Structure-dependent microkinetic modeling: methodology and applications

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Laboratory of Catalysis and Catalytic Processes LCCP

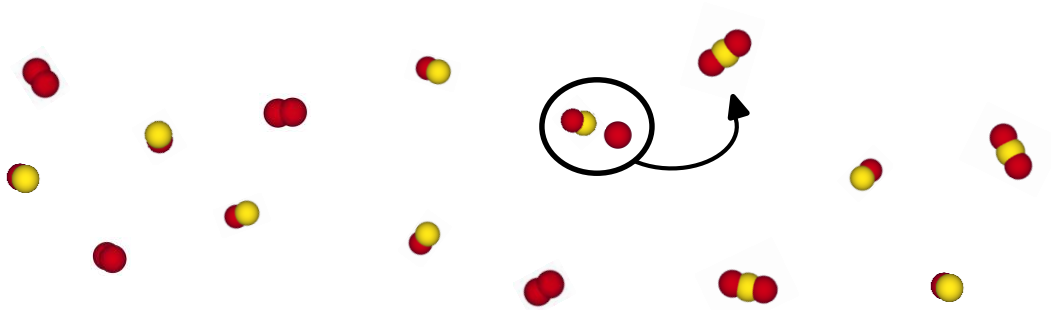
POLITECNICO MILANO 1863

March 22nd, 2018

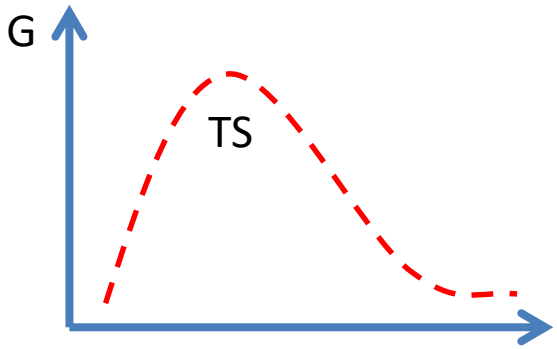
Pregl Lecture - Kemijski inštitut

National Institute of Chemistry – Ljubljana, Slovenia

Catalysis is a kinetic phenomenon



Catalyst: functional material with specific “active sites”



$$r \propto \exp\left(-\frac{G^{TS}}{RT}\right)$$

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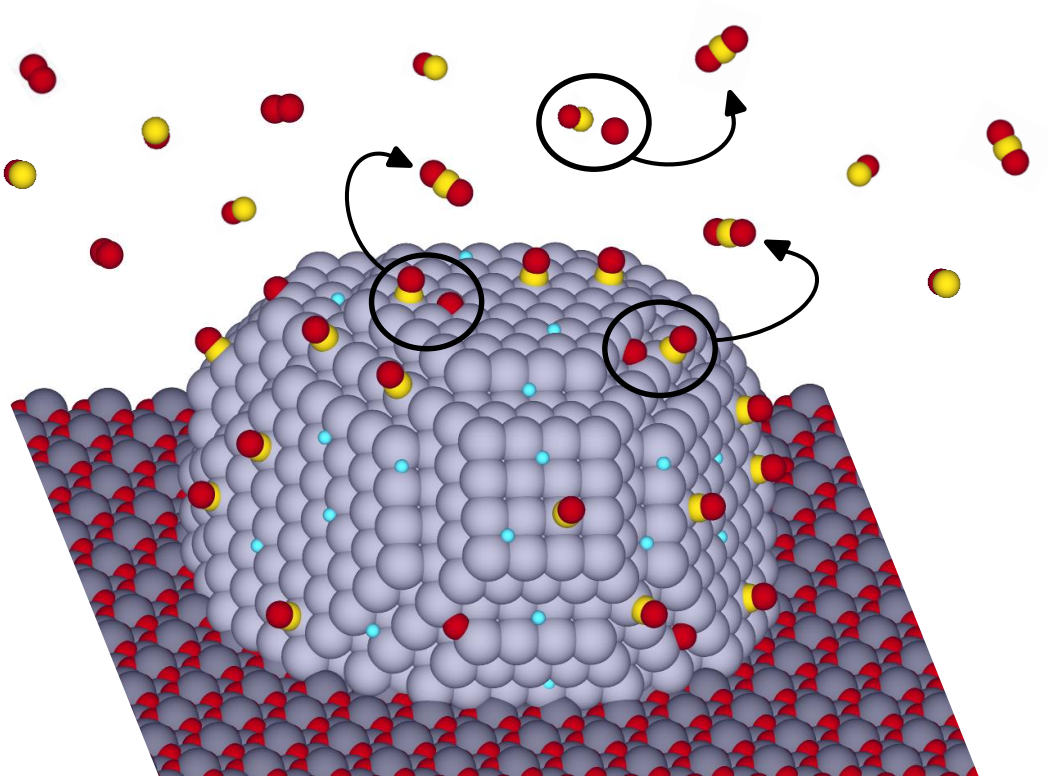

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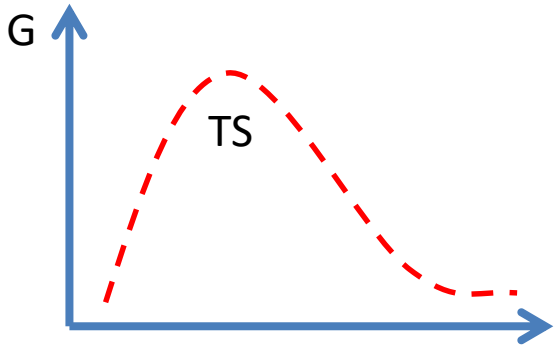

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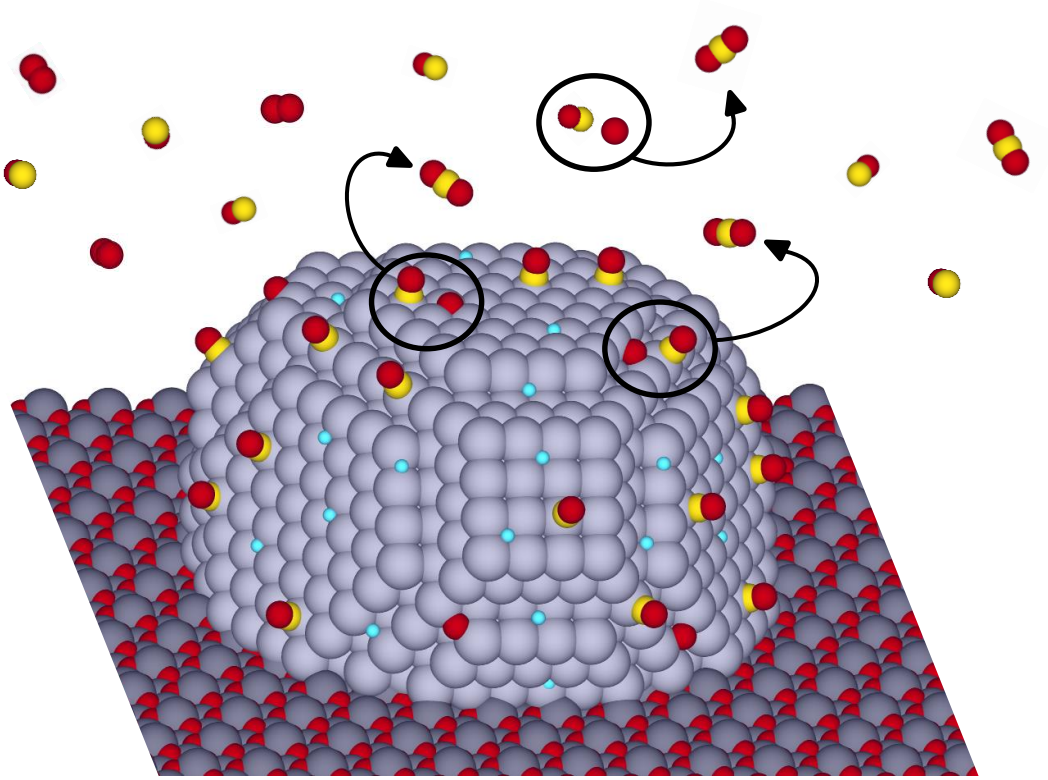
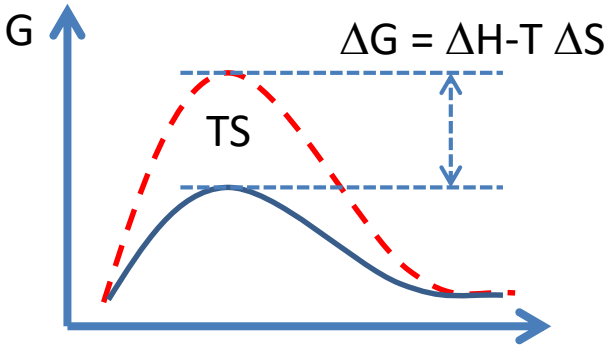


Catalyst: functional material with specific “active sites”, which provide a stabilization of the free energy of the TS



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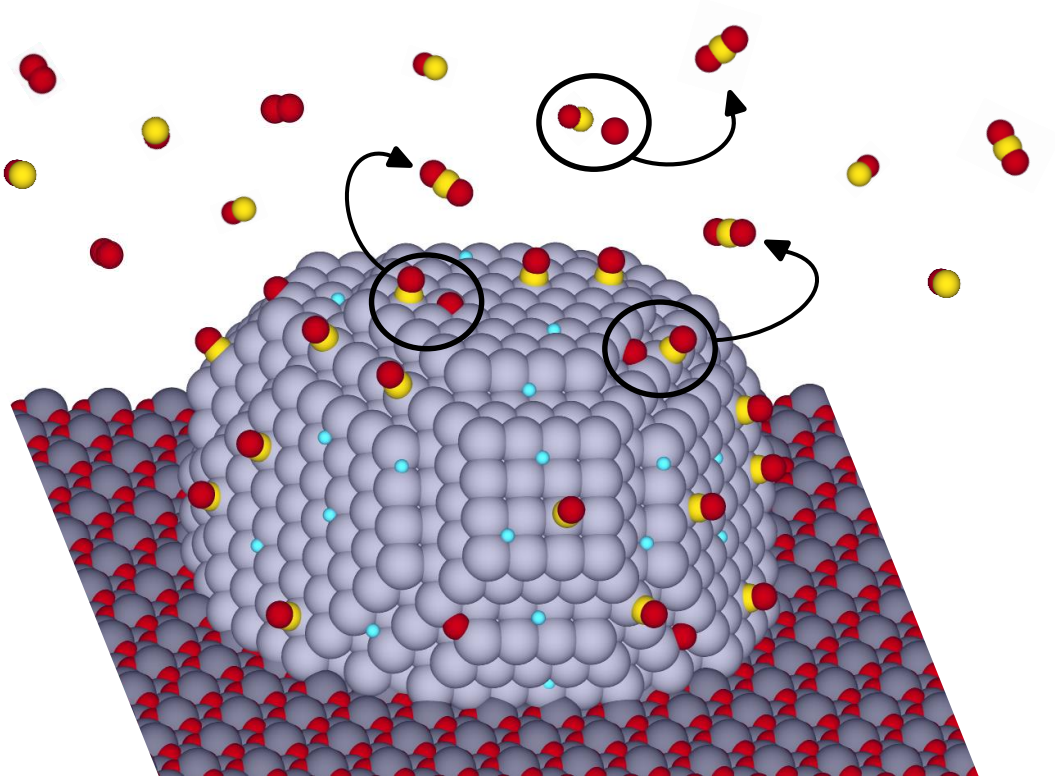

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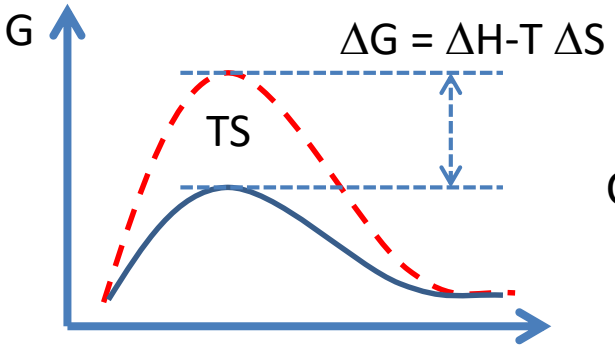

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G depends not only on H and S, but also on the local chemical potential

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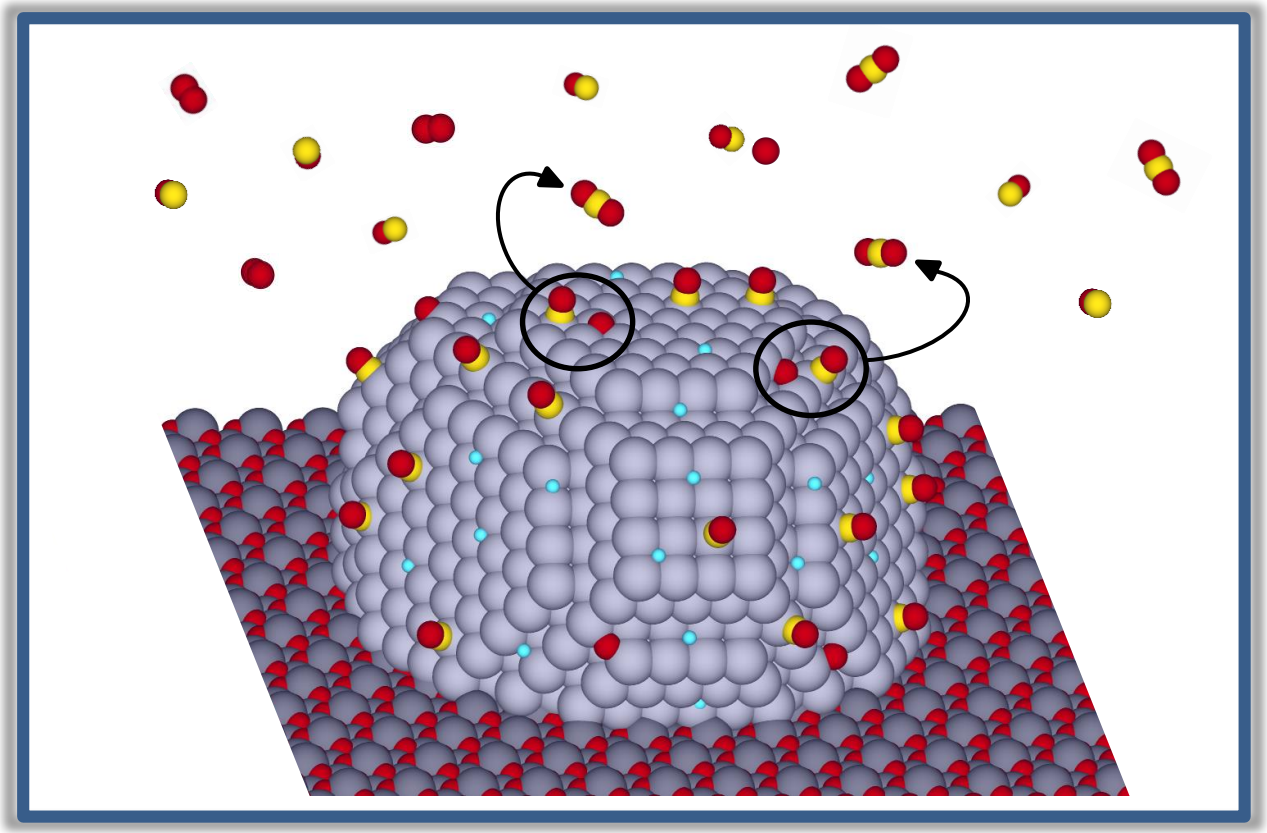

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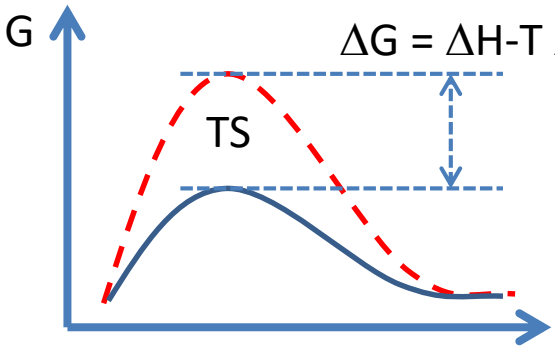

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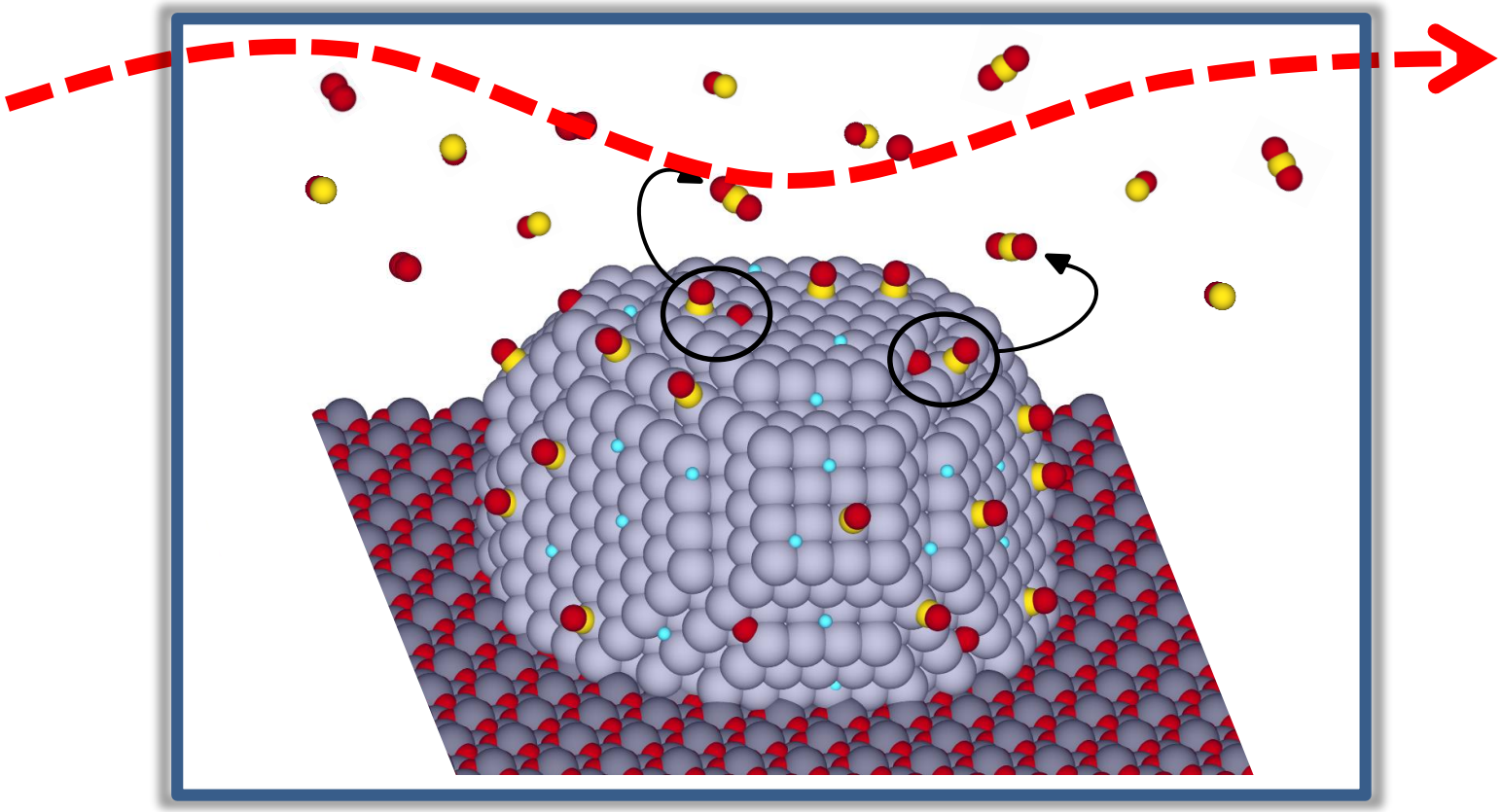

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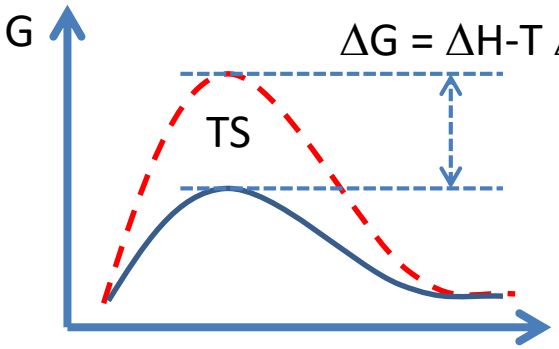

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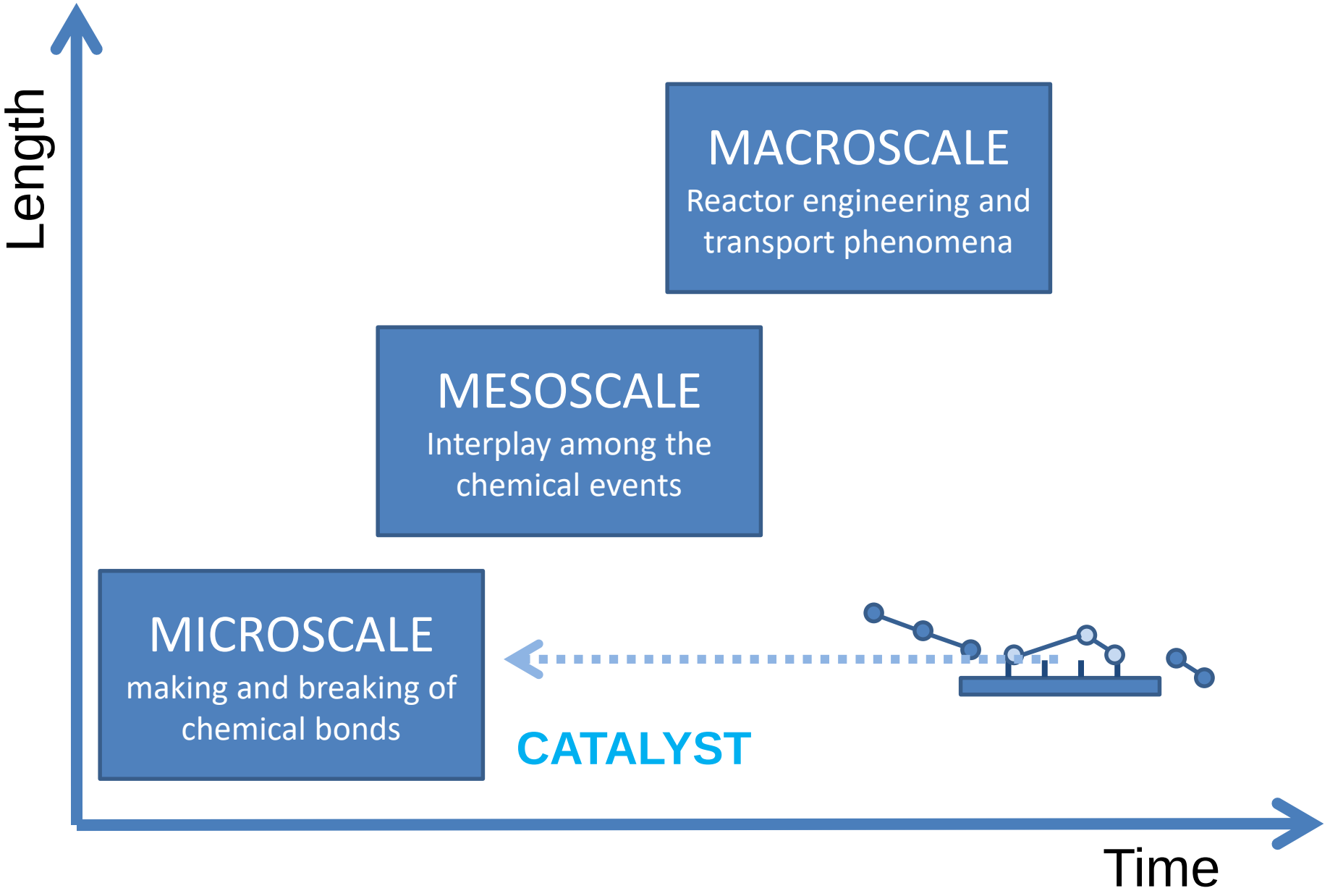
A multiscale functionality



