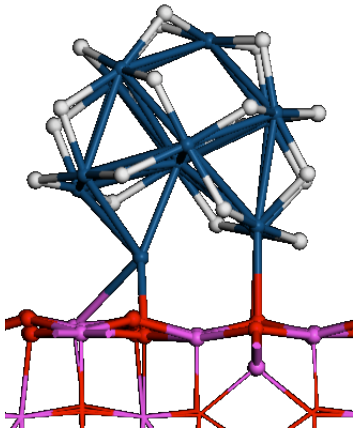
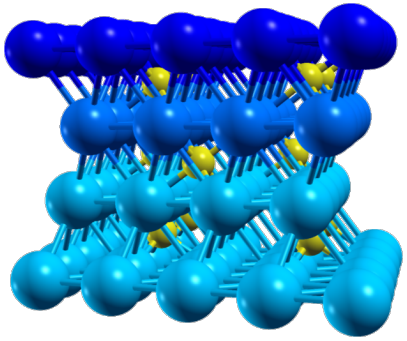
Computational Catalysis



Philippe Sautet

Institute of Chemistry
University of Lyon



Quantum Chemistry

Erwin Schrödinger

Mathematics

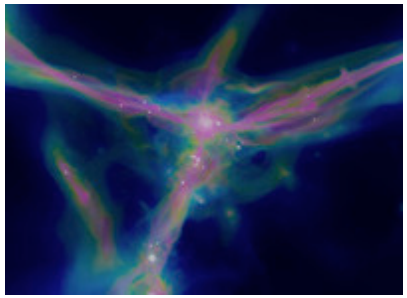
Physics

Computer science

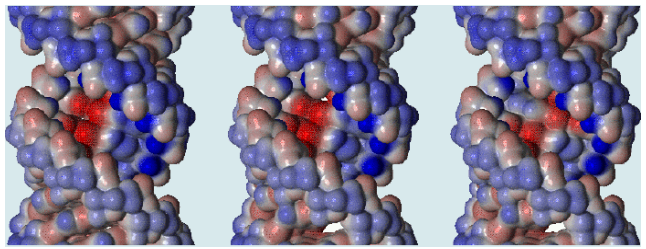
$H_{el}\Psi = E_{el}\Psi$

Materials science
Chemistry

Astronomy

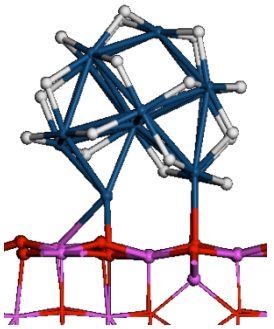


Life science



DNA

Quantum Chemistry



Catalysis ?

Erwin Schrödinger

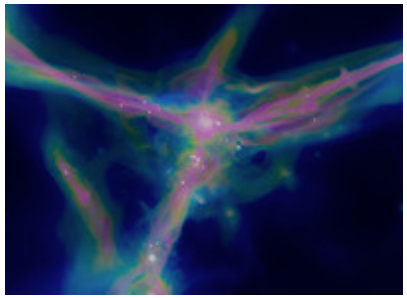
Mathematics

Materials science
Chemistry

Physics

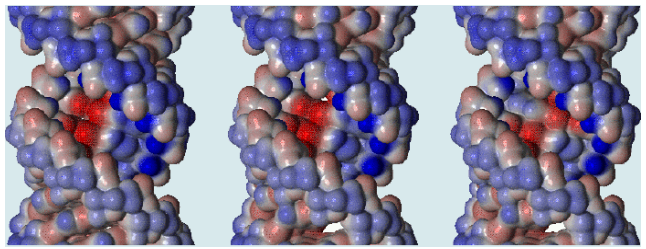
$H_{el}\Psi = E_{el}\Psi$

Astronomy



Computer science

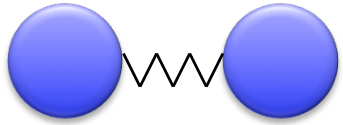
Life science



DNA

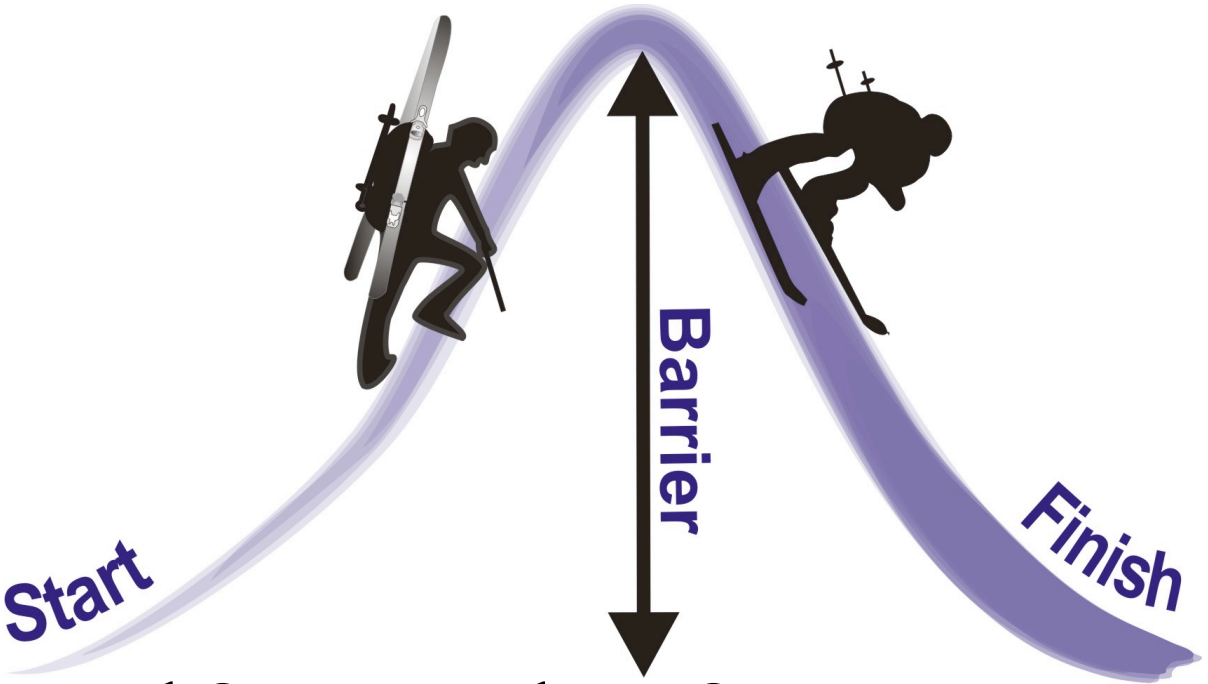
Breaking bonds

Breaking bonds requires energy



Chemical reaction

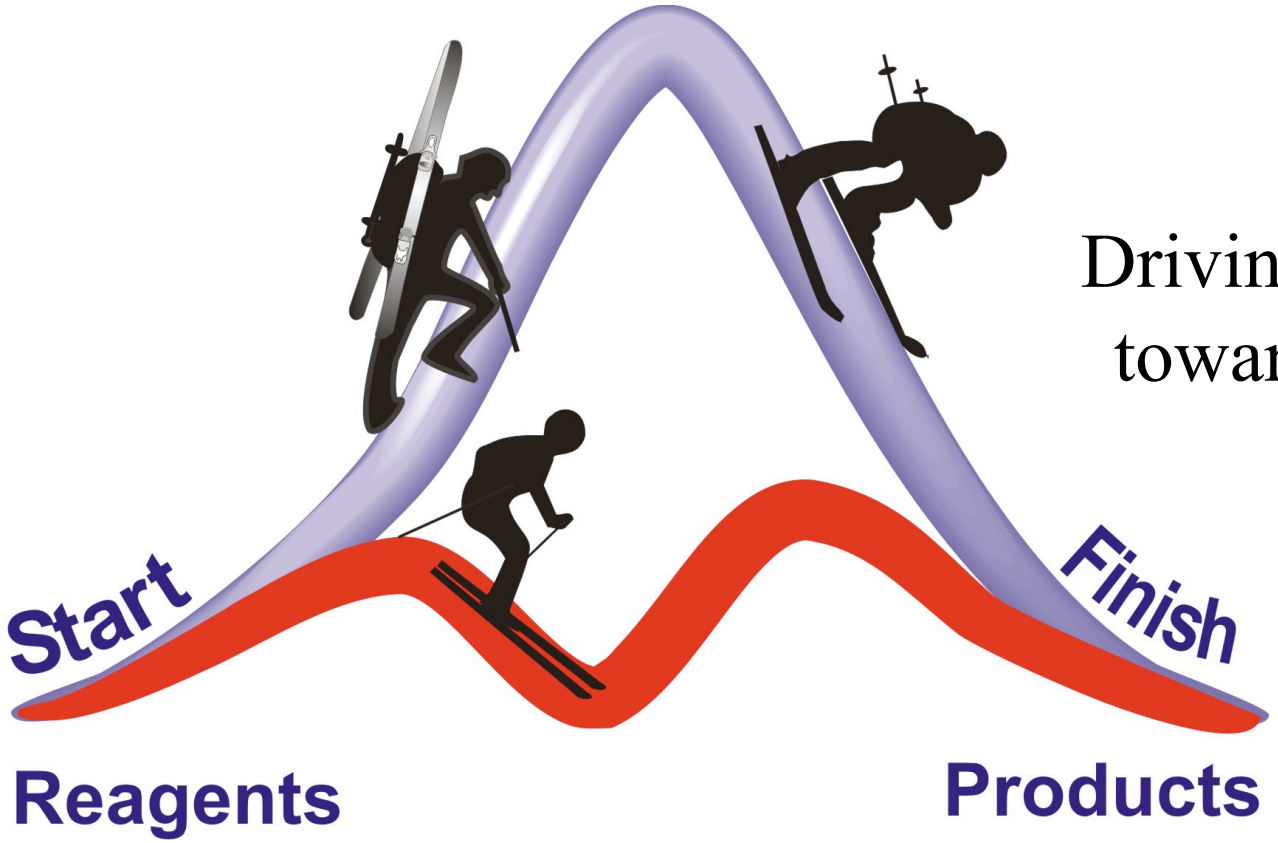
energy: heat
pressure
reactant



Selectivity control ? By products?

Making chemical reactions easier with catalysis

Lowering the energy barrier, finding an easy path



Driving chemical reaction towards wanted product

without catalyst

with catalyst

Outline

1. Introduction to Density Functional Theory
2. Applications to heterogeneous catalysis

Some References

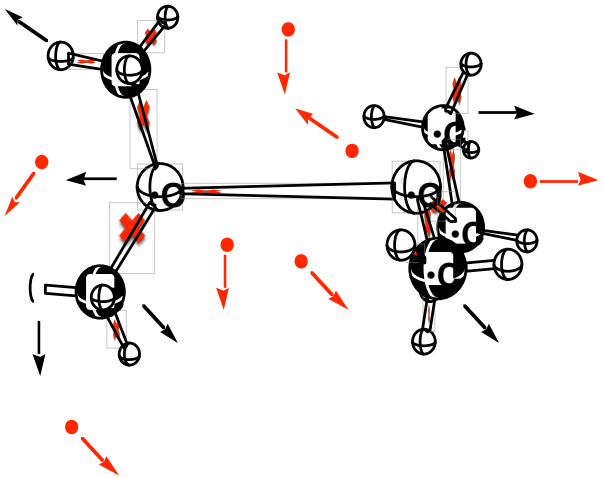
- Koch & Holthausen, *A Chemist's Guide to Density Functional Theory.*
- Par & Yang, *Density Functional Theory of Atoms & Molecules.*
- Kohanoff & Gidopoulos, Density Functional Theory: Basics, New Trends and Applications, in *Handbook of Molecular Physics and Quantum Chemistry.*
- *Sautet & van Santen,* Computational Methods in Catalysis and Materials Science, Wiley-VCH (2009)
- P. Sautet "Quantum chemistry as a tool for an atomic scale description of heterogeneous catalyst" in Characterization of Solid Materials and Heterogeneous Catalysts: From Structure to Surface Reactivity, M. Che and J. C. Védrine Edts, Wiley (2012)

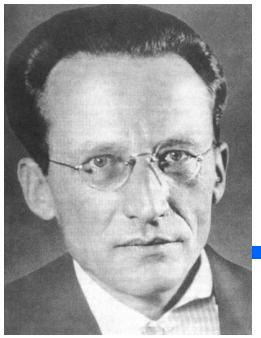
And of course…

- Hohenberg & Kohn, Phys. Rev. 136, B864 (1964).
- Kohn & Sham, Phys. Rev. 140, A1133 (1965).

- *p* nuclei
- *n* electrons

- N body problem (N=n+p)





Schrödinger equation

Erwin Schrödinger 1925

$$H\Psi = E\Psi$$

- Ψ, the many-body wavefunction, contains all the information that can be obtained about a microscopic physical system.
- Ψ is complicated!… 4 variables per electron…
- Much of electronic structure theory is concerned with obtaining approximate solutions to Ψ.

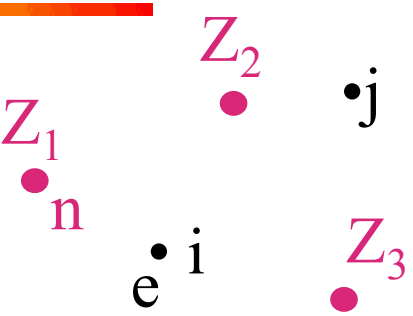
$$\Psi(r_1, s_1, r_2, s_2, \cdots, r_N, s_N)$$

$$\left|\Psi(r_1, s_1, r_2, s_2, \cdots, r_N, s_N)\right|^2$$ Probability to find electrons at r_1, s_1, ..., r_N, s_N

Born-Oppenheimer Approximation

$$H\Psi = E\Psi$$

$$H = T_n + T_e + V_{nn} + V_{ne} + V_{ee}$$



• Electrons move much more rapidly than nuclei…consider the nuclei as fixed

$$H_{el}\Psi = E_{el}\Psi$$

$$H_{el} = T_e + V_{ne} + V_{ee}$$

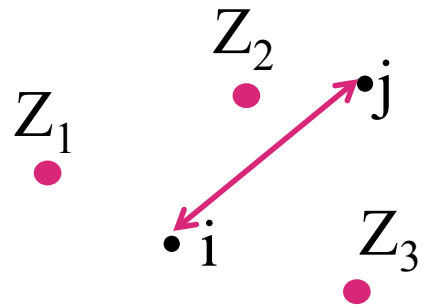
$$E_{TOT} = E_{el} + E_{nn}$$

• This adiabatic approximation is usually very good $m_Z >> m_e$….worst case, the proton, is 1800:1

• In certain cases, however, quantum nuclear effects can be important, for e.g. solid H, H diffusion, enzymes, H tunnel effect.

Hamiltonian

$$H_{el}\Psi = E\,\Psi$$



$$\hat{H}_{el} = \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee}$$

$$\hat{T}_e = \sum_{i=1}^{N}\left(-\tfrac{1}{2}\nabla_i^2\right)$$

$$\hat{V}_{ne} = \sum_{i=1}^{N} v(r_i)$$

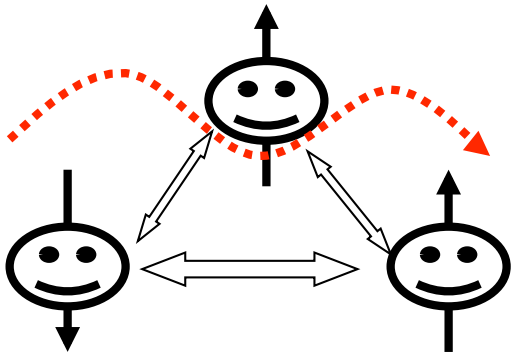
$$\hat{V}_{ee} = \sum_{i<j}^{N} \frac{1}{|r_i - r_j|}$$

$$v(r_i) = -\sum_{I=1}^{P} \frac{Z_I}{|R_I - r_i|}$$

$$\nabla_i^2 = \frac{\delta^2}{\delta x_i^2} + \frac{\delta^2}{\delta y_i^2} + \frac{\delta^2}{\delta z_i^2}$$

Hamiltonian

$$\hat{V}_{ee} = \sum_{i<j}^{N} \frac{1}{|r_i - r_j|}$$



- V_{ee} is the problem term; motion of the electrons is strongly coupled

first route : ab initio quantum chemistry

Wavefunction methods: non-interacting reference systems -> Ψ_0

Hartree (1928, no exchange or correlation)

Hartree-Fock (1930, exact exchange)

Post Hartree-Fock (exact, very small systems, 20 atoms)

Density Functional Theory

The idea:

Ψ is too complicated to determine. Instead use the electron density, $\rho(r)$, as the fundamental variable.

Electron density

$$\rho(r_1) = N \int \cdots \int \left|\Psi(r_1, s_1, r_2, s_2, \cdots, r_N, s_N)\right|^2 dr_2 \cdots dr_N ds_1 \cdots ds_N$$

3 variables ← 4N variables

$$\int \rho(r) dr = N$$

- Is there enough information in the electronic density ?

External potential

$$H_{el}\Psi = E\,\Psi$$

$$\hat{H}_{el} = \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee}$$

$$\hat{T}_e = \sum_{i=1}^{N}\left(-\tfrac{1}{2}\nabla_i^2\right)$$

$$\hat{V}_{ne} = \sum_{i=1}^{N} v(r_i)$$

$$\hat{V}_{ee} = \sum_{i<j}^{N} \frac{1}{|r_i - r_j|}$$

$$\nabla_i^2 = \frac{\delta^2}{\delta x_i^2} + \frac{\delta^2}{\delta y_i^2} + \frac{\delta^2}{\delta z_i^2}$$

V_{ext}

Density Functional Theory

Hohenberg and Kohn (1964) Theorem I:

1. *"…that the external potential V_{ext} is (to within a constant) a unique functional of $\rho(r)$; since, in turn $V_{ext}(r)$ fixes H we see that the full many particle ground state is a unique functional of $\rho(r)$"*

…electron density determines H, therefore, determines all properties of the system.

$$\rho_0 \Rightarrow H \Rightarrow \Psi_0 \Rightarrow E_0$$ (…and all other properties)

Density Functional Theory

Hohenberg and Kohn (1964) Theorem II:

The variational minimum of the energy is exactly equivalent to the true ground-state energy.

$$E[\rho_{trial}] \geq E_0$$

Analogous for the variationnal principle for wavefunctions

Density Functional Theory

- …decompose the energetic contributions to the total density:

$$\hat{H}_{el} = \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee}$$

$$E_0[\rho_0] = T_e[\rho_0] + E_{ne}[\rho_0] + E_{ee}[\rho_0]$$

Kinetic energy
easy

easy

$$\int \rho(r) v(r)\, dr$$

?????

