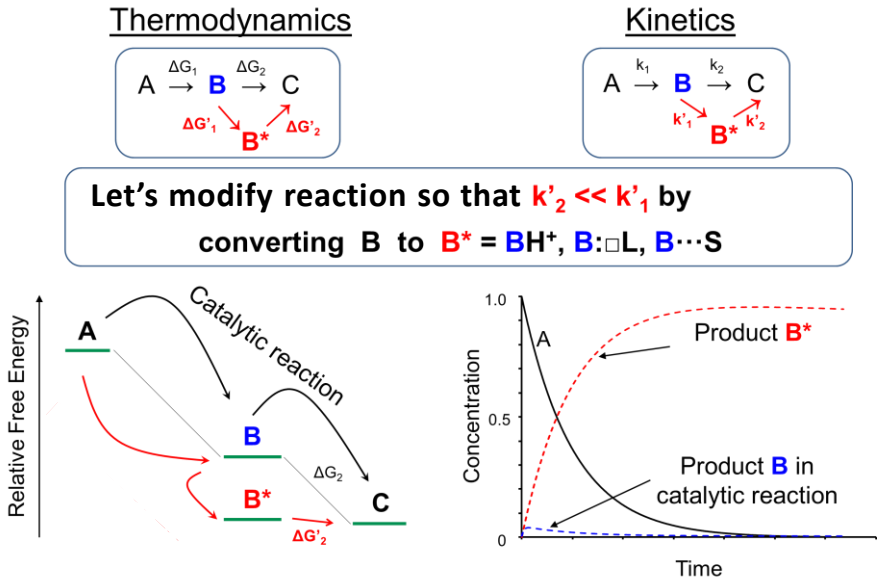
Big question: hydrogen release!!!

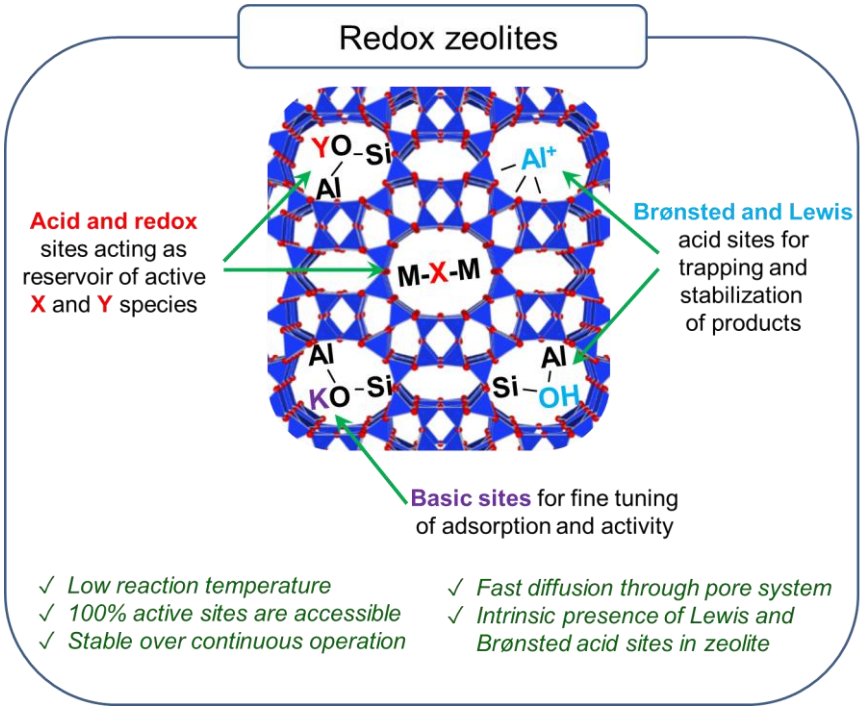


Palagin *et al.*, *ACS Catal.* **9**, 10365 (2019)

Thermodynamics → stabilize/modify products ← suitable materials ← theory

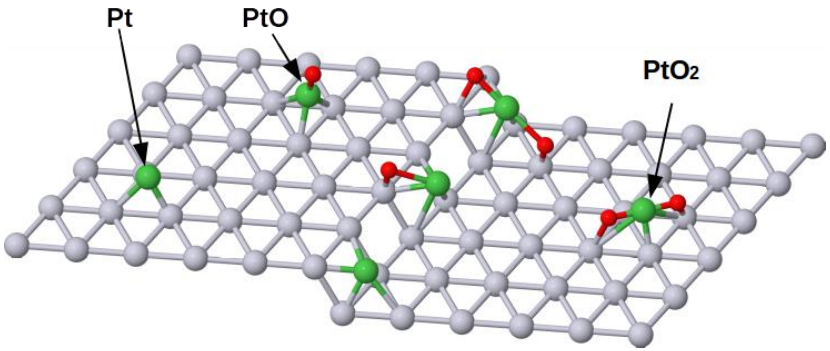
Application outlook: Enabling thermodynamically challenging reactions



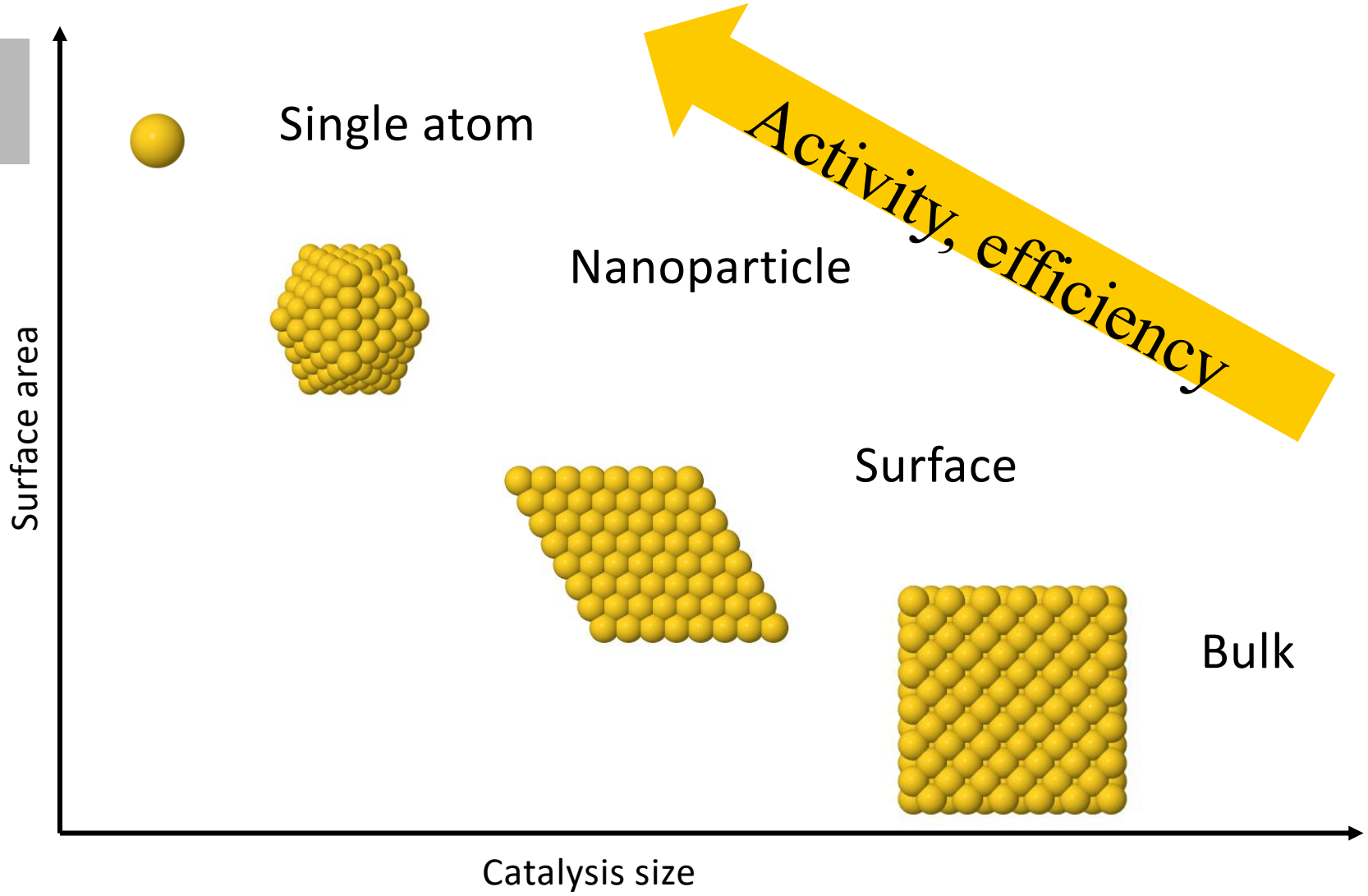


TheoCat@LSK highlights:

1) Methane to Methanol
2) Water gas shift
3) Supported nanoparticles
4) Theory development