A multiscale functionality

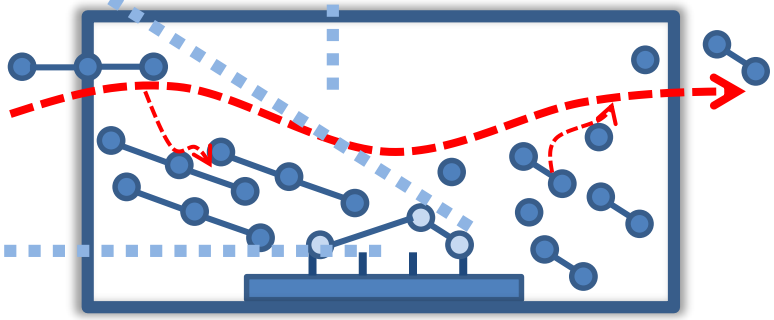
Length

CATALYTIC PROCESS

OBSERVED FUNCTIONALITY

MACROSCALE
Reactor engineering and transport phenomena

MESOSCALE
Interplay among the chemical events

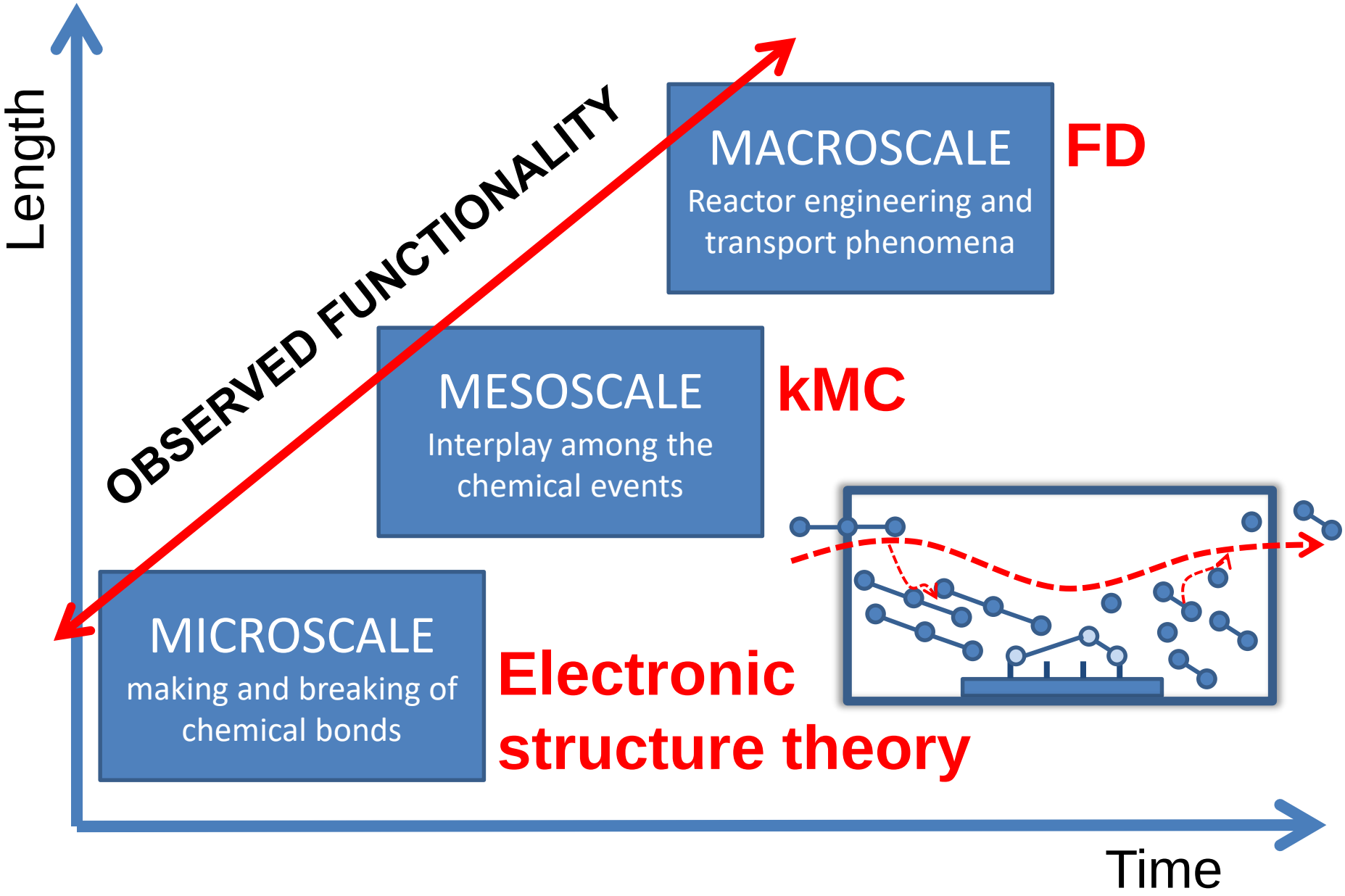


MICROSCALE
making and breaking of chemical bonds

CATALYST

Time

Functional-based design



Need of bridging the scales

Length

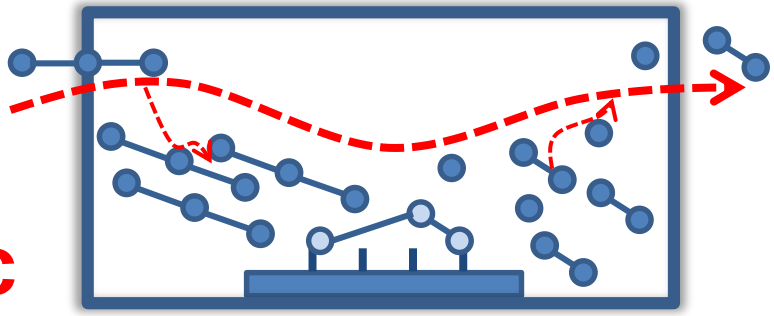
OBSERVED FUNCTIONALITY

MACROSCALE
Reactor engineering and transport phenomena

FD

MESOSCALE
Interplay among the chemical events

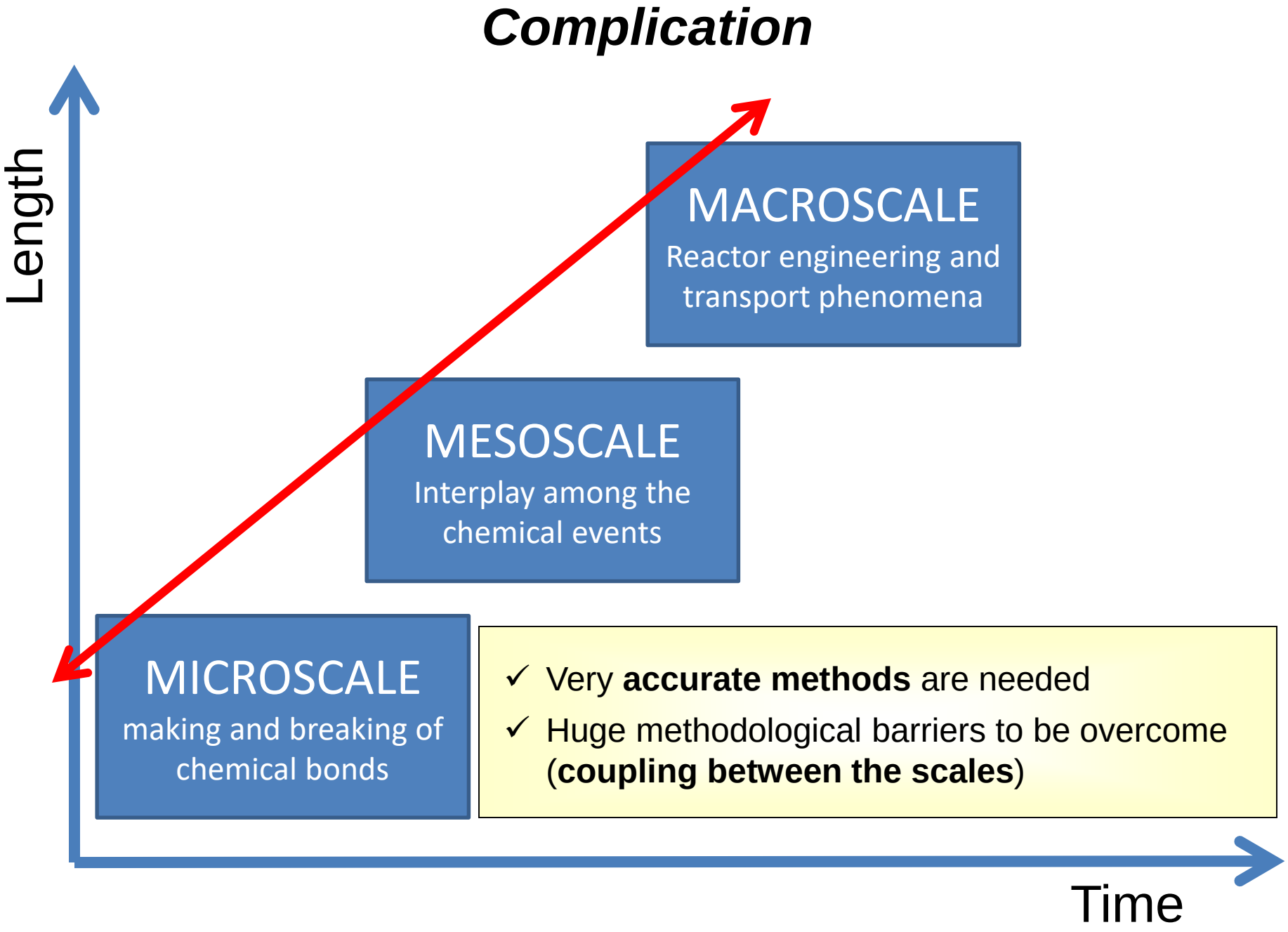
kMC

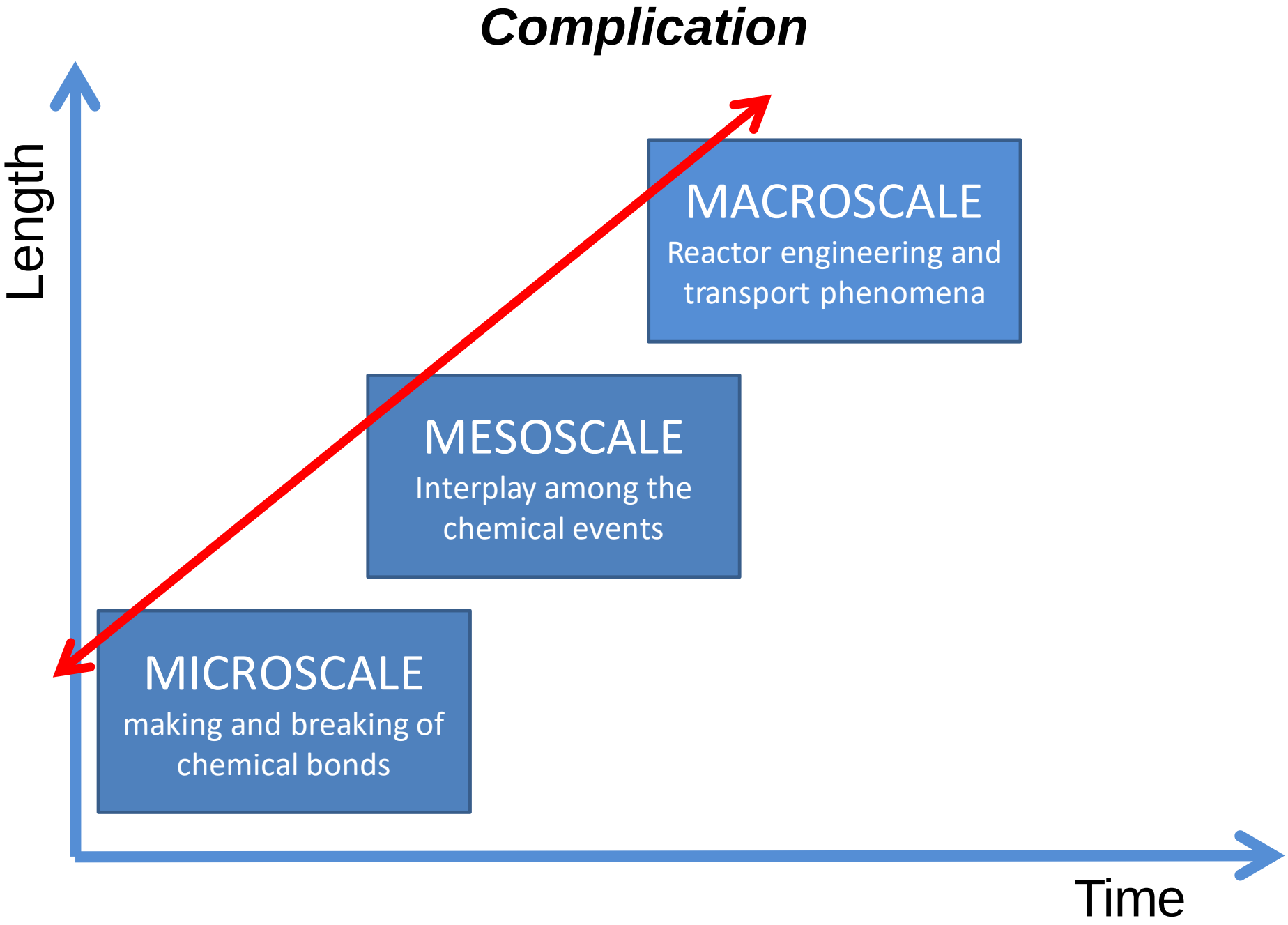


MICROSCALE
making and breaking of chemical bonds

Electronic structure theory

Time


Complication
Length
MACROSCALE
Reactor engineering and transport phenomena
MESOSCALE
Interplay among the chemical events
MICROSCALE
making and breaking of chemical bonds
✓ Very **accurate methods** are needed
✓ Huge methodological barriers to be overcome (**coupling between the scales**)
Time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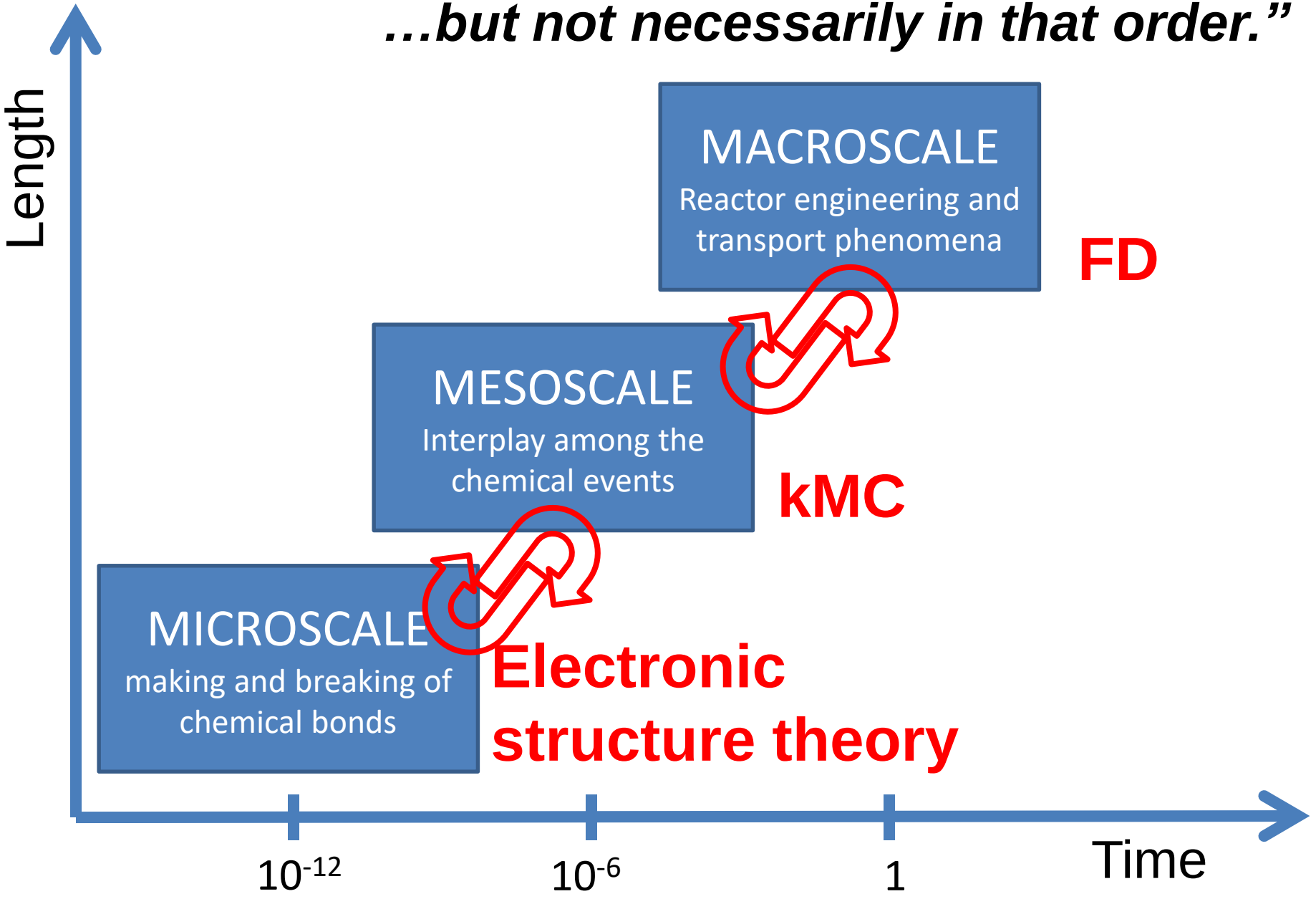
"First things first…

…but not necessarily in that order."



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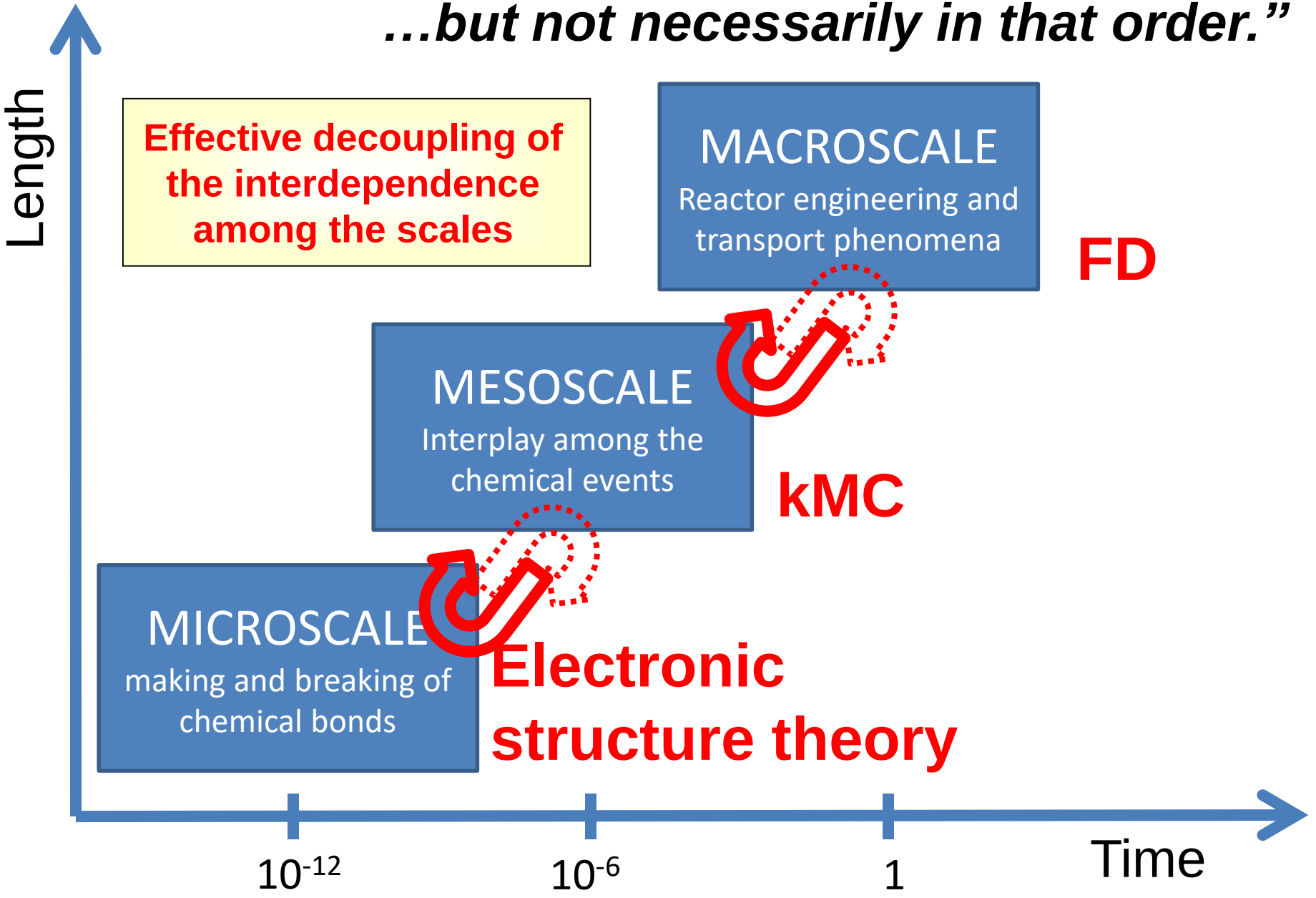
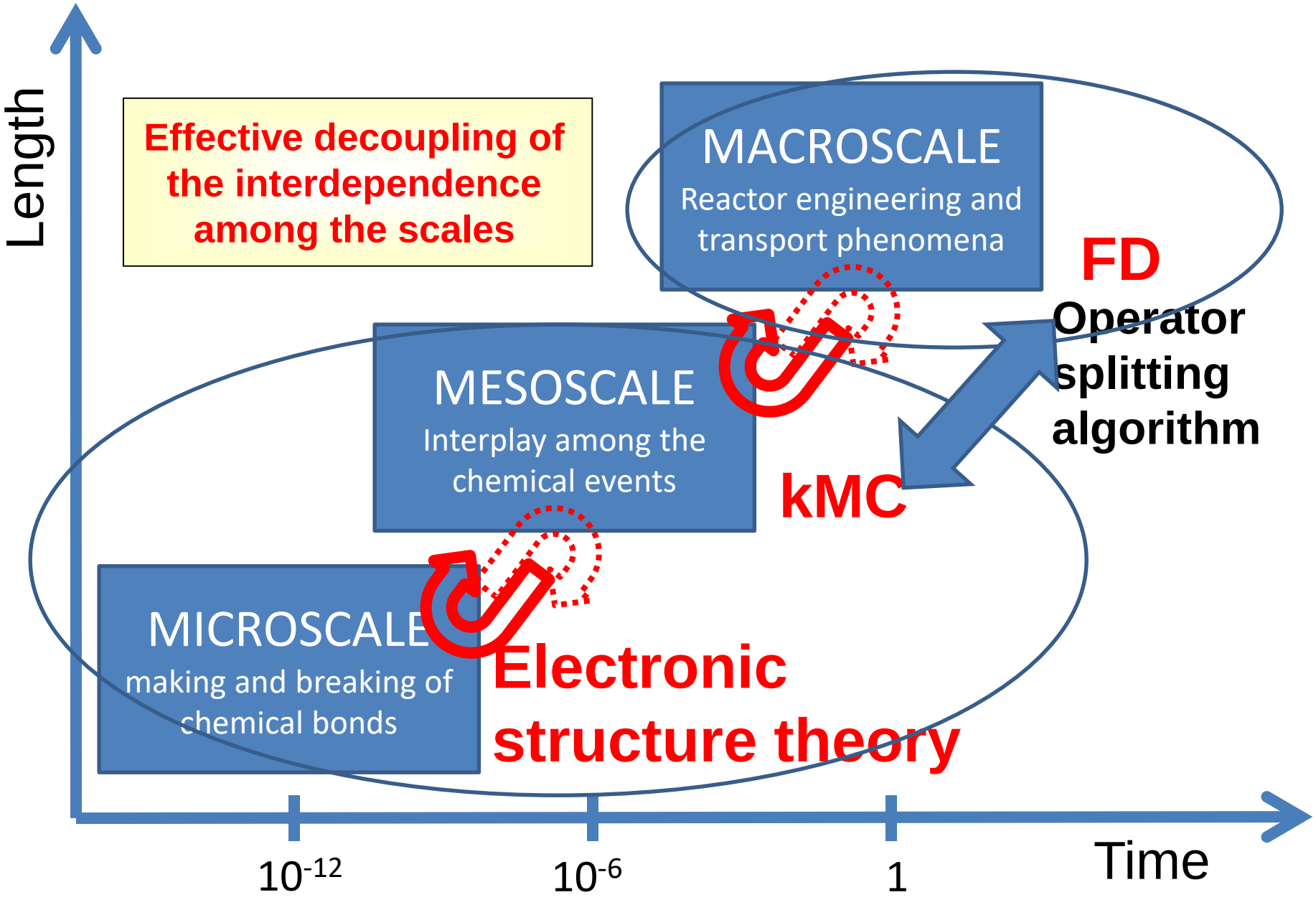