Density Functional Theory

$$E_{ee}[\rho] = \tfrac{1}{2}\int\int \frac{1}{r_{12}}\rho(r_1)\rho(r_2)d\vec{r}_1 d\vec{r}_2 + E_{ee-nc}[\rho]$$

Classical (Coulomb) *non-classical*

Exchange & Correlation

$$E_0[\rho_0] = T_e[\rho_0] + E_{ne}[\rho_0] + E_{ee-cl}[\rho] + E_{XC}[\rho]$$

Minimize the total energy functional by applying the variational principle:

Density Functional Theory

Kohn & Sham (1965)

- introduced the idea of a ***non- interacting reference system composed of one electron wavefunctions.***
- The density resulting from the sum of the non-interacting, **Kohn-Sham orbitals**, exactly equals the ground state density of the real (interacting) system:

$$\rho_s(\vec{r}) = \sum_i^N \sum_s \varphi(\vec{r},s)^2 = \rho_0(\vec{r})$$

- Then obtain the exact kinetic energy of the non-interacting system:

$$T_s = -\tfrac{1}{2} \sum_i^N \varphi_i \nabla^2 \varphi_i$$

- …which is not the true kinetic energy of the interacting system:

$$T_s \neq T \quad (T_s \leq T)$$

Density Functional Theory

• …get the resulting set of SCF equations (Kohn-Sham):

$$\left(-\tfrac{1}{2}\nabla^2 - \sum_A^M \frac{Z_A}{r_{1A}} + \int \frac{1}{r_{12}}\rho(\vec{r}_2)d\vec{r}_2 + V_{XC}\right)\varphi_i(r) = \varepsilon_i\varphi_i(r)$$

$$\left(-\tfrac{1}{2}\nabla^2 + V_{ne} + V_H + V_{XC}\right)\varphi_i(r) = \varepsilon_i\varphi_i(r)$$

• V_{XC} is simply defined as the functional derivative of E_{XC} with respect to ρ:

$$V_{XC} \equiv \frac{\delta E_{XC}}{\delta_\rho}$$

Self interaction

• In principle exact, but don't know form of E_{XC}

LDA, GGA and further

Exchange & Correlation

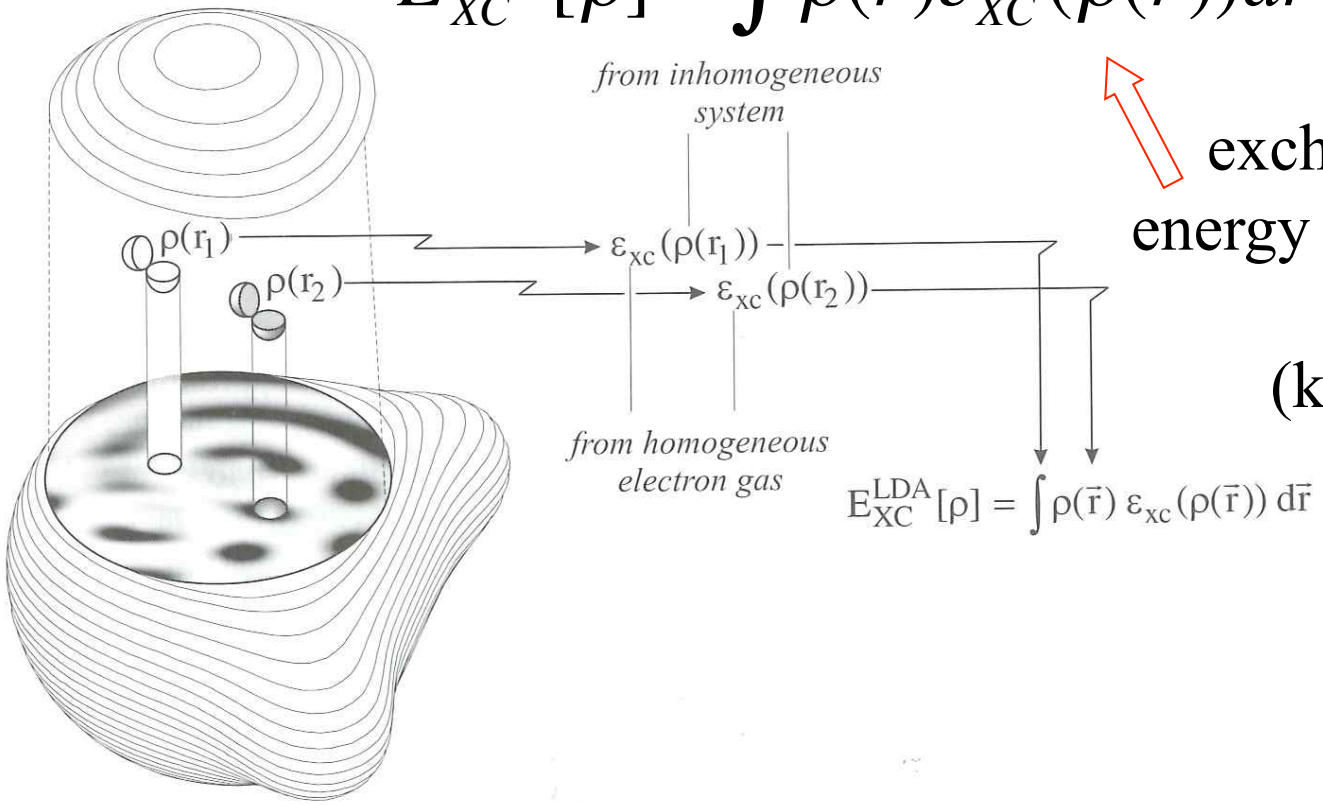
DFT IN PRINCIPLE EXACT

DFT IN PRACTICE APPROXIMATE E_{XC}

$$V_{XC} \equiv \frac{\delta E_{XC}}{\delta_\rho}$$

Local Density Approximation

$$E_{XC}^{LDA}[\rho] = \int \rho(\vec{r})\varepsilon_{XC}(\rho(\vec{r}))d\vec{r}$$



exchange-correlation energy of uniform electron gas (known exactly)

$\varepsilon_{XC}(\rho_0)$

ρ_0

From Koch & Holthausen, *A Chemist's Guide to Density Functional Theory*

Exchange & Correlation

•Generalized Gradient Approximation:

•…the exchange-correlation energy has a gradient expansion

• However, gradient expansion difficult…ill-behaved.

•…can easily violate one or more of the exact conditions required for the echange-correlation hole…forcing functionals to obey these rules yielded big improvements in the early nineties:

$$E_{XC}[\rho] = \int \rho(\vec{r})\varepsilon_{XC}(\rho(\vec{r}))d\vec{r} + \int F_{XC}[\rho(\vec{r}),\nabla\rho(\vec{r})]dr$$

Asked to satisfy various formal conditions

Exchange & Correlation

- ***…some trends within the LDA***
- Favours more homogeneous systems
- Overbinds molecules & solids (within 10%)
- Chemical trends usually correct
- Bad for weak bonds, especially H bonds
- Self interaction…affects dissociation limit & ionization energies

- ***…some trends of the GGAs***
- Improve binding energies & atomic energies
- Improve bond length & angles
- Improve energetics, bond lengths & dynamical properties of H_2O and ice.
- 4d-5d transition metal lattice constants worse than LDA
- Semiconductors are marginally better described

Summary

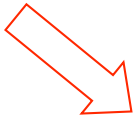
$$H\Psi = E\,\Psi$$

$$H = T_n + T_e + V_{nn} + V_{ne} + V_{ee}$$

Adiabatic Approximation

$$H_{el}\Psi = E_{el}\Psi$$

$$H_{el} = T_e + V_{ne} + V_{ee}$$



Wavefunction methods: non-interacting reference systems -> Ψ_0

Hartree (no exchange or correlation)

Hartree-Fock (exact exchange)

Post Hartree-Fock

Density based approaches (DFT)

$\rho_0 \Rightarrow H \Rightarrow E_0$

KS non-interacting reference system -> ρ_0

In principle exact, but don't know form of E_{XC}

Some Comparisons

• ***Atomization energies of small main group molecules*** (taken from Koch & Holthausen)

	Mean absolute (kcal/mol)	Maximum absolute (kcal/mol)
HF[a]	74.5	170.0
LDA	43.6	
GGA (BLYP)[a]	5.0	15.8
GGA (B3LYP)[a]	5.2	31.5

• There are many different types of GGA exchange-correlation functionals.
• Their performance is usually tested on 'training sets'…large groups of small molecules, mainly from the first two rows of the periodic table. Here the "G2" training set was used[a].

Some Comparisons

• ***H-bonds***: H_2O-H_2O dimer (taken from Koch & Holthausen)

	HF	BLYP	B3LYP	PW91	Experiment
ΔE(kcal/mol)	**3.5**	4.2	4.6	4.6	5.4±0.7
O-O (Deviation/A)	0.086	-0.003	-0.033		2.952

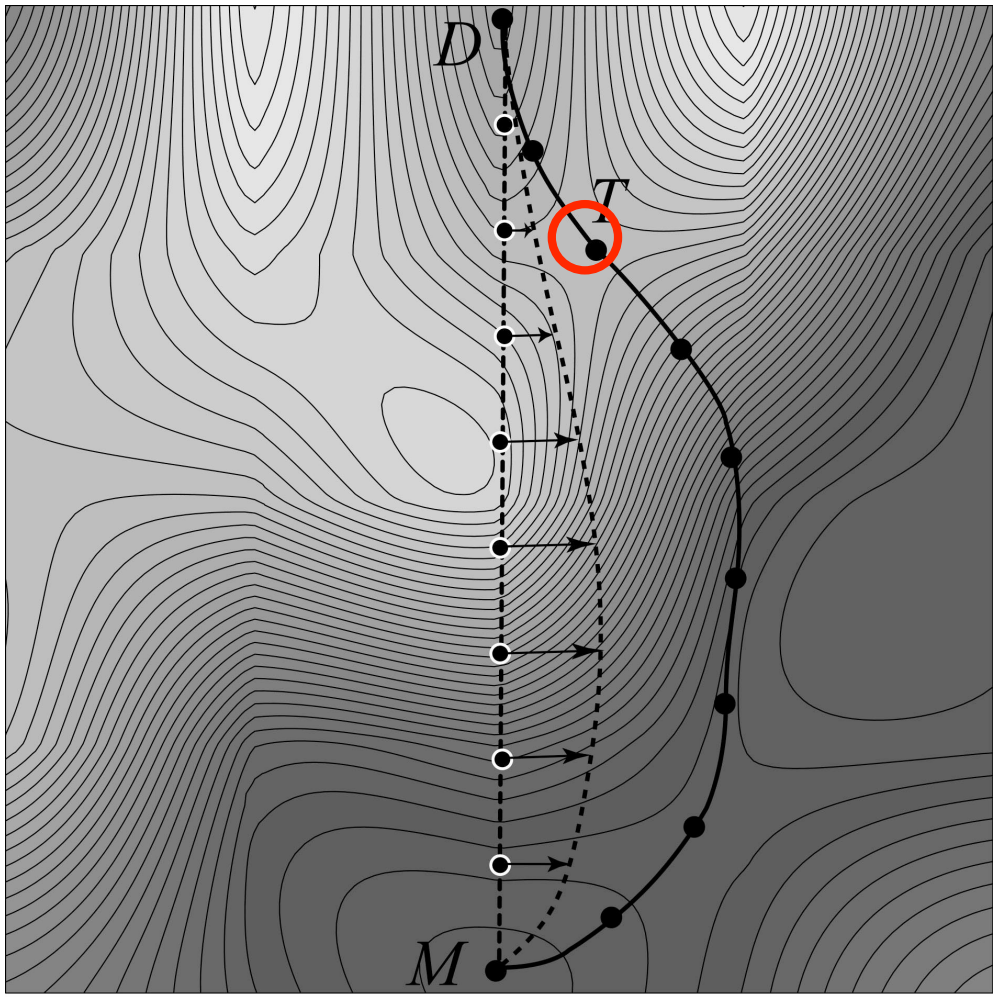
• All approaches ignore dispersion interactions (induced-dipole induced-dipole interactions.

Chemisorption systems (Hammer et al. Physical Review B, Vol. 59, 7413 (1999))

	$E_{chem,\beta}$					E^{exp}_{chem}
	LDA	PW91	PBE	revPBE	RPBE	
O(fcc)/Ni(111)	-6.68	-5.38	-5.27	-4.83	-4.77	-4.84 [a]
O(hol)/Ni(100)	-6.97	-5.66	-5.55	-5.10	-5.03	-5.41 [a]
O(hol)/Rh(100)	-6.64	-5.34	-5.23	-4.77	-4.71	-4.56 [a]
O(fcc)/Pd(111)	-5.34	-4.08	-3.98	-3.54	-3.49	
O(hol)/Pd(100)	-5.39	-4.14	-4.04	-3.59	-3.53	
σ_O	1.84	0.57	0.47	0.22	0.24	
CO(fcc)/Ni(111)	-2.85	-1.99	-1.88	-1.52	-1.49	-1.35 [a]
CO(hol)/Ni(100)	-3.05	-2.11	-2.00	-1.62	-1.58	-1.26 [a]
CO(brd)/Rh(100)	-3.02	-2.28	-2.16	-1.84	-1.81	-1.19 [a]
CO(fcc)/Pd(111)	-2.95	-2.07	-1.96	-1.59	-1.56	(-1.47) [b]
CO(brd)/Pd(100)	-2.77	-1.98	-1.87	-1.53	-1.50	-1.69 [a]
σ_{CO}	1.58 (1.49)	0.78 (0.64)	0.67 (0.54)	0.39 (0.25)	0.37 (0.23)	

- Very big improvement!

Reaction paths and transition states



- Potential energy surface
- Large number of degrees of freedom
- explorer in the dark

Nudged elastic band

Optimisation of TS
with quasi-newton method

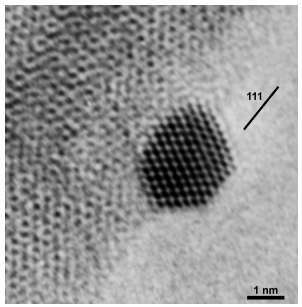
Vibrational characterization
of transition state

Outline

1. Introduction to Density Functional Theory
2. Applications to heterogeneous catalysis

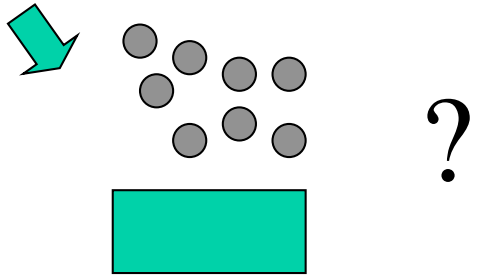
Heterogeneous Catalysis

Surface of solid catalyst



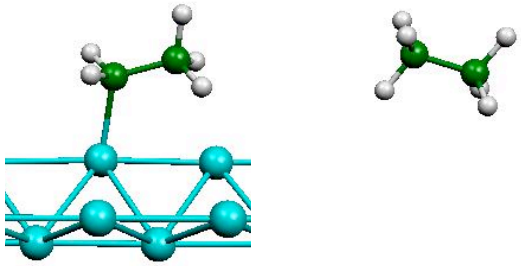
Surface structure
Reconstruction
Segregation
Steps, defects

Gas pressure Temperature



Active sites ?

Chemical reaction



Reaction pathways, kinetics and selectivity

Heterogeneous Catalysis

Active sites ?

Chemical reaction

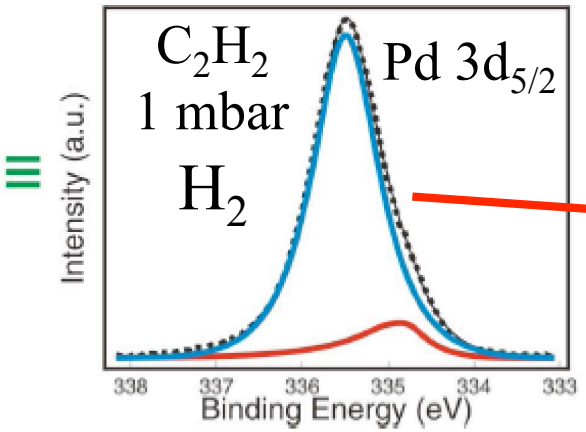
- Metal surface under gas pressure

- Supported nanometer size Pt particles under hydrogen

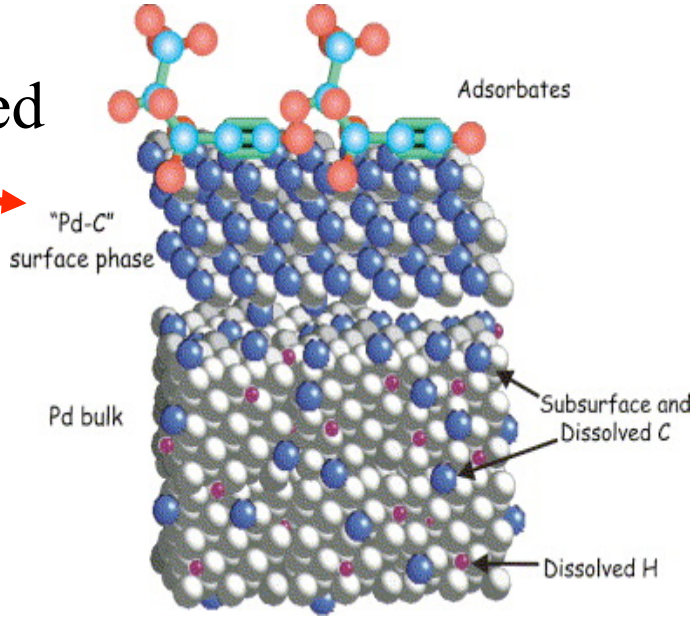
- Butadiene hydrogenation: Why is PtSn selective ?

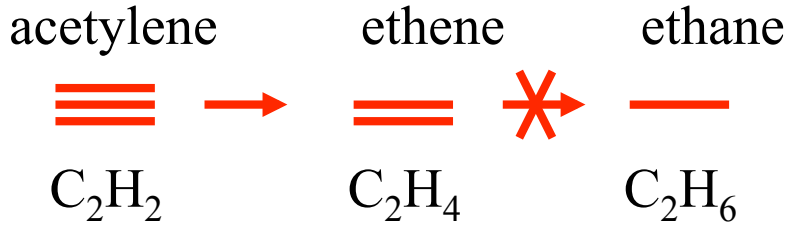
Selective hydrogenation of alkynes

- ***Pd is selective for hydrogenation of alkynes in alkenes***
- Recent models propose the formation of a Pd-C phase from in situ XPS



Alkynes:
Pd-C phase formed





[1] D. Teschner, R. Schlögl et al J. Catal. 242, 26 (2006)
[2] D. Teschner, R. Schlögl, et al *Science 320*, 86 (2008)

Selective hydrogenation of alkynes

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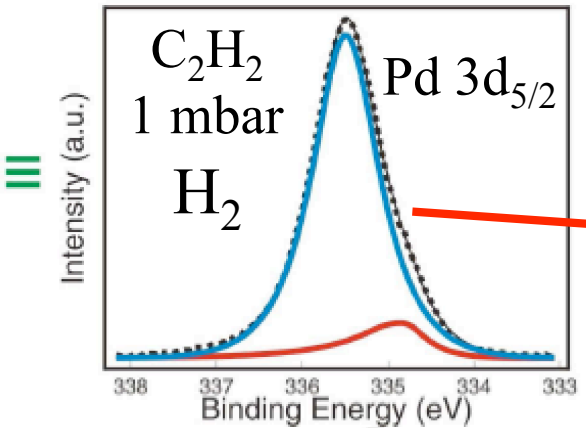
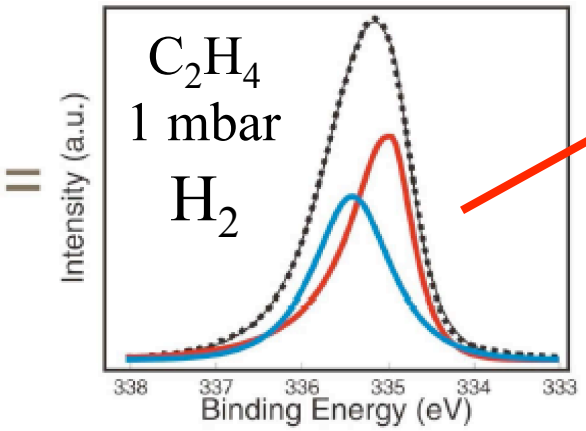
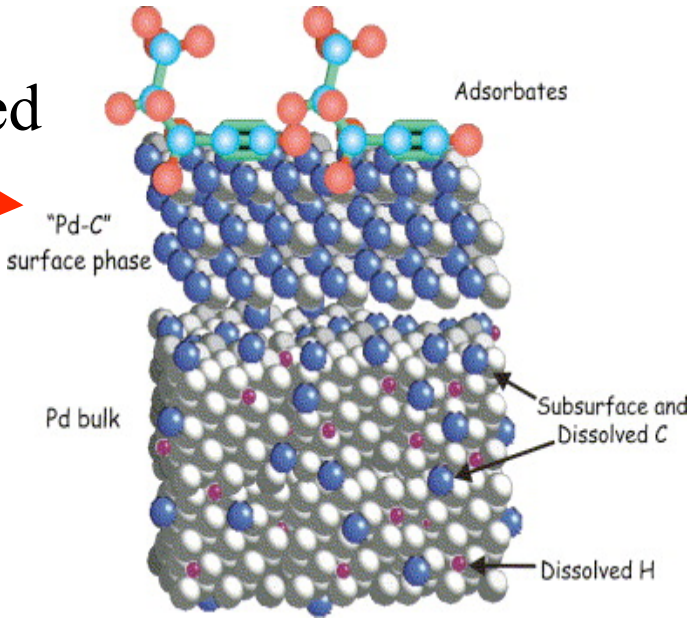