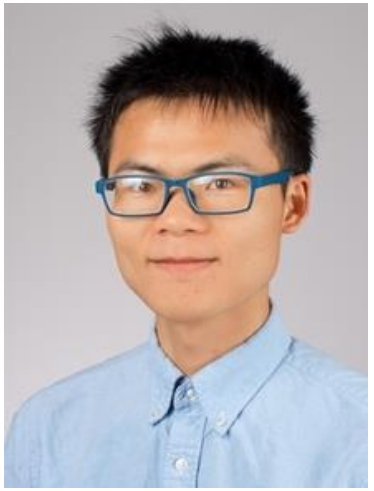
Nanoparticle activity



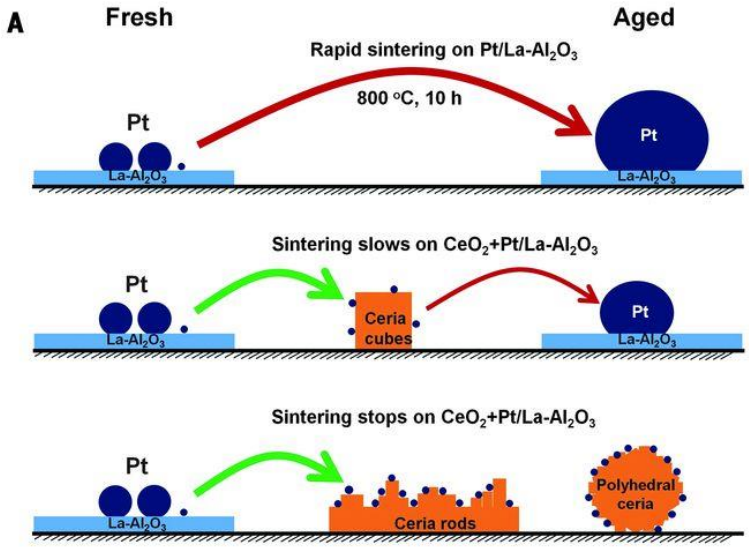
Pt sintering @ Al_2O_3 and CeO_2

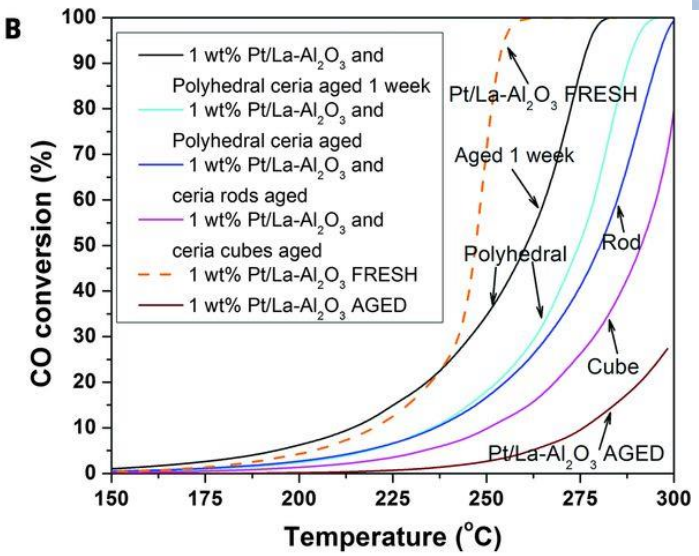
WGS: $CO + H_2O \leftrightarrow CO_2 + H_2$

LTS: @ Pt/CeO_2



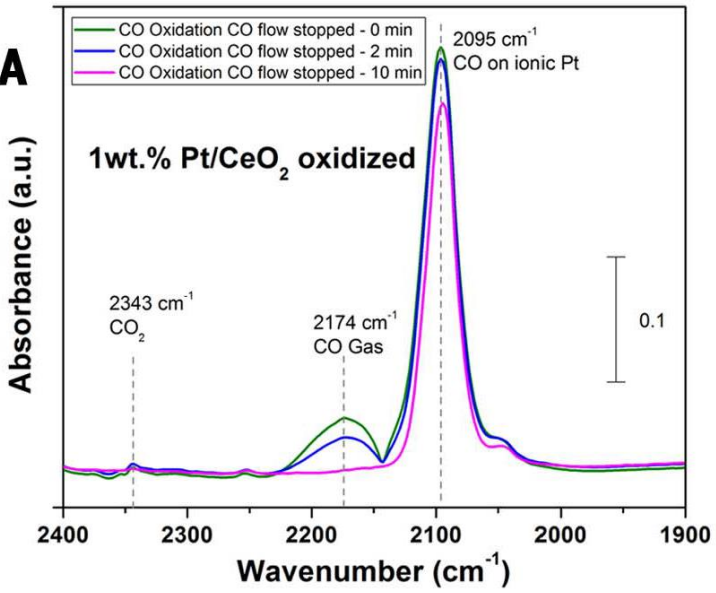
Xing Wang

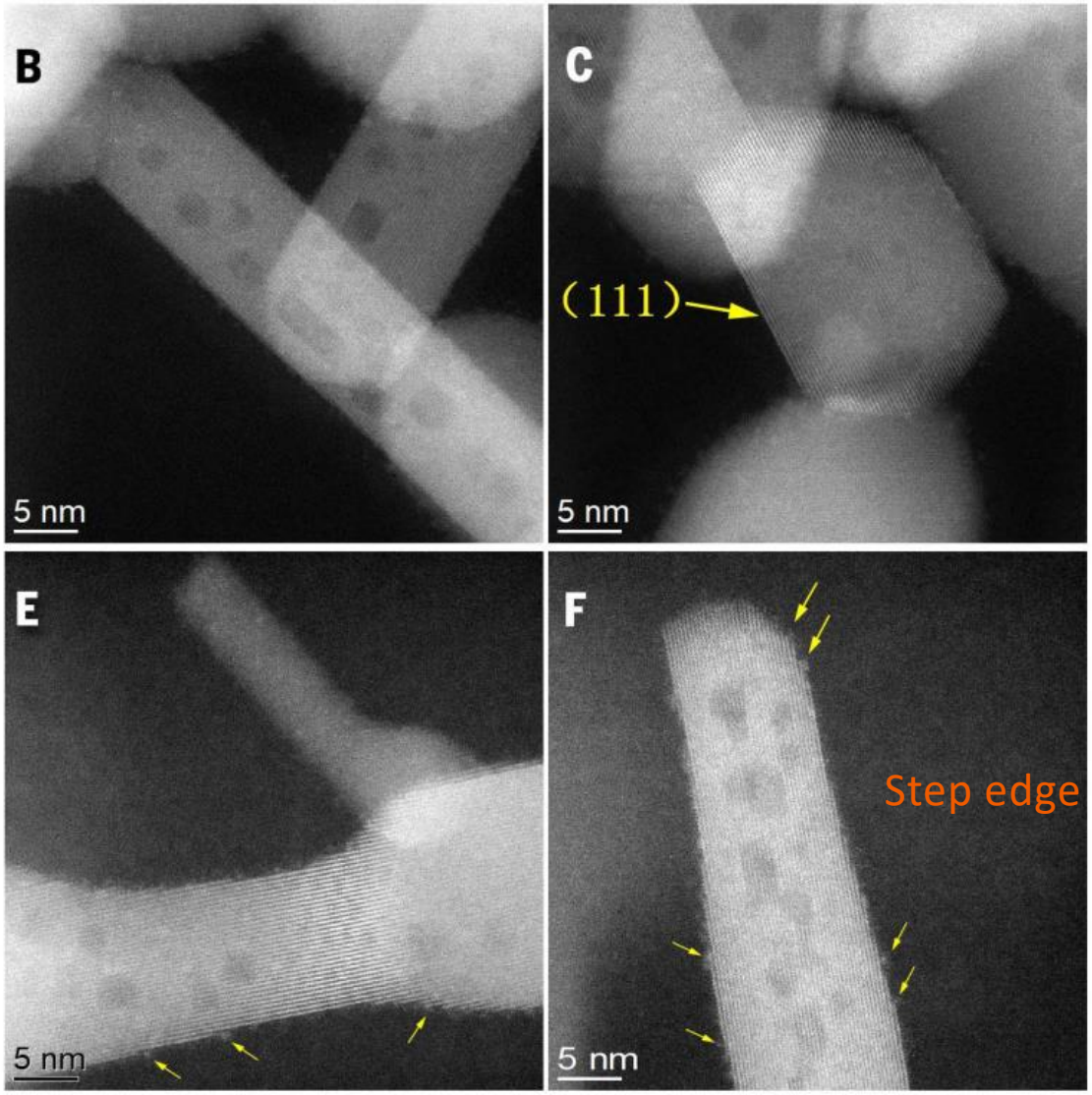




J. Jones *et al.*, *Science* **353**, 150 (2016)

Single-atom Pt@CeO_2 catalysts





[1]. Jones, John, et al. *Science* 353.6295 (2016): 150-154.

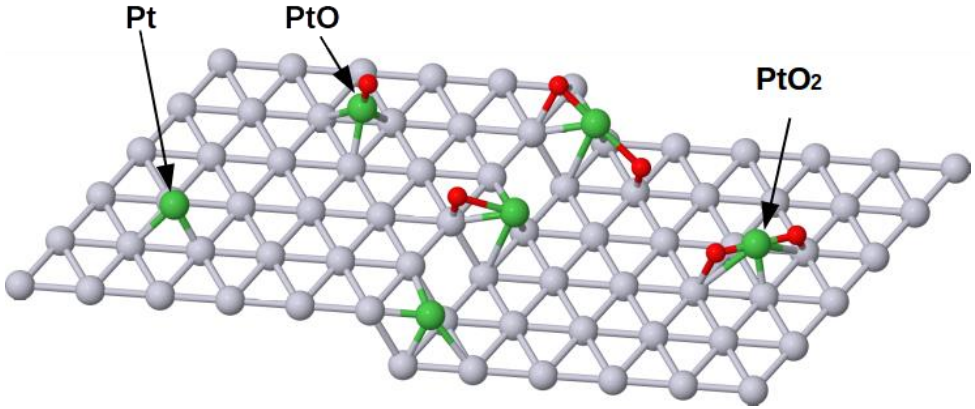
Outline

- Why?
- Which site?
- What kind of structure?
- How to compare with experiment?
- Can we predict something unknown?

DFT calculations could help!