Coupling CFD and microkinetic models



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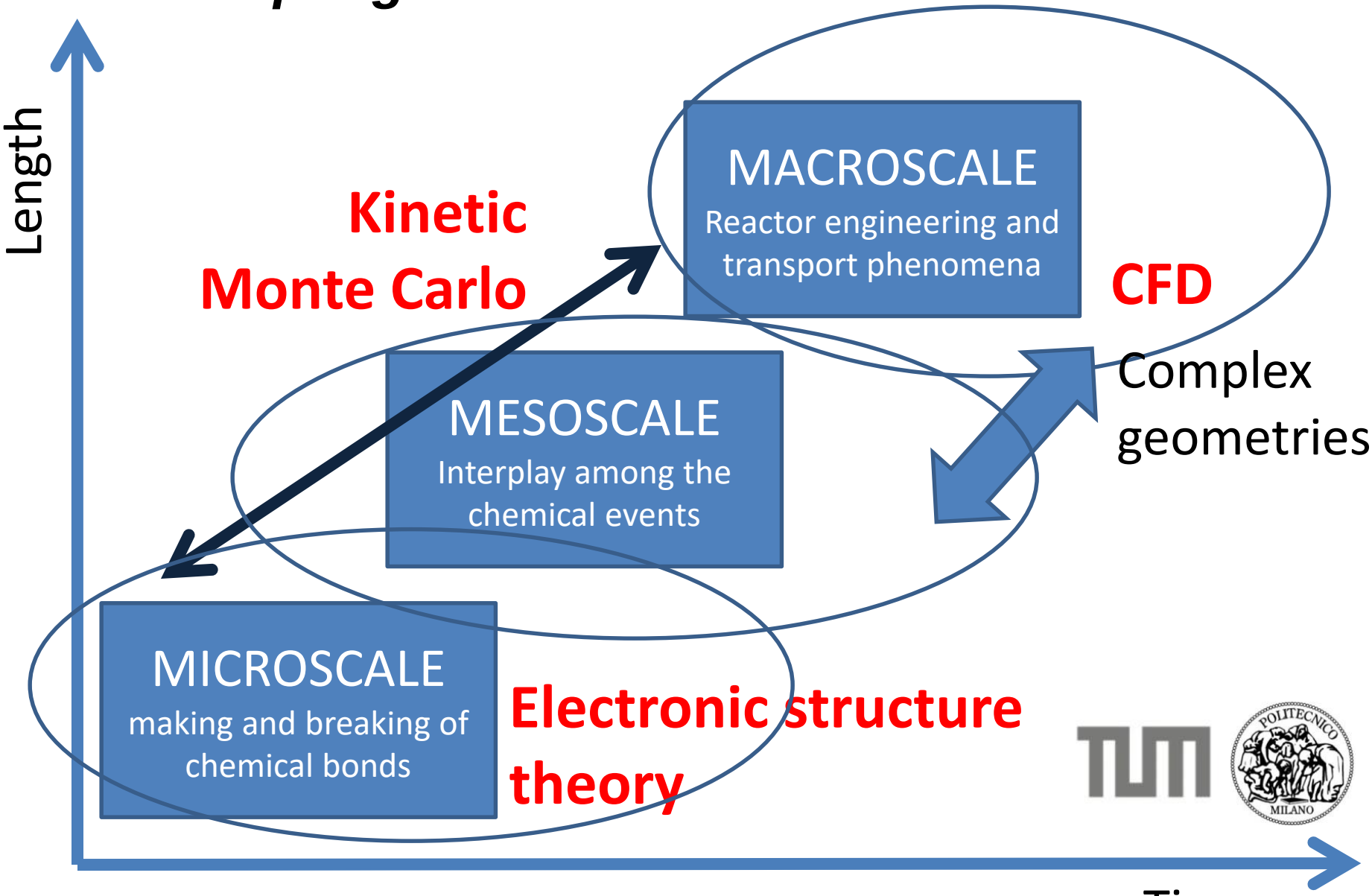

S. Matera, M. Maestri, A. Cuoci, K. Reuter, ACS Catalysis, 2014

Effective decoupling of interdependencies

- Continuum equations need boundary conditions for the mass fluxes j^{α} at the surface:

$$j_n^{\alpha} = v^{\alpha} M^{\alpha} \mathbf{TOF}$$

- **Coupled problem**: to determine the TOF with 1p-kMC the pressures at the surface are needed, but the pressure field depends on the TOF
- **kMC too expensive** for direct coupling to the flow solver

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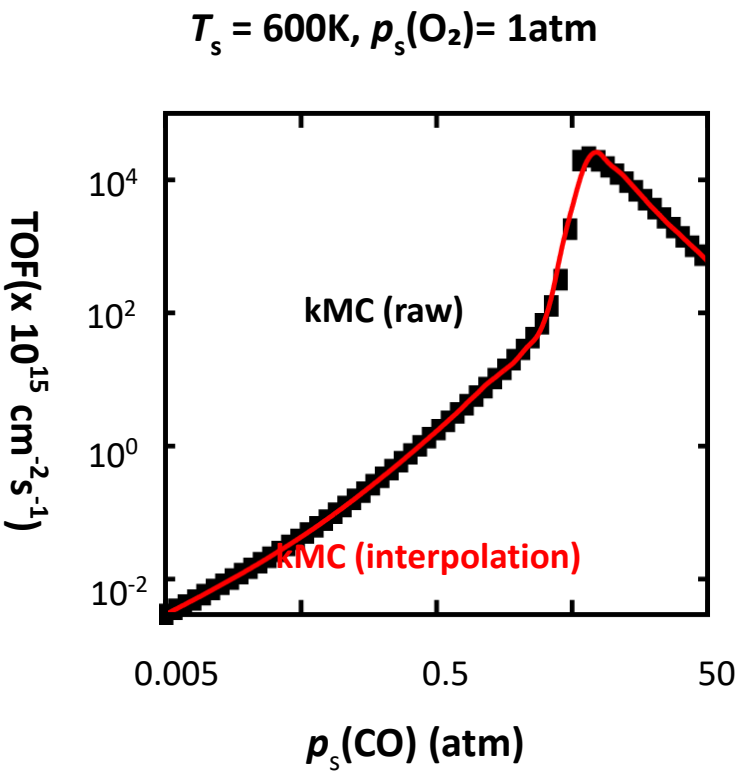
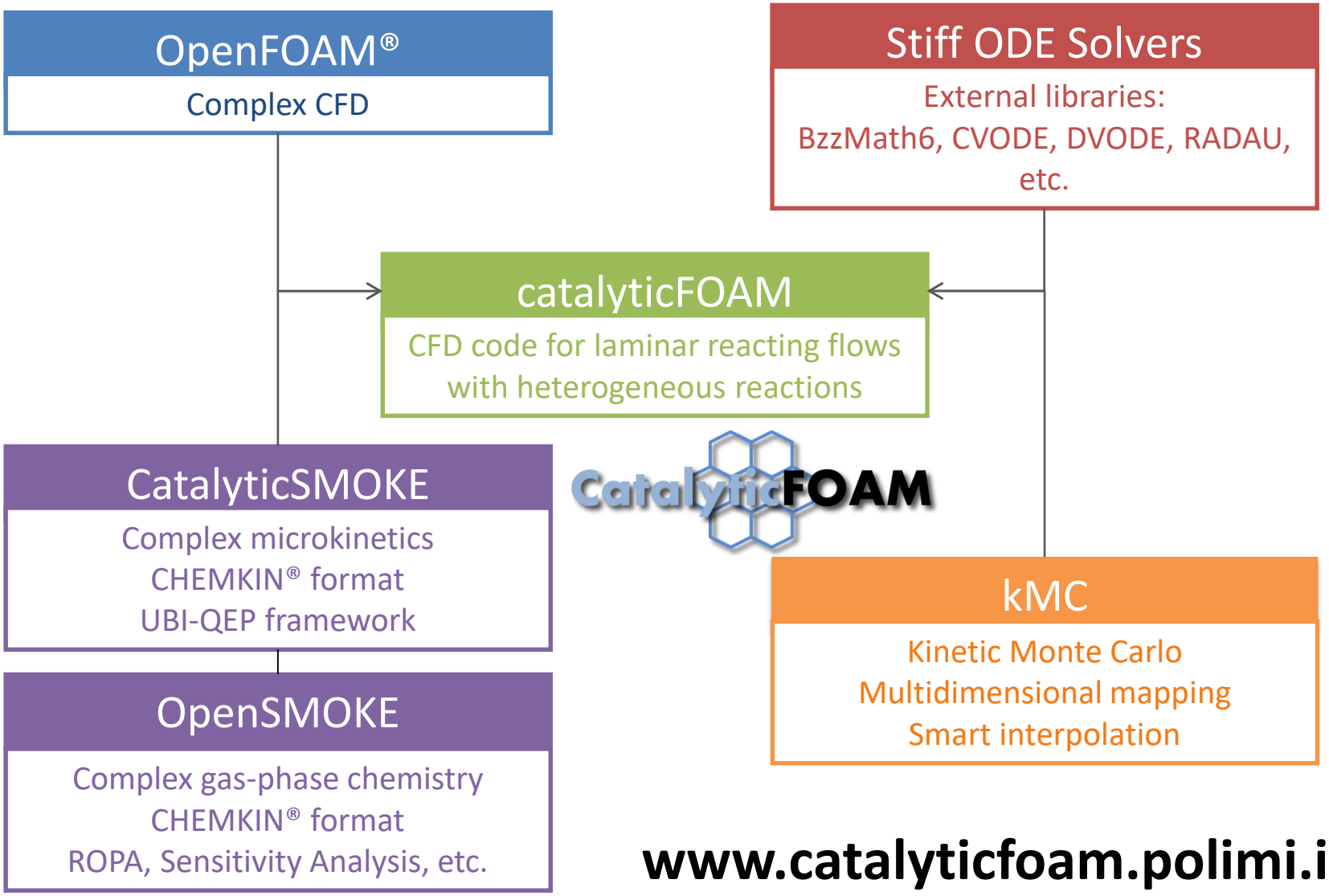
- **Coupled problem**: to determine the TOF with 1p-kMC the pressures at the surface are needed, but the pressure field depends on the TOF
- **kMC too expensive** for direct coupling to the flow solver
- **Run kMC beforehand and interpolate (Modified Shepard)**
- **The interpolated function will be then used during CFD**



S. Matera and K. Reuter, *Catal. Lett.* **133**, 156-159 (2009); *Phys. Rev. B* **82**, 085446 (2010).

catalyticFOAM multiscale framework

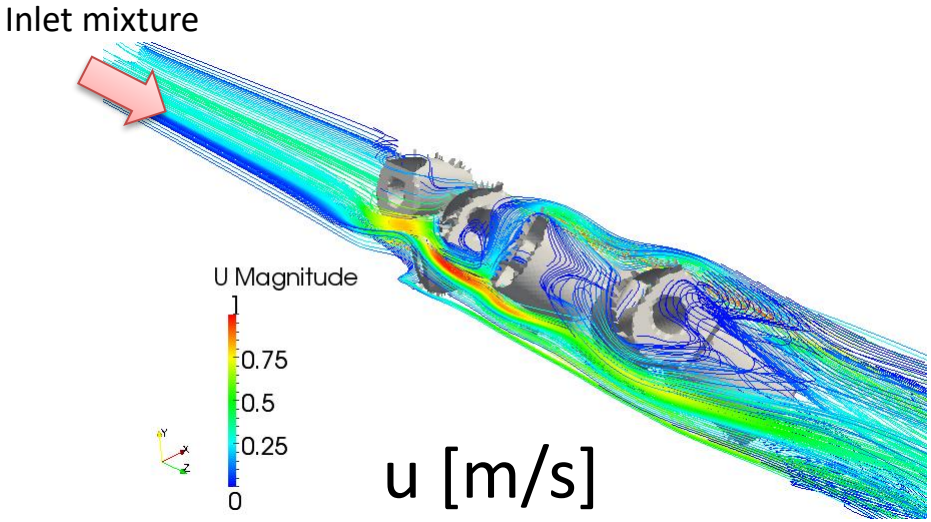


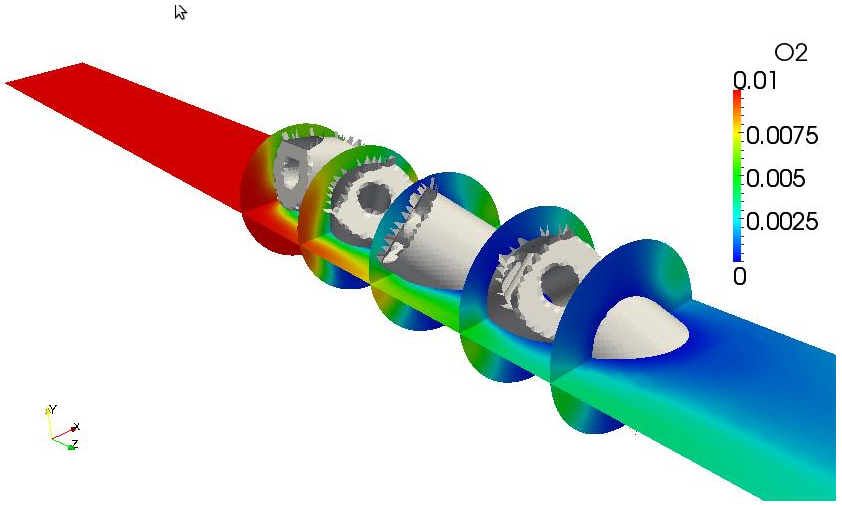
www.catalyticfoam.polimi.it

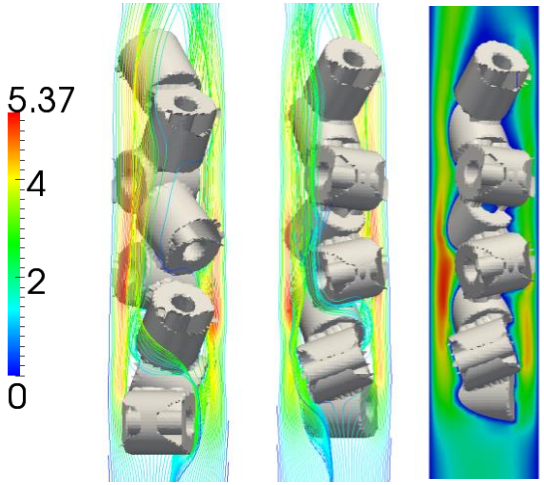
M. Maestri and A. Cuoci, *Chemical Engineering Science*, *96*, *2013*, *106-117*

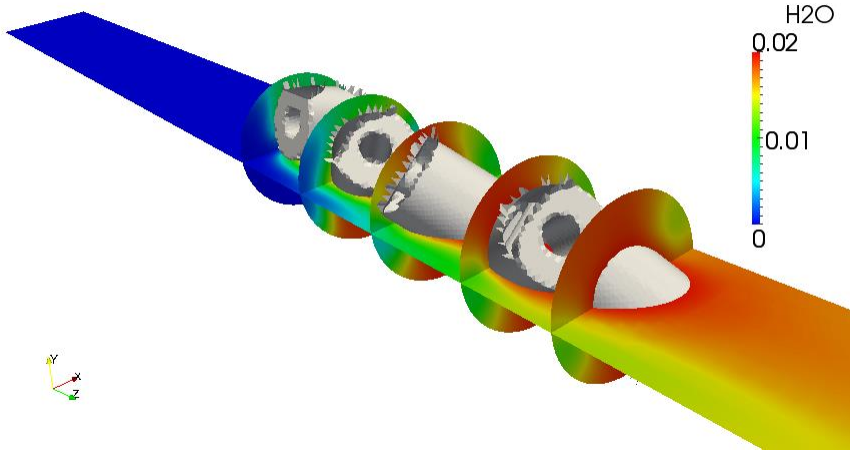
T. Maffei et al., *Chemical Engineering Journal*, *283*, *2016*, *1392-1404*

Show-case: Rashig-ring bed



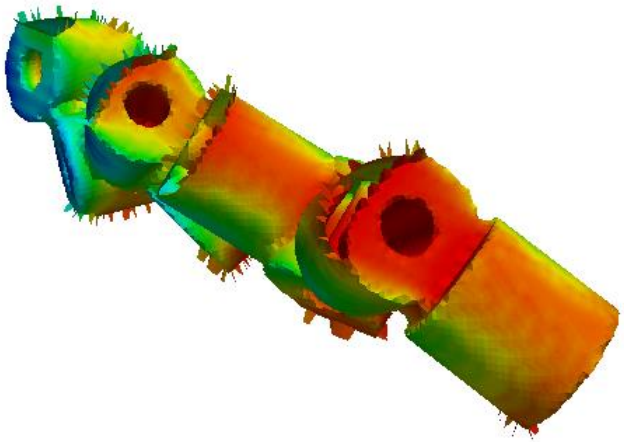


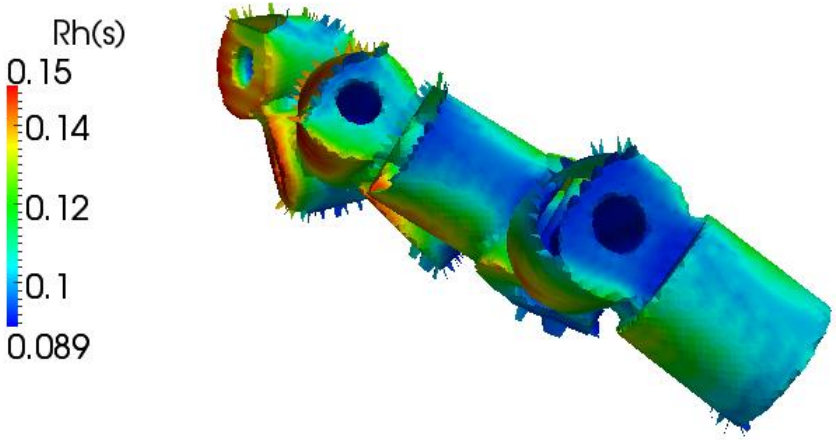




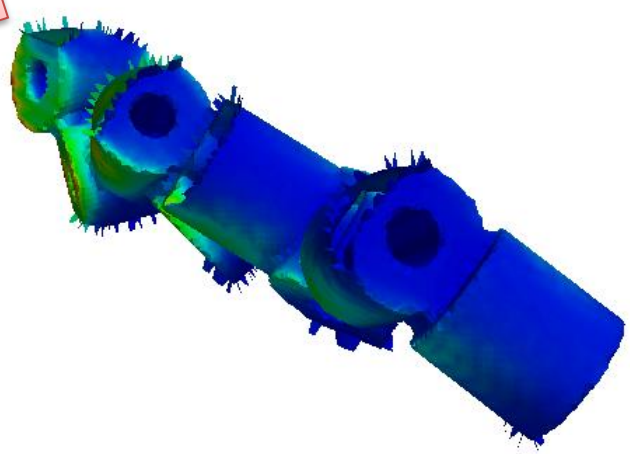
Show-case: Rashig-ring bed

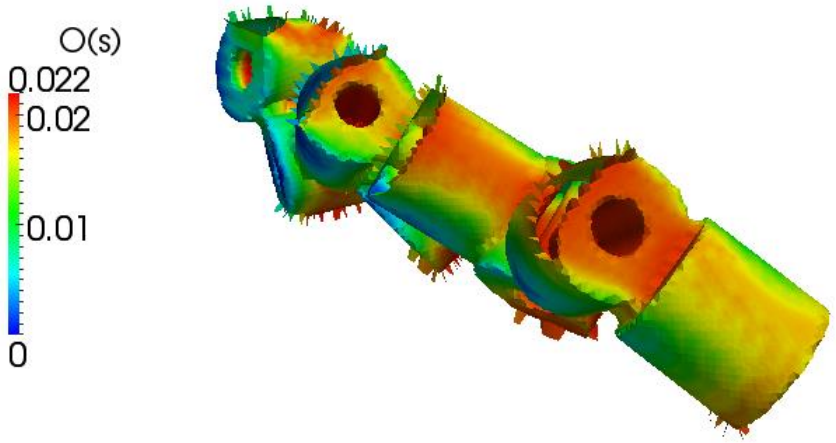
Adsorbed species at the catalyst surface