Alkynes:
Pd-C phase formed



Alkenes:
No Pd-C phase



[1] D. Teschner, R. Schlögl et al J. Catal. 242, 26 (2006)
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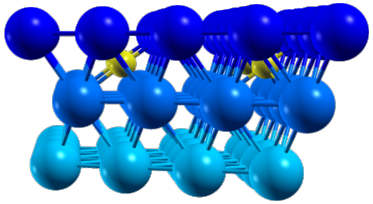
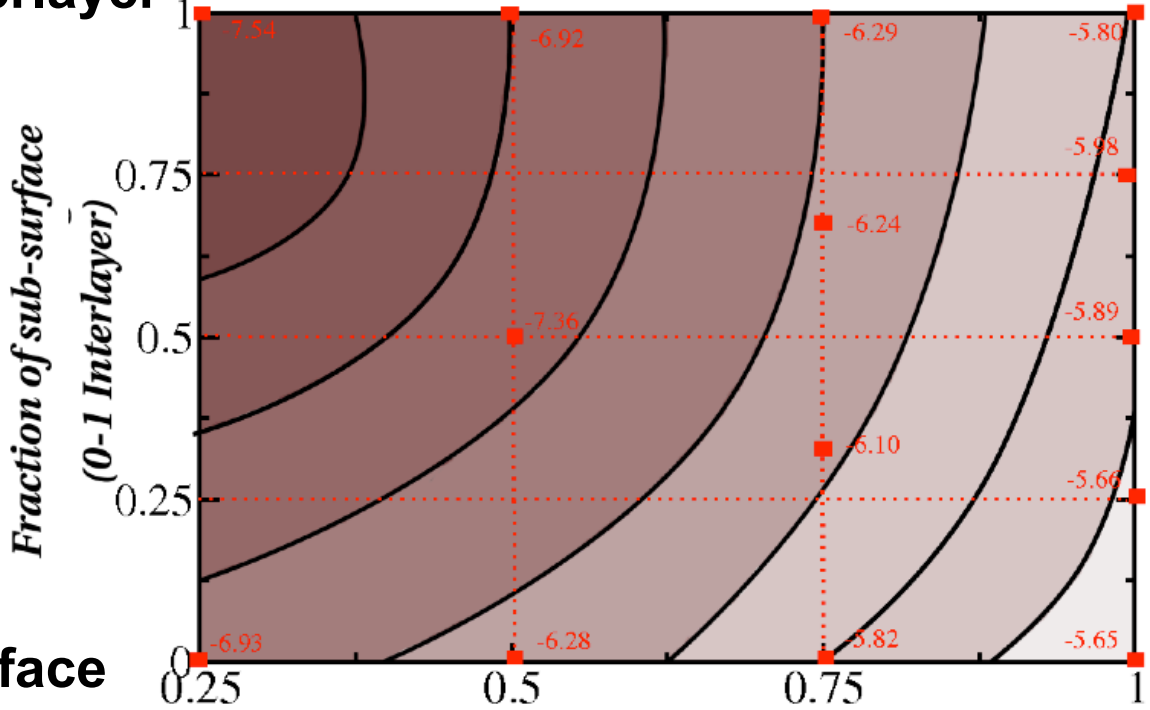
C on Pd(111): surface and subsurface

All C in 1st interlayer

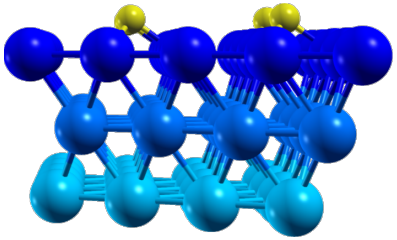


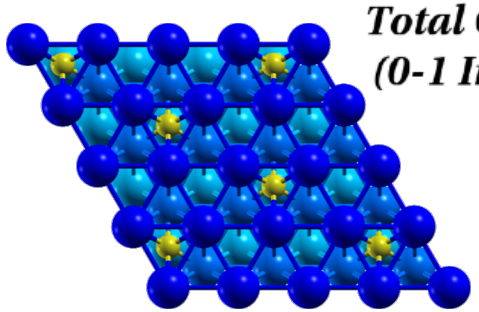
average carbon adsorption energy

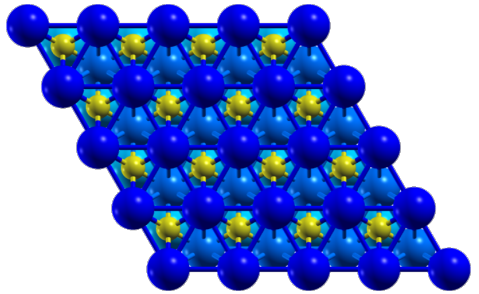


dark = more stable

All C on surface



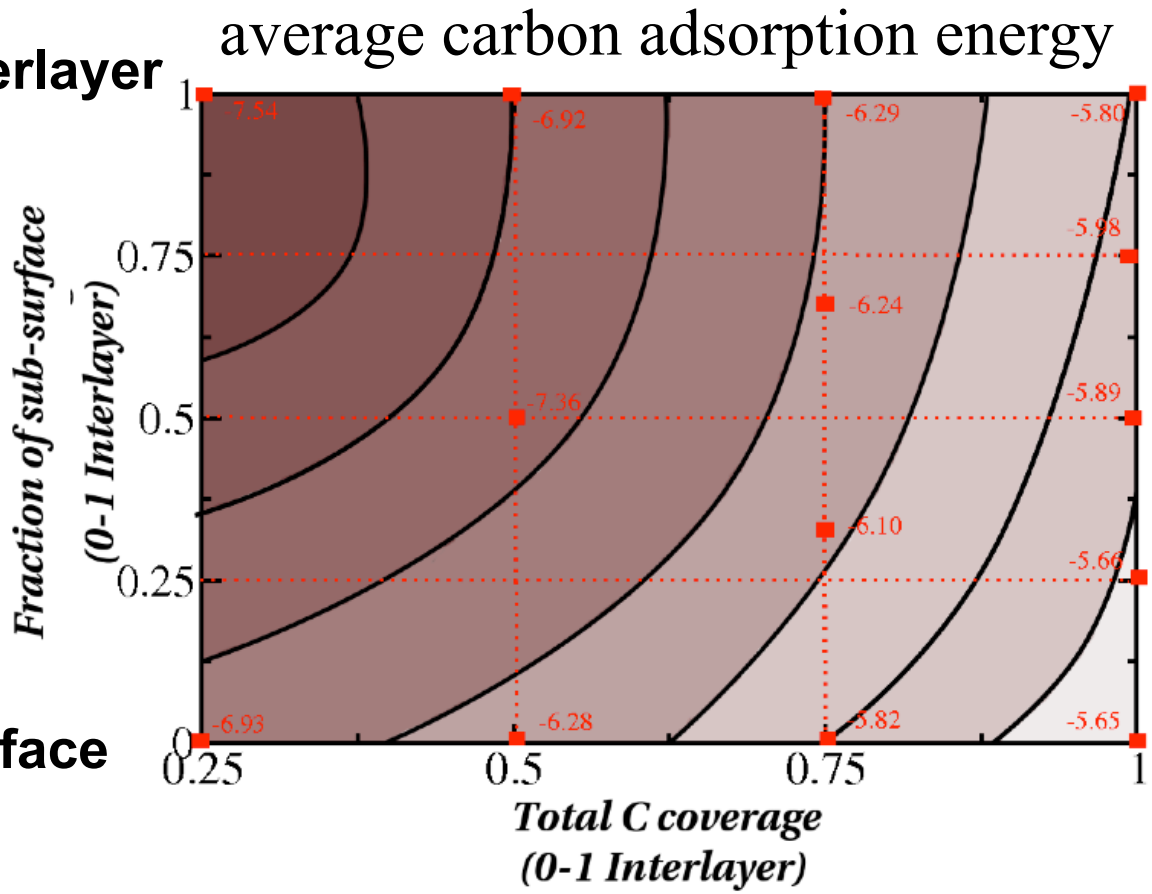




√3x√3, θ=1/3 ML

C on Pd(111): surface and subsurface

All C in 1st interlayer

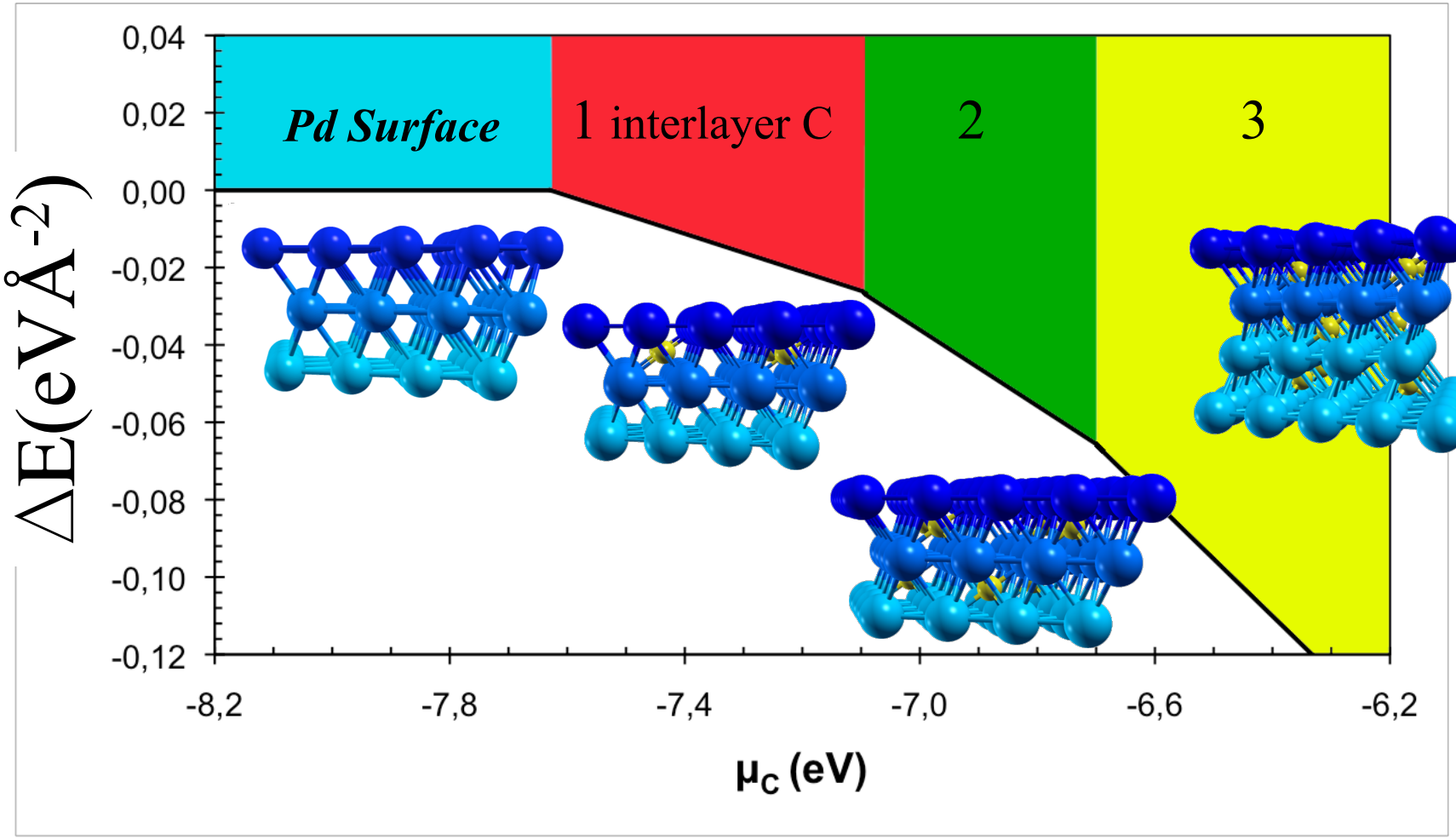


dark = more stable

All C on surface

- C prefers to be in the ***first interlayer***, rather than on the surface (by 60 kJ.mol^{-1})
- Repulsion in one interlayer after a coverage of 1/3 ML

Pd or Pd-C : stable termination vs μ_C



- Thickness of the Pd_{75}-C_{25} phase controlled by C chemical potential

Detre Teschner, PS et al, Angewandte Chemie 47, 9274 (2008)

The chemical potential of carbon is controlled by the reactant

$$C_2H_2 \leftrightarrow 2C + H_2$$

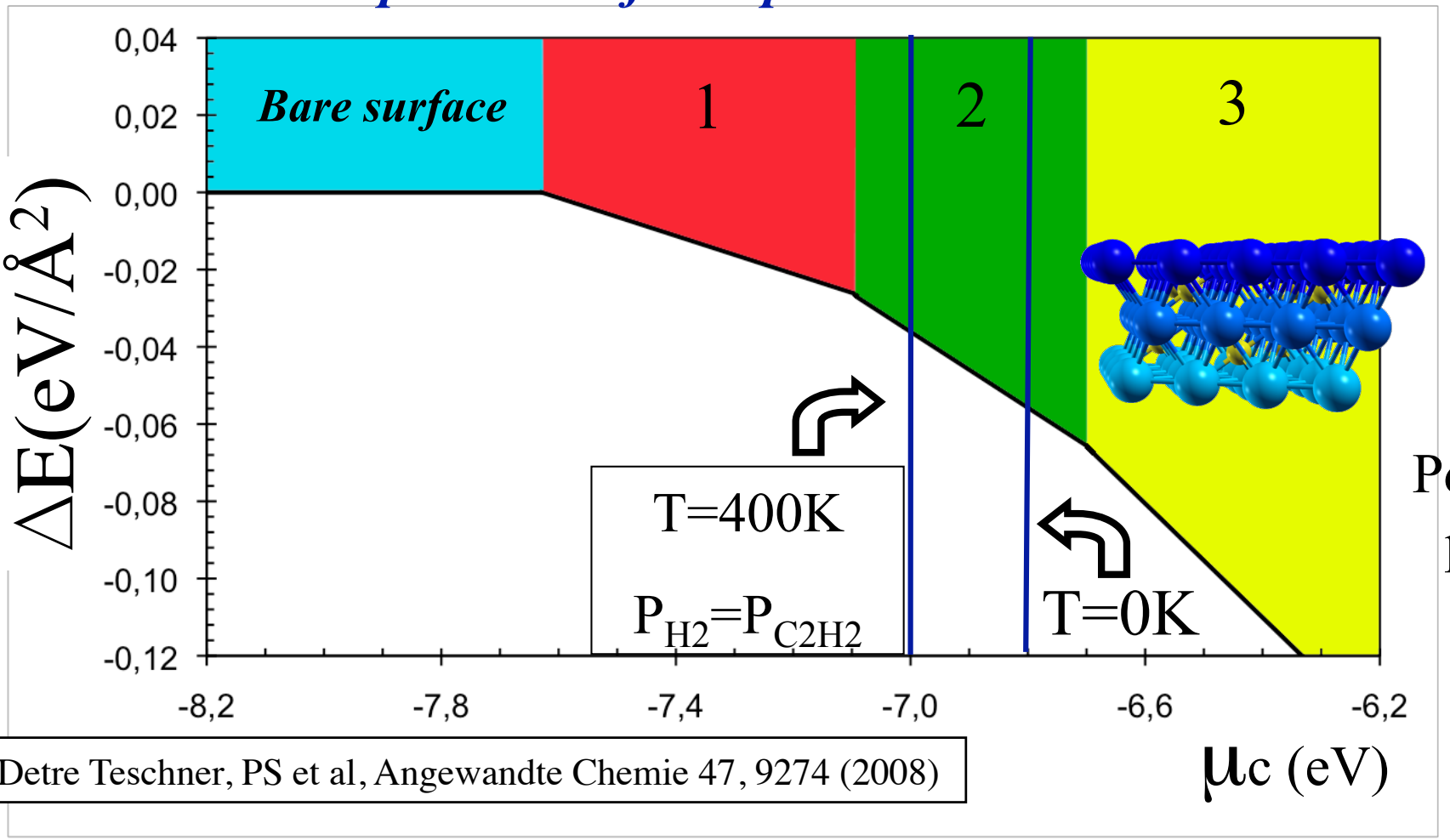
$$\mu_C = \frac{\mu_{C2H2} - \mu_{H2}}{2}$$

$$\mu_{C2H2}\left(T, p_{C2H2}\right) = \mu_{C2H2}{}^{0}\left(T\right) + kTLn\left(\frac{p_{C2H2}}{p^0}\right)$$

$$\mu_{H2}\left(T, p_{H2}\right) = \mu_{H2}{}^{0}\left(T\right) + kTLn\left(\frac{p_{H2}}{p^0}\right)$$

Pd surface under C_2H_2

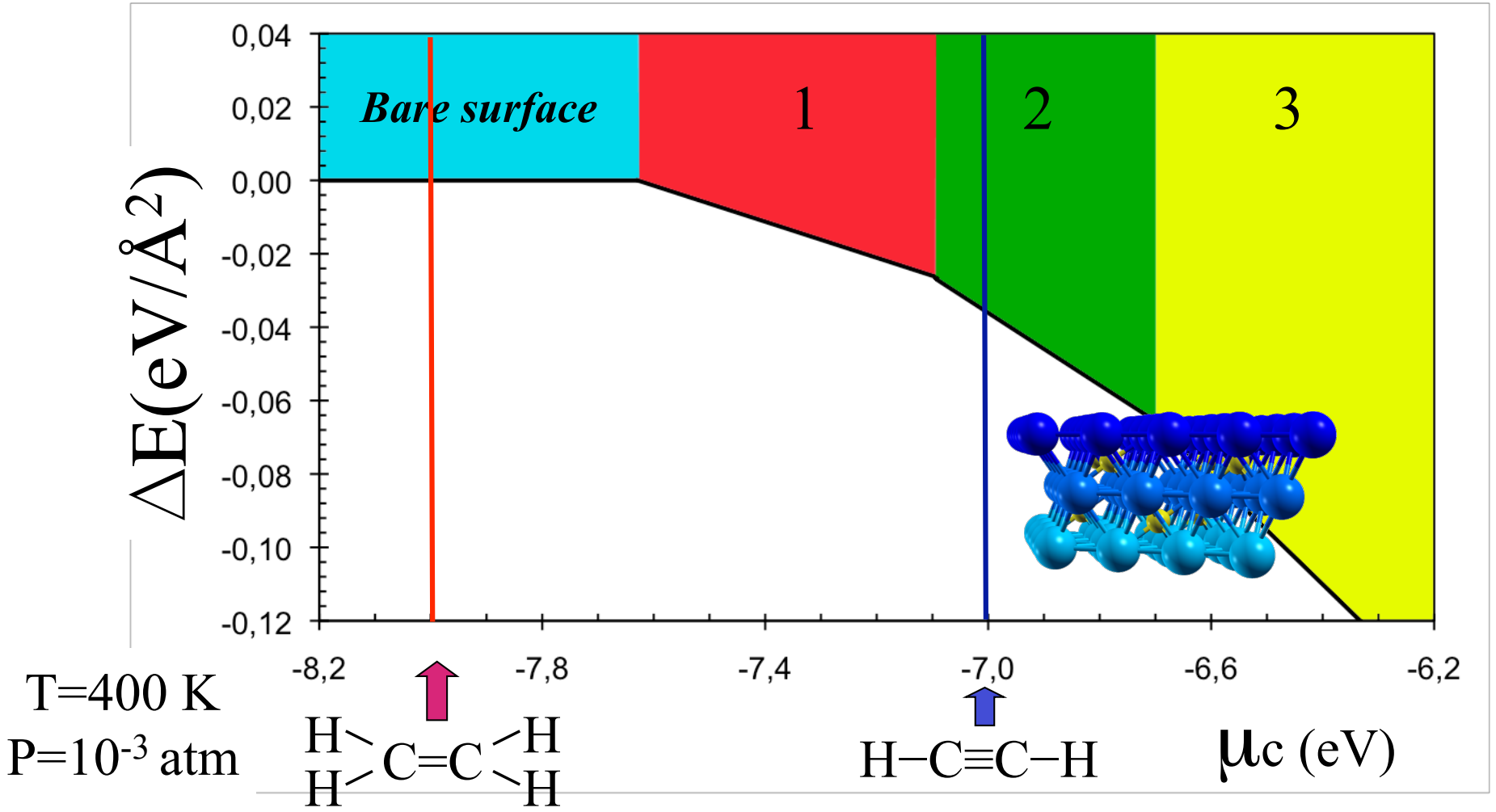
The chemical potential of C depends on the external conditions