Mobile Pt species

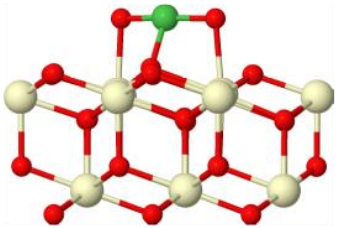
At high temperature, the evaporation of platinum species could be volatile Pt atom, PtO and PtO_2 species

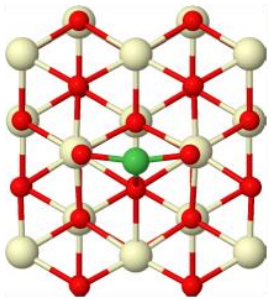


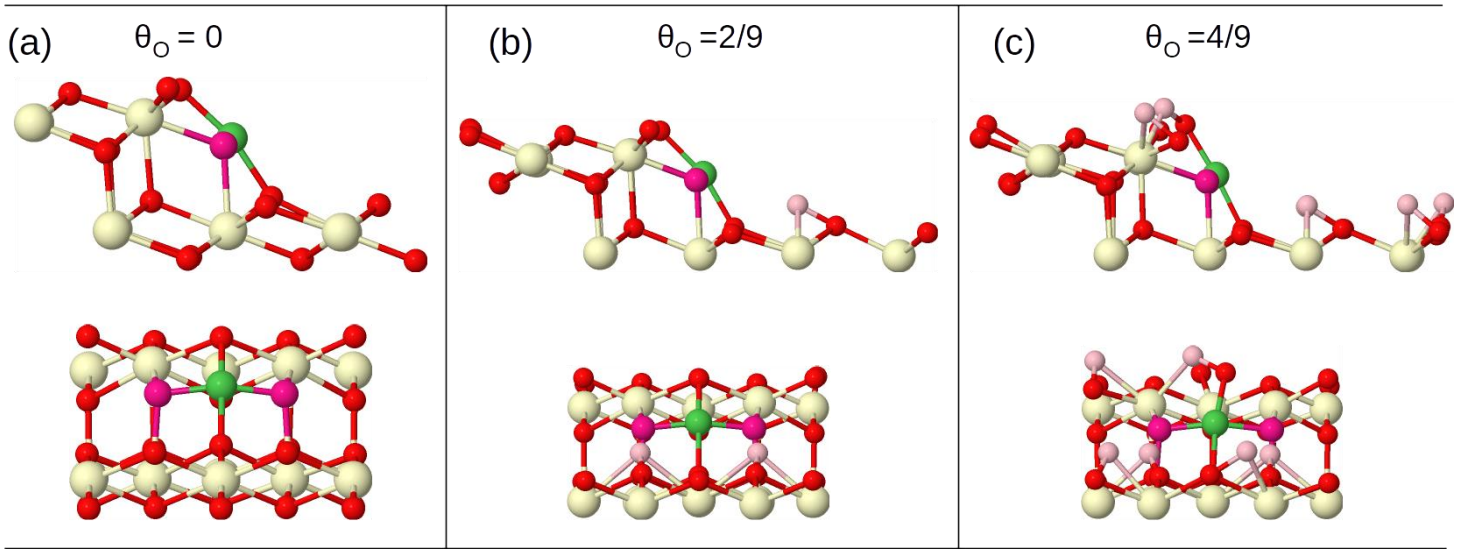
Surface	Binding energy (eV)		
	Pt	PtO	PtO_2
Pt(111)	−4.45	−3.94	−2.92
Pt(111) step	−5.48	−4.76	−3.58

Product	Reaction	Enthalpy of Formation (eV)
PtO (gas)	$Pt + \frac{1}{2} O_2 \longrightarrow PtO$	−2.00
PtO_2 (gas)	$Pt + O_2 \longrightarrow PtO_2$	−4.40
Pt_{ads}	$Pt + Pt(111) \longrightarrow Pt/Pt(111)$	−4.45
PtO_{ads}	$Pt + \frac{1}{2} O_2 + Pt(111) \longrightarrow PtO/Pt(111)$	−5.94
PtO_{2_ads}	$Pt + O_2 + Pt(111) \longrightarrow PtO_2/Pt(111)$	−7.32

PtO_2 on perfect and stepped CeO_2





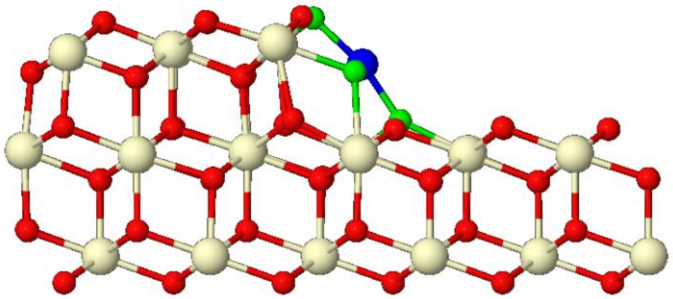


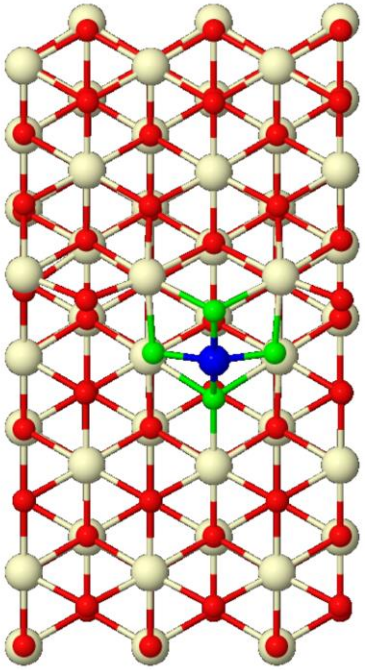
Surface	E_b (eV)	$d1_{Pt-O}$ (Å)	$d2_{Pt-O}$ (Å)	$d3_{Pt-O}$ (Å)	$d4_{Pt-O}$ (Å)
CeO_2	−3.32	1.86	1.86	2.04	2.06
CeO_2, $\theta_O = 2/9$	−3.43	1.87	1.87	2.04	2.06
CeO_2, $\theta_O = 4/9$	−3.06	1.90	1.91	2.01	2.03

$[PtO_4]$ on CeO_2 surface

Calculated 2093 cm^{-1}

Experimental 2095 cm^{-1}





$[PtO_4]$

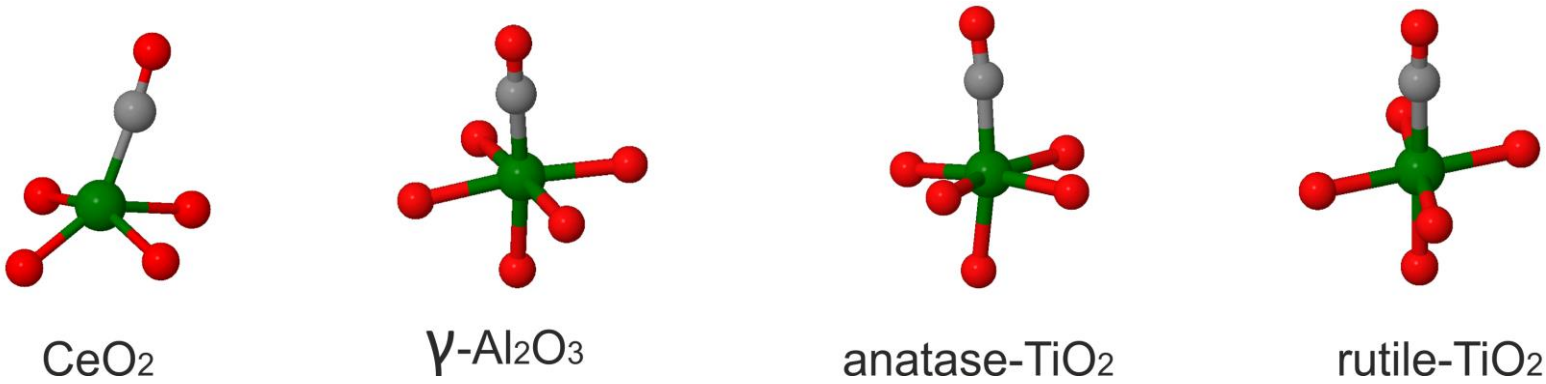
J. Jones *et al.*, *Science* **353**, 150 (2016)

X. Wang *et al.*, *Phys. Chem. Chem. Phys.* **19**, 30513 (2017)

Suitable geometrical motifs

[PtO_4]

[PtO_5]



CeO_2 | γ-Al_2O_3 | anatase-TiO_2 | rutile-TiO_2

PCCP,
19, 30513 (2017)