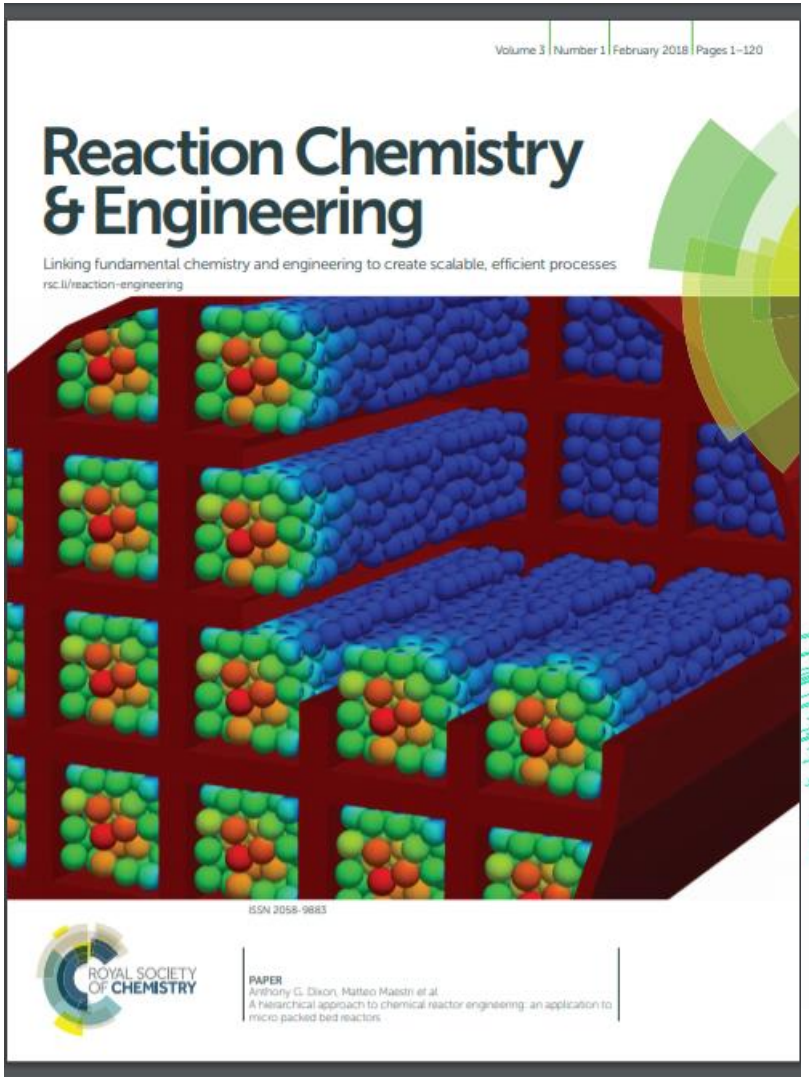


Inlet mixture

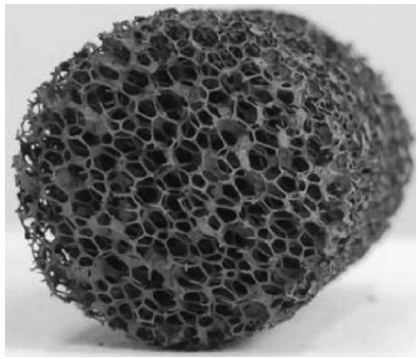


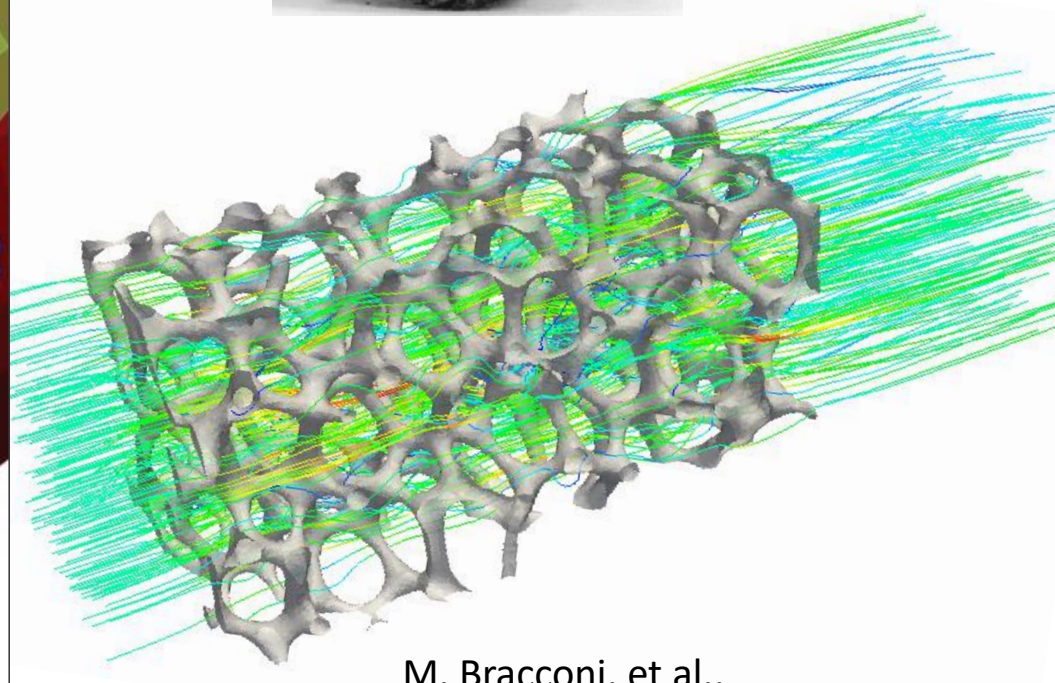


Complex domains



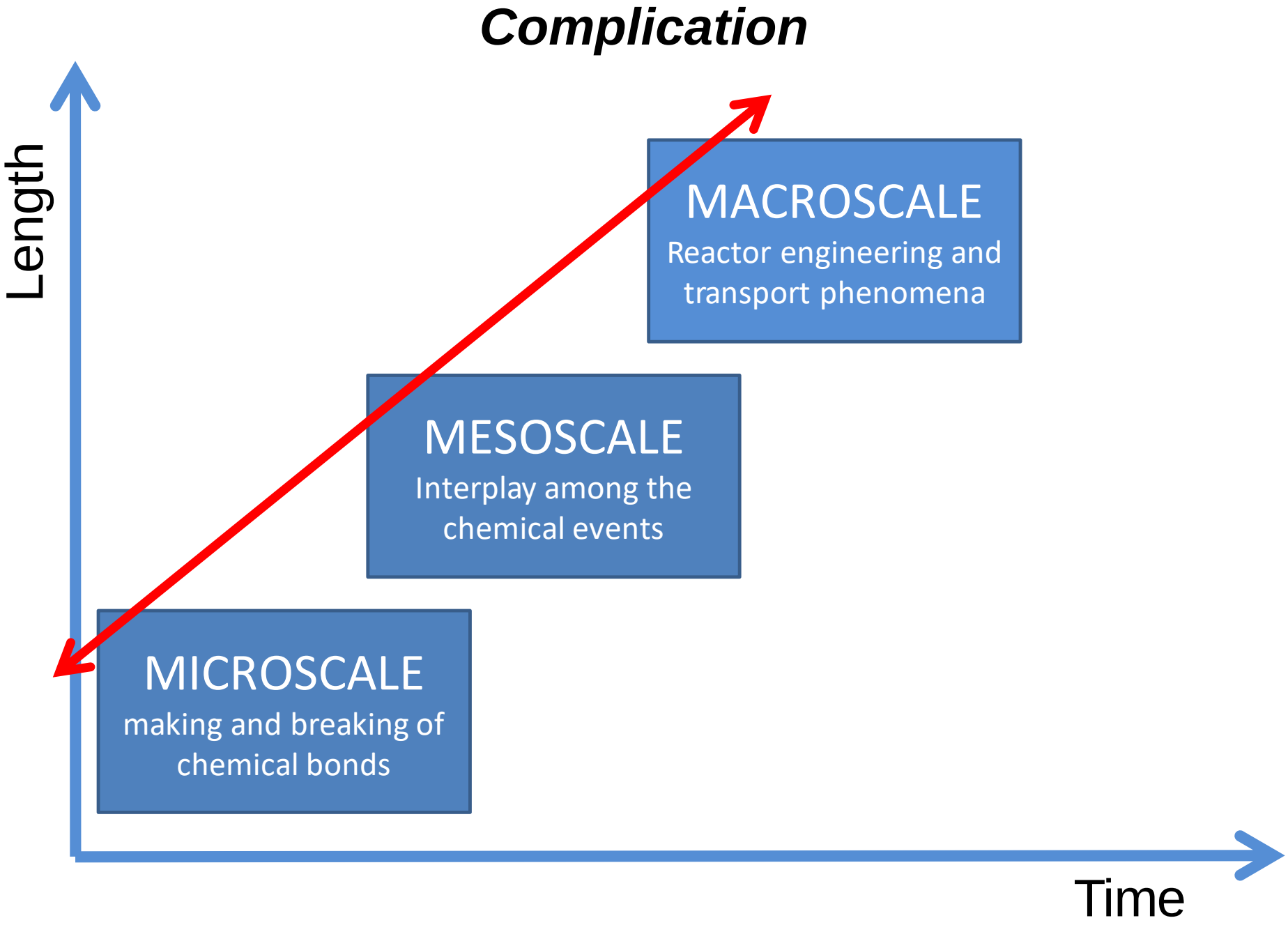
S. Rebughini, M. Bracconi, A.G. Dixon, M. Maestri,
Reaction Chemistry and Engineering, 3, 2018, 25 - 33





M. Bracconi, et al.,
Chemical Engineering Journal, 315, 2017, 608-620

M. Bracconi et al., *AIChE Journal, 63, 2017, 95-104*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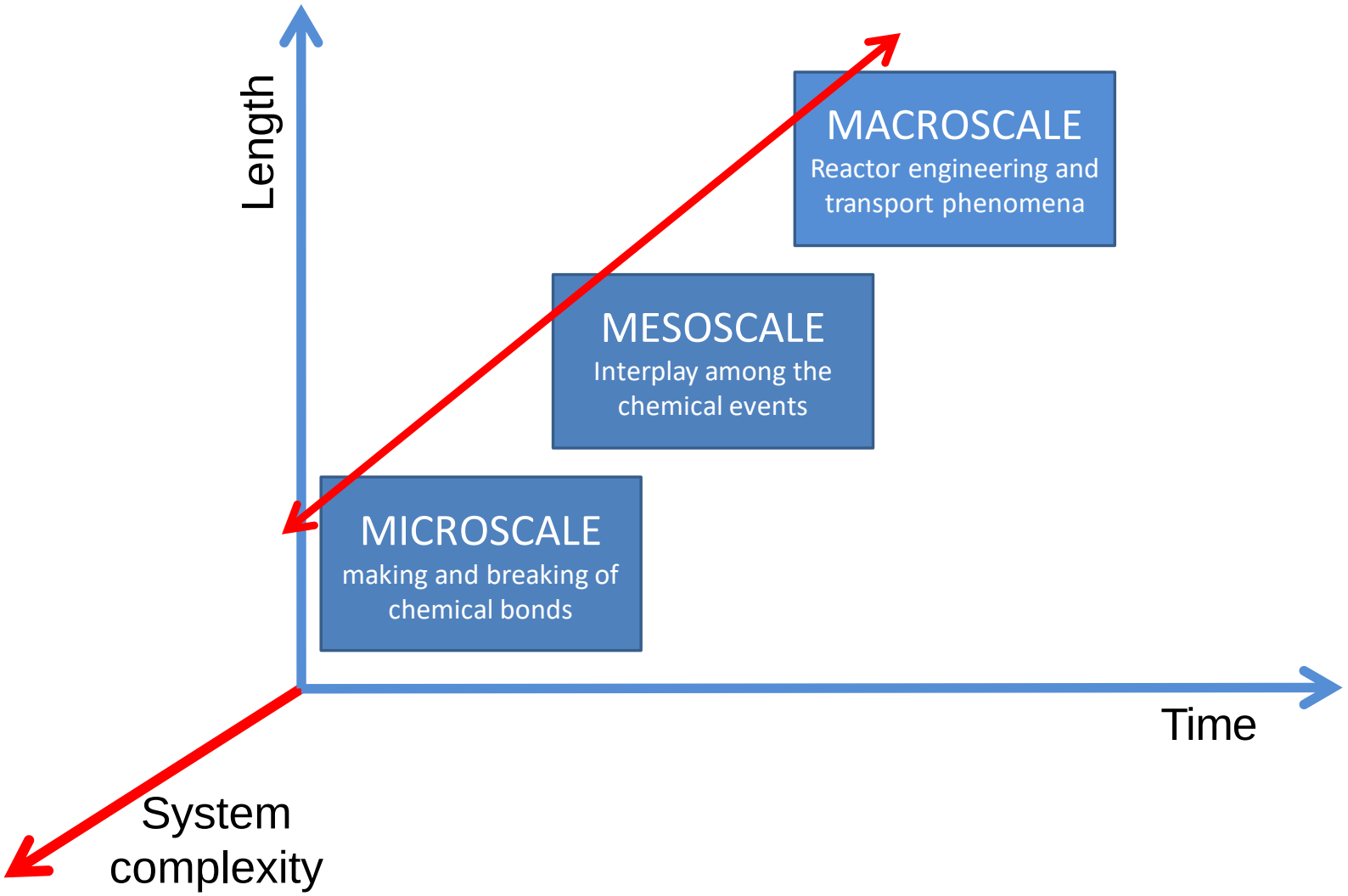
Complication + complexity



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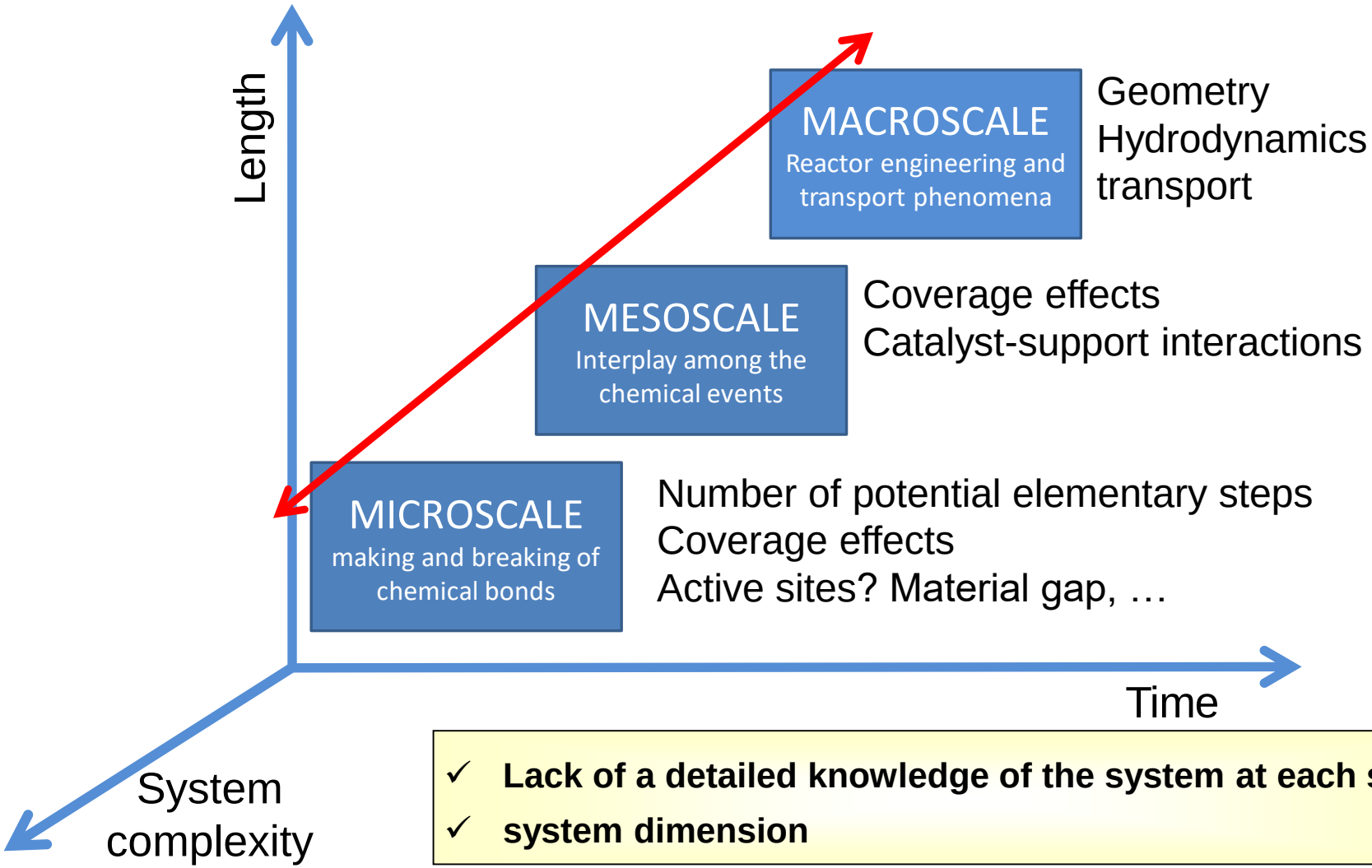
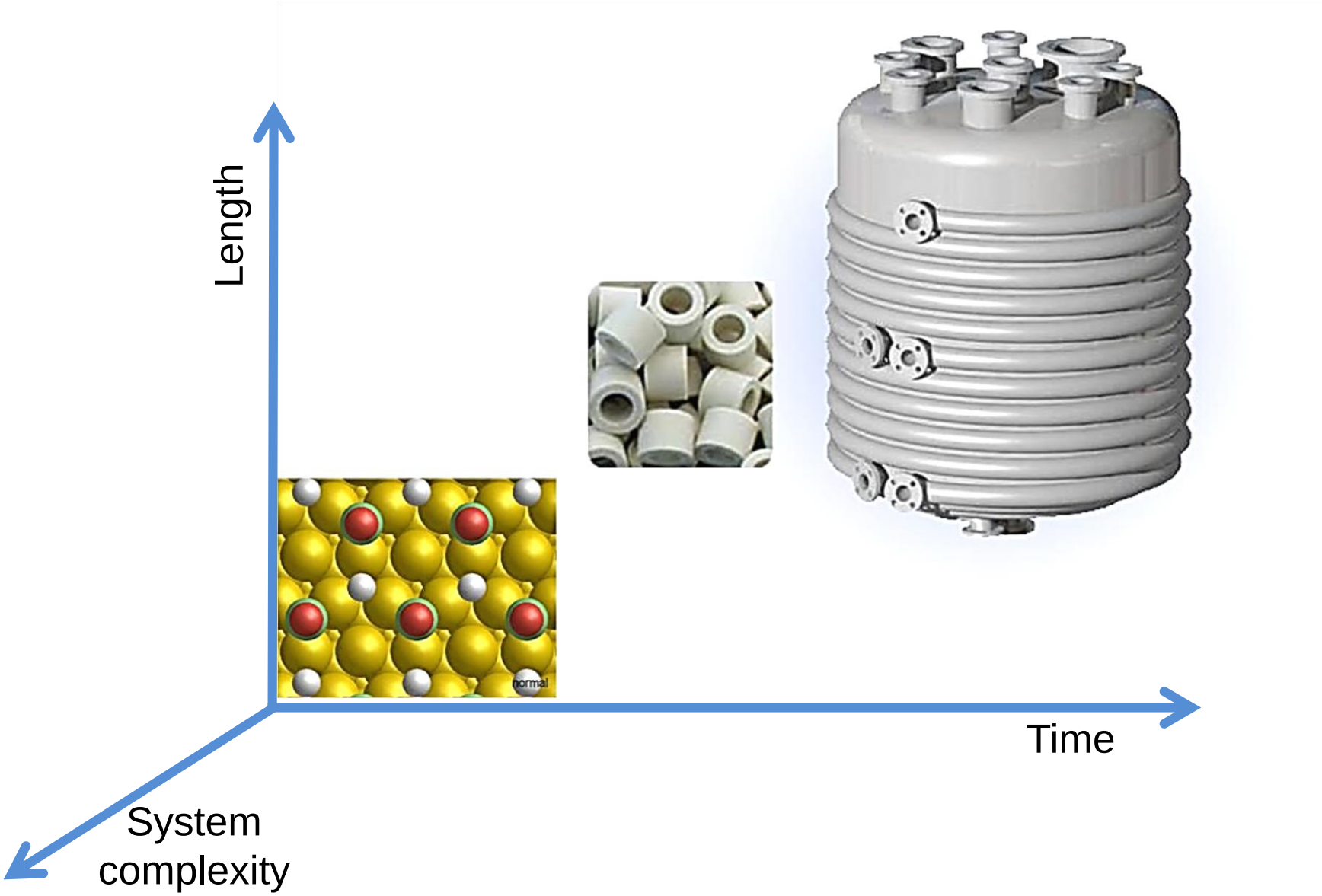


- ✓ **Lack of a detailed knowledge of the system at each scale**
- ✓ **system dimension**

The complication and complexity trap



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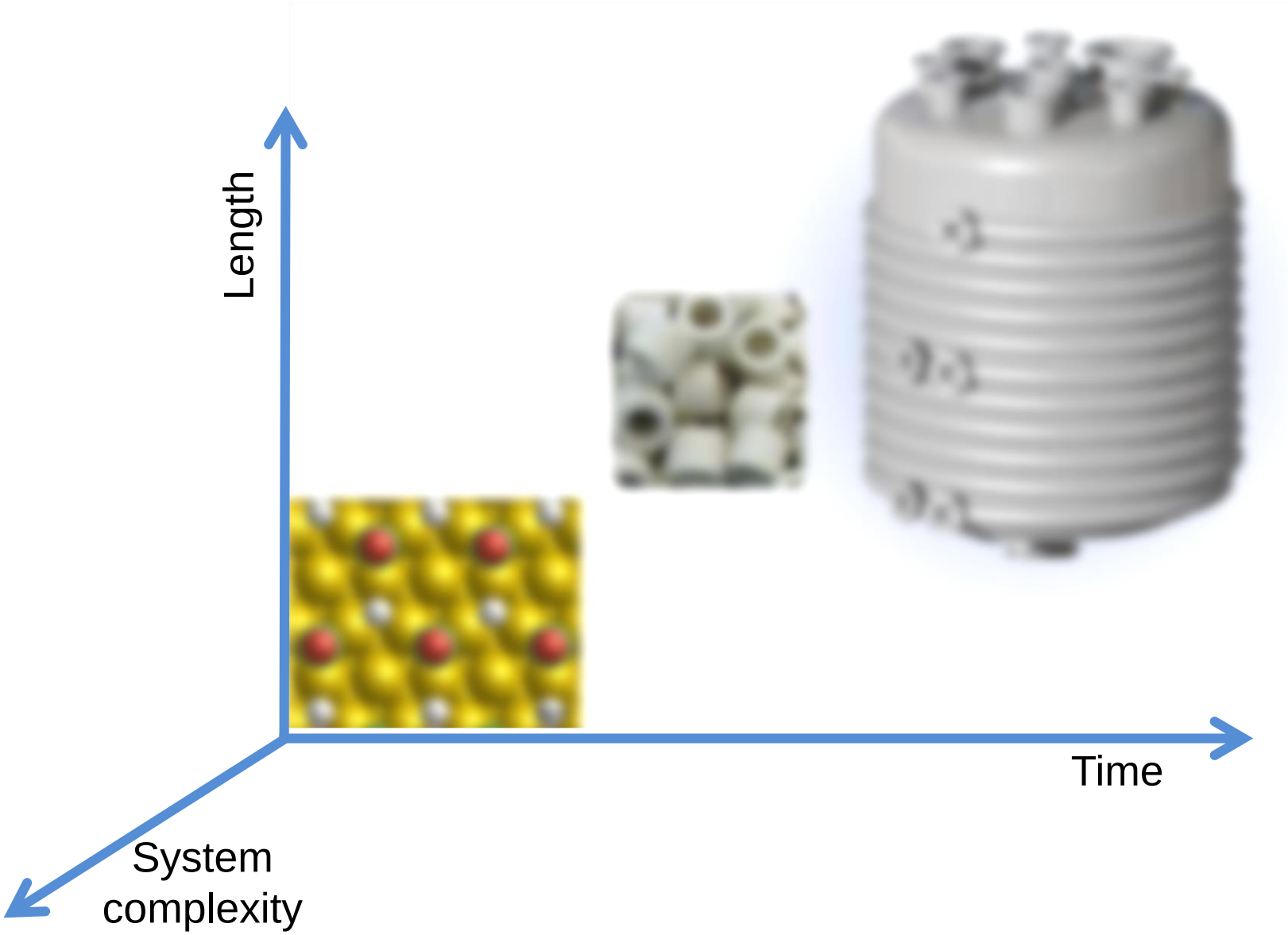