Detre Teschner, PS et al, Angewandte Chemie 47, 9274 (2008)

- Pd core level shift: + 0.5 to +0.6 eV (N. Seriani et al, J. Chem. Phys. 132, 024711 (2010))
- Reasonable barriers for C_2H_2 decomposition

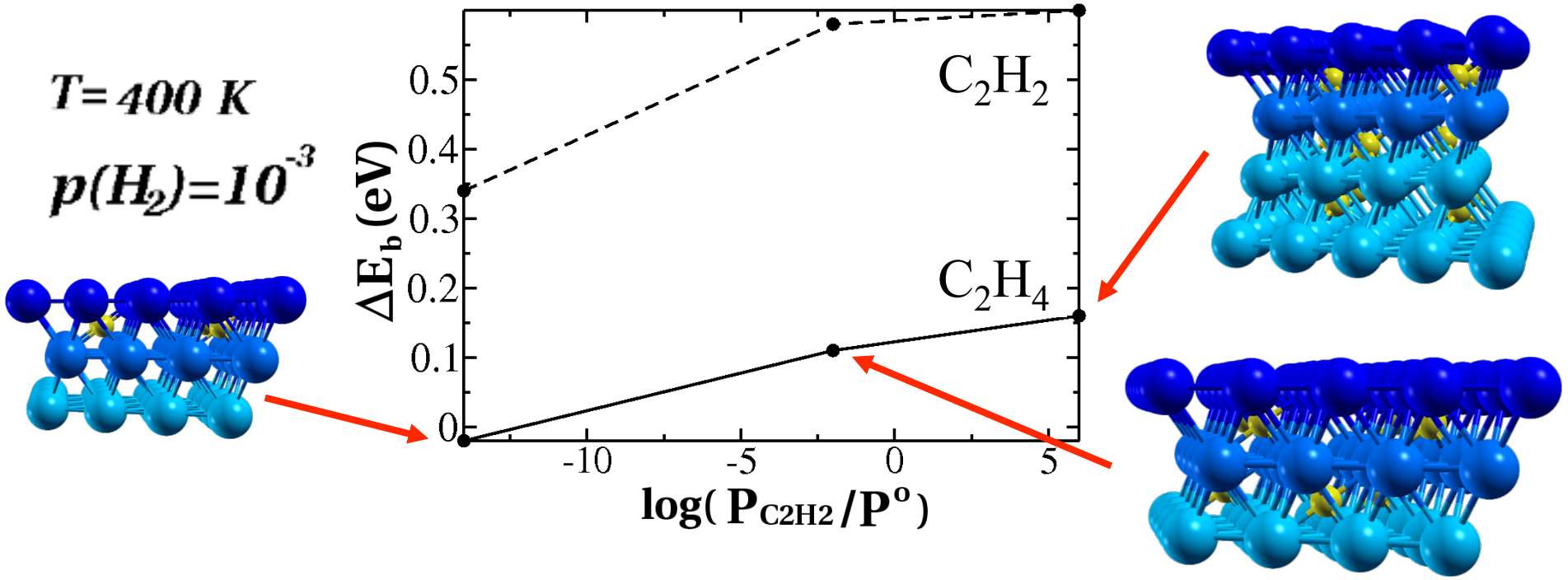
Nature of the Pd surface: influence of reactant



- Chemical potential of C in alkyne favors Pd-C formation, but not with alkenes

Detre Teschner, Zsolt Révay, János Borsodi, Michael Hävecker, Axel Knop-Gericke, Robert Schlögl
D. Milroy, S. David Jackson, Daniel Torres, Philippe Sautet, Angewandte Chemie 47, 9274 (2008)

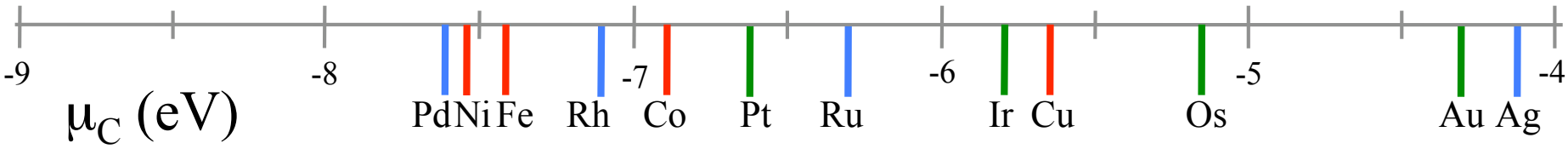
Influence of PdC on C_2H_2 and C_2H_4 adsorption

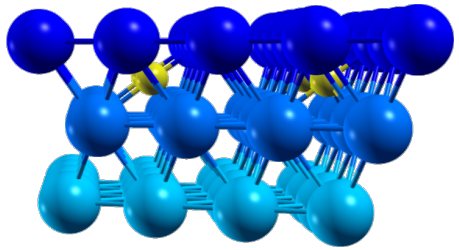


- Minor changes in the geometry of adsorbate
- Decrease of the C_2H_2 adsorption energy (-2 eV on Pd(111))
- **Decrease of C_2H_4 adsorption (-0.9 eV on Pd(111))**
  - Therefore the PdC phase increases the selectivity by favouring the desorption of the double bond

See also: Garcia-Mota, et al. J. Catal. 273, 92 (2010)

Critical C chemical potential for surface carbide formation



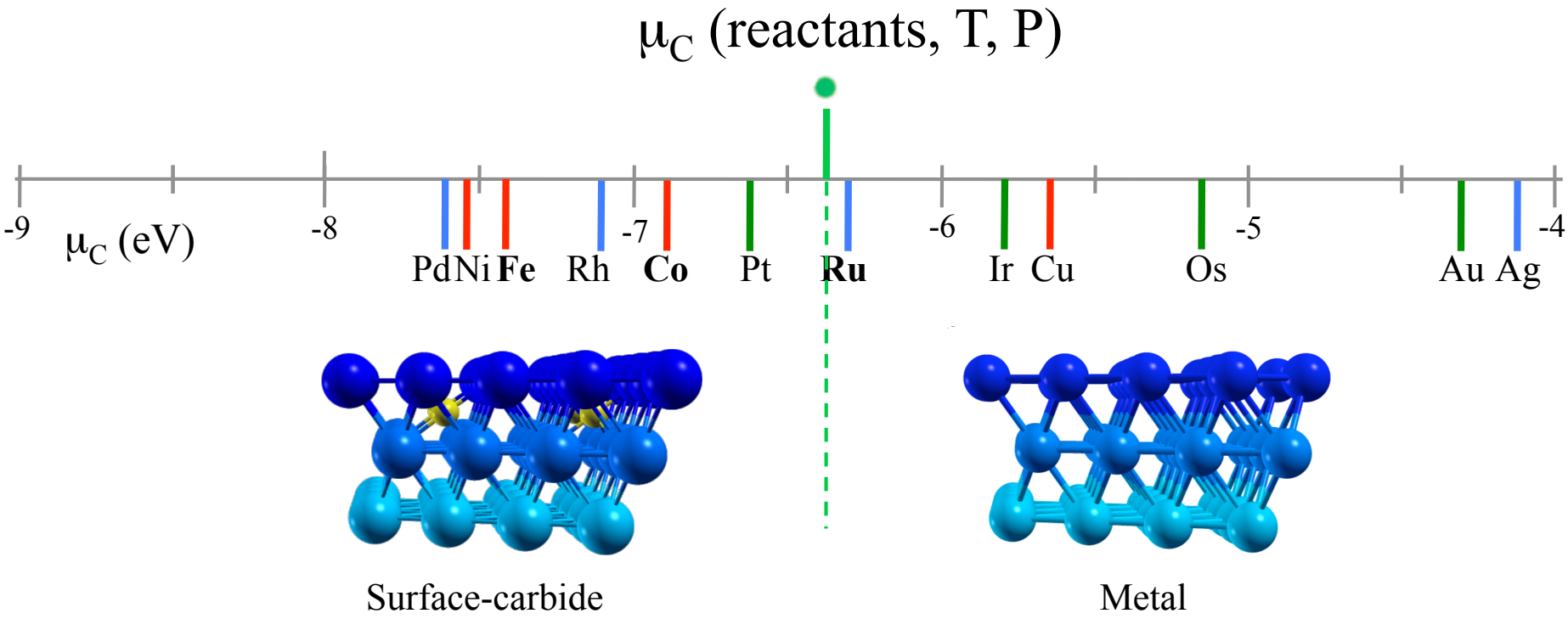


Surface-carbide

8	9	10	11
Fe	Co	Ni	Cu
Ru	Rh	Pd	Ag
Os	Ir	Pt	Au

PS, F. Cinquini, ChemCatChem 2010, 2, 636

In reaction conditions



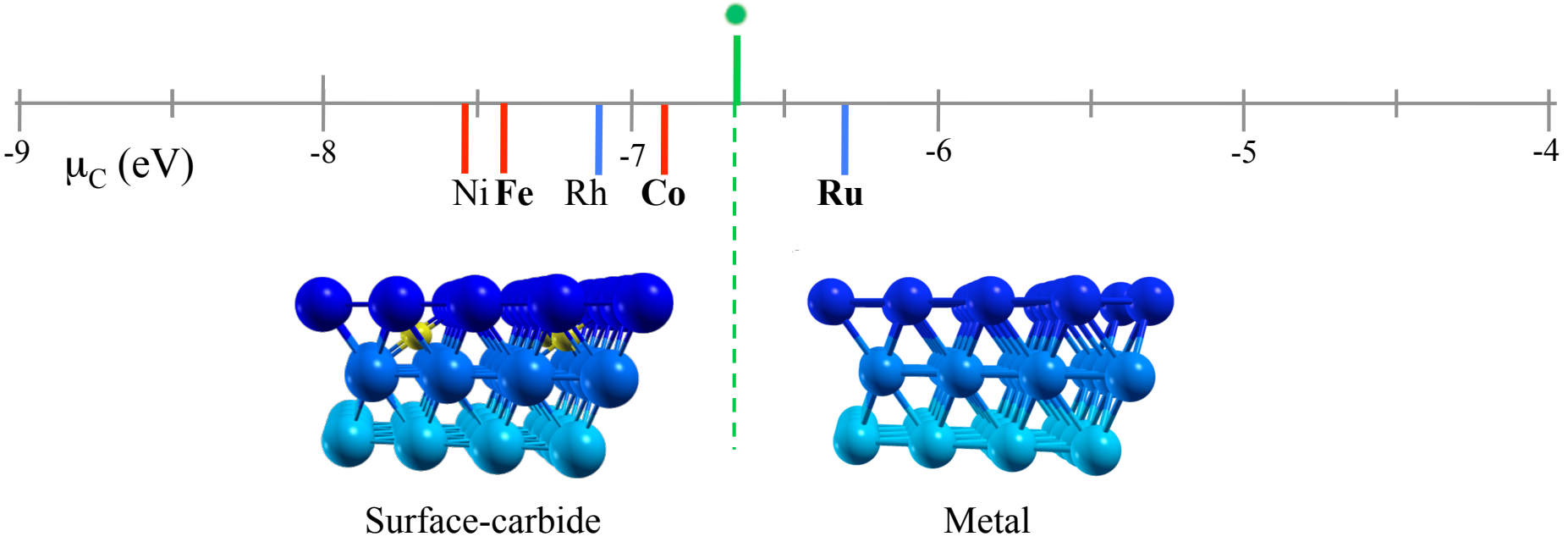
PS, F. Cinquini, ChemCatChem 2010, 2, 636

CO as a carbon source

$nCO + 2n\,H_2 \rightarrow nH_2O + (CH_2)_n$ Fischer-Tropsch

$CO + H_2 \rightarrow H_2O + C$

T=450 K
P= 1 atm



Surface-carbide

Metal

PS, F. Cinquini, ChemCatChem 2010, 2, 636

Heterogeneous Catalysis

Active sites ?

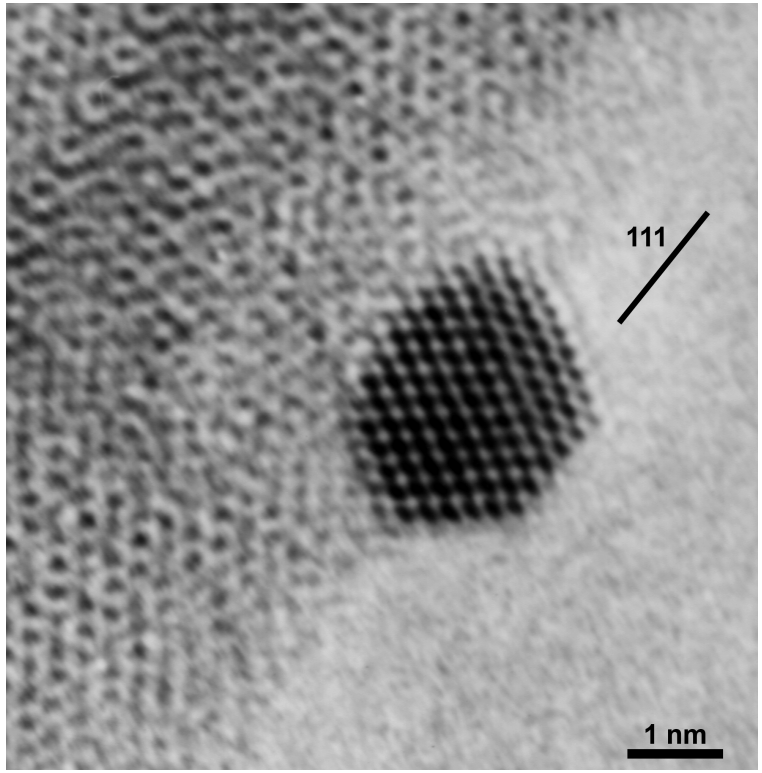
Chemical reaction

- Metal surface under gas pressure

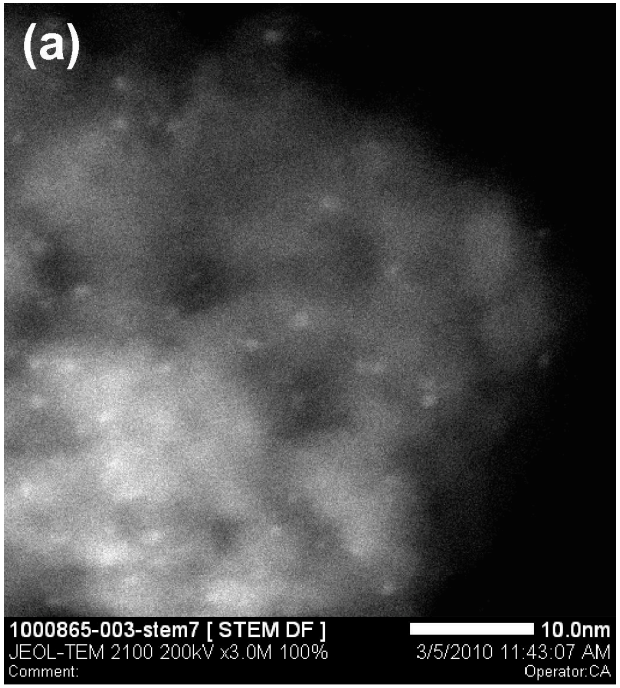
- Supported nanometer size Pt particles under hydrogen

- Butadiene hydrogenation: Why is PtSn selective ?

Pt particles on γ-alumina



Particle size 0.6 – 1.1 nm

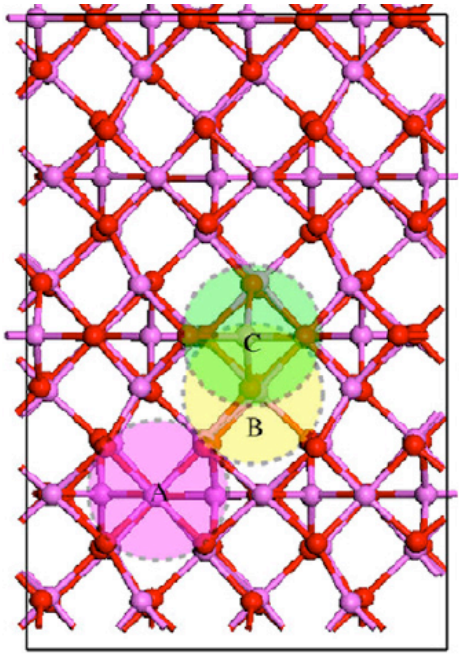


A. Jael et al, J. Catal. 272 (2010) 275

$Pt_{10} - Pt_{20}$

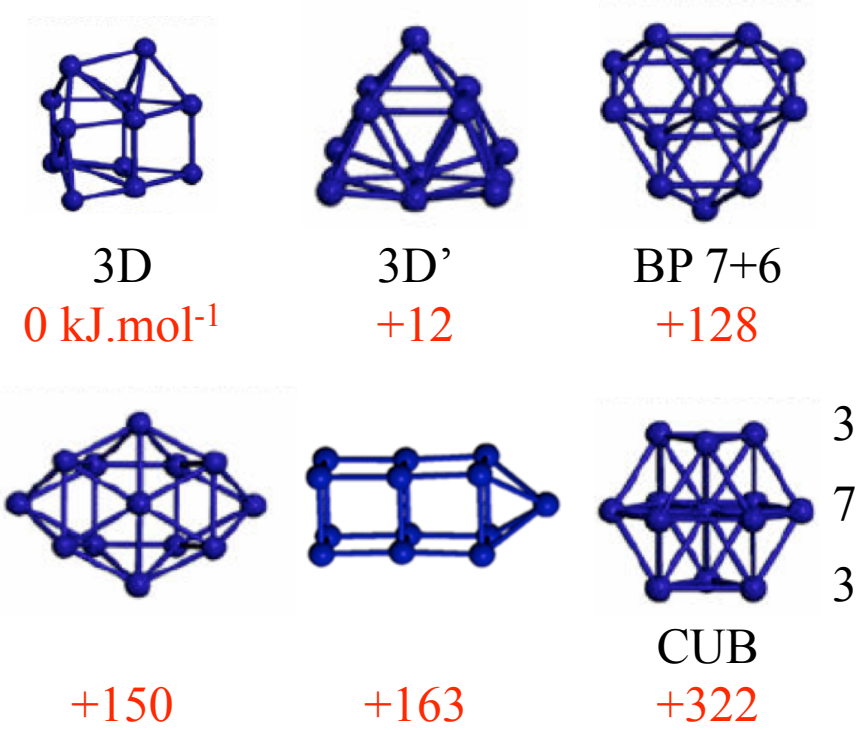
Pt_{13} particles on the γ-Al_2O_3 support

(100)



(100) is fully dehydrated

relevant Pt_{13} shapes



3D
0 kJ.mol^{-1}

3D'
+12

BP 7+6
+128

3
7
3
CUB
+322

+150

+163

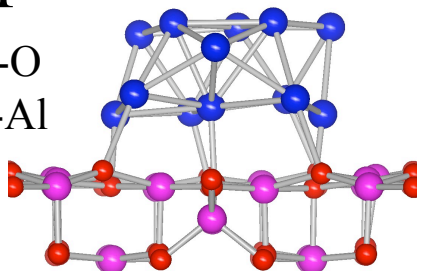
In vacuum

C-.H. Hu, C. Chizallet, ..., P. Sautet, H. Toulhoat, P. Raybaud, J. Catal. 274 (2010) 99

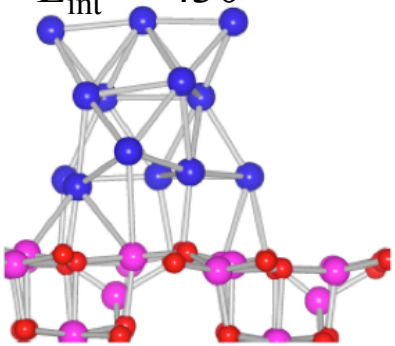
Pt_{13} particles on γ-Al_2O_3 (100)