PCCP

PAPER

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View Journal | View Issue

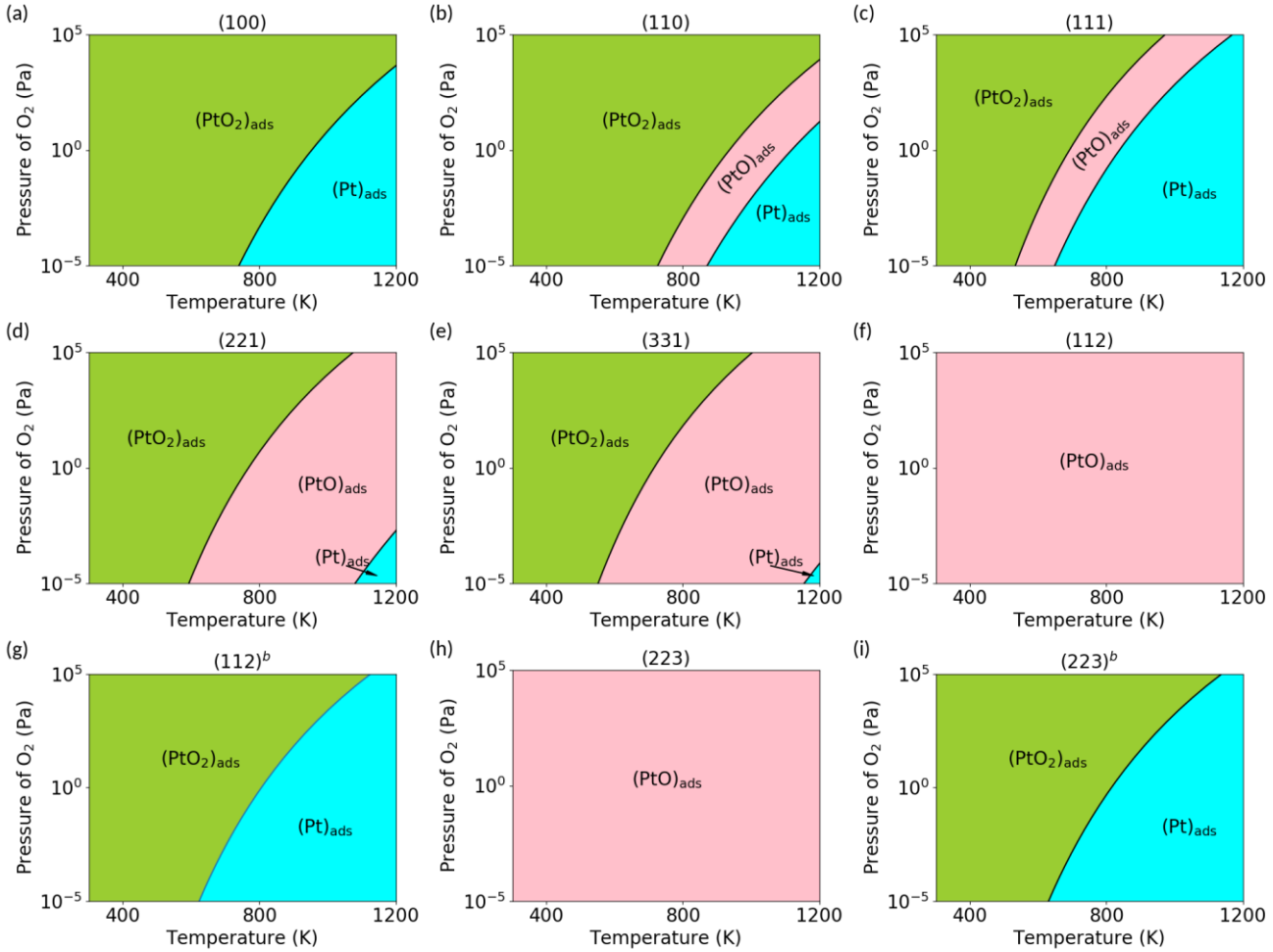
Check for updates

Cite this: *Phys. Chem. Chem. Phys.*, 2017, **19**, 30513

Ostwald ripening *versus* single atom trapping: towards understanding platinum particle sintering†

Xing Wang,[ab] Jeroen A. van Bokhoven*[ab] and Dennis Palagin *[b]

Stability under different conditions



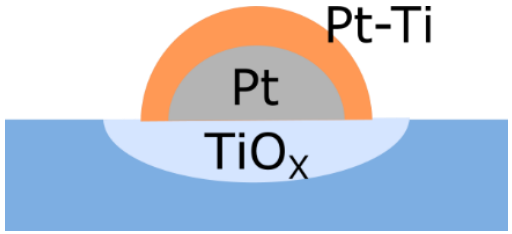
Atomically dispersed platinum on low index and stepped ceria surfaces: phase diagrams and stability analysis†

Xing Wang,[ab] Jeroen A. van Bokhoven [ab] and Dennis Palagin [*b]

PCCP,
22, 28 (2020)

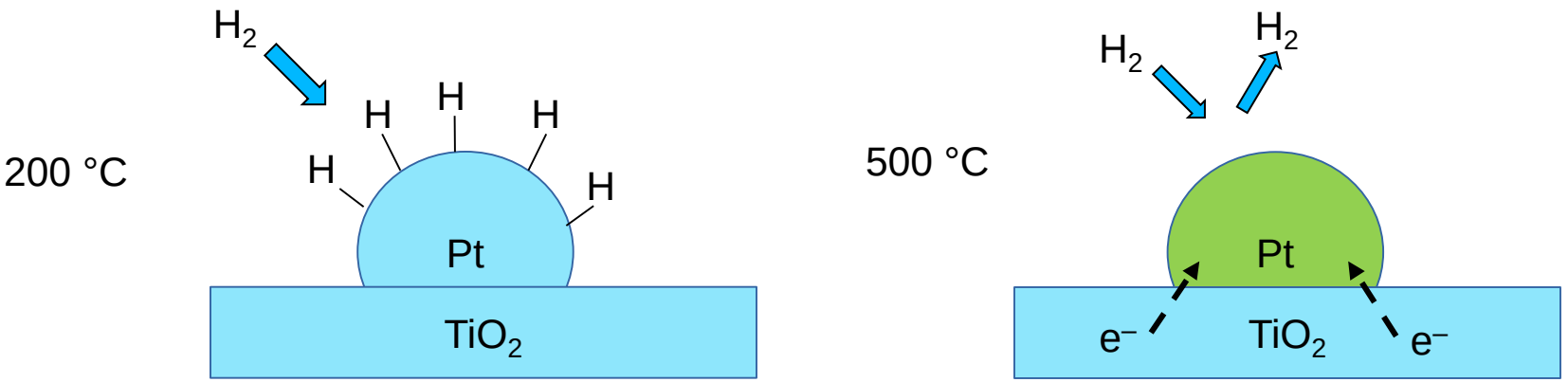
TheoCat@LSK highlights:

1) Methane to Methanol
   a) active sites
   b) mechanism
2) Water gas shift
3) Supported nanoparticles
4) Theory development



Strong metal support interaction (SMSI)

1978, SMSI



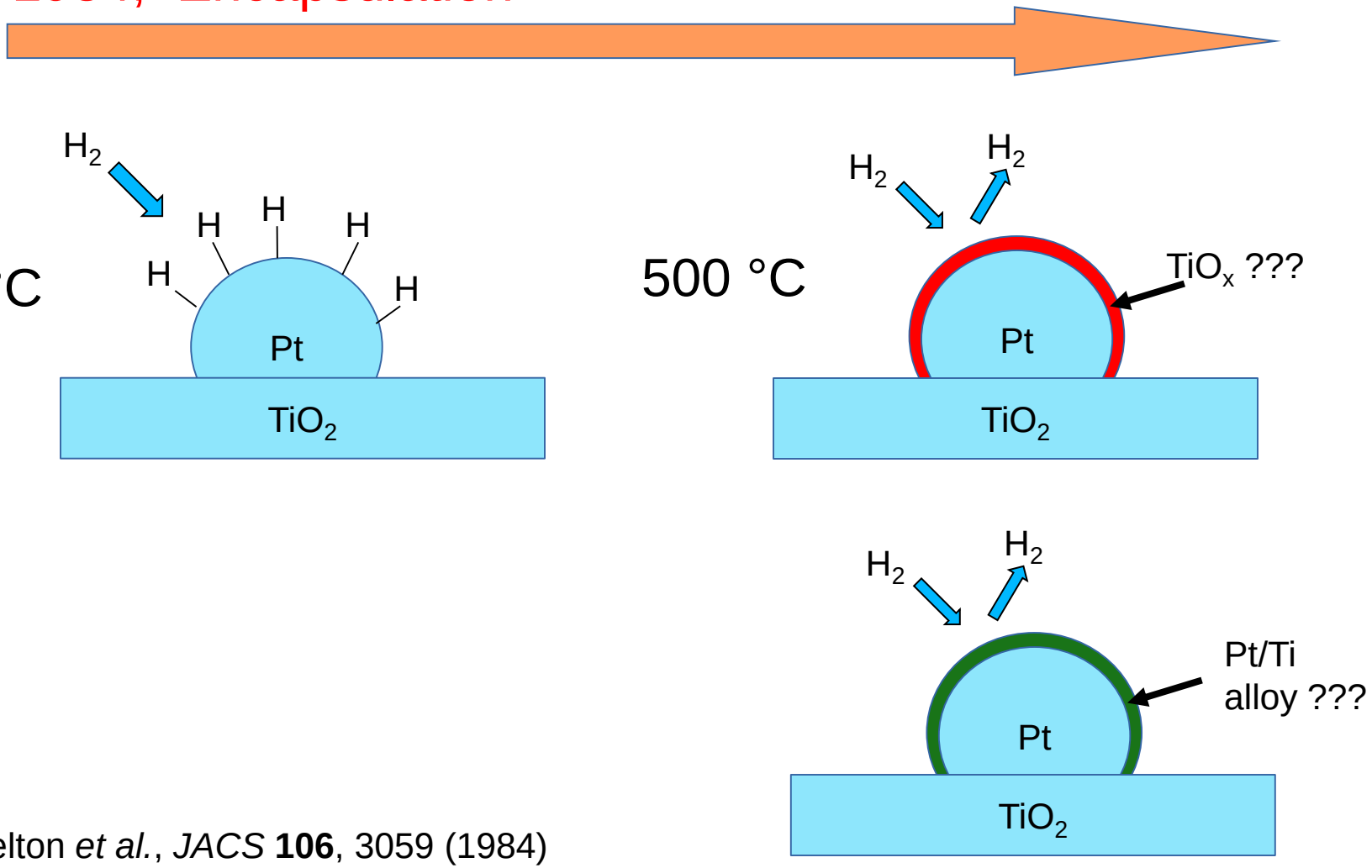
Metals	Oxides
Ru, Rh, Pd, Os, Ir, Pt	TiO_2, Nb_2O_5, Ta_2O_5
	~~Sc_2O_3, Y_2O_3, ZrO_2~~

S.J. Tauster *et al.*, *JACS* **100**, 170 (1978)

S.J. Tauster *et al.*, *Science* **211**, 1121 (1981)

Formation of alloy or encapsulation?