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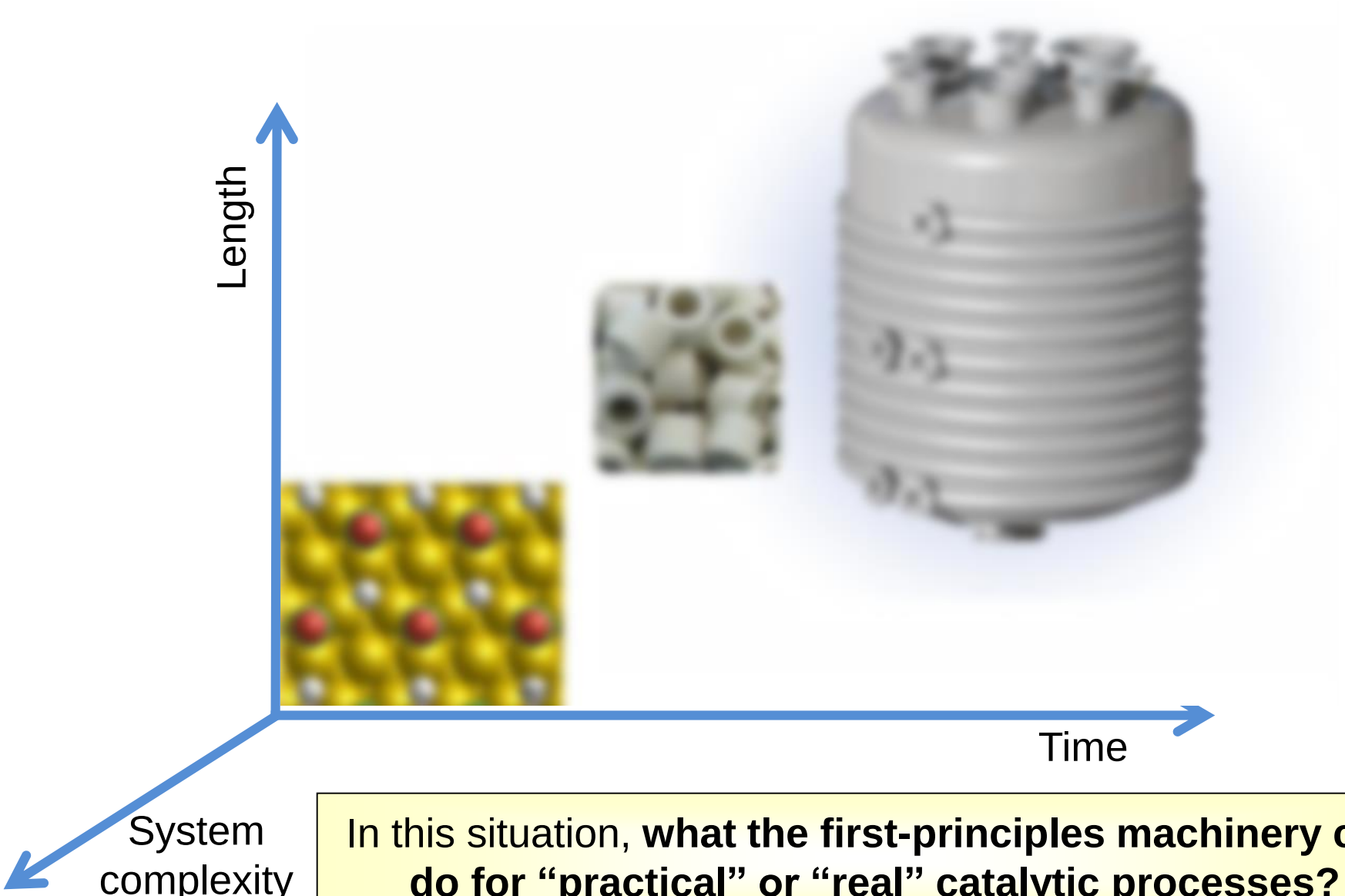
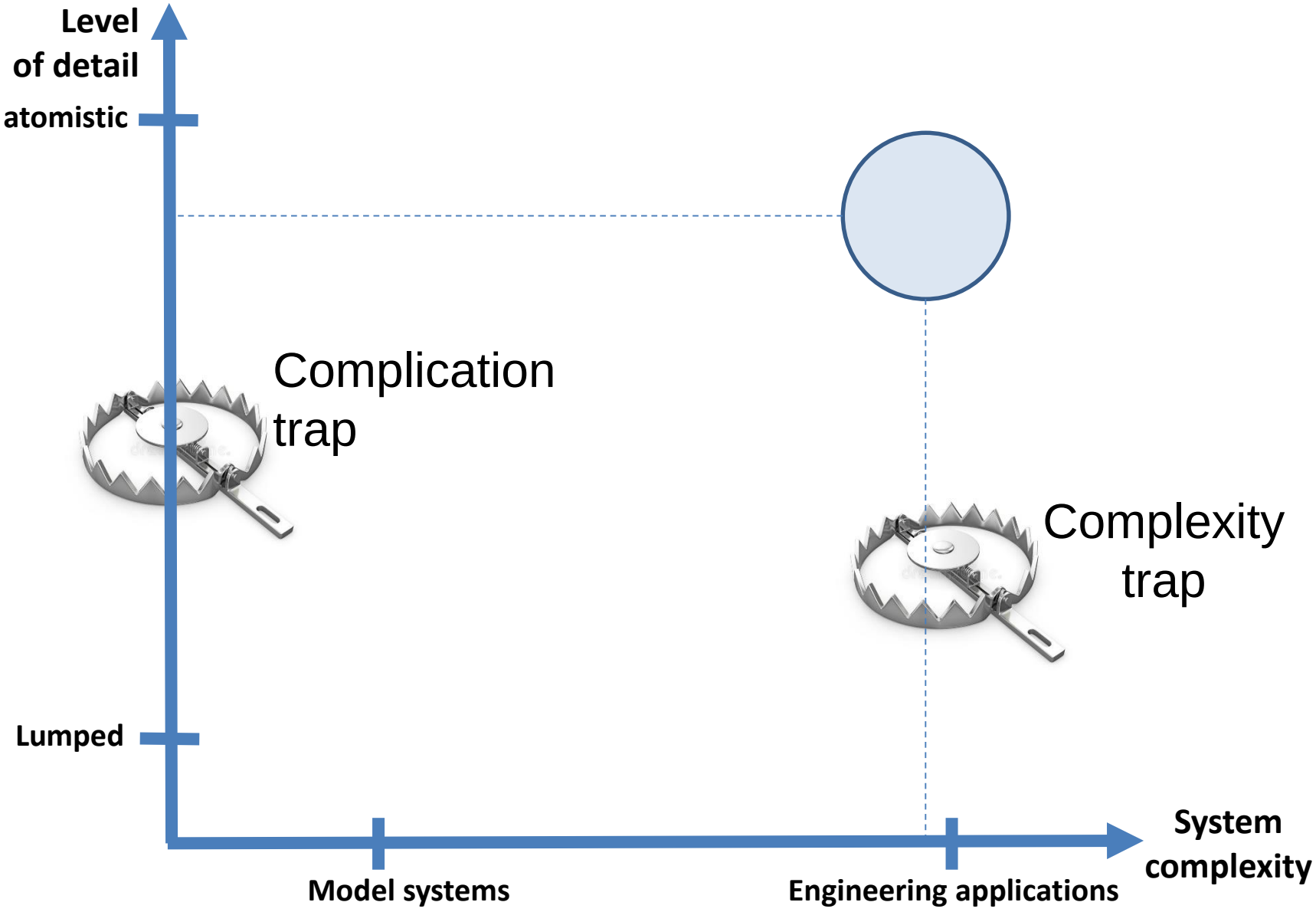


In this situation, **what the first-principles machinery can do for “practical” or “real” catalytic processes?**

The complication and complexity trap



M. Maestri, *Chem. Commun.*, *2017,53, 10244-10254*

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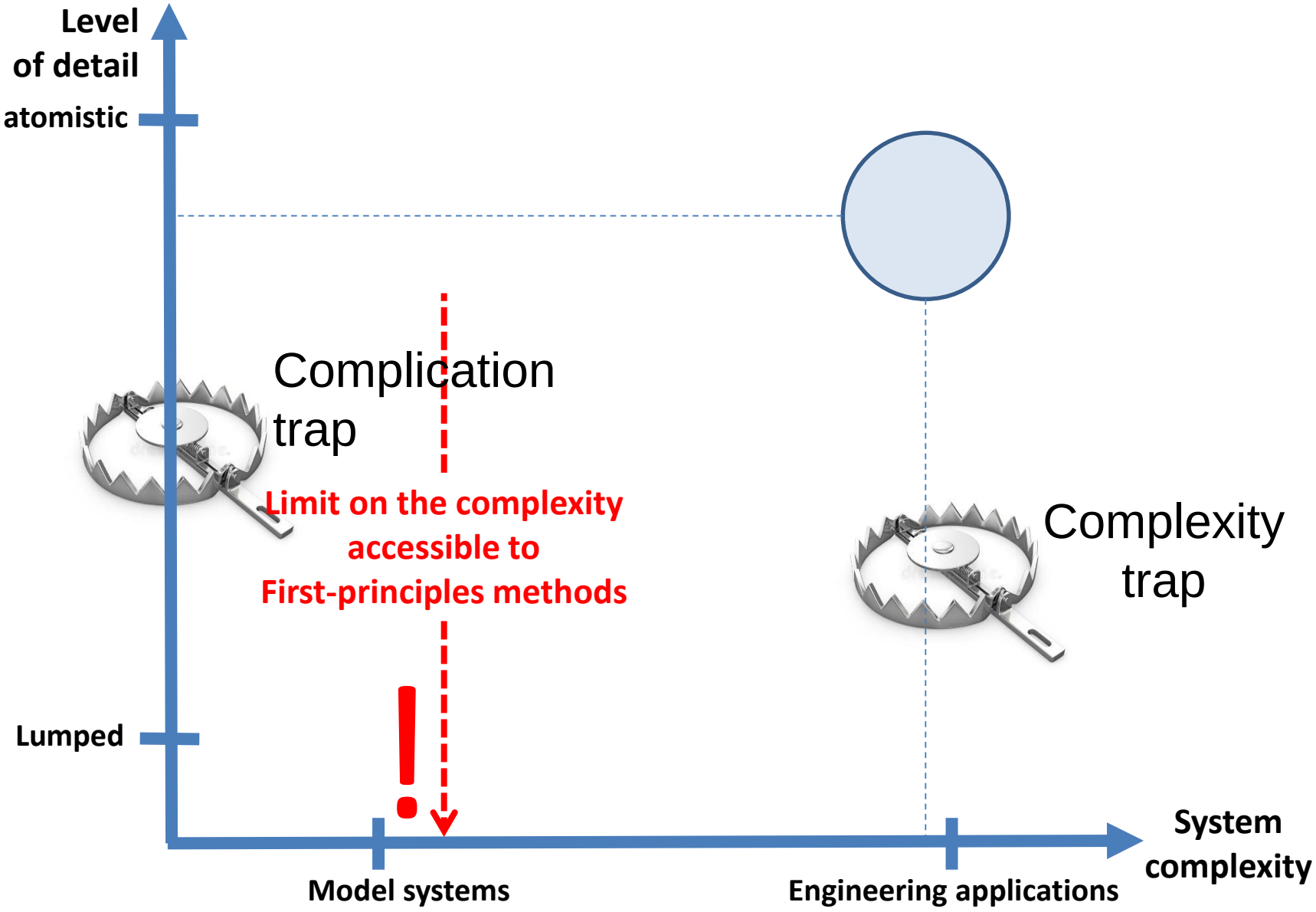

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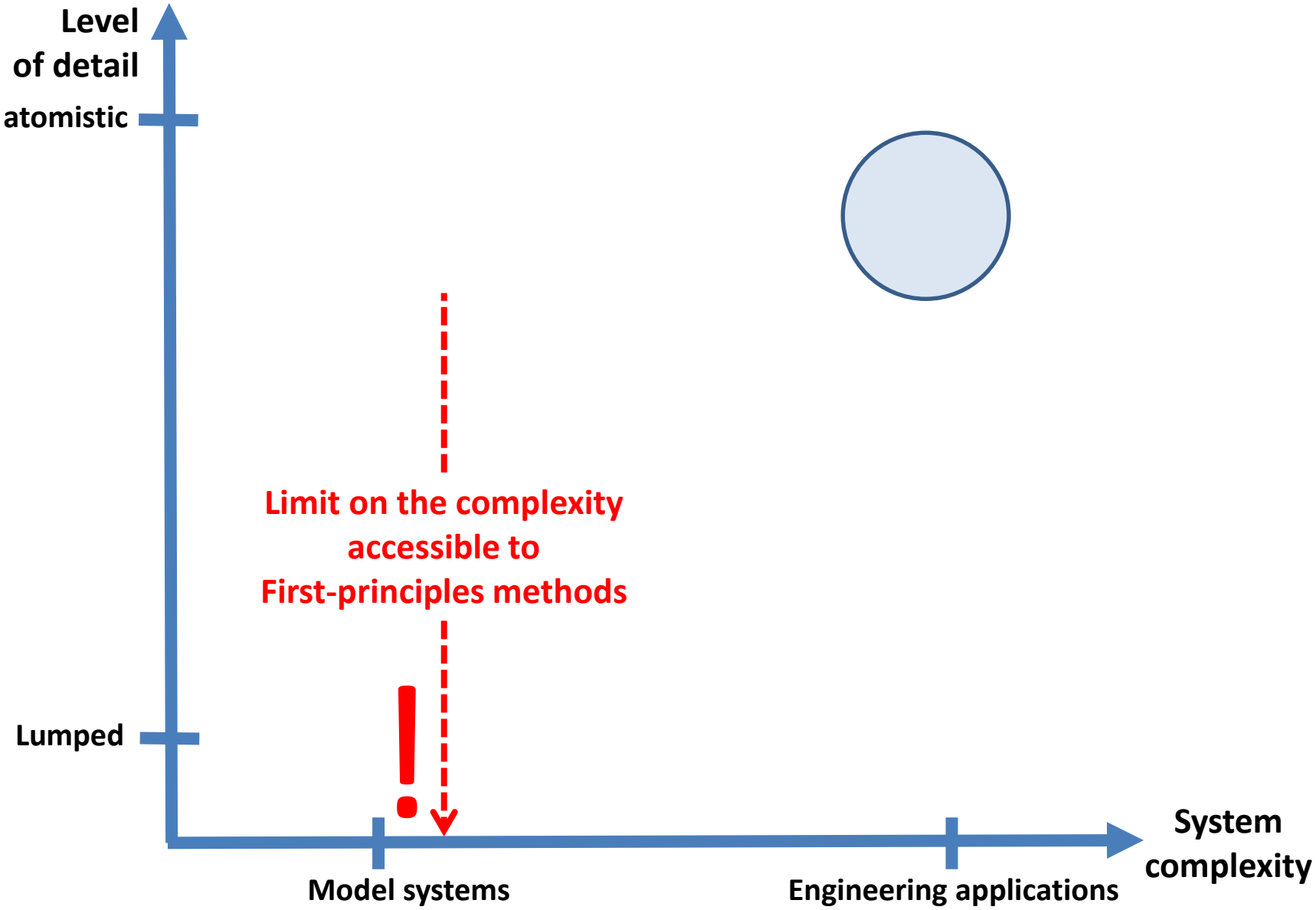
Hierarchical multiscale approach



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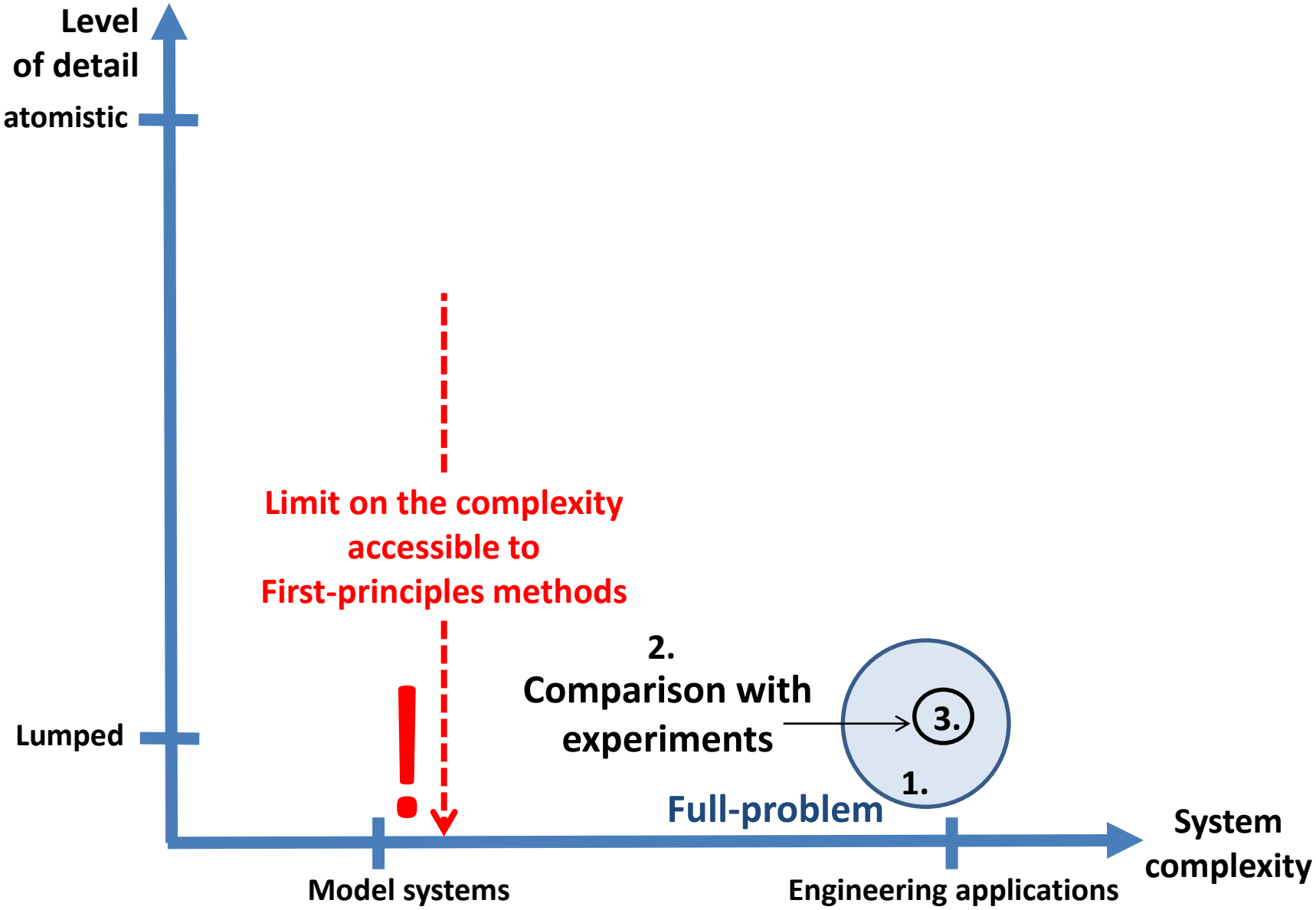

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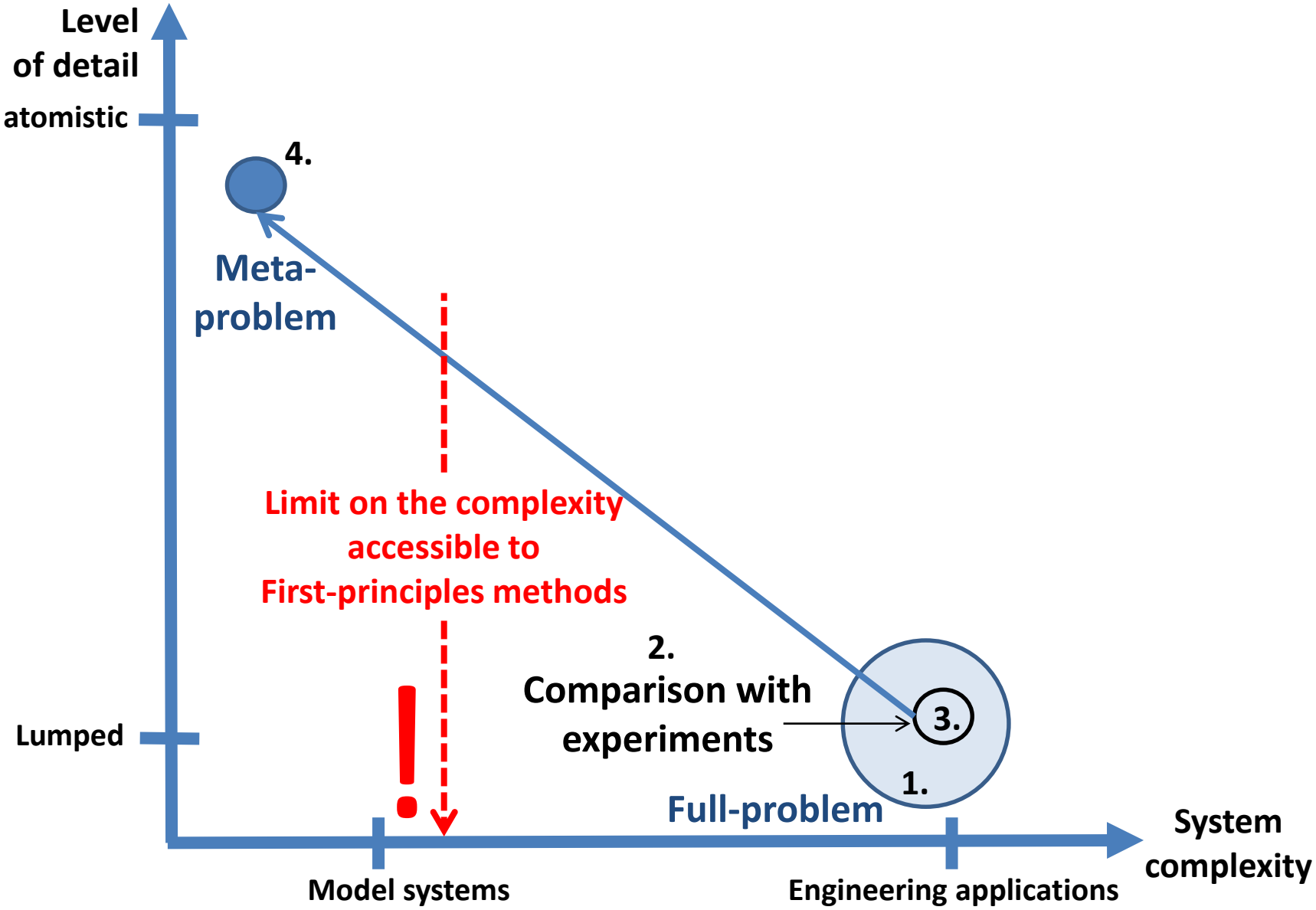