E = 0 kJ.mol^{-1}
(E_{gas} = +136)
E_{int} = -783

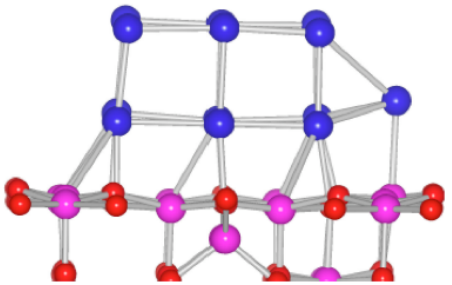
BP
8 Pt-O
6 Pt-Al

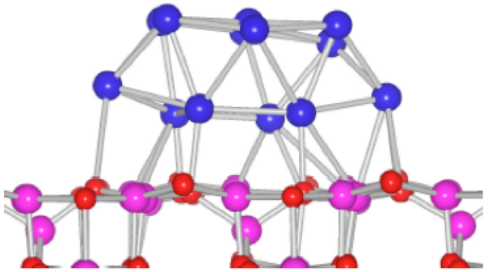


E = +25
(E_{gas} = +12)
E_{int} = -430

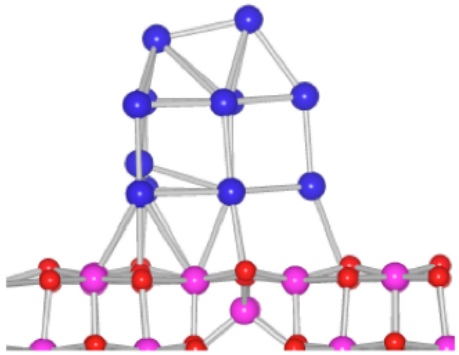


E = +26
(E_{gas} = +163)
E_{int} = -704

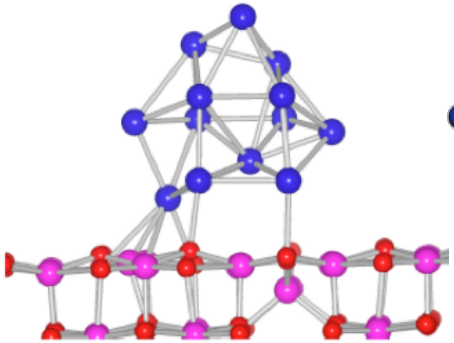




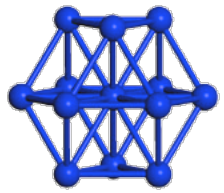
E = +62
(E_{gas} = +150)
E_{int} = -646



E = + 62
(E_{gas} = 0)
E_{int} = -300



E = +150
(E_{gas} = +322)
E_{int} = -331



CUB

Al O Pt

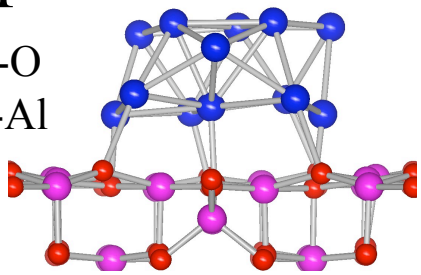
C-H. Hu, C. Chizallet, C. Mager-Maury, M. Corral-Valero, P. Sautet, H. Toulhoat and P. Raybaud, **Journal of Catalysis** 274, 99-110 (2010)

Pt_{13} particles on γ-Al_2O_3 (100)

E = 0 kJ.mol^{-1}
(E_{gas} = +136)
E_{int} = -783

BP

8 Pt-O
6 Pt-Al



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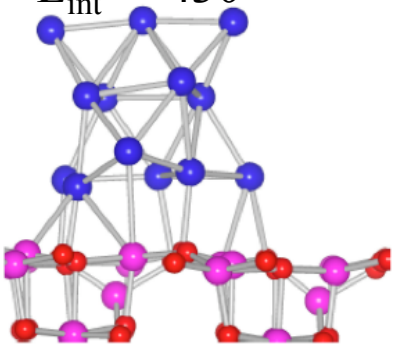

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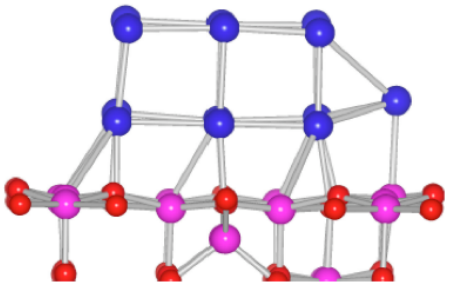

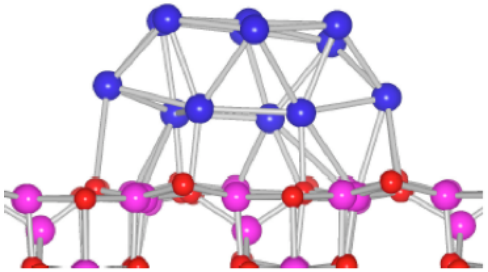

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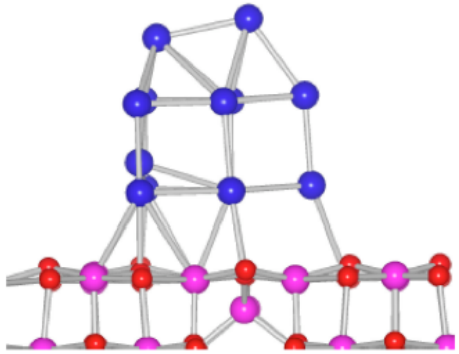
E_{int} = -646



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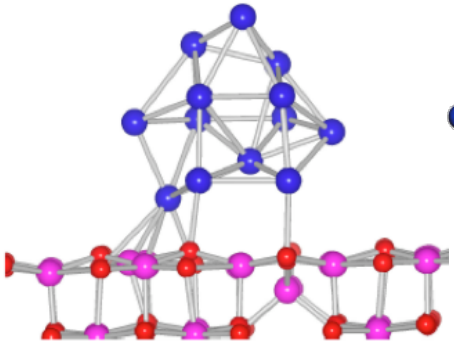

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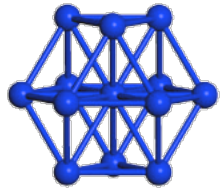

CUB

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8 Pt-O
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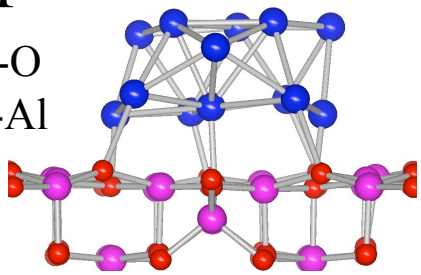

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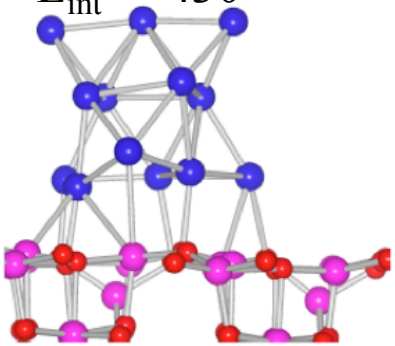

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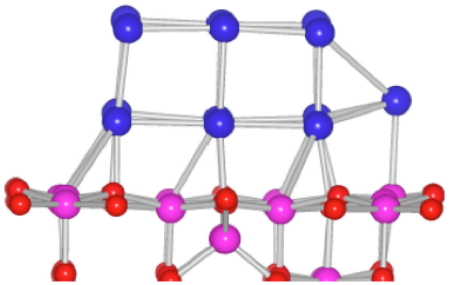
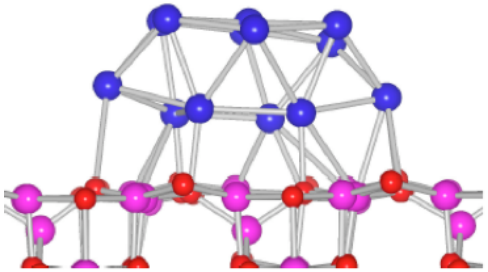
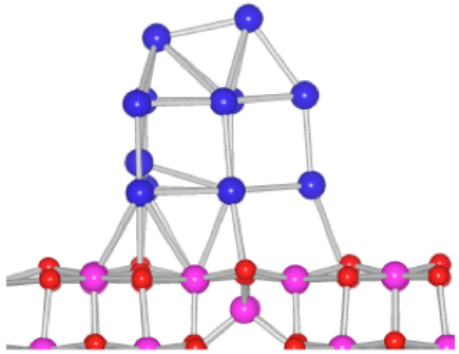
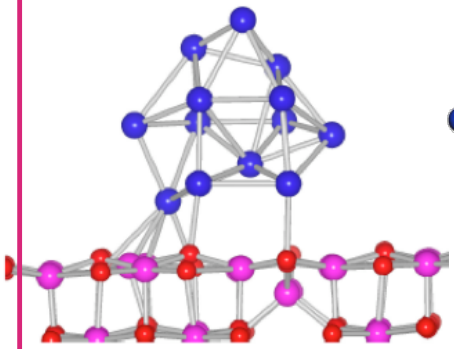


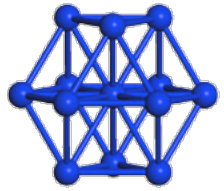


$E = +62$
($E_{gas} = +150$)
$E_{int} = -646$



$E = +62$
($E_{gas} = 0$)
$E_{int} = -300$





CUB

$E = +150$
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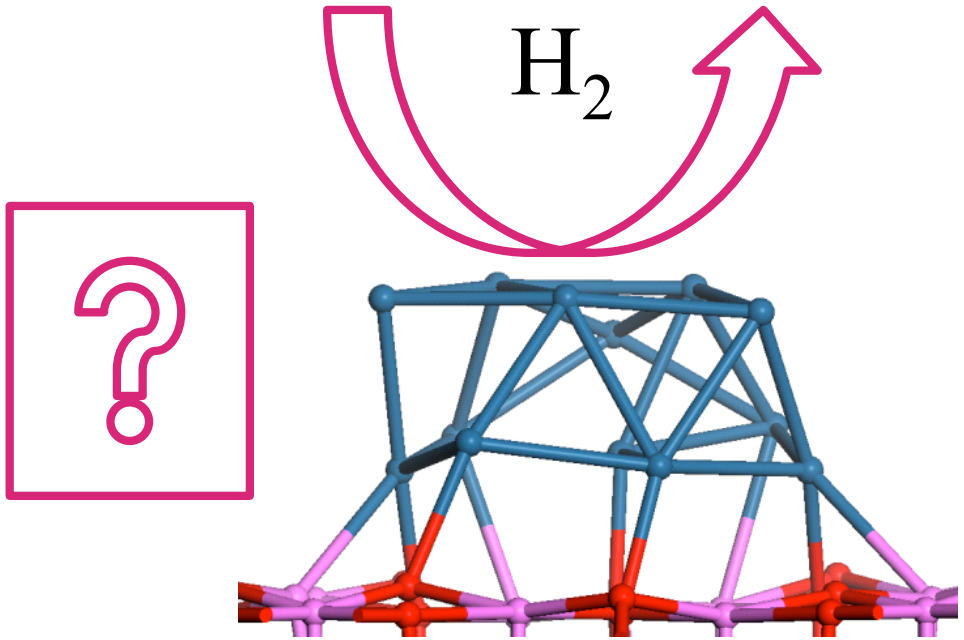
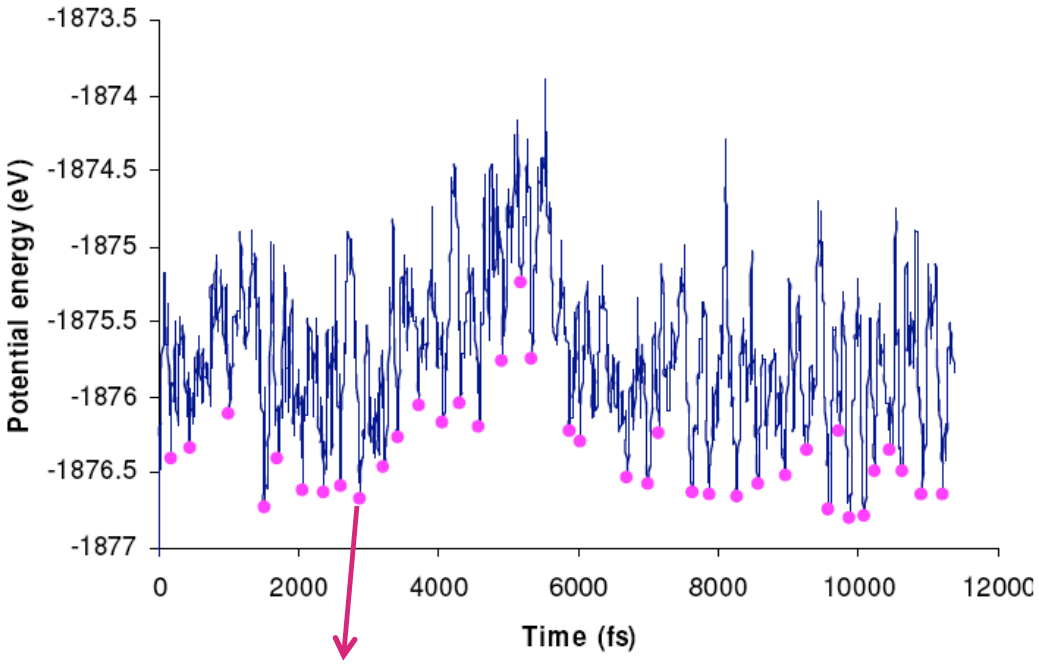
Al O Pt

C-H. Hu, C. Chizallet, C. Mager-Maury, M. Corral-Valero, P. Sautet, H. Toulhoat and P. Raybaud, **Journal of Catalysis** 274, 99-110 (2010)

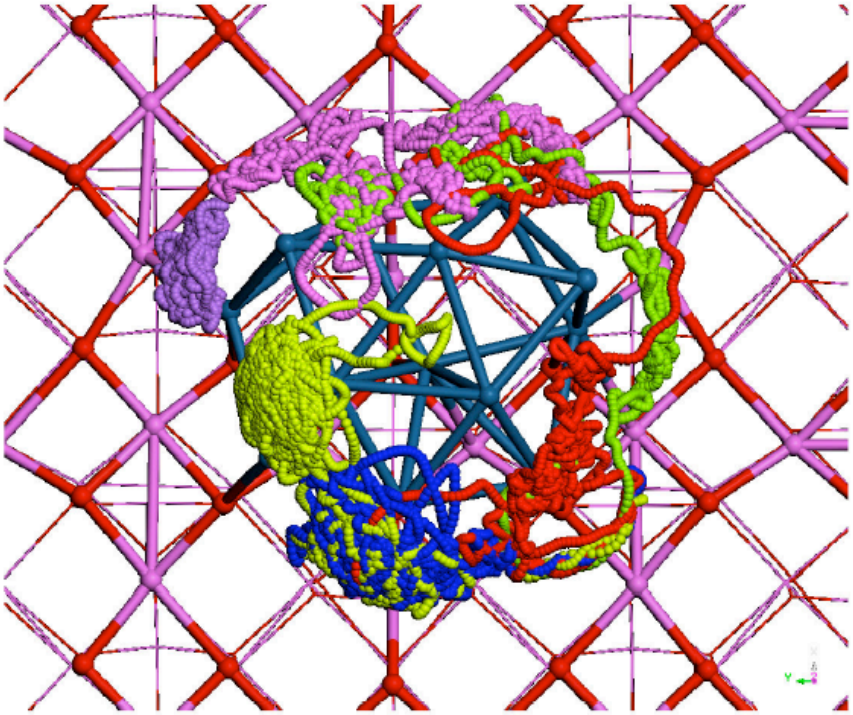
Pt_{13} on γ-Al_2O_3 under a pressure of H_2



Pt_{13} + 6 H on γ-Al_2O_3 (100)



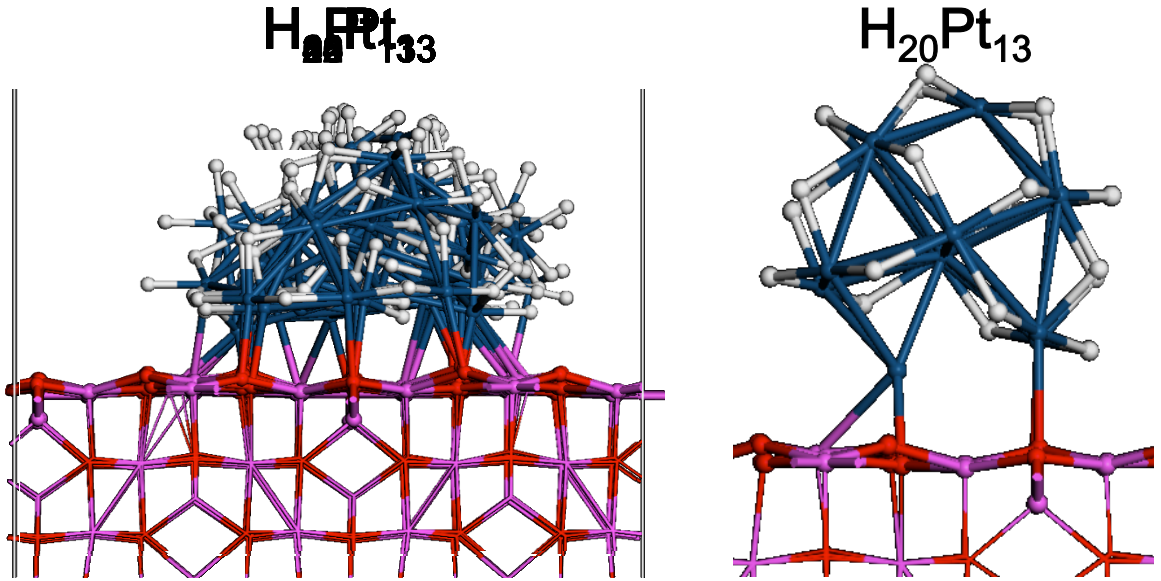
Subsequent complete optimisation



Velocity scaled MD, 1200 K, 12 ps, m_H=10
Pt_{13} and alumina frozen

C. Mager-Maury, C. Chizallet, P. Sautet, P. Raybaud ChemCatChem 3 (2011) 200

Hydrogen adsorption: $Pt_{13}/(100)\ \gamma{-}Al_2O_3$



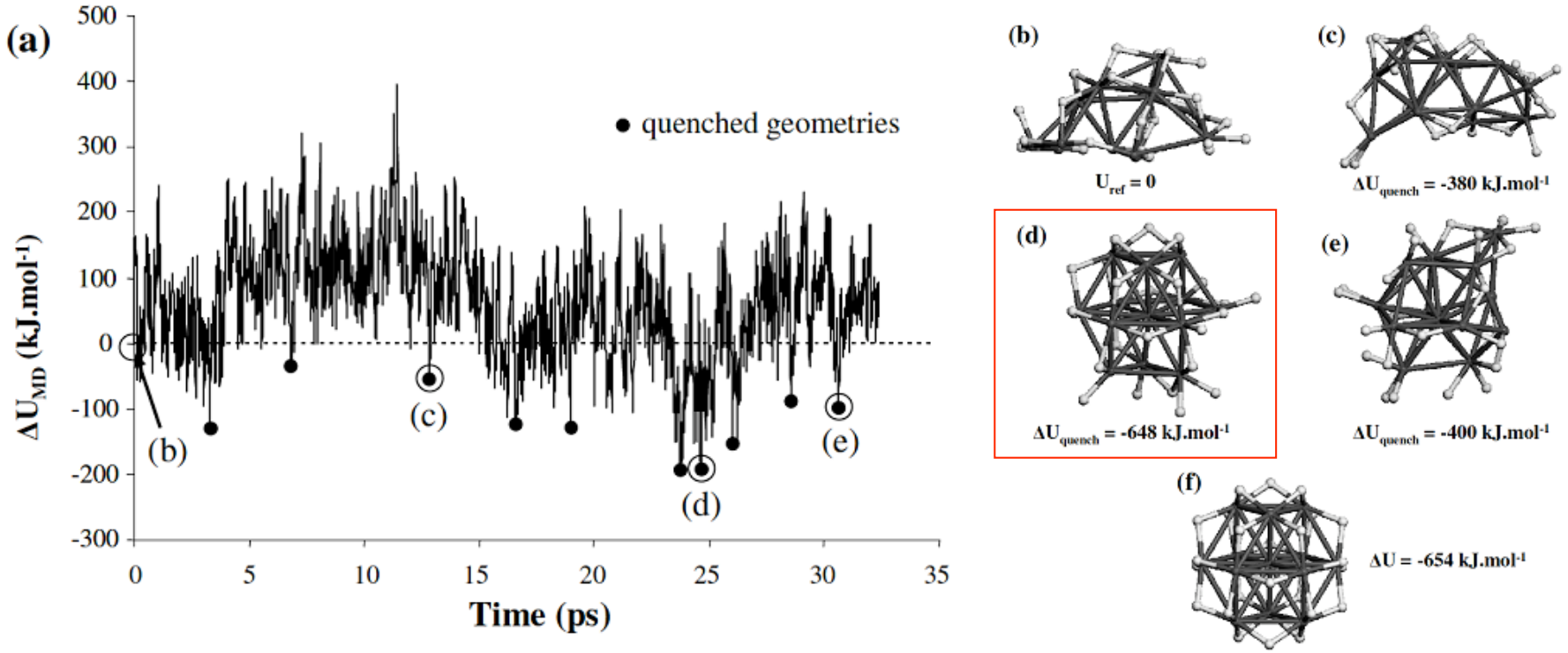
Strong structural deformation of the Pt_{13} cluster
Weakening of the metal support interaction