1984, Encapsulation

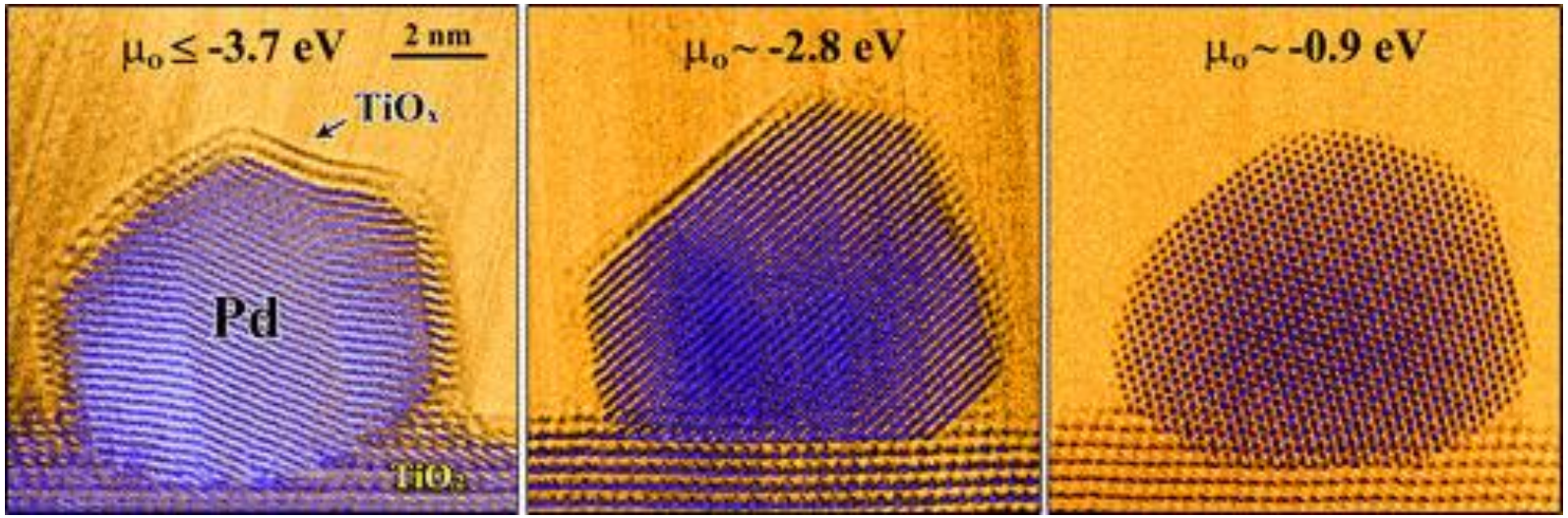


D.N. Belton *et al.*, *JACS* **106**, 3059 (1984)

Electron microscopy as direct evidence

2016
in situ TEM

Dynamical Observation



S. Zhang *et al.*, *Nano Lett.***16**, 4528 (2016)

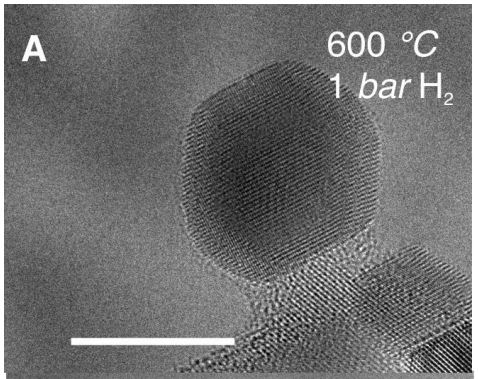
Questions and challenges:

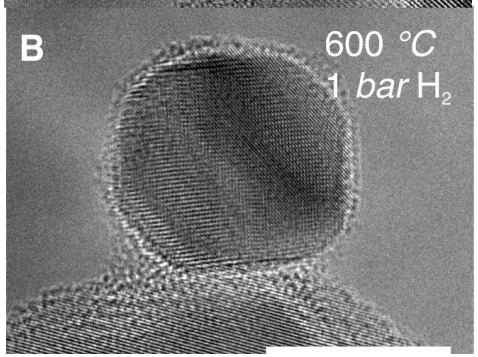
1. Mechanism of SMSI in Pt@TiO_2: alloy or partially reduced overlayer?

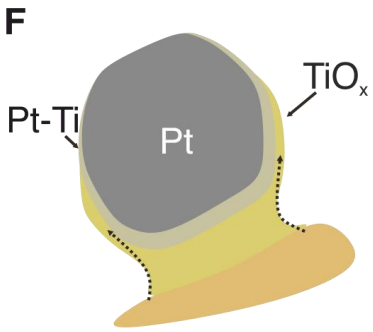
2. Thermodynamic driving force behind the surface overlayer growth?

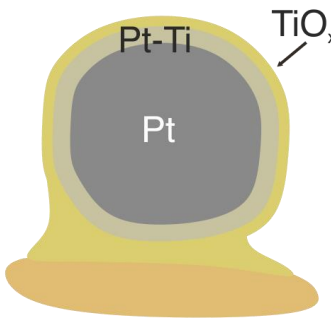
3. Any way to predict and control the SMSI?

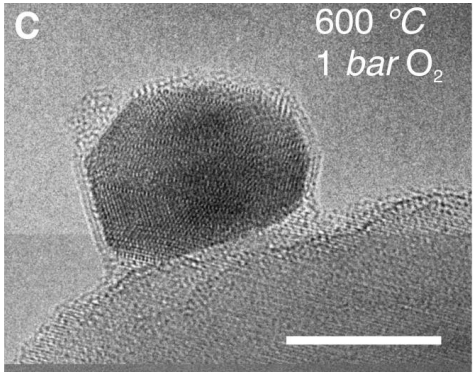
Evolution and dynamics of the overlayer in SMSI