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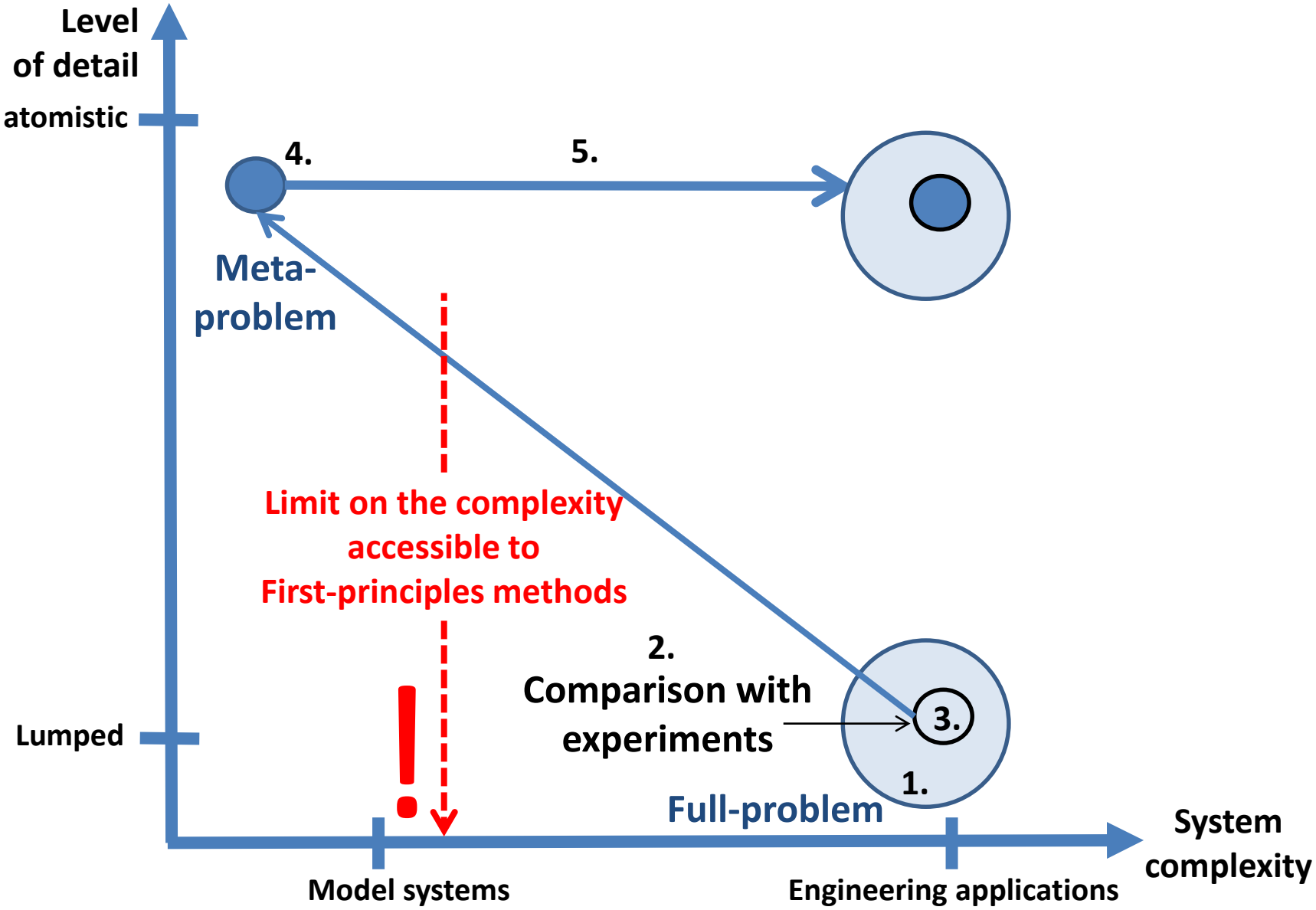

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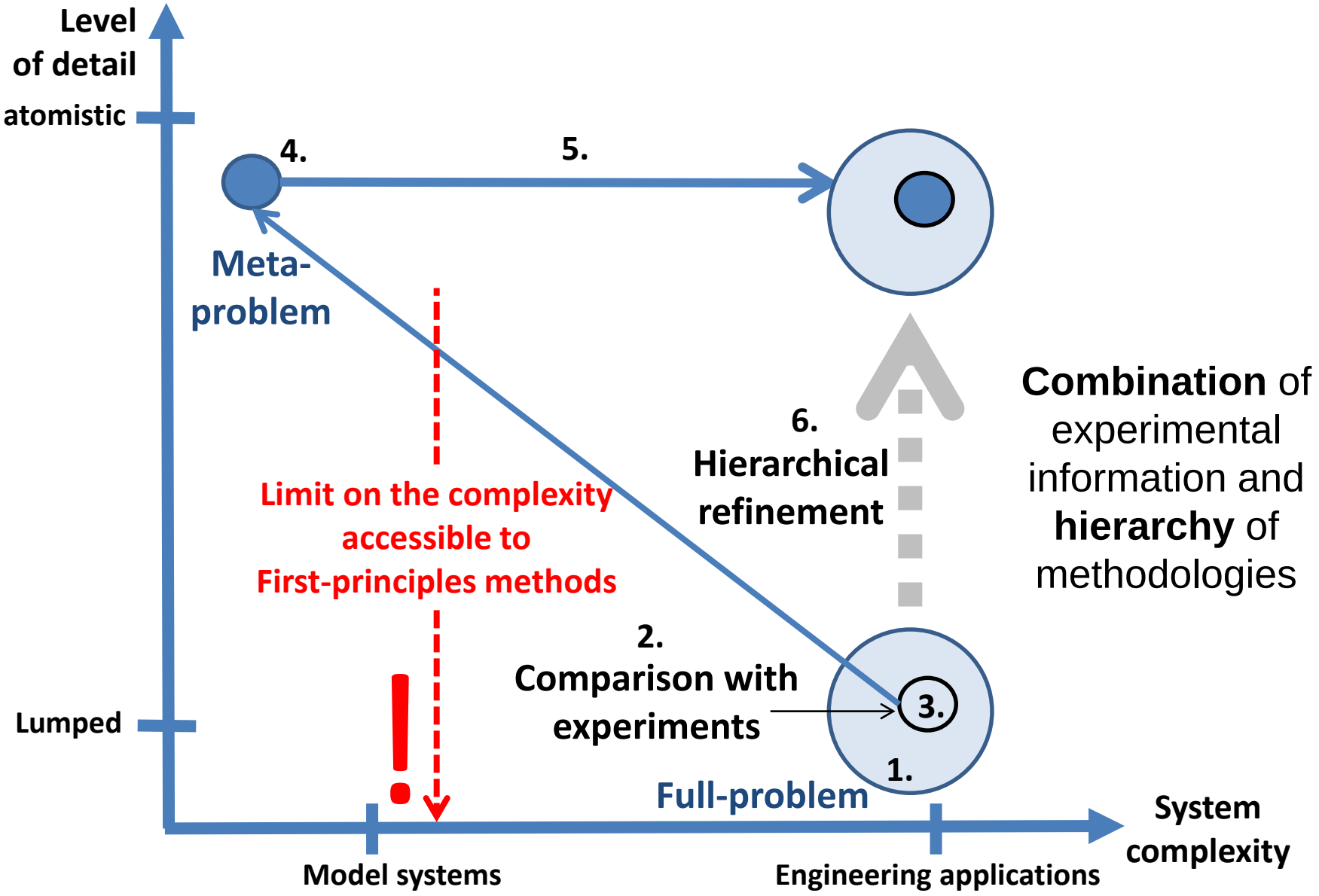

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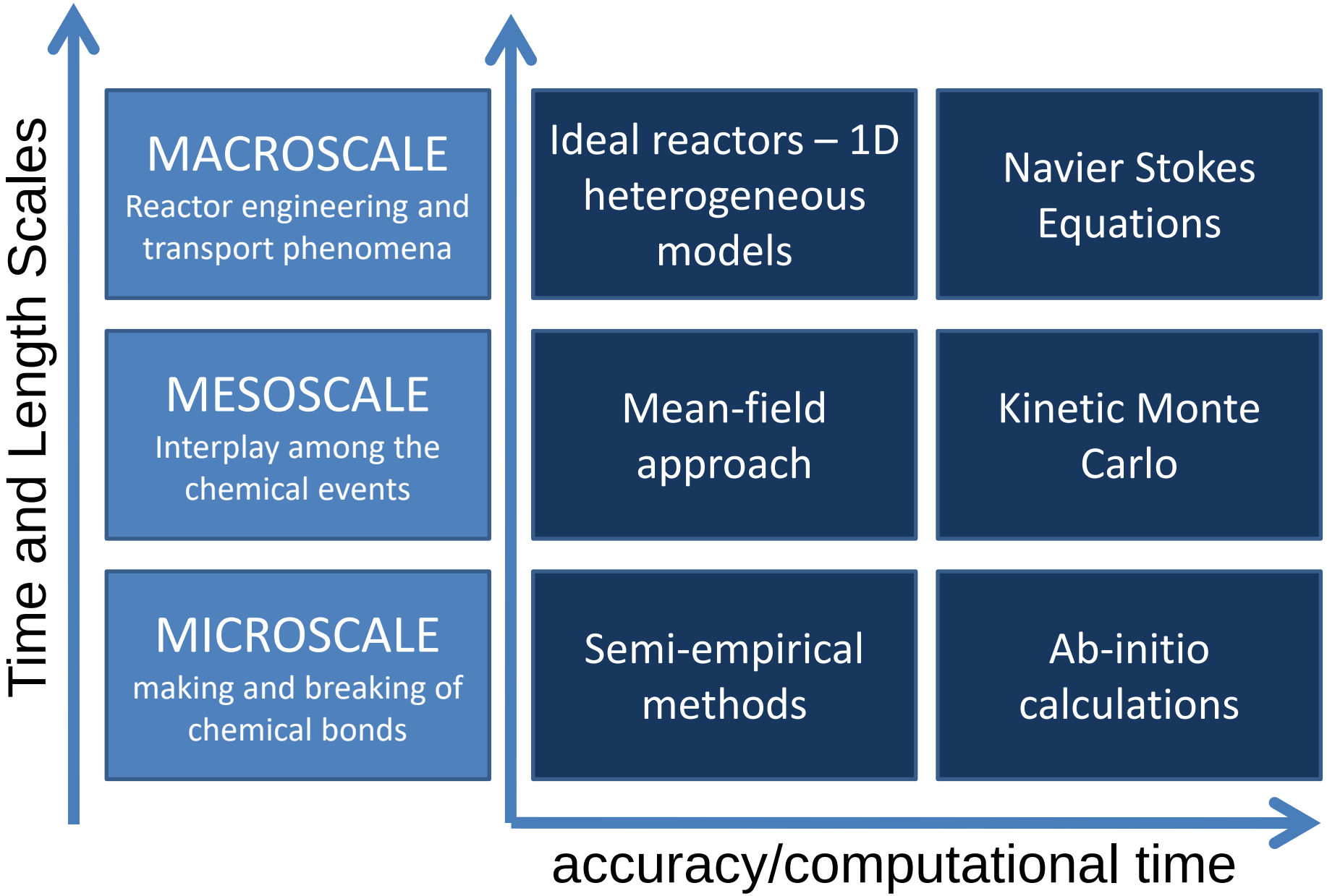

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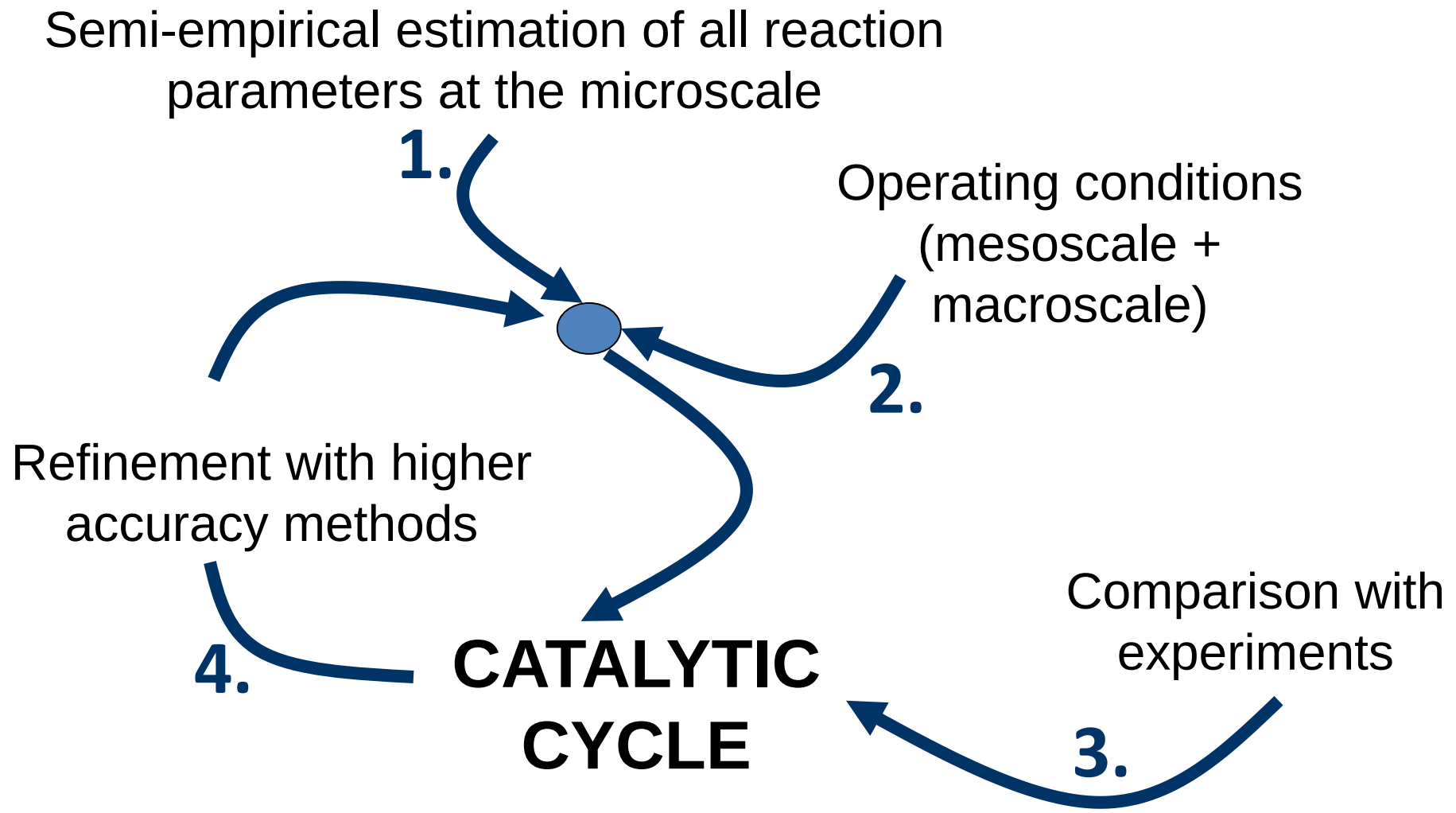
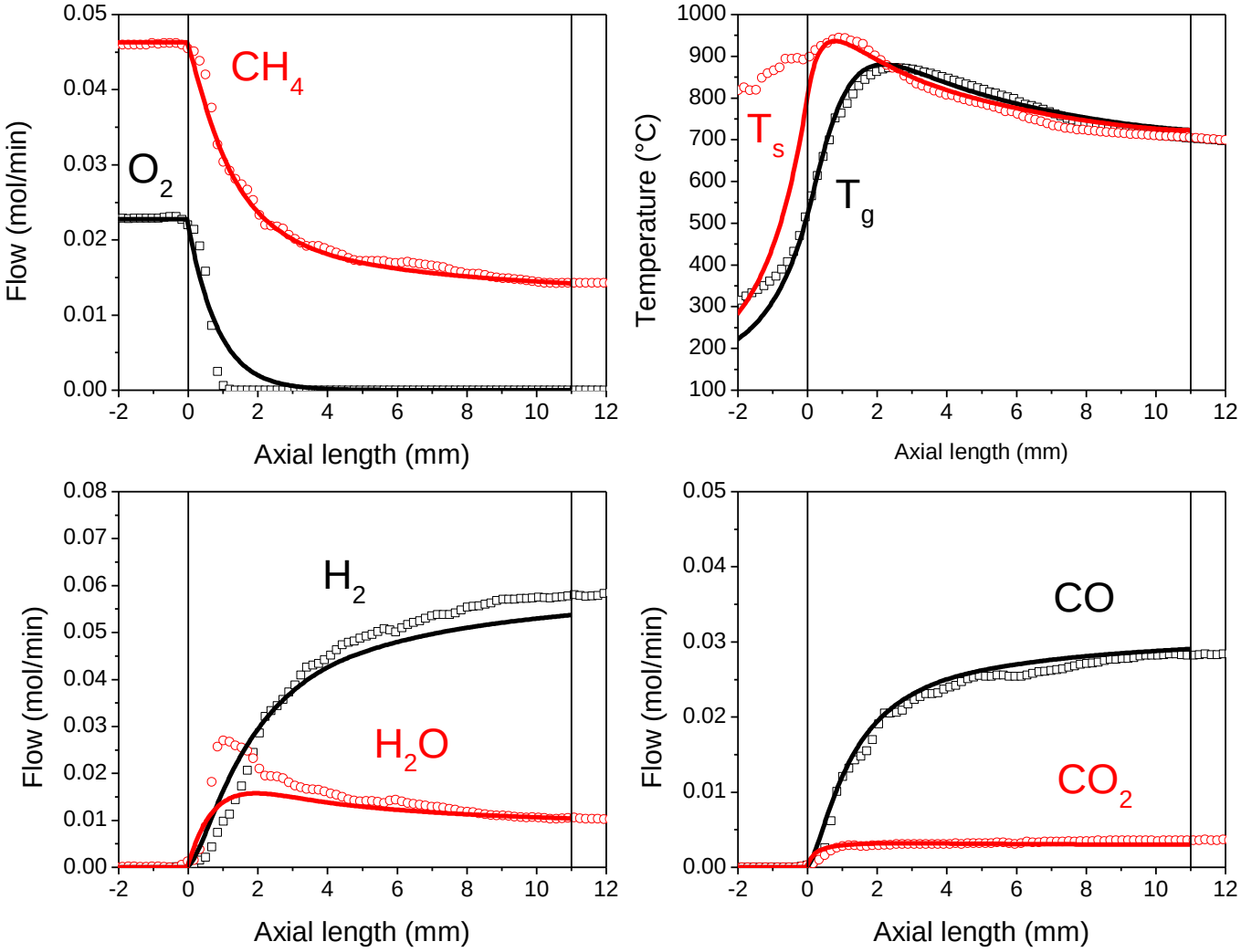


M. Maestri, Chem.Comm., 2017

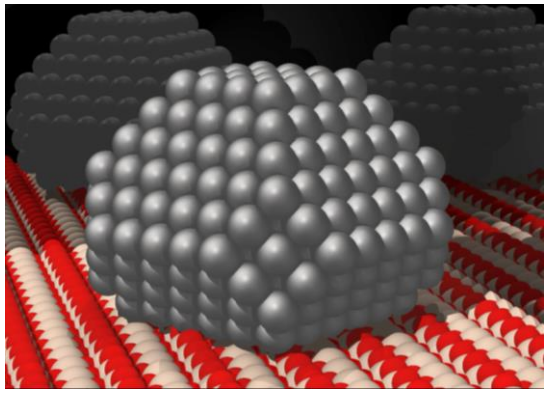
CH_4 CPOX on Rh experiments on foams



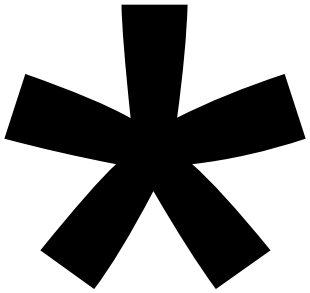
Symbols: experiments – Lines: **DFT-refined model**