⇒ Change of the morphology under reductive environment
⇒ Cuboctahedron is stabilized at high $p(H_2)$

C. Mager-Maury, C. Chizallet, P. Sautet, P. Raybaud ChemCatChem 3 (2011) 200

Hydrogen adsorption: structural reconstruction

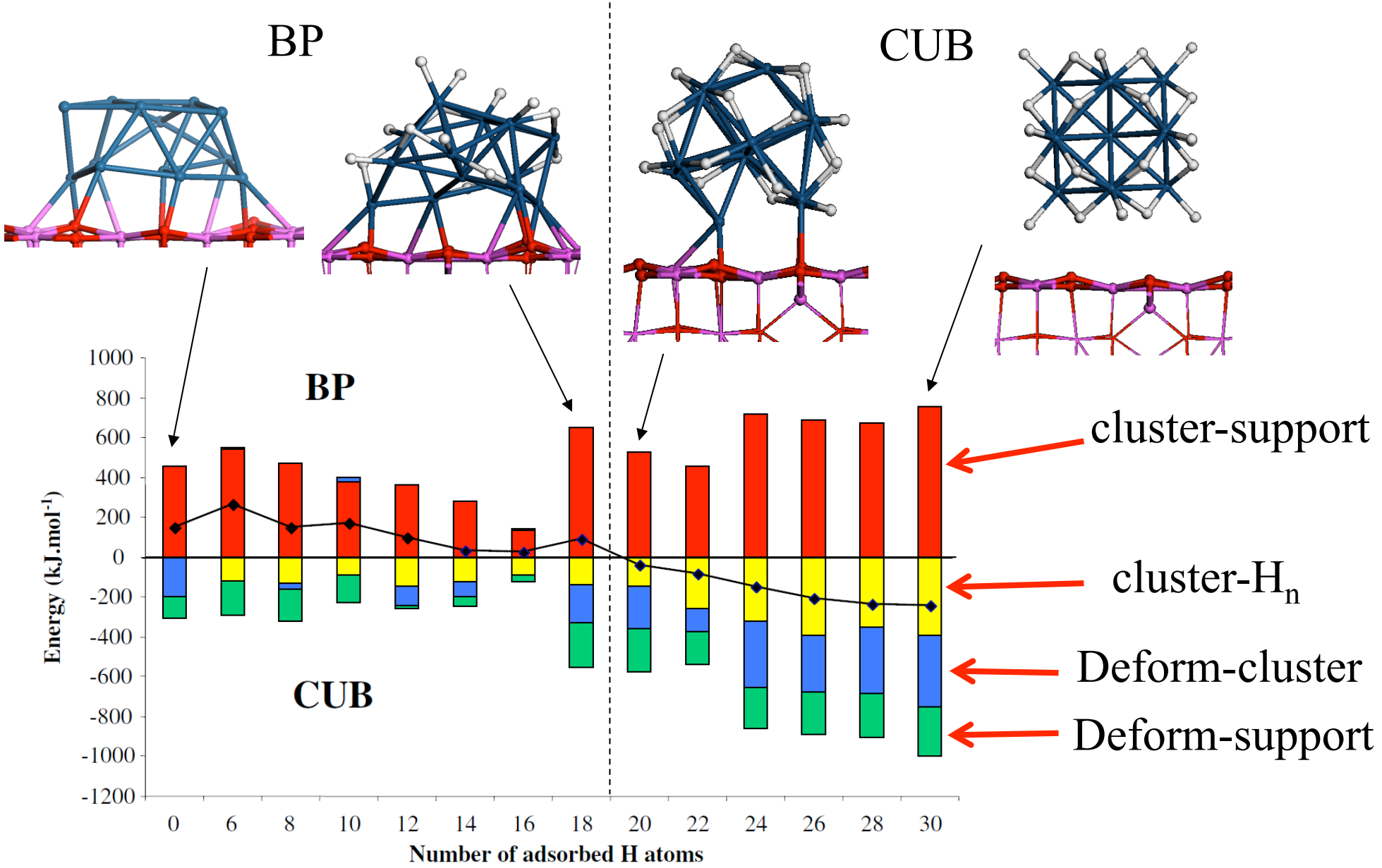
Gas phase molecular dynamic at n(H)=24



From BP to CUB transformation

C. Mager-Maury, C. Chizallet, P. Sautet, P. Raybaud ChemCatChem 3 (2011) 200

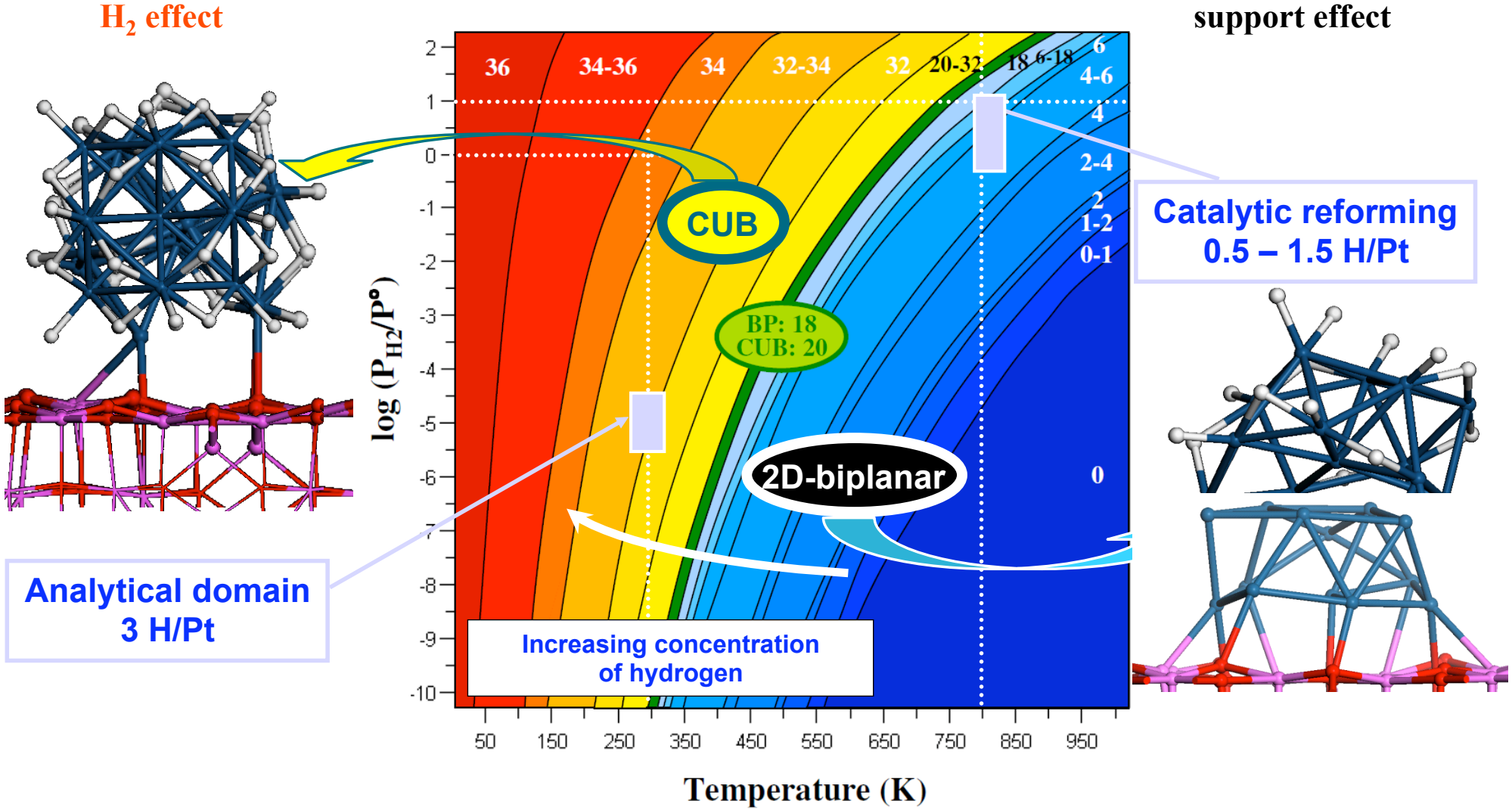
Effect of Hydrogen: structural reconstruction



C. Mager-Maury, C. Chizallet, P. Sautet, P. Raybaud ChemCatChem 3 (2011) 200

Influence of H_2 on the structural properties of $Pt_{13}/\gamma\text{-}Al_2O_3$-(100)

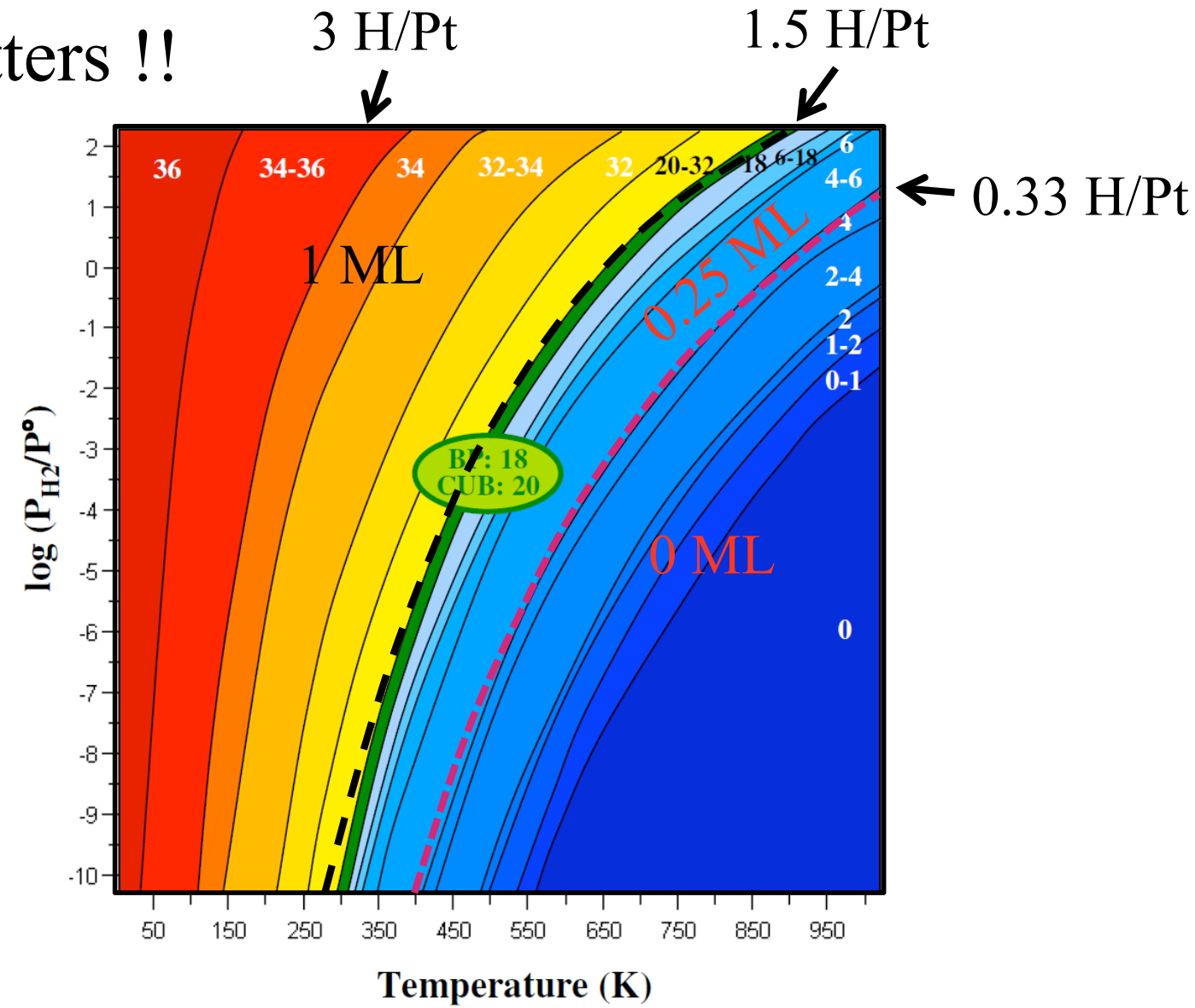
Phase diagram of Pt_{13}-H_n/(100) Al_2O_3 as a function of T and P



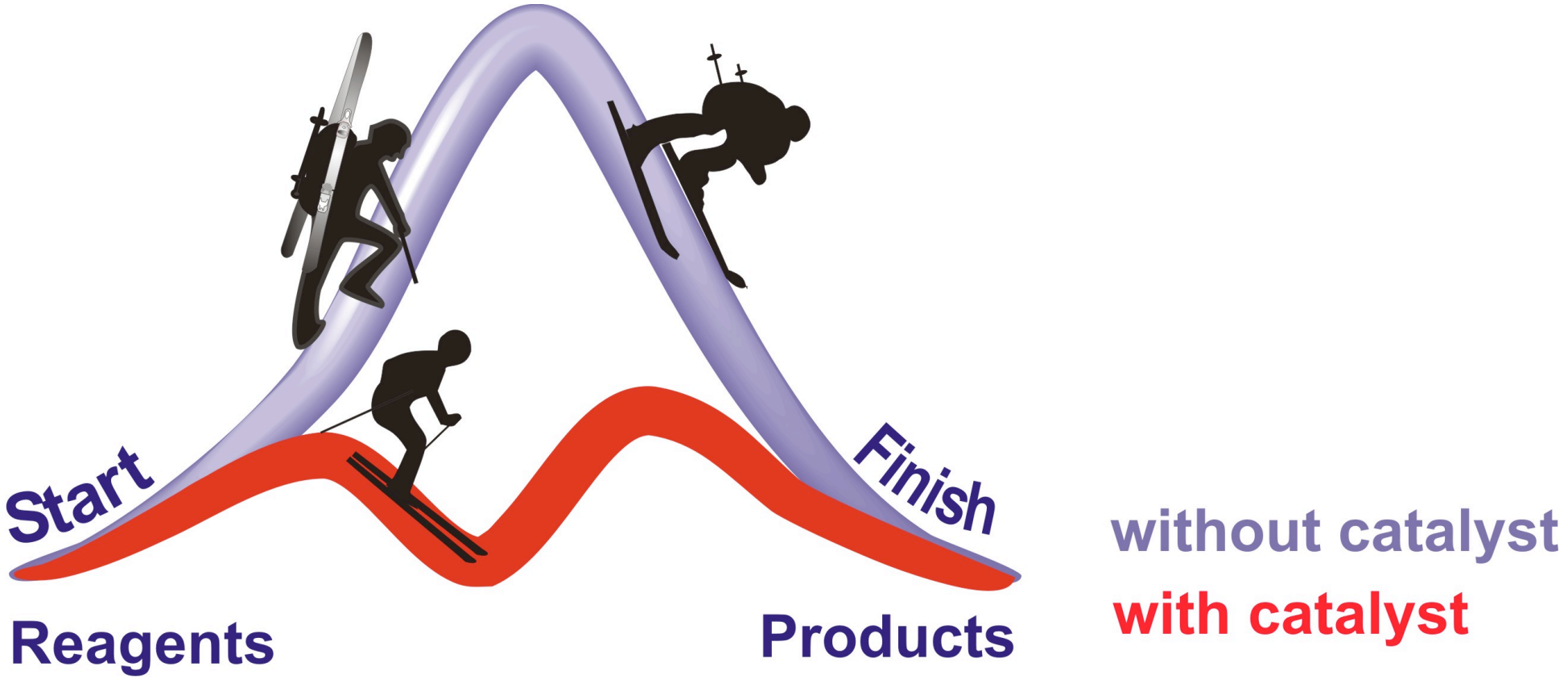
C. Mager-Maury, C. Chizallet, P. Sautet, P.Raybaud ChemCatChem 3 (2011) 200

Hydrogen on Pt_{13} on γ-Al_2O_3 versus Pt(111)

Size matters !!