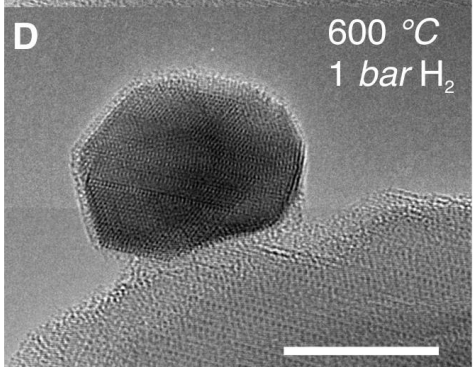


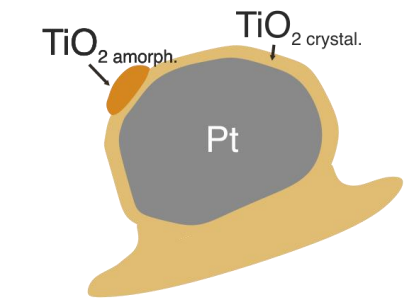


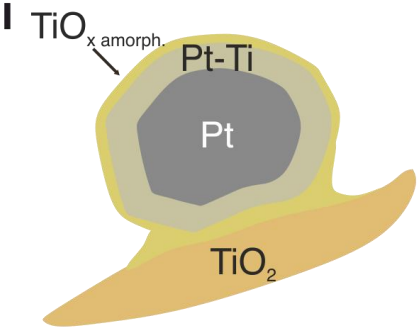




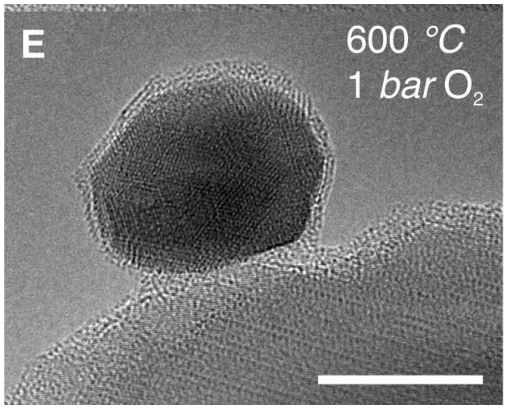


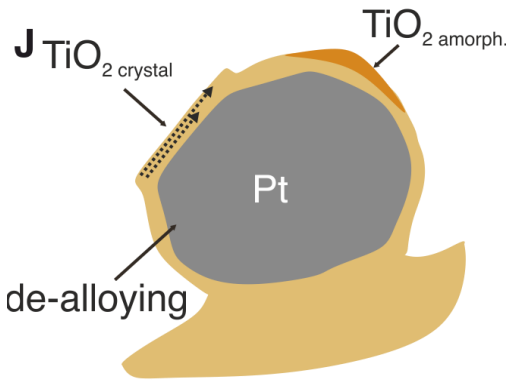




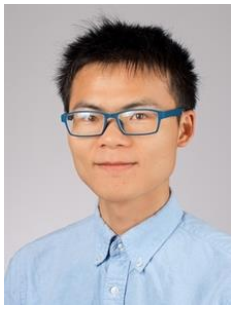


Arik Beck

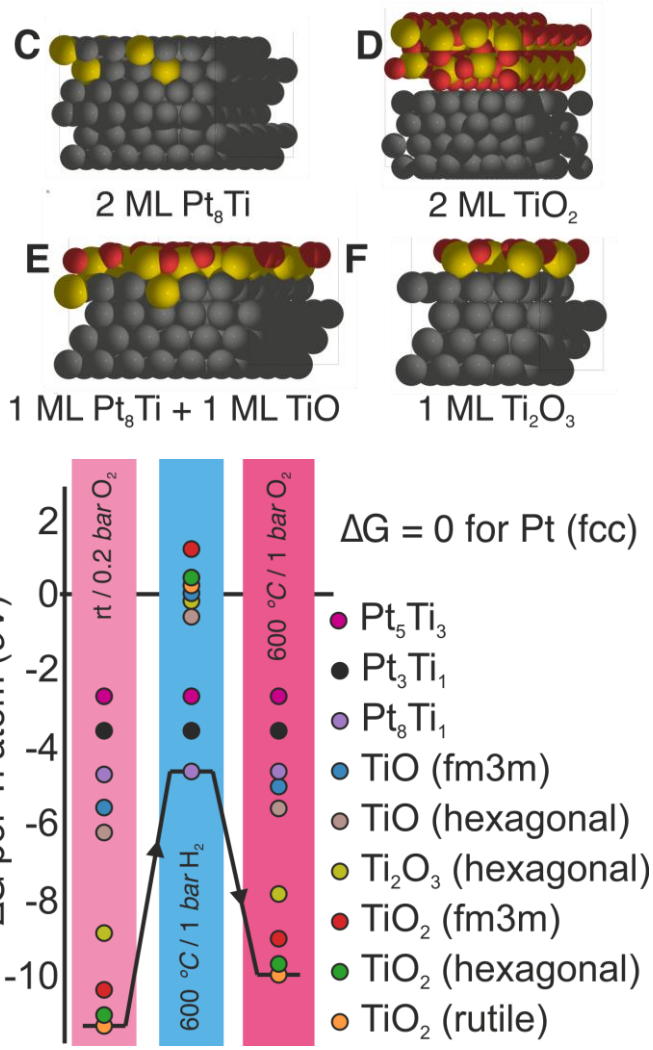


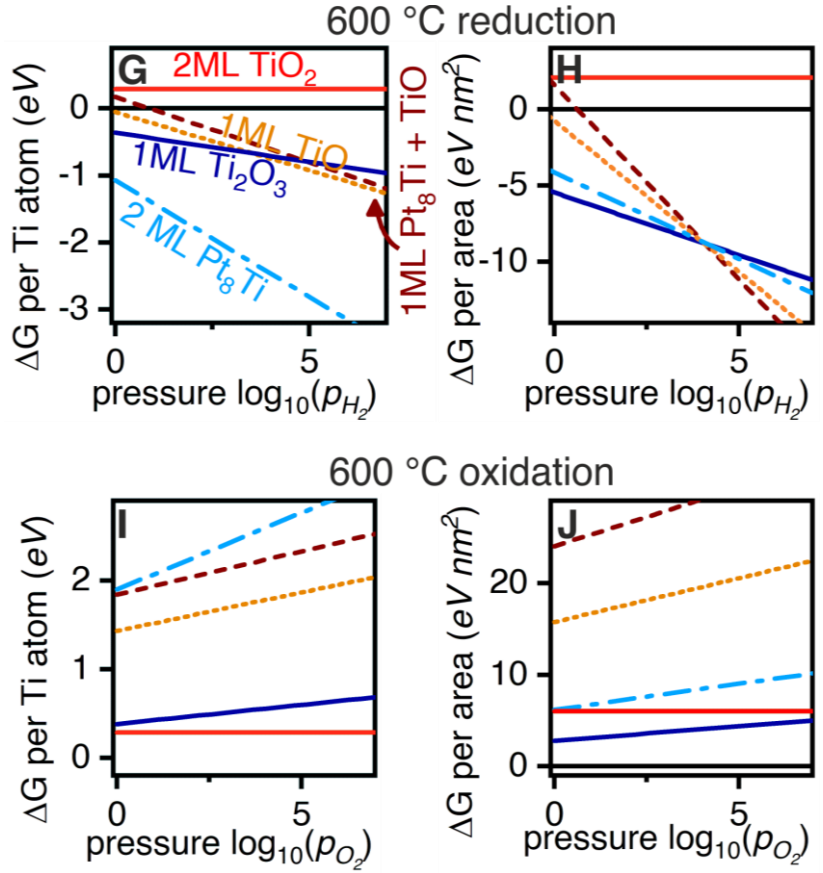


Evolution and dynamics of the overlayer in SMSI



Xing Wang





- Mixture of reduced titania and surface alloy is the most stable under hydrogen atmosphere.
- Under oxygen at 600°C surface alloy becomes thermodynamically unfavourable and segregation into oxidized titania phase and platinum metal surface occurs.

Questions and challenges/First conclusions

1. Mechanism of SMSI: alloy or overlayer?

The migration of reduced titanium oxide onto the platinum particle surface and the formation of an alloy are competing mechanisms during high temperature reduction.

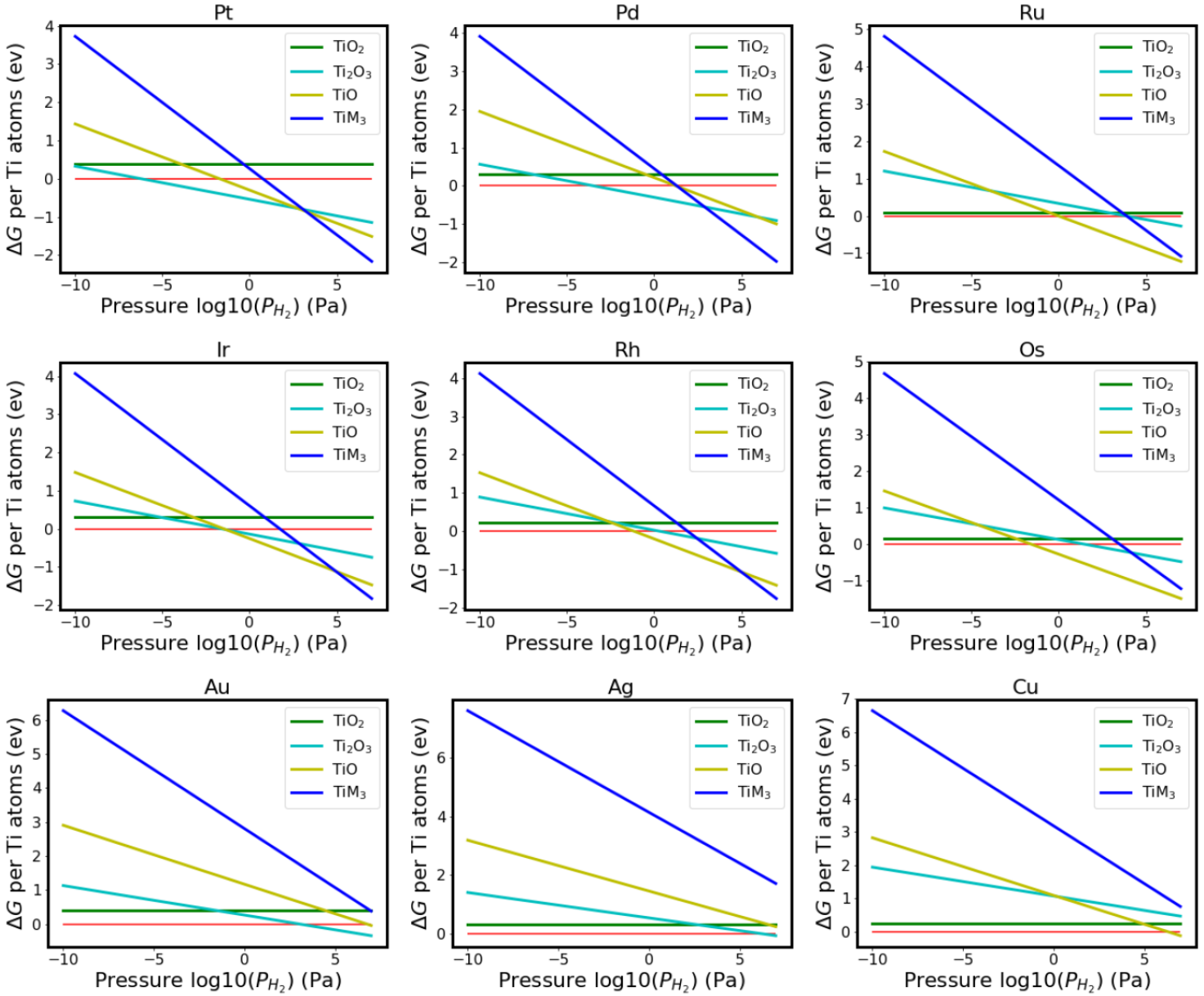
2. Thermodynamic driving force behind the surface overlayer growth?

Subsequent exposure to oxygen segregates the titanium from the alloy, and a thicker titania overlayer forms. This thicker fully oxidized overlayer is stable in oxygen.

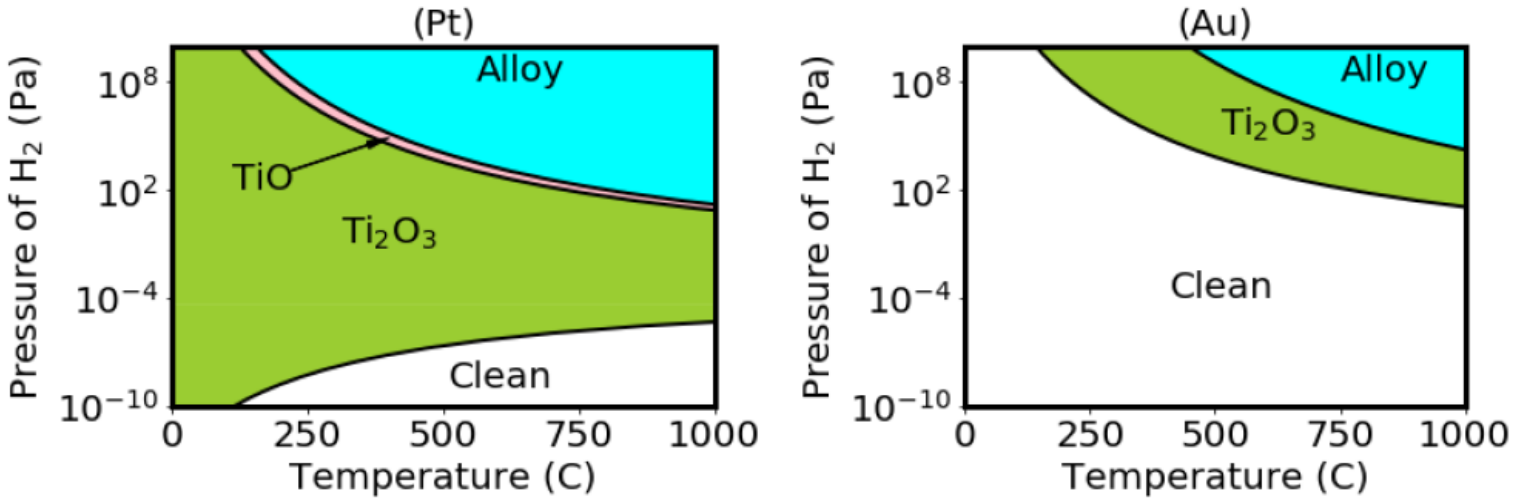
3. Any way to predict and control the SMSI?

A. Beck, X. Huang, L. Artiglia, M. Zabilskiy, X. Wang, P. Rzepka, D. Palagin, M. Willinger, J. A. van Bokhoven, *Nature Communications* **11**, 3220 (2020)

Phase diagrams: 600°C



Phase diagrams: temperature and pressure



- The stability range of overlayers is sensitive to the temperature and pressure.
- At higher temperatures and higher hydrogen partial pressures, the alloy overlayers are energetically favorable.
- By either lowering the temperature or the hydrogen partial pressure, the overlayers transform in the following order: alloy → TiO → Ti_2O_3 → clean surfaces.