A. Donazzi, M. Maestri et al., J. Catal., 2010

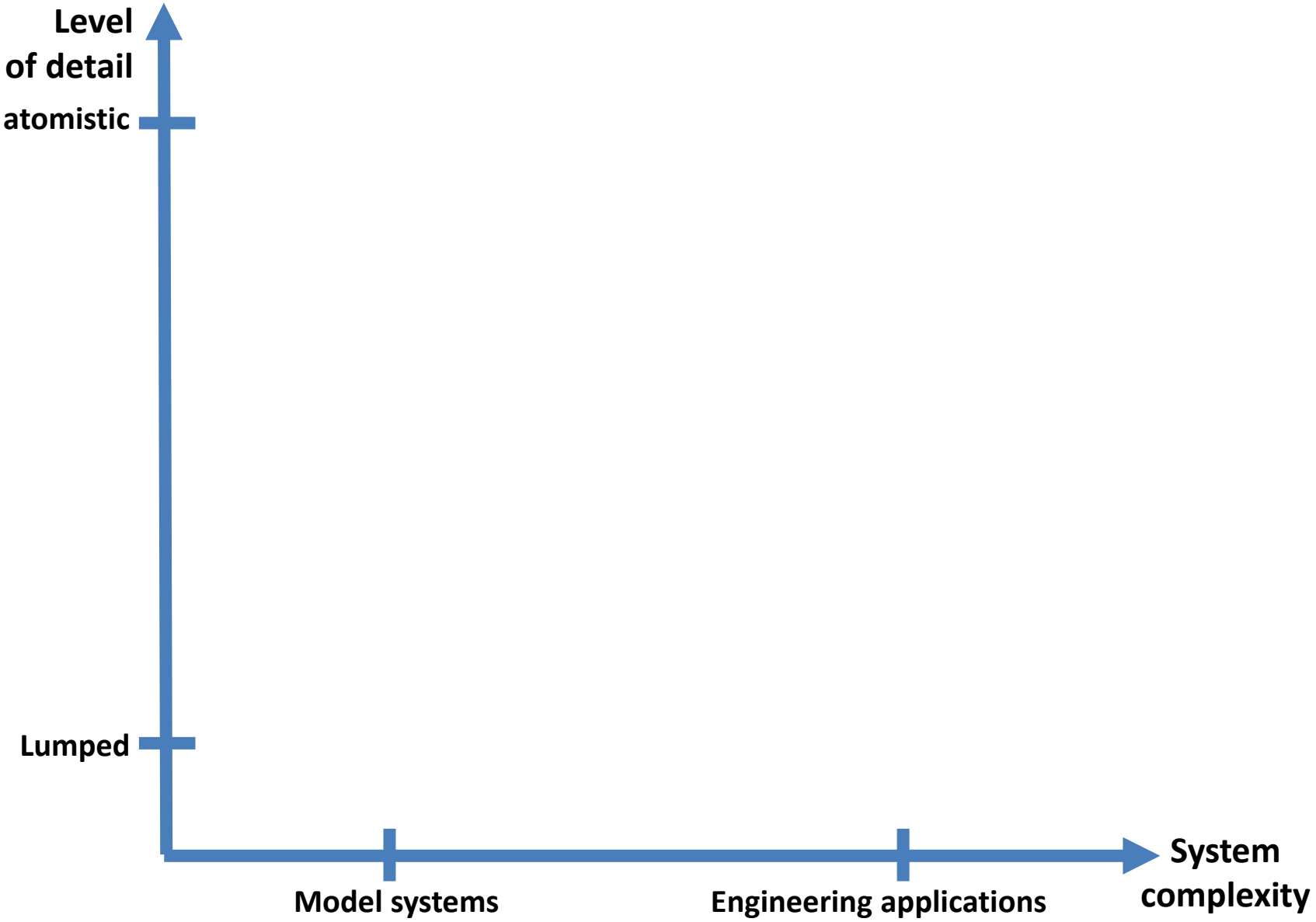
Structure-less microkinetic modeling



Gap



State-of-the-art microkinetic modeling



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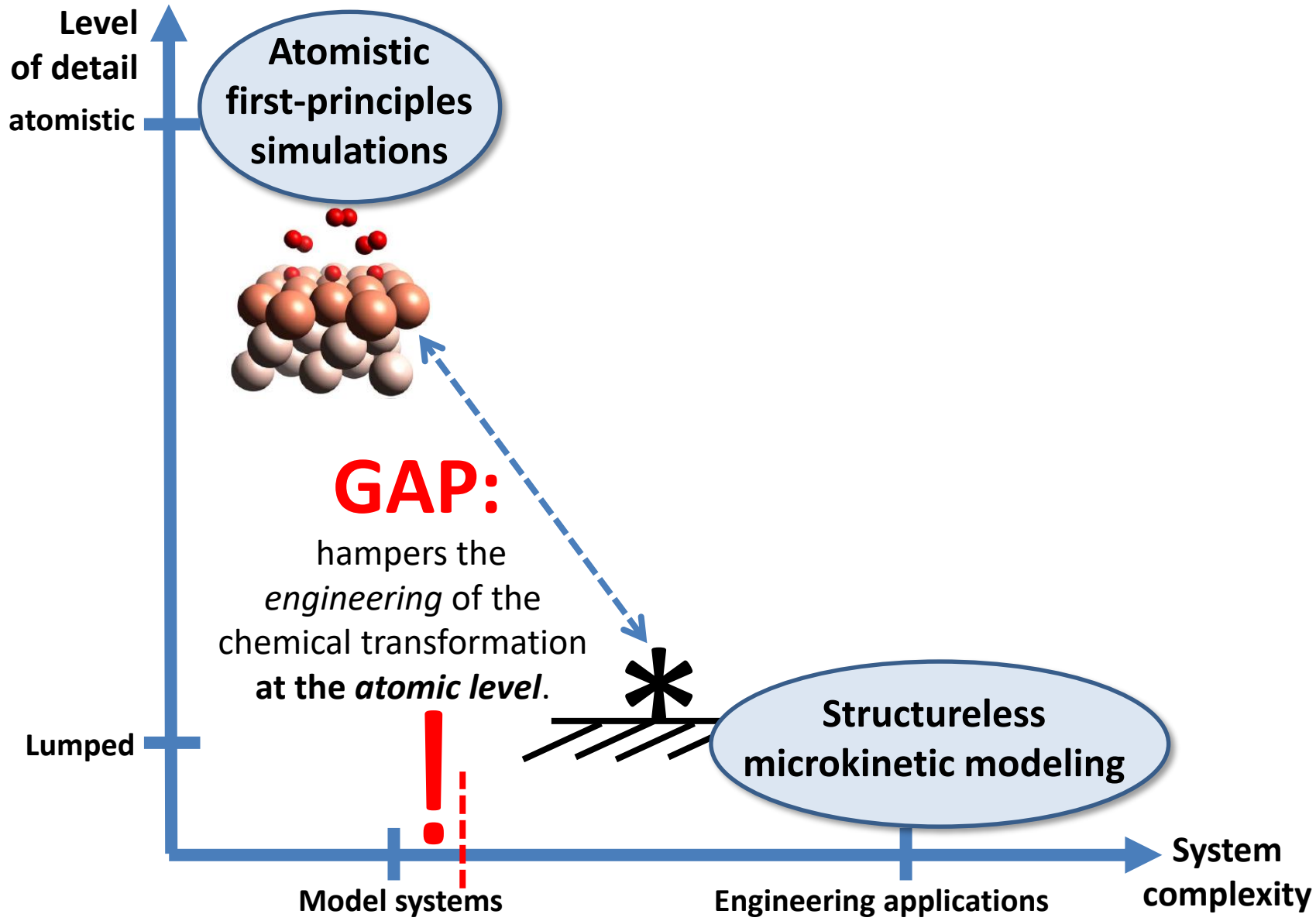
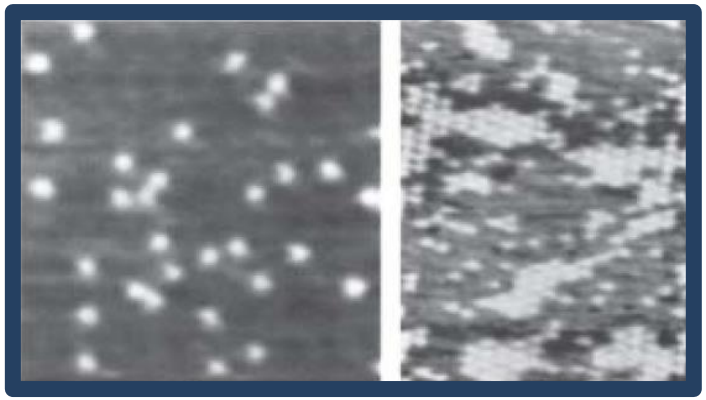
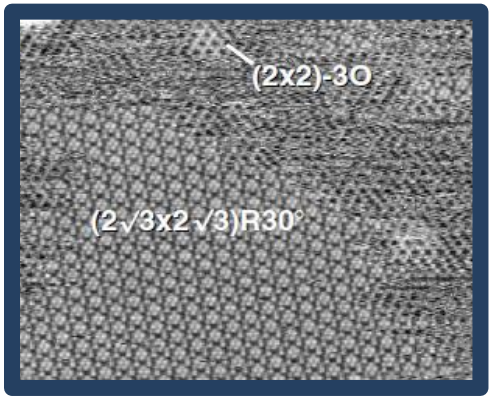


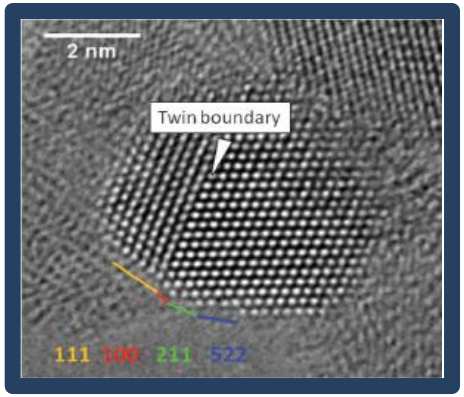
Catalysts have a "living" character

"A catalyst is a substance which affects the rate of a chemical reaction without being part of its end products"

- W. Ostwald (1909)



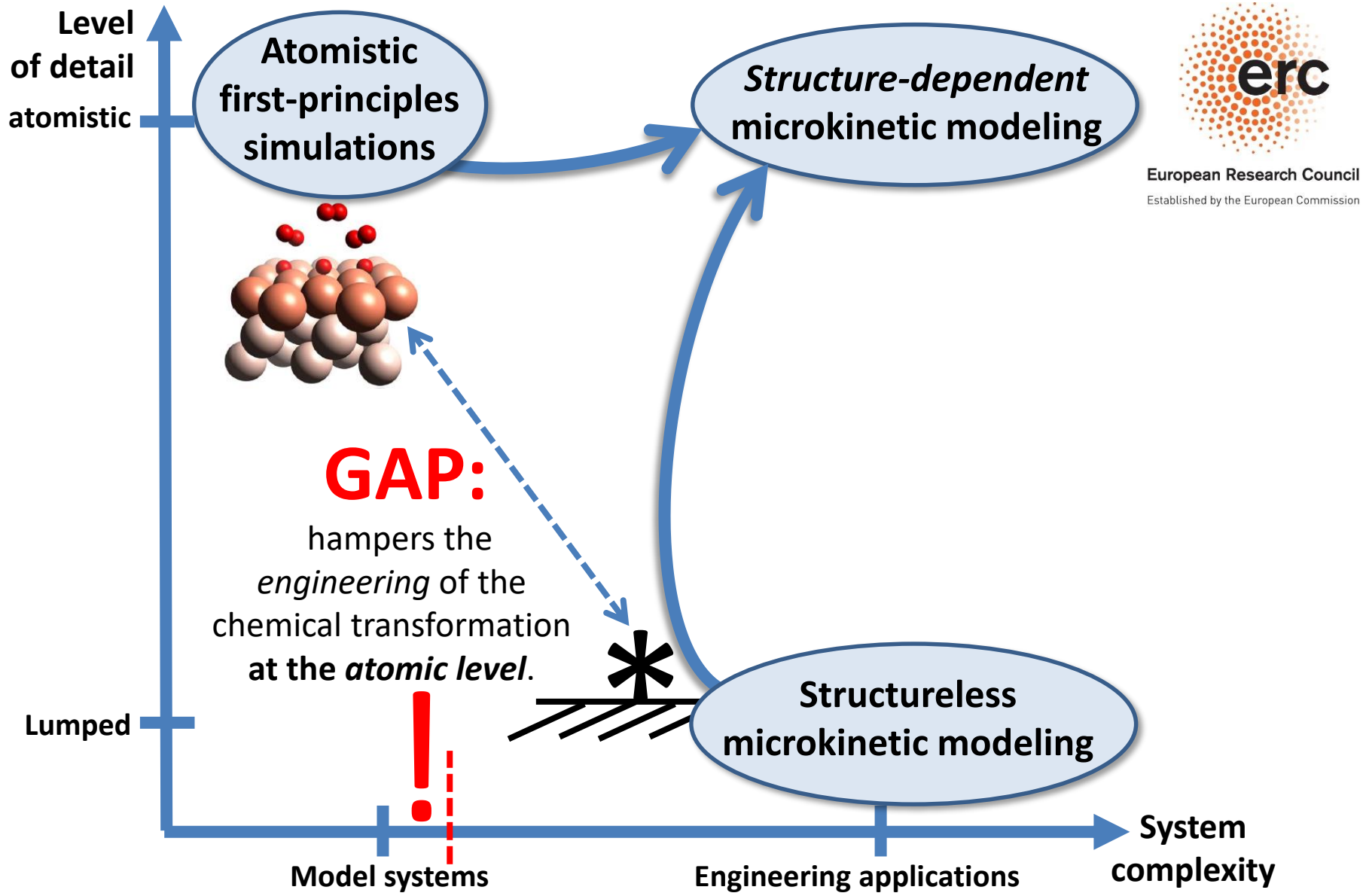




"The entity of a catalyst solid has a living character"

R. Schlögl

From structure-less to structure-dependent microkinetic modeling



European Research Council
Established by the European Commission

Outline

- ✓ Theoretical methods for the prediction of dynamic changes of nanoparticles and phase transformation.
- ✓ Parametrization of kinetic parameters on different sites.
- ✓ Novel experimental tools: spectroscopy & kinetically relevant data.
- ✓ Confinement effects: «physical» catalysis

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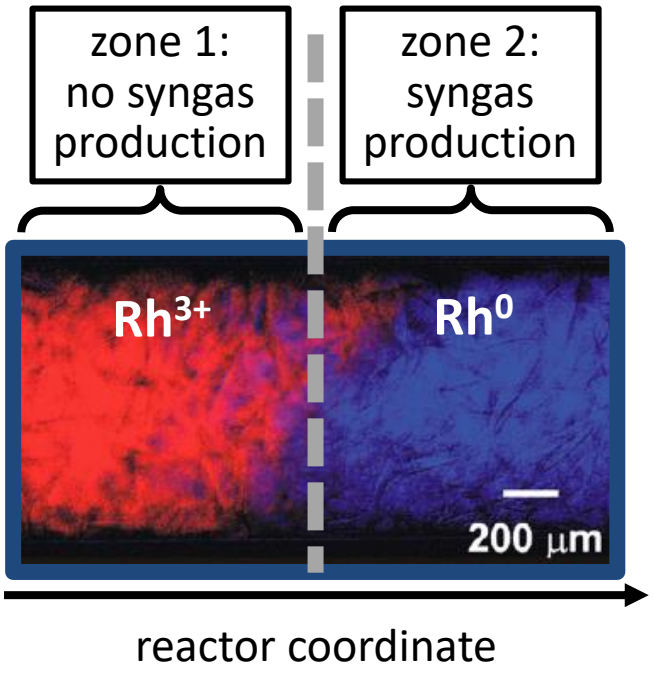
CH_4 CPO on Rh/Al_2O_3



J. Grunwaldt et al., J. Phys. Chem. B 110, 8674-8680 (2006)

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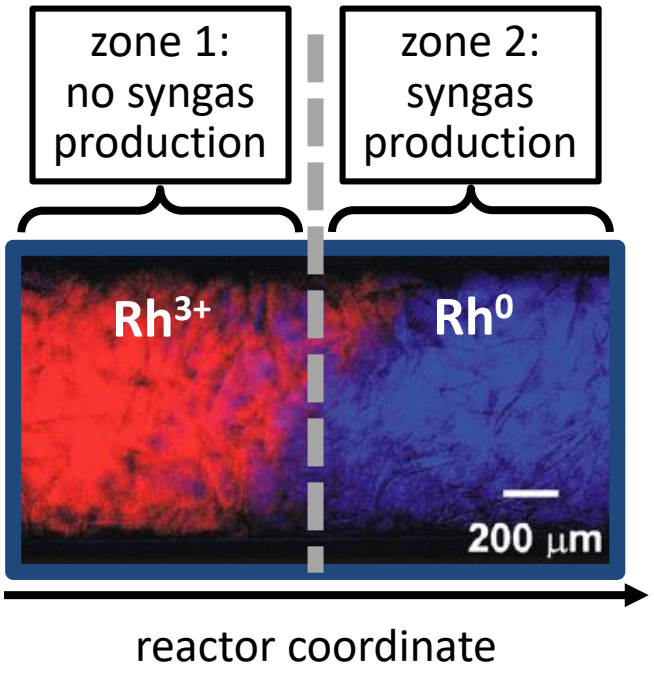

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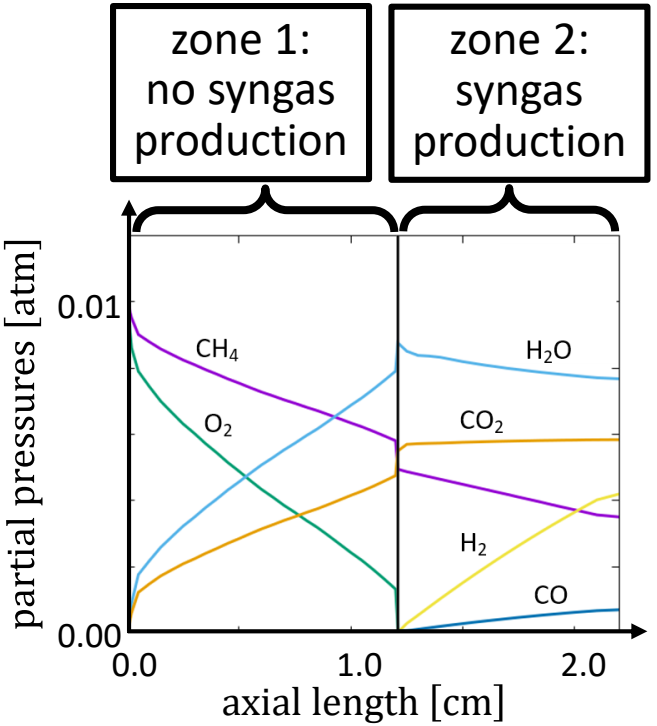
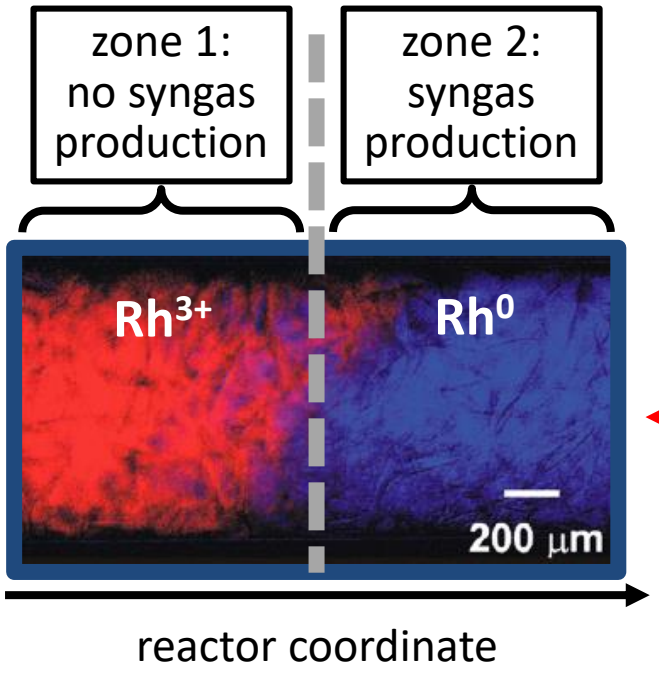


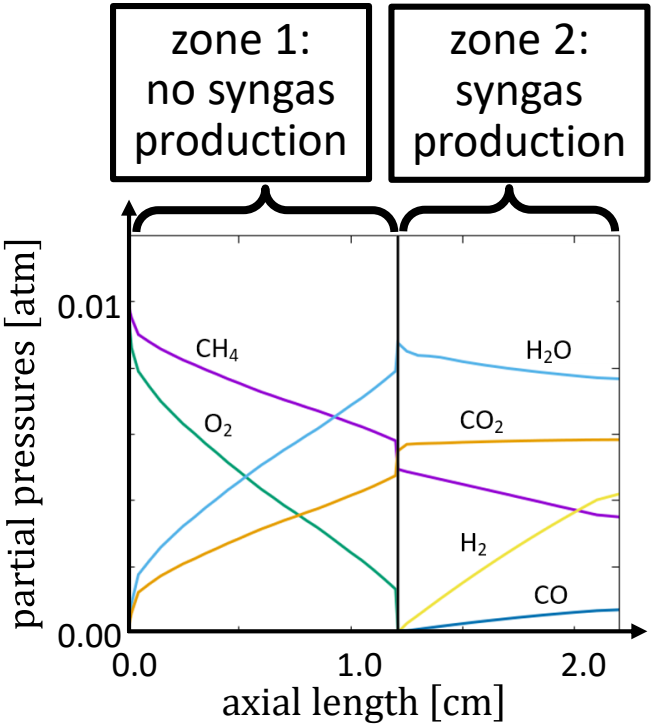
M. Maestri et al., Top. Catal. 52, 13–20, 1983–1988 (2009)

STRUCTURE-LESS MICROKINETIC MODEL

CH_4 CPO on Rh/Al_2O_3



MATERIAL GAP



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STRUCTURE-LESS MICROKINETIC MODEL

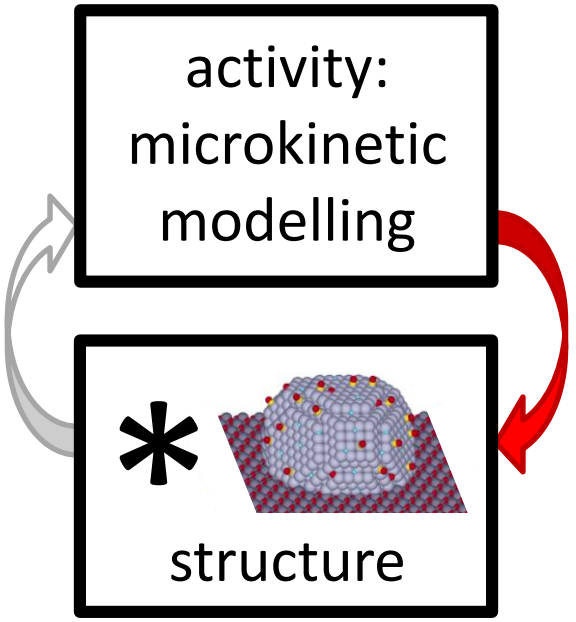
Coupling microkinetic modeling and ab-initio thermodynamics

Methods:

- *Ab initio* thermodynamics
- Wulff-Kaichew construction

Rh nanoparticles morphology in a CH_4 CPO reactor:

- zone 1 (MARI: O*)
- zone 2 (MARIs: CO* & H*)



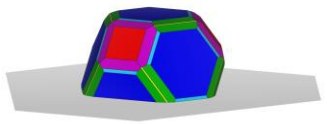
R. Cheula, A. Soon, M. Maestri, Cat. Sci. Tech., 2018

Coupling microkinetic modeling and ab-initio thermodynamics

reactor modelling → gas species partial pressures, most abundant reaction intermediates

ab initio thermodynamics → bulk structure (lowest Ω), surfaces morphology (lowest γ)

Wulff-Kaishew construction → catalyst 3D shape, active sites distribution



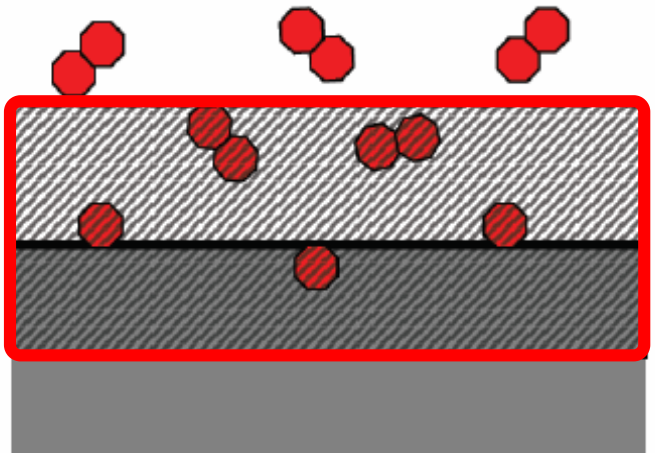
R. Cheula, A. Soon, M. Maestri, Cat. Sci. Tech., 2018