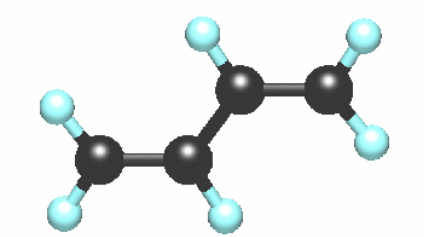


Molecular reactivity on catalysts



Selective hydrogenation

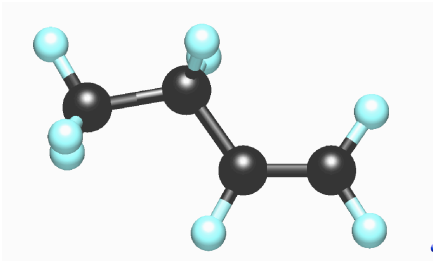
Important industrial process : selective hydrogenation of dienes into mono-olefins



$CH_2=CH-CH=CH_2$

Butadiene

H_2

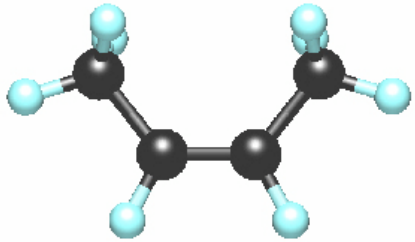


$CH_2=CH-CH_2-CH_3$

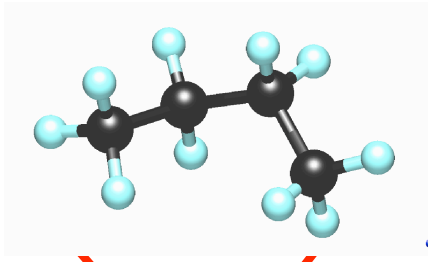
1-Butene

$CH_3-CH_2=CH_2-CH_3$

2-Butene



H_2



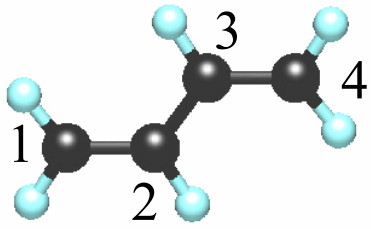
$CH_3-CH_2-CH_2-CH_3$

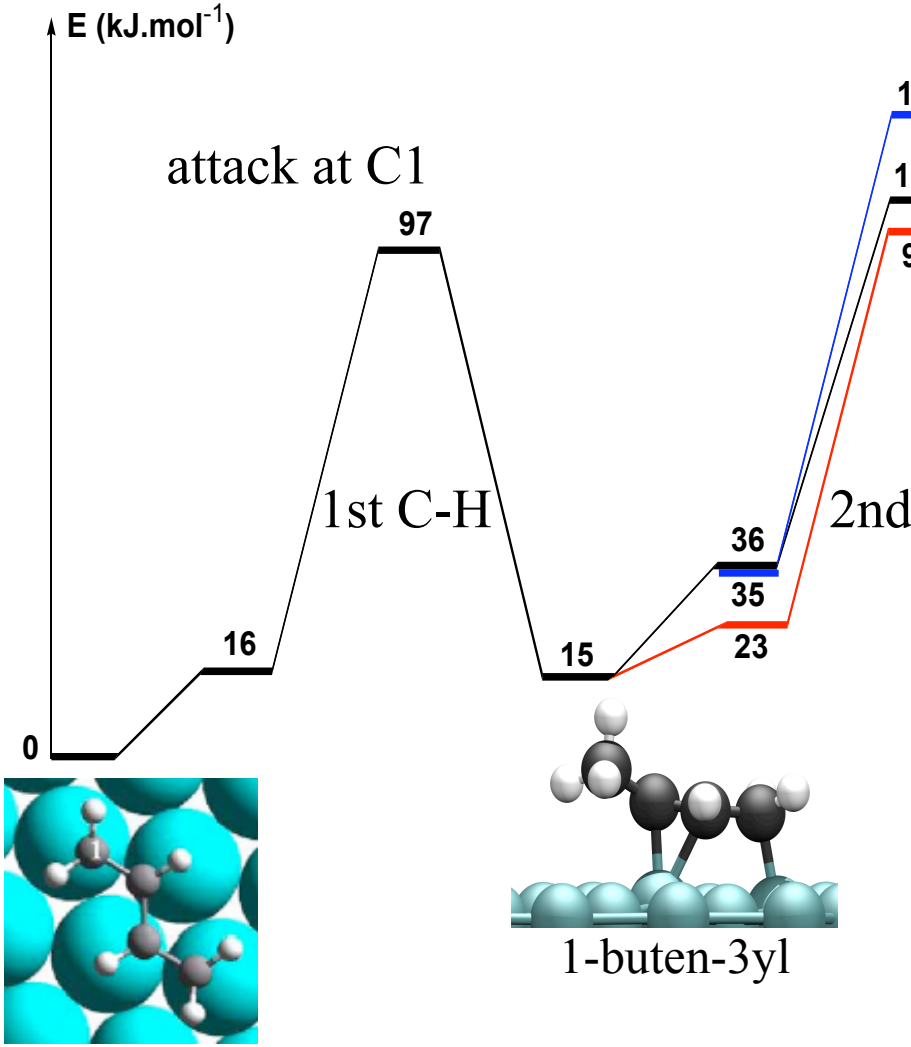
Butane

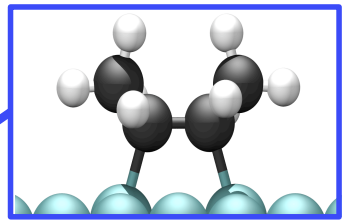
Byproduct

Challenge : search for catalysts able to avoid the total hydrogenation

Platinum is non selective !!

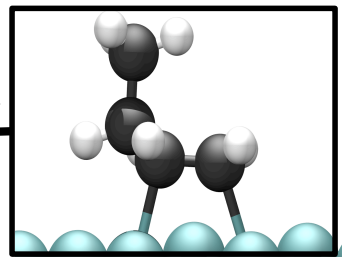






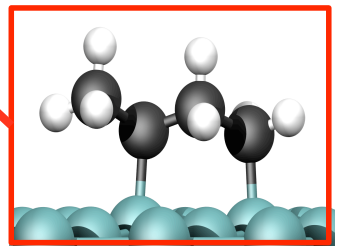
C1+C4

Selective
2-butene



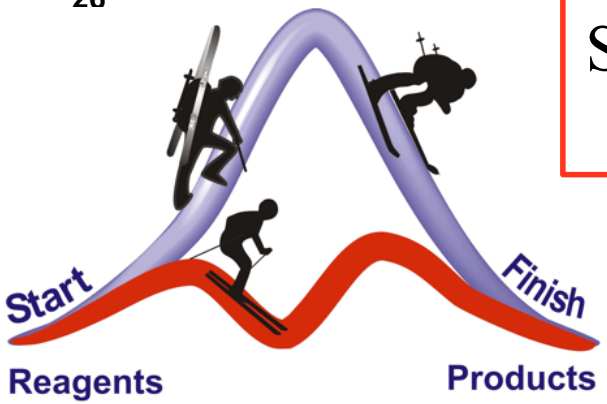
C1+C2

Selective
1-butene



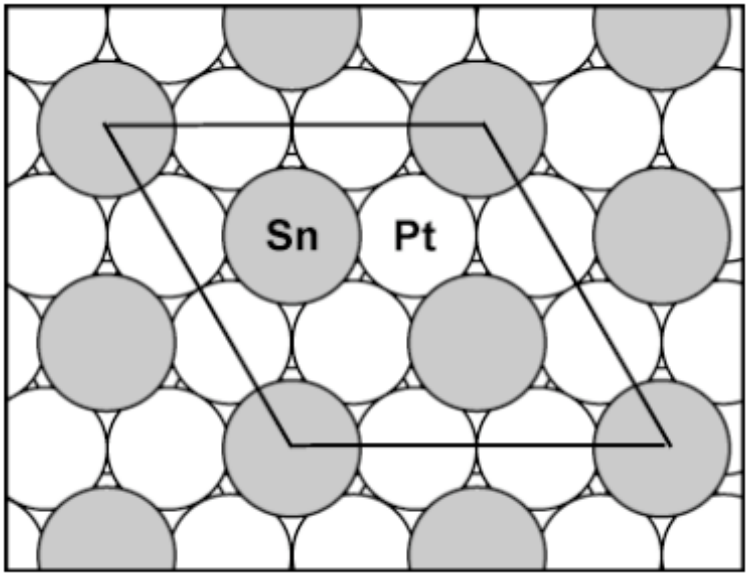
C1+C3

Non - Sel
butane-1,3-diyl

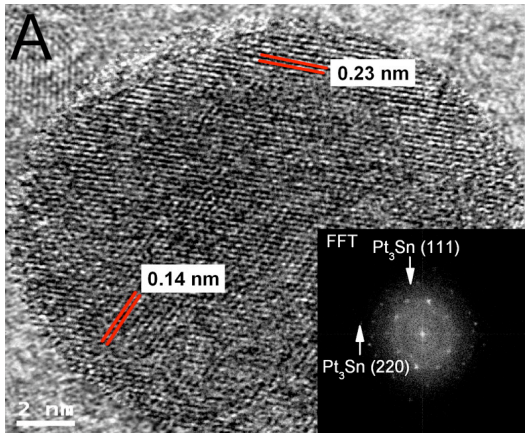


Strong M-C bonds !

Pt-Sn catalyst



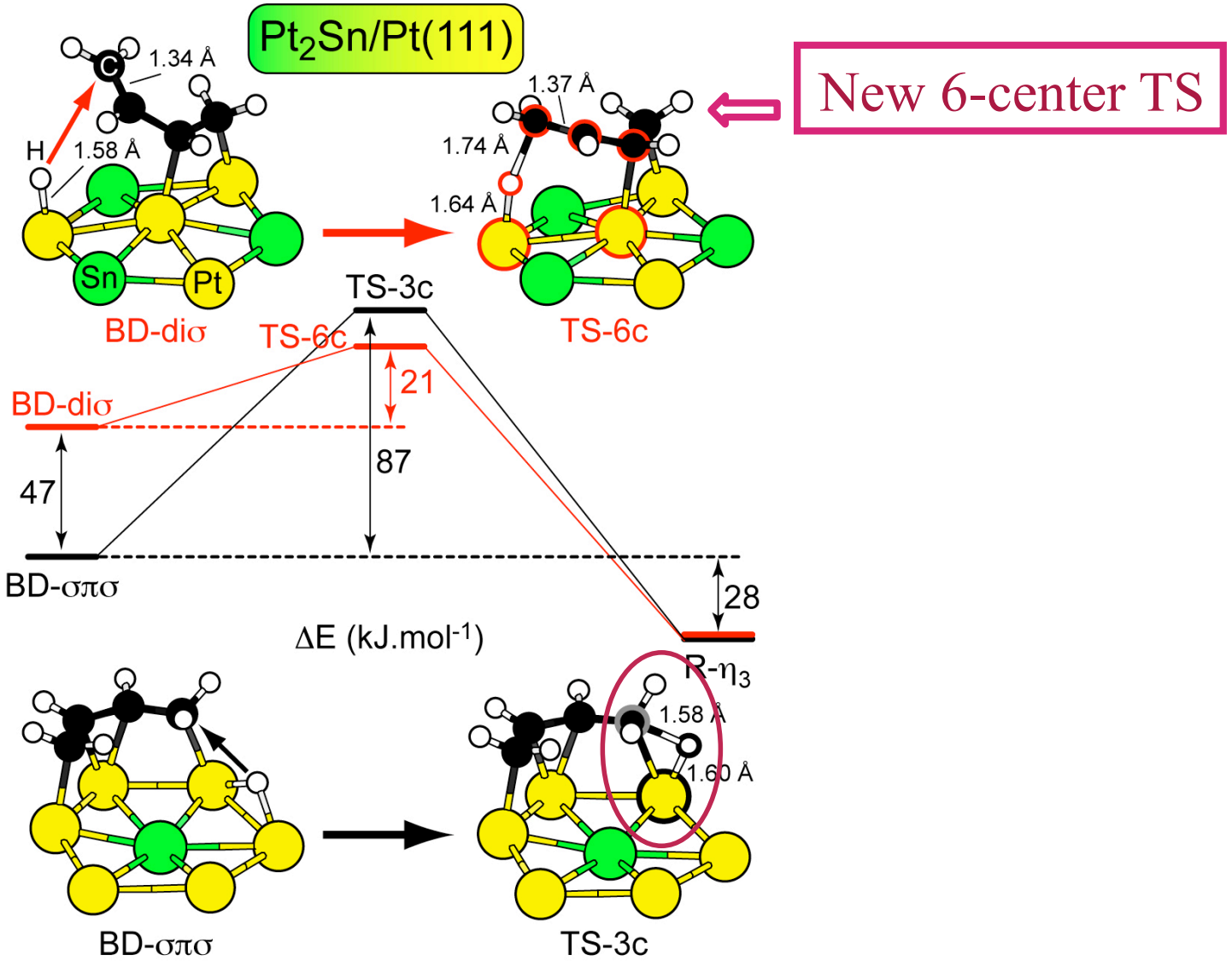
$Pt_2Sn/Pt(111)$



B.K. Vu et al

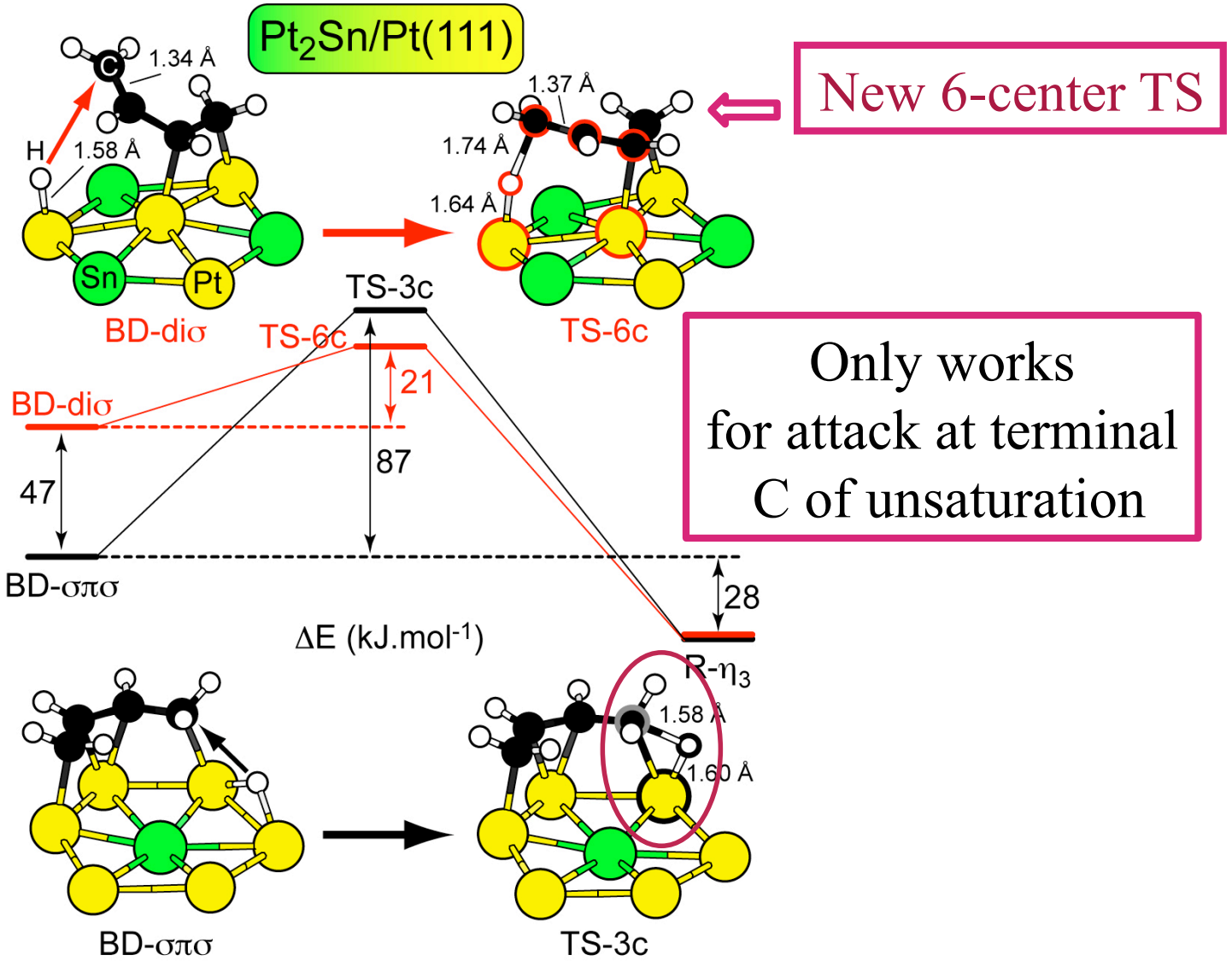
Weakening M-C interaction with Sn

Butadiene hydrogenation: new pathway



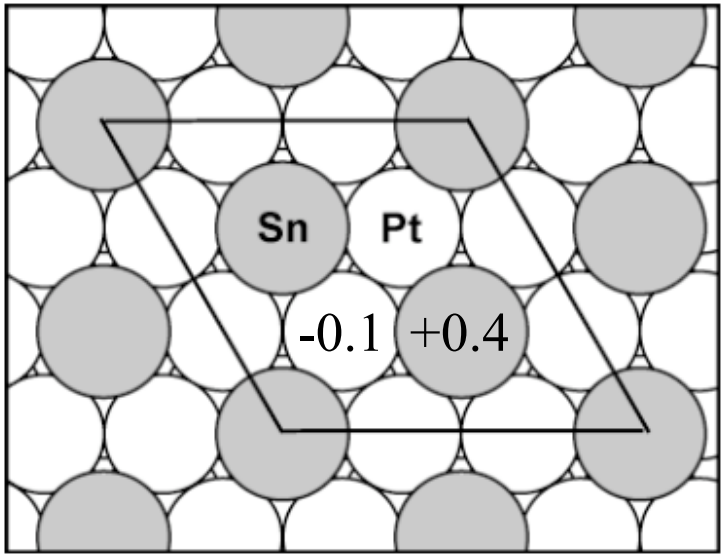
D. Loffreda, F. Delbecq and P. Sautet, J. Phys. Chem. Lett., 1, 323-326 (2010)

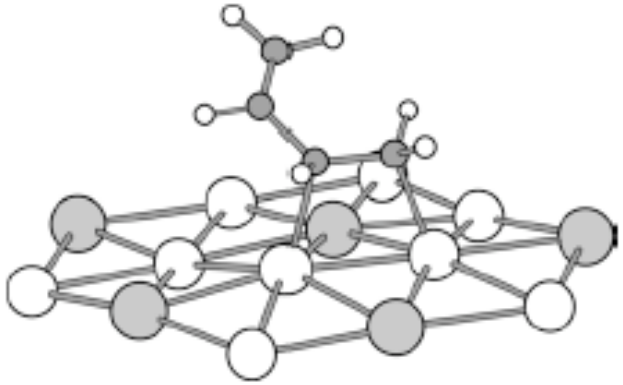
Butadiene hydrogenation: new pathway



D. Loffreda, F. Delbecq and P. Sautet, J. Phys. Chem. Lett., 1, 323-326 (2010)

Electronic effect of Sn





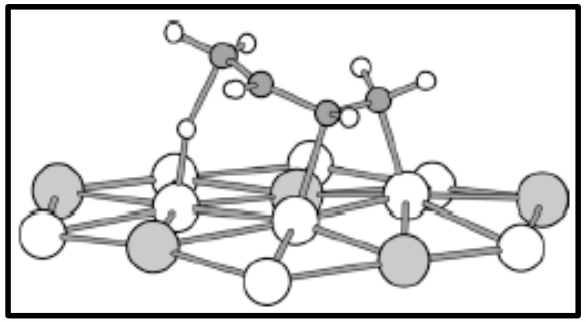
Butadiene half decoordination cost : 47 kJ.mol^{-1} (vs 71 on Pt)

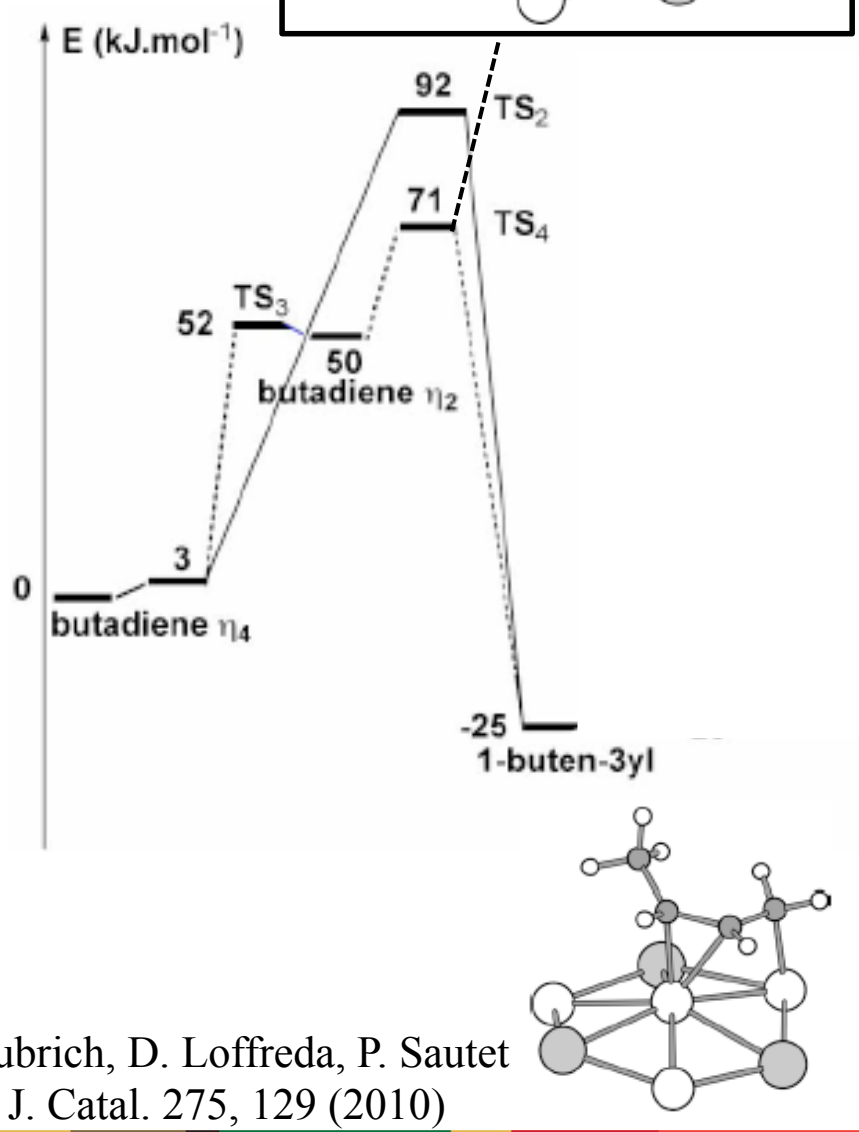
Additional electronic density on Pt
Increased Pauli repulsion with π electrons
Pt d-band center is lowered