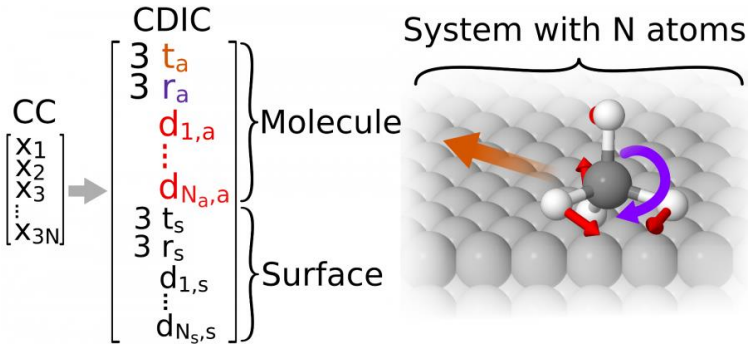
Conclusions

1) The oxide–metal interaction strength at the interfaces changes substantially, ranging from particularly strong (Pt and Pd) to relatively weak (Cu and Ag).
2) Surface has to be reducible to facilitate strong interaction with the metal through the electron transfer from the cation to the metal.
3) The oxide/metal configurations are sensitive to the reducing atomosphere used to induce the SMSI.
4) It is possible to correlate SMSI to alloy formation energy

X. Wang, A. Beck, J. A. van Bokhoven, D. Palagin,
“Thermodynamic insights into strong metal-support interaction of transition-metals and titania” (2020)

TheoCat@LSK highlights:

1) Methane to Methanol
   a) active sites
   b) mechanism
2) Water gas shift
3) Supported nanoparticles
4) Theory development

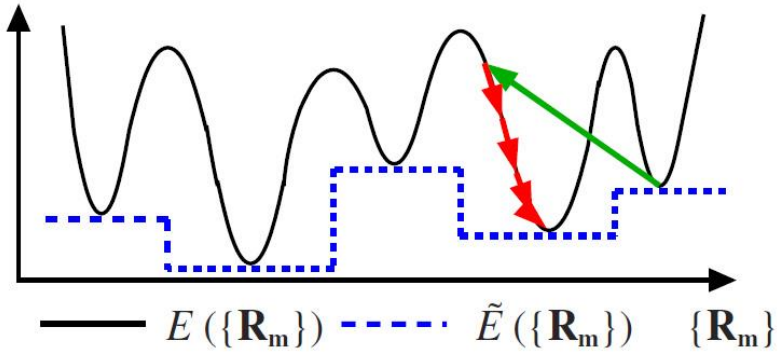


Global optimization is good...

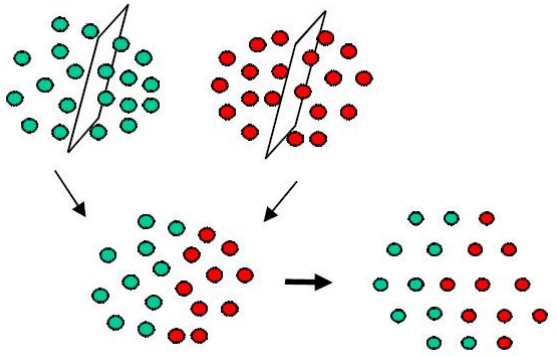
- We deal with simulations of very complex systems
- DFT + computational power makes the calculation of electronic PES easy (easier), but...
- the larger the system, the more complicated the shape of the PES is
- exact knowledge of structure is crucial to everything else
- local optimization of several chemically sensible structures is not sufficient

That's what global optimization is for

basin hopping (BH):



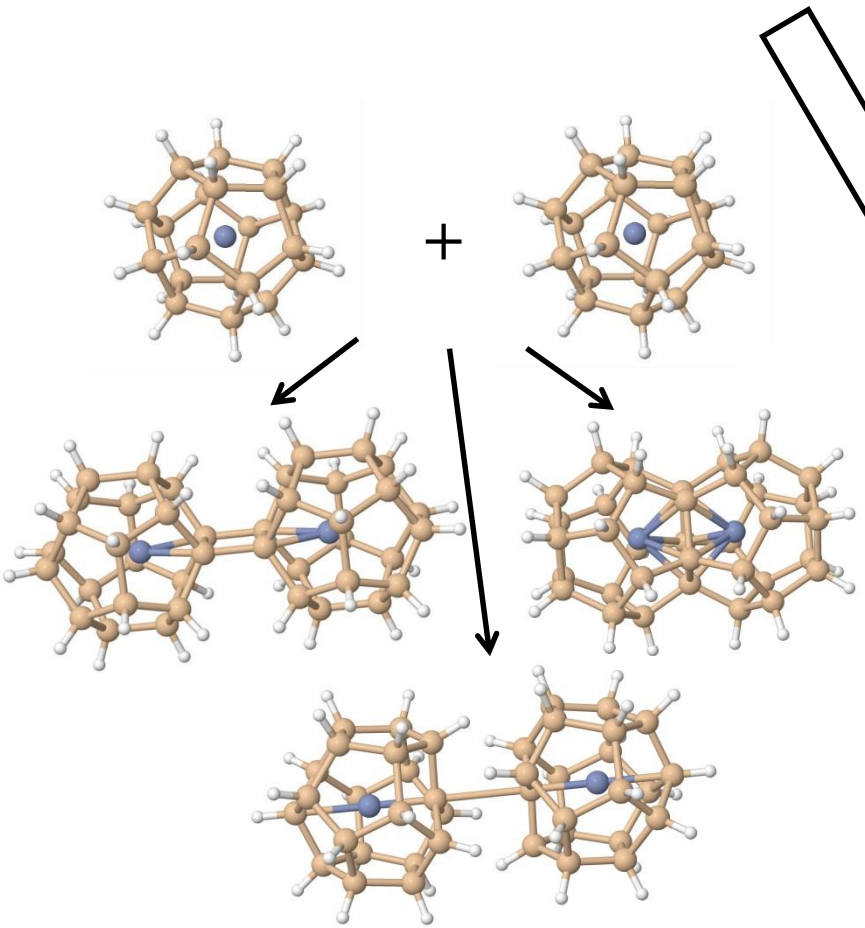
genetic algorithms (GA):

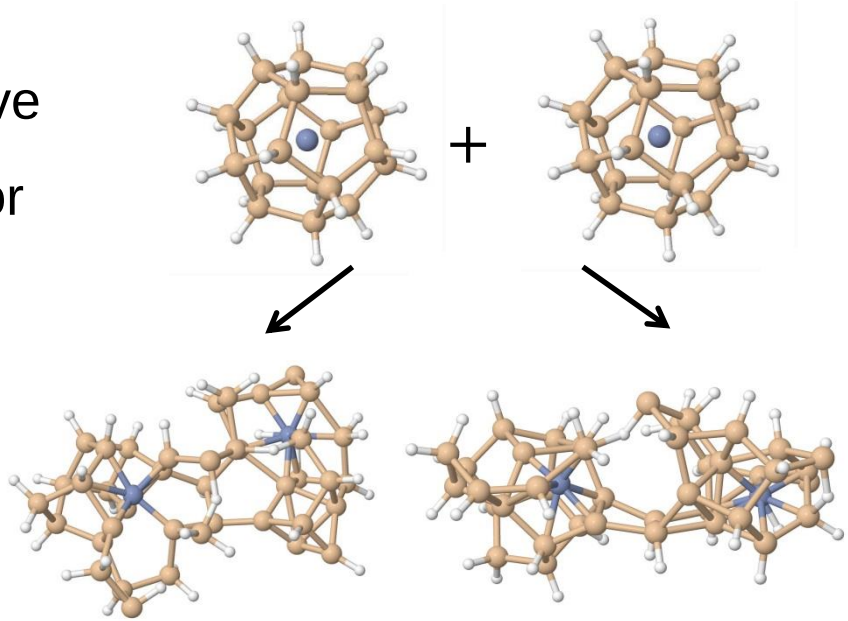


D. J. Wales, J. P. K. Doye, *J.* Phys. Chem. A **101**, 5111 (1997)

but: materials science is a special case

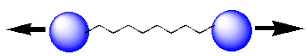
- Sampling all of the PES is expensive
- Most of the minima are irrelevant for materials science applications



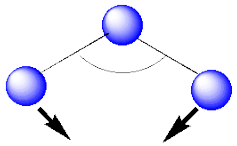


- Relevant reaction pathways
- Chemically-relevant intermediates
- Low-lying structures retaining original structural motifs