Weakening of adsorption energy (kJ.mol^{-1})

	Pt	Pt_2Sn
Butadiene	150	74
Butene	101	49

attack at C1

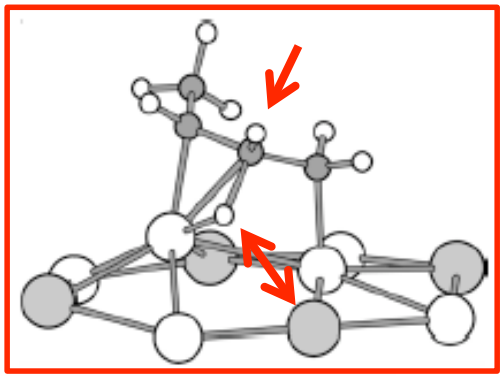


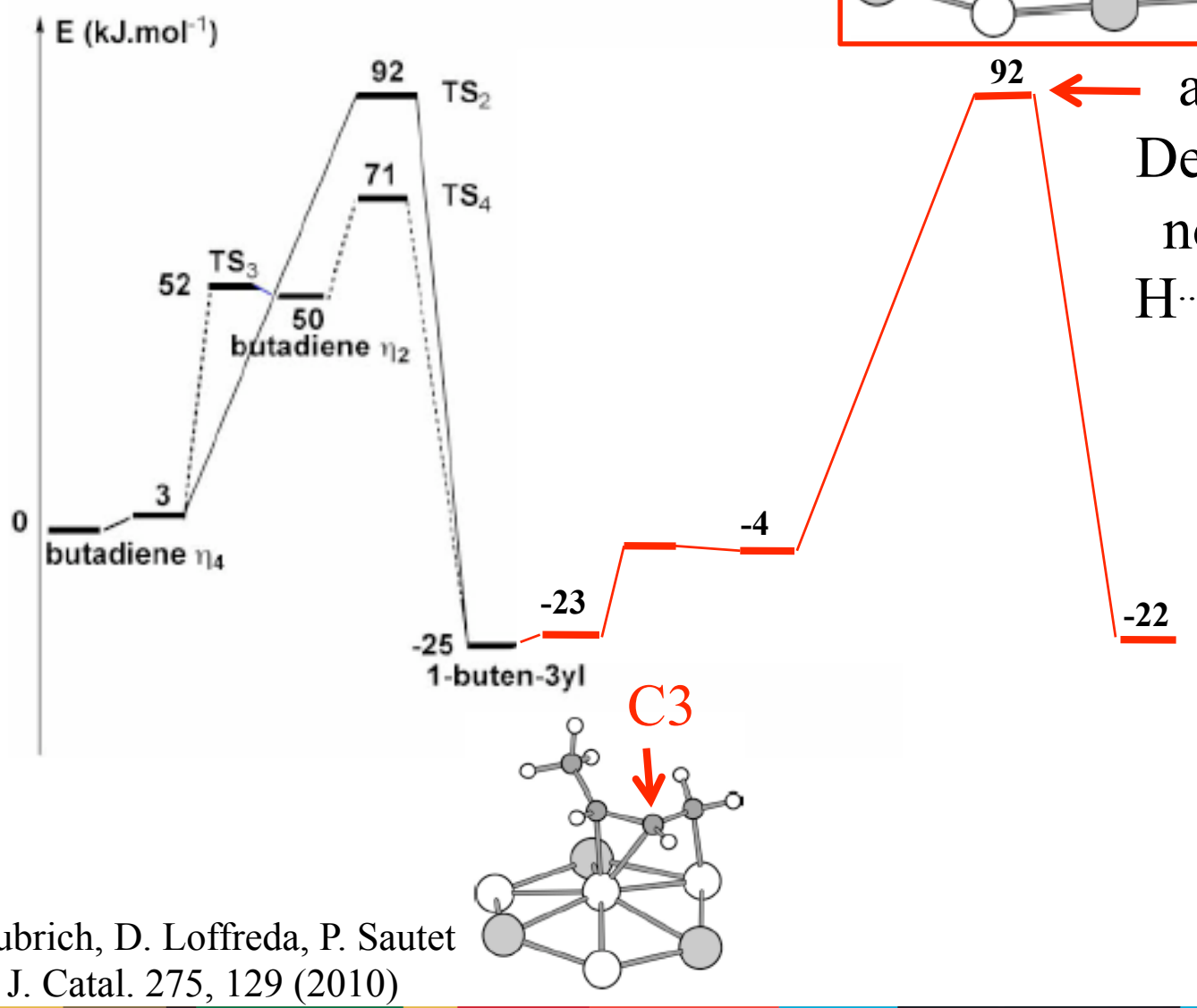


F. Vigné, J. Haubrich, D. Loffreda, P. Sautet
F. Delbecq, J. Catal. 275, 129 (2010)

attack at C1+C3

Platinum-Tin



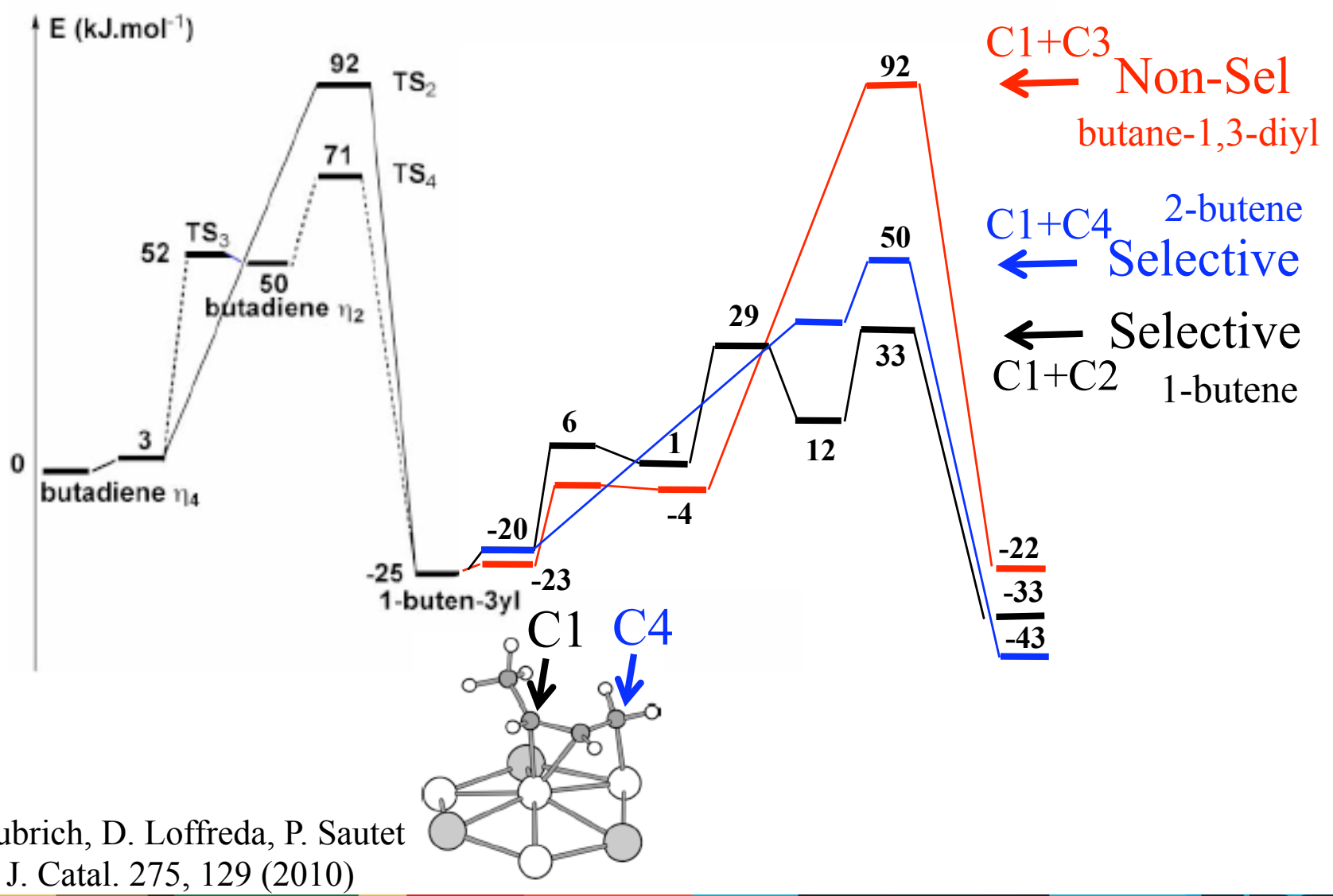


F. Vigné, J. Haubrich, D. Loffreda, P. Sautet
F. Delbecq, J. Catal. 275, 129 (2010)

Platinum-Tin : selective !

attack at C1+C2

C1+C4



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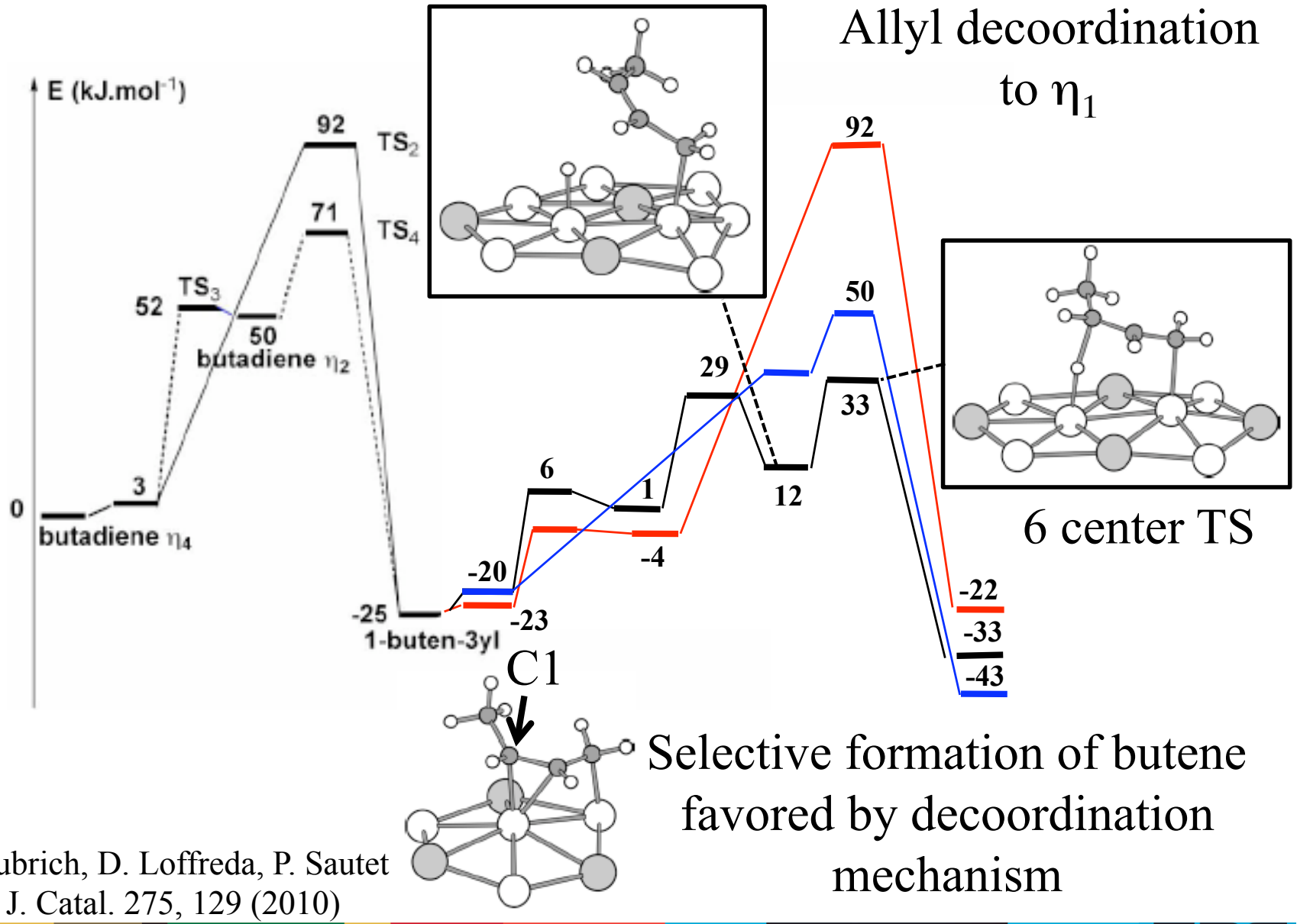
attack at C1+C2

Platinum-Tin : selective !



Allyl decoordination to η_1

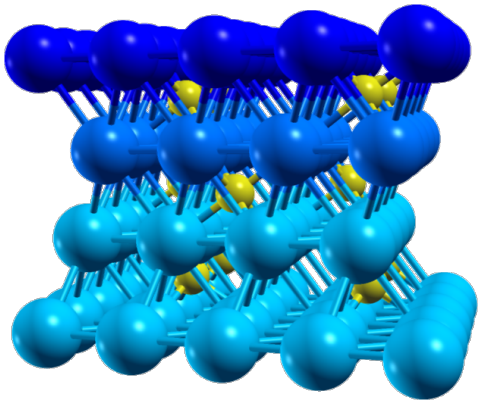
6 center TS

Selective formation of butene favored by decoordination mechanism

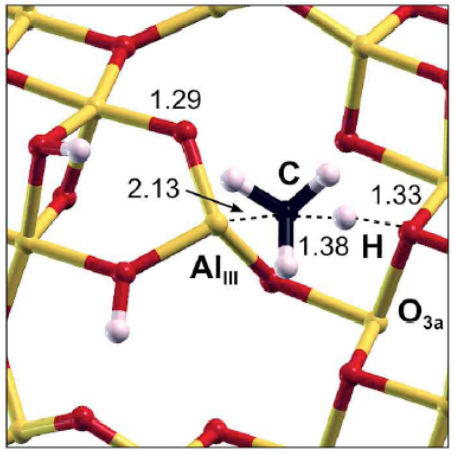
F. Vigné, J. Haubrich, D. Loffreda, P. Sautet
F. Delbecq, J. Catal. 275, 129 (2010)

Computational chemistry and catalysis

acetylene



metastable



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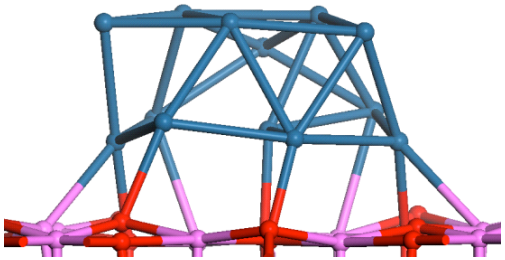
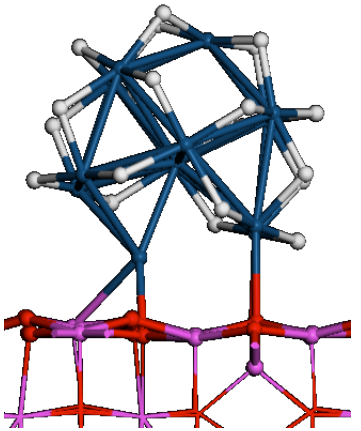
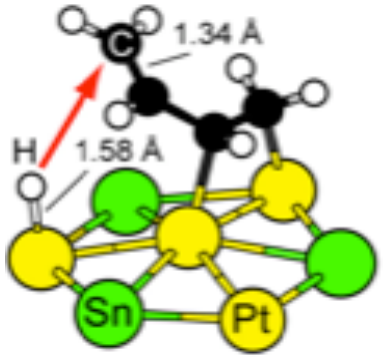


metastable

+ H_2





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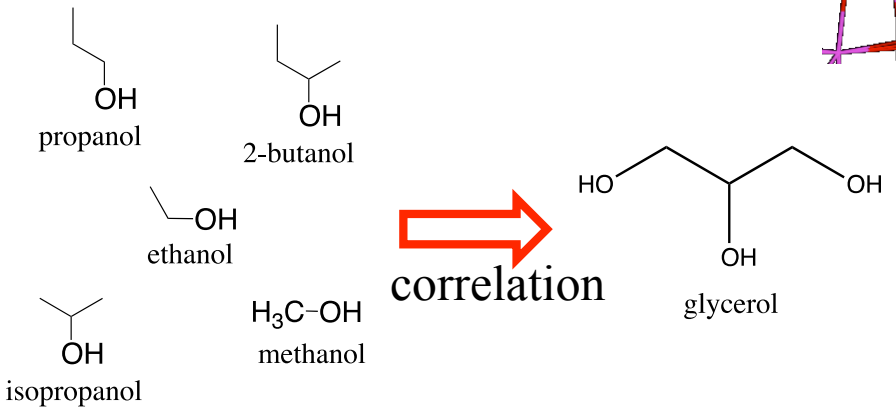

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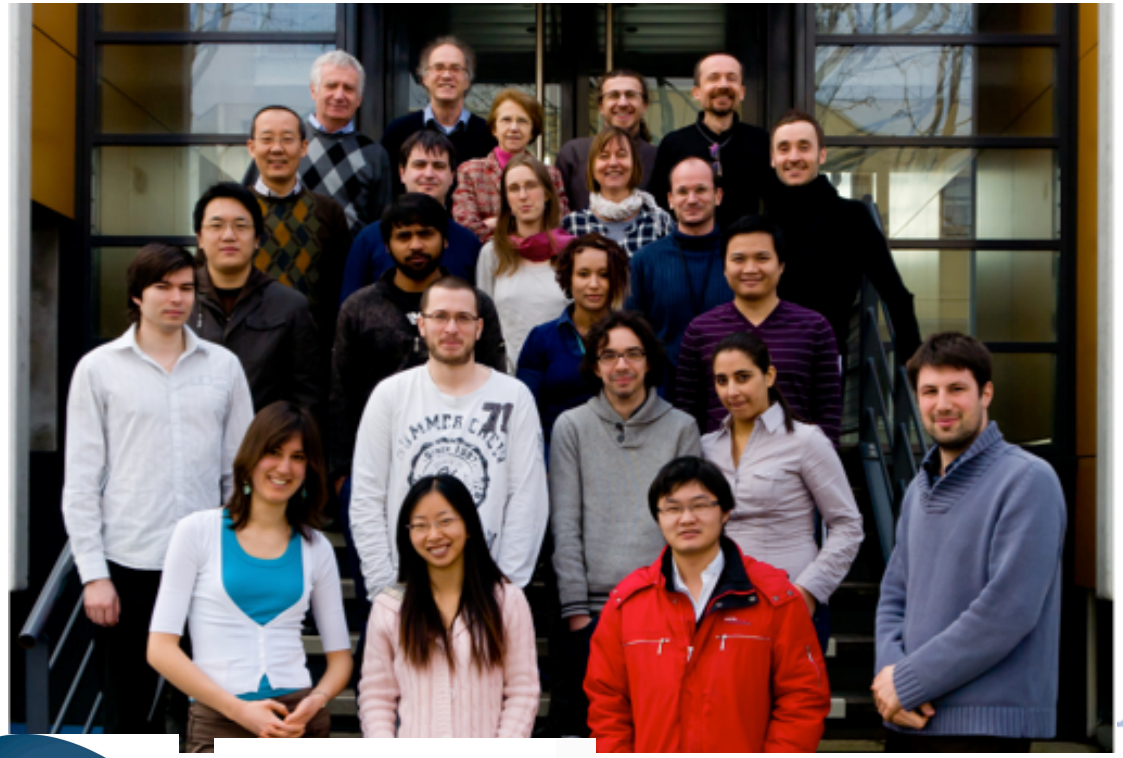
Lyon + ETH Zurich : C. Coperet, R. Wischert

FHI Berlin: D. Teschner, A. Knop-Gericke, R. Schlögl

IFPEN: P. Raybaud, C. Chizallet, M. Digne



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