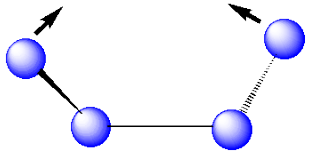
Optimization with delocalized internals



Bond Stretching



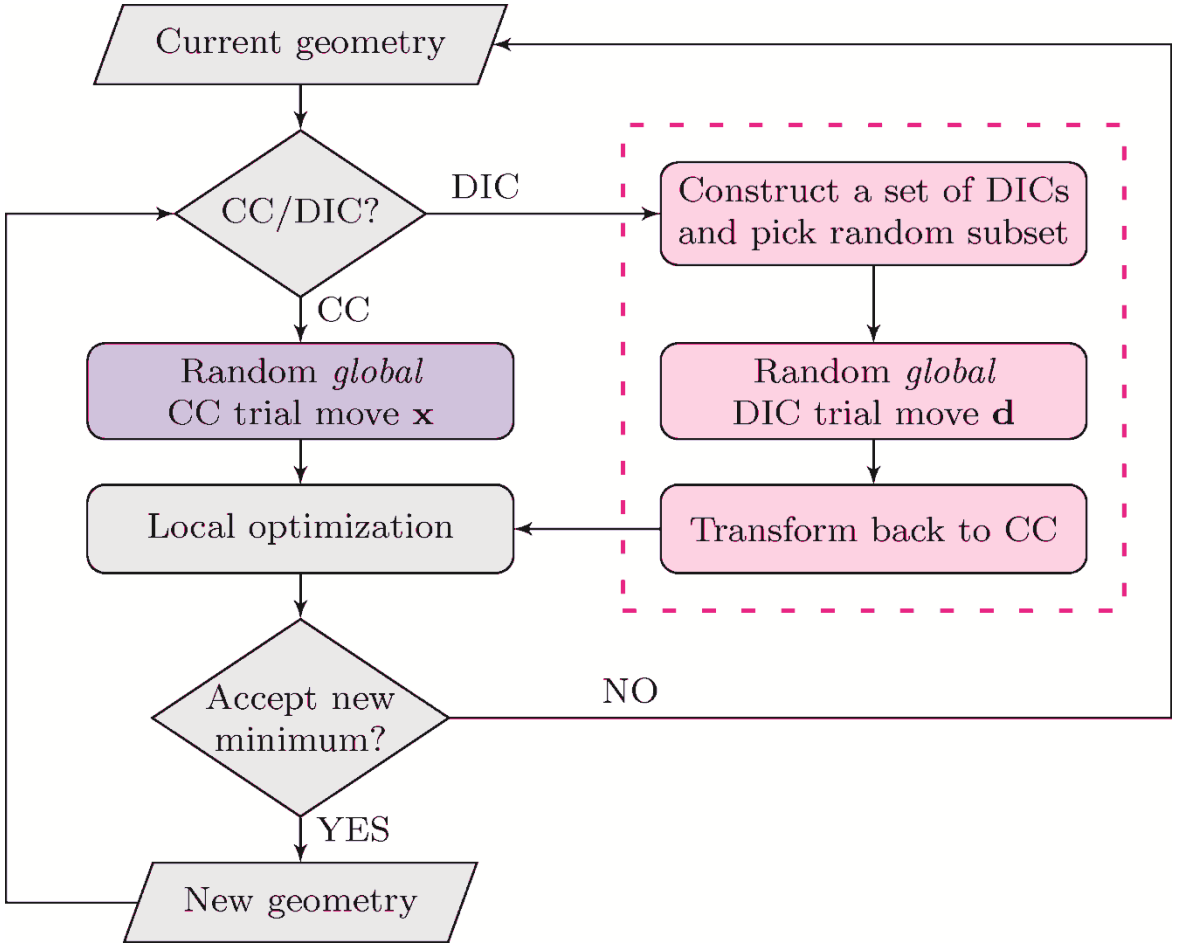
Valence angle bending



Torsion

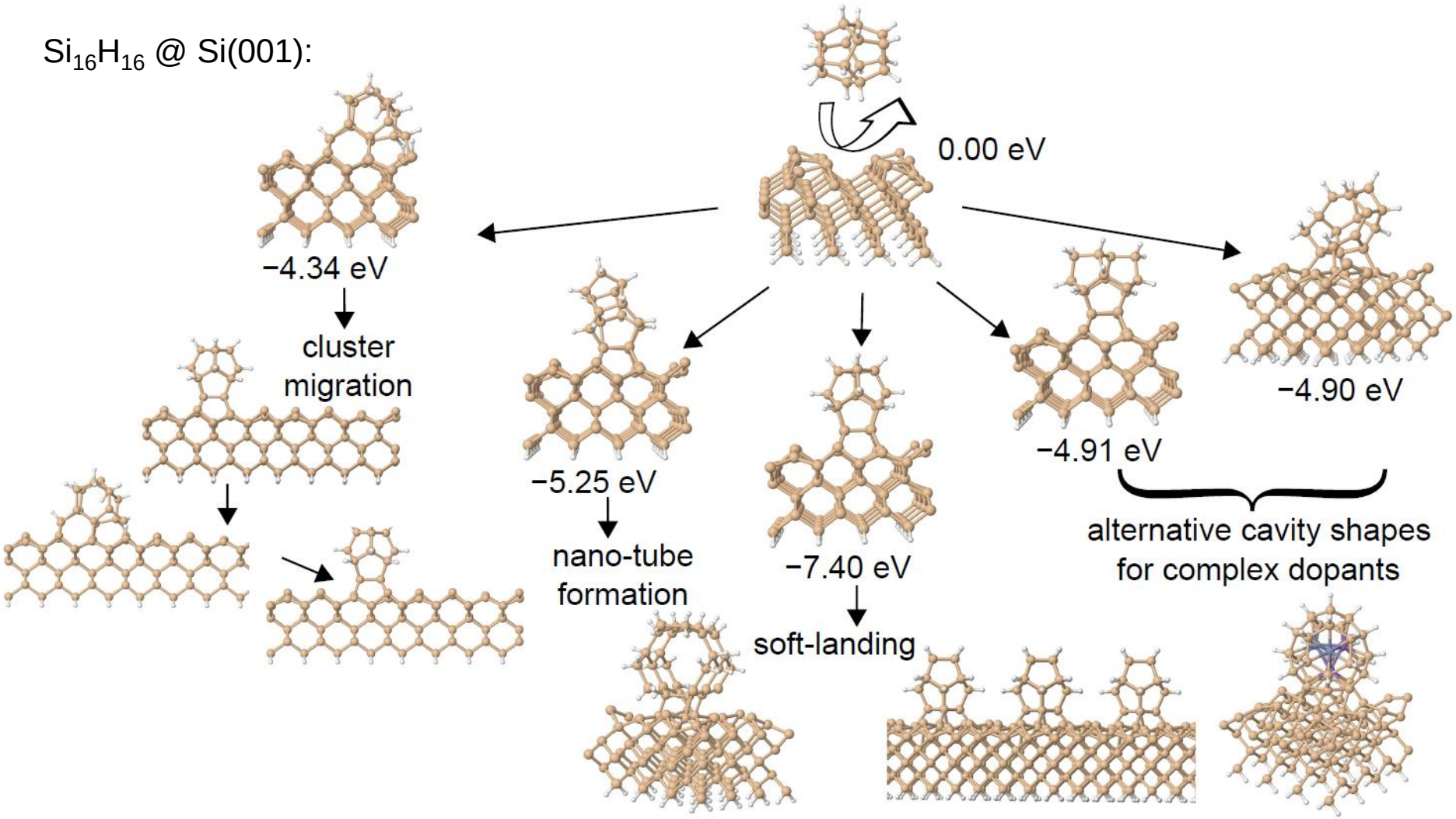
$$\mathbf{q} = B\mathbf{x}$$

$$B = \frac{d\mathbf{q}}{d\mathbf{x}}$$



Optimization with delocalized internals

$Si_{16}H_{16}$ @ Si(001):

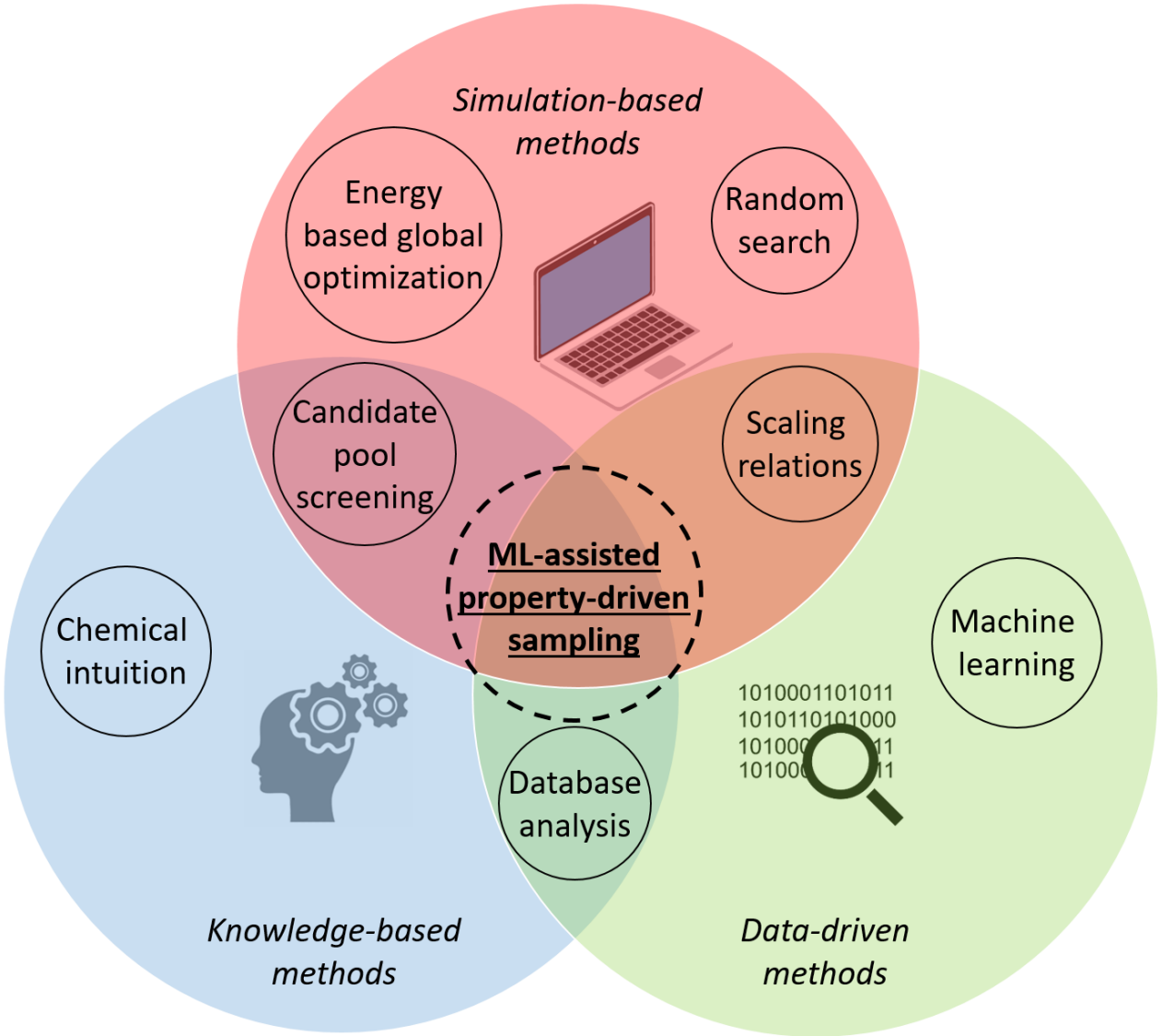


Efficient identification of relevant low-lying isomers!

C. Panosetti *et al.*, *Nano Lett.* **15**, 8044 (2015)

K. Krautgasser *et al.*, *J. Chem. Phys.* **145**, 084117 (2016)

Outlook: what's next for theoretical materials science?



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Interested in a PhD project?

Contact me!

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