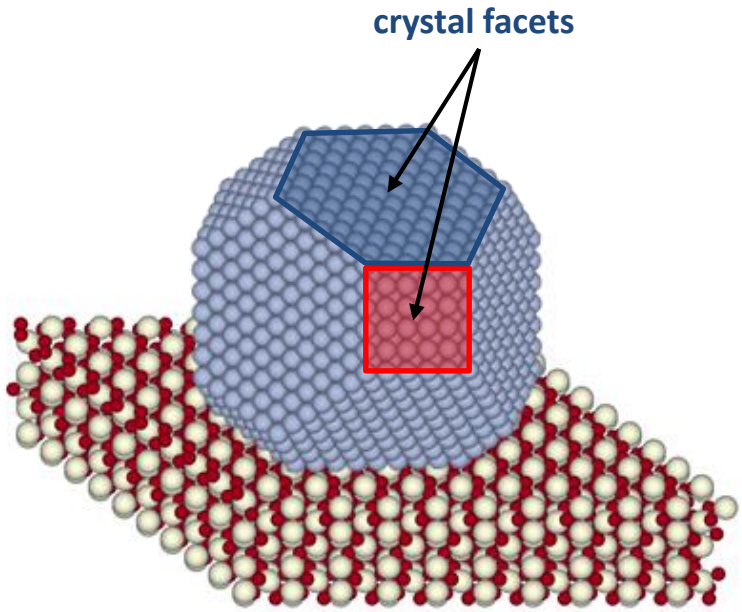
Prediction of catalyst structure in reaction

Ab-initio Thermodynamics

$$\gamma^{surf}_{Rh+O^*}(T,P,P_{O_2}) = \frac{1}{S}\left(G^{surf}_{Rh+O^*}(T,P) - N_{Rh}G^{bulk}_{Rh}(T,P) - N_{O^*}\mu_{O^*}(T,P_{O_2})\right)$$

$$\Omega_{Rh_xO_y}(T,P,P_{O_2}) = \frac{1}{x}G^{bulk}_{Rh_xO_y}(T,P) - G^{bulk}_{Rh}(T,P) - \frac{y}{x}\,\mu_O(T,P_{O_2})$$

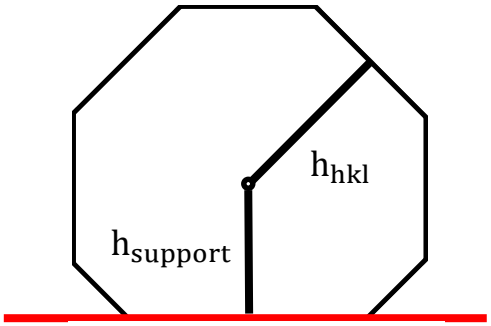


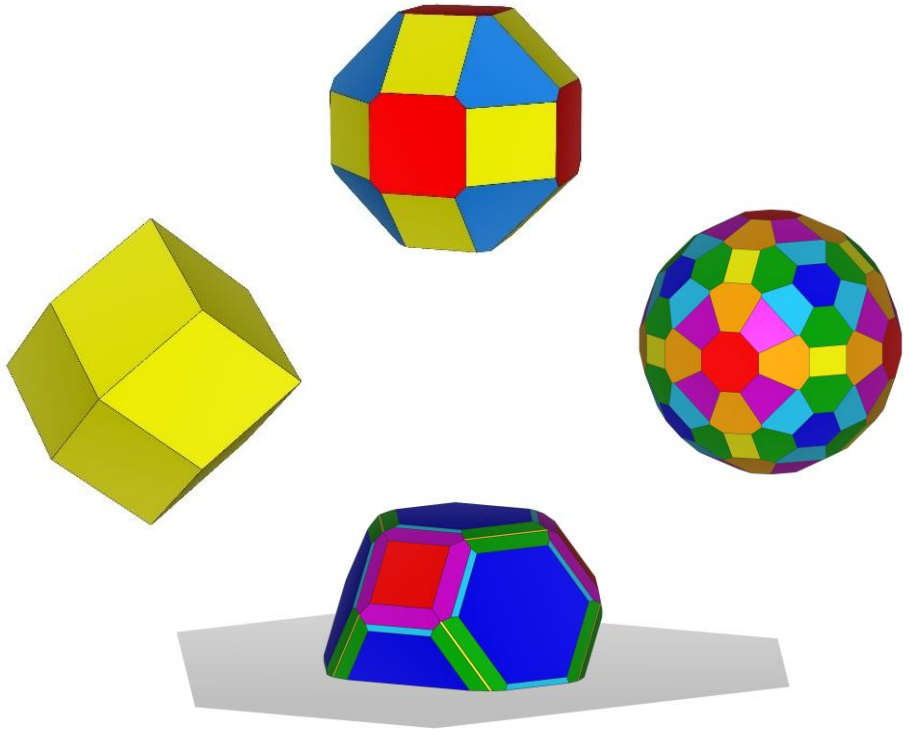


Prediction of catalyst structure in reaction

$$h_{hkl} = \lambda\, \gamma_{hkl}(T, P_i)$$

$$h_{support} = \lambda\, \gamma_{support}(T, P_i)$$





size-independent

The atomistic Wulff construction method is applied to estimate nanoparticles shapes, accounting for both energetic and geometric characteristics of catalyst surfaces.

Coupling microkinetic modeling and ab-initio thermodynamics

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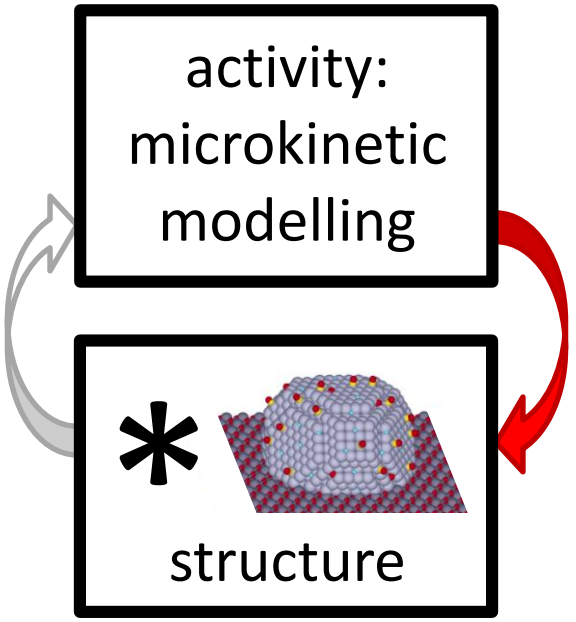
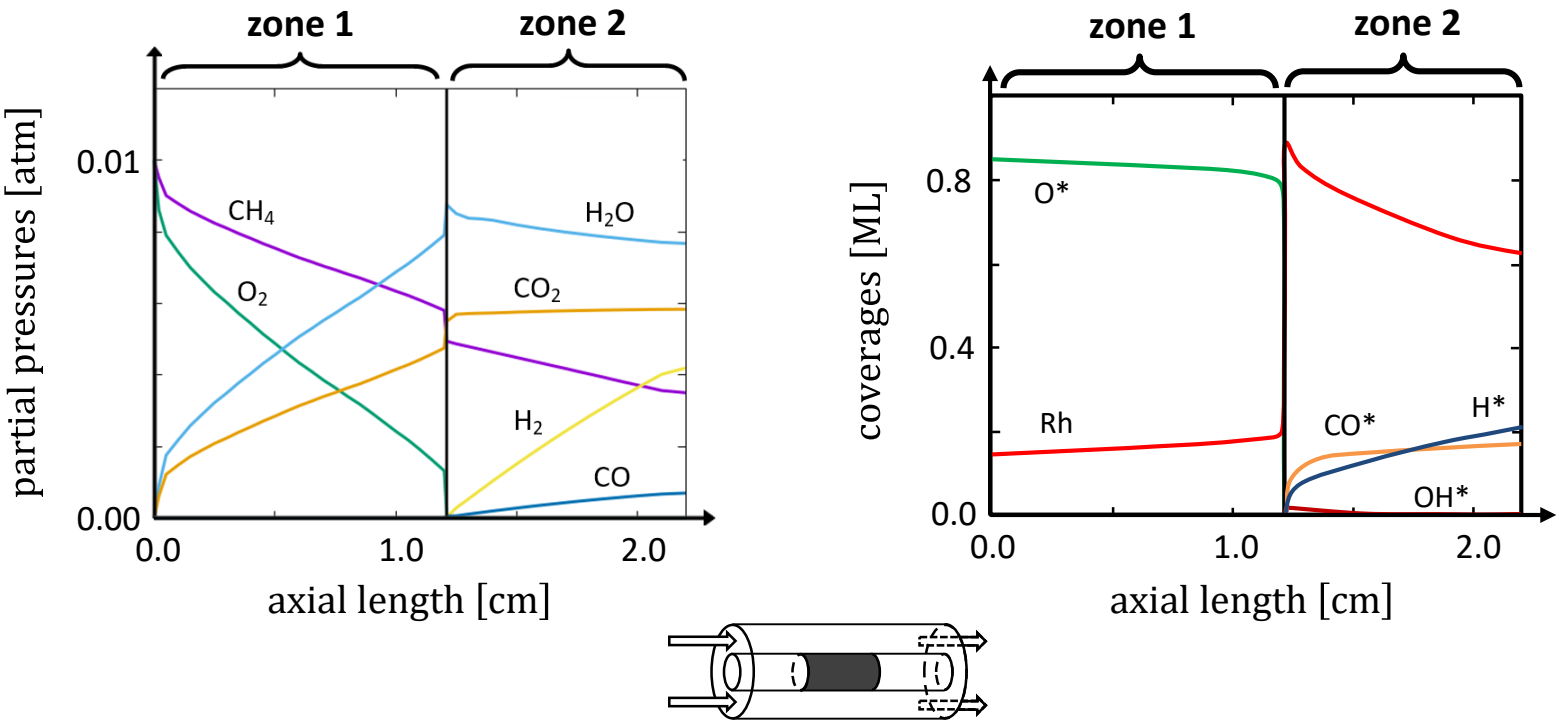


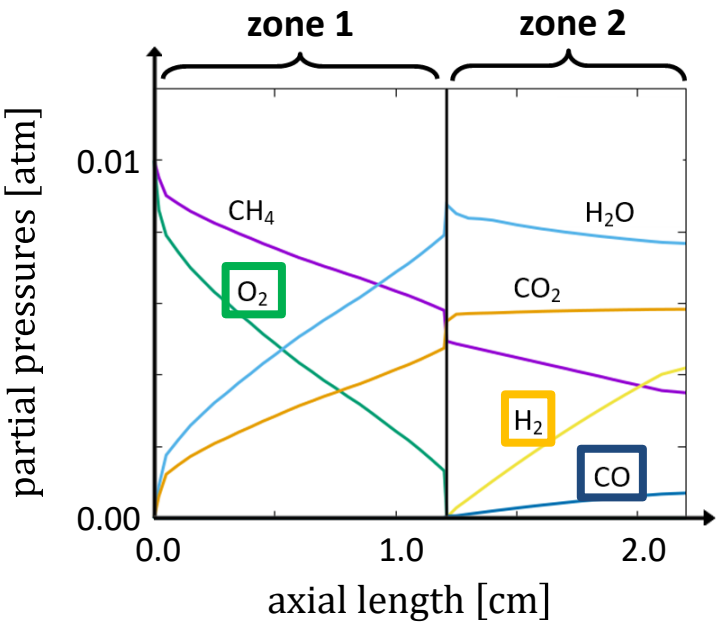
R. Cheula, A. Soon, M. Maestri, Cat. Sci. Tech., 2018

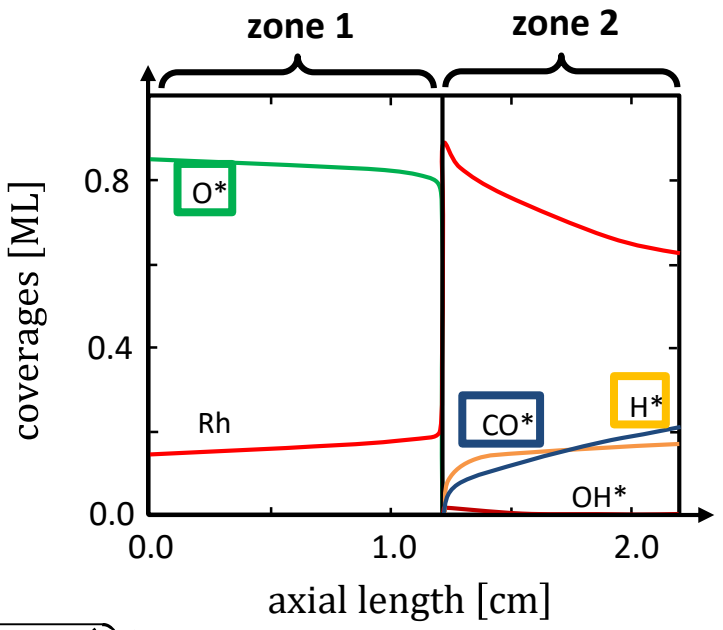
Gas and adsorbate species axial profiles by reactor modelling

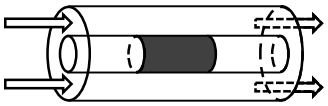


annular reactor, T = 773 K, P = 1 atm, GHSV = 2E6 $Nl/kg_{cat}/h$

Gas and adsorbate species axial profiles by reactor modelling

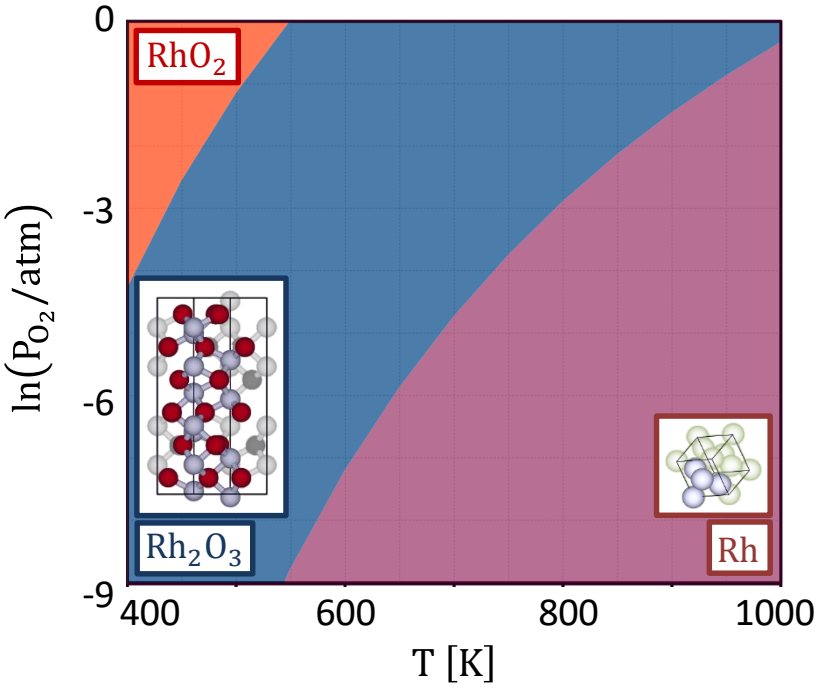






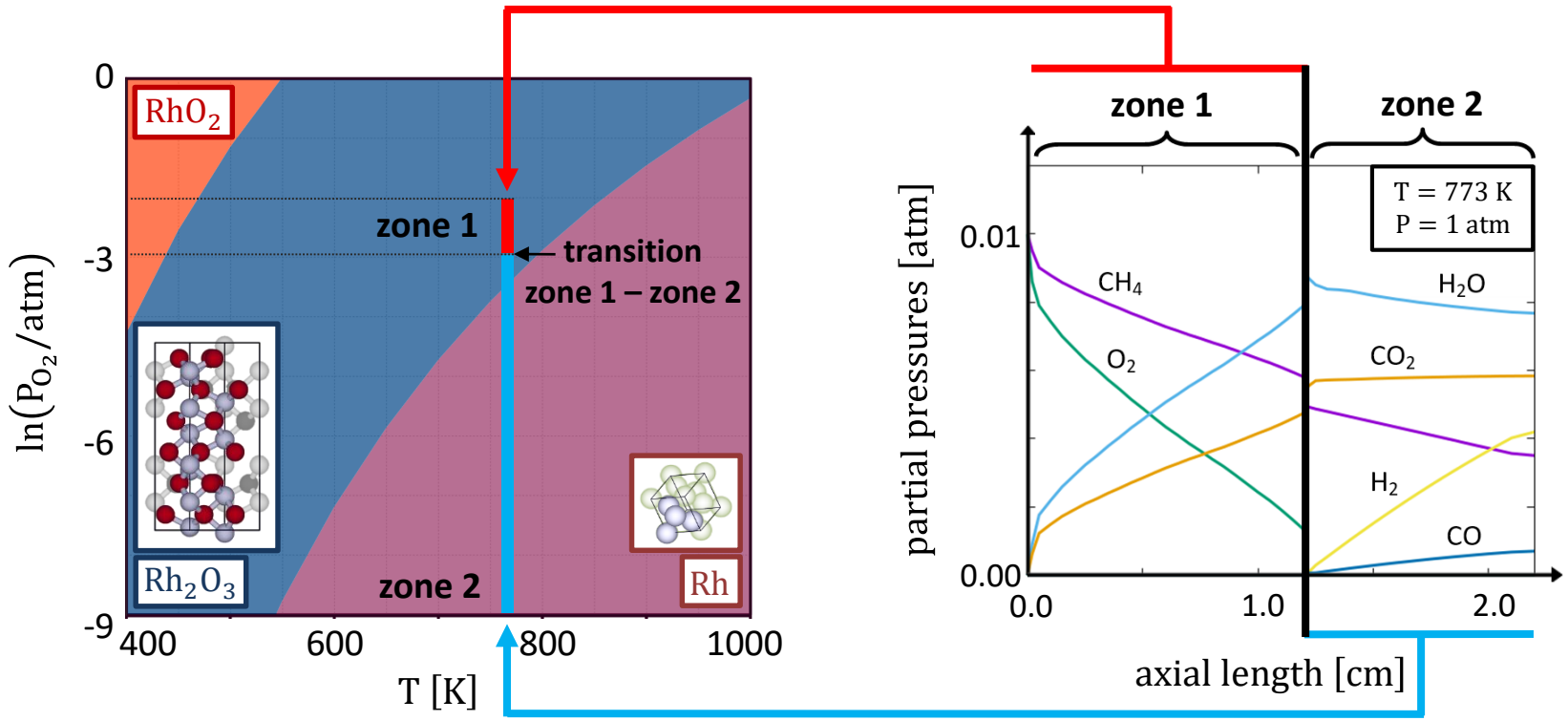
annular reactor, T = 773 K, P = 1 atm, GHSV = 2E6 $Nl/kg_{cat}/h$

Bulk phase diagram of Rh and Rh oxides

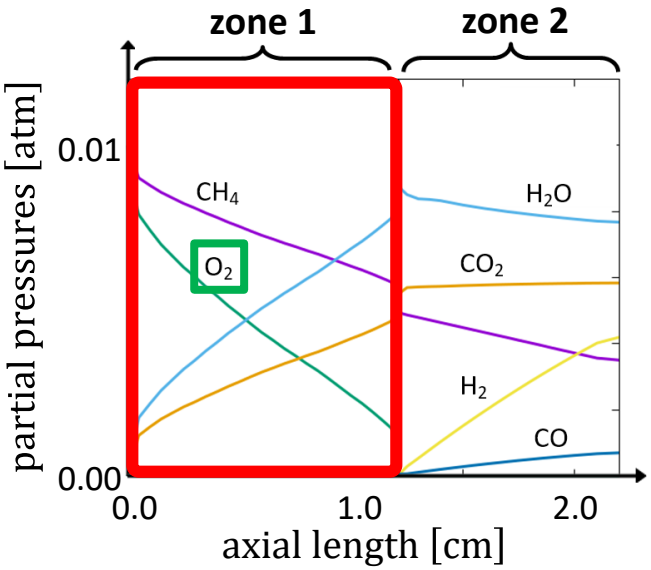


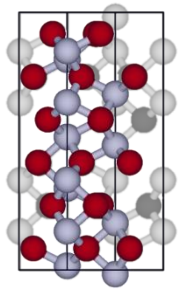
Plane waves
PBE ultrasoft
pp
DFT+U

Bulk phase diagram of Rh and Rh oxides

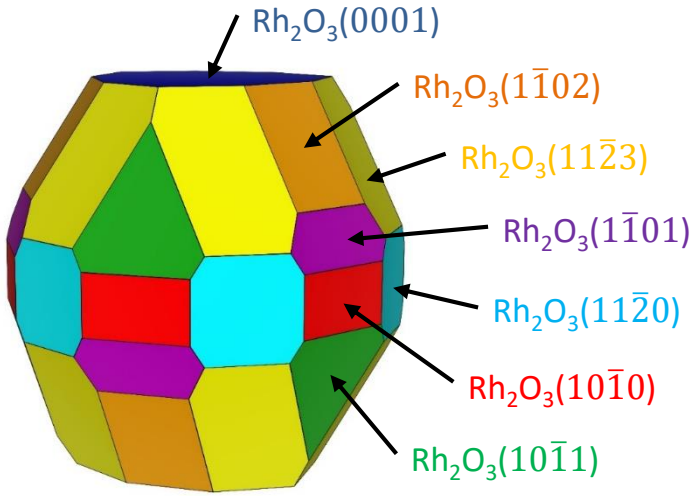


Rh_2O_3 catalyst morphology in zone 1 of the reactor

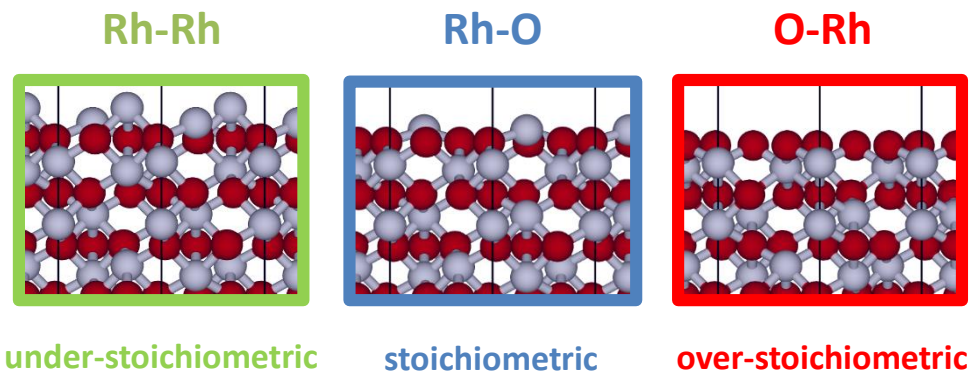


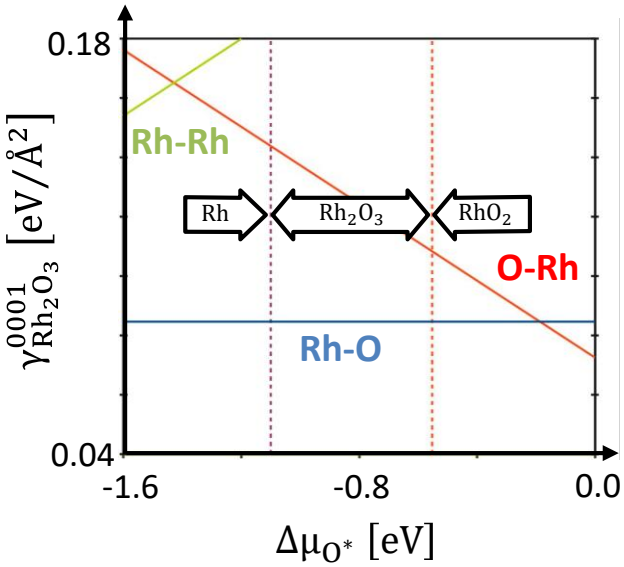


corundum Rh_2O_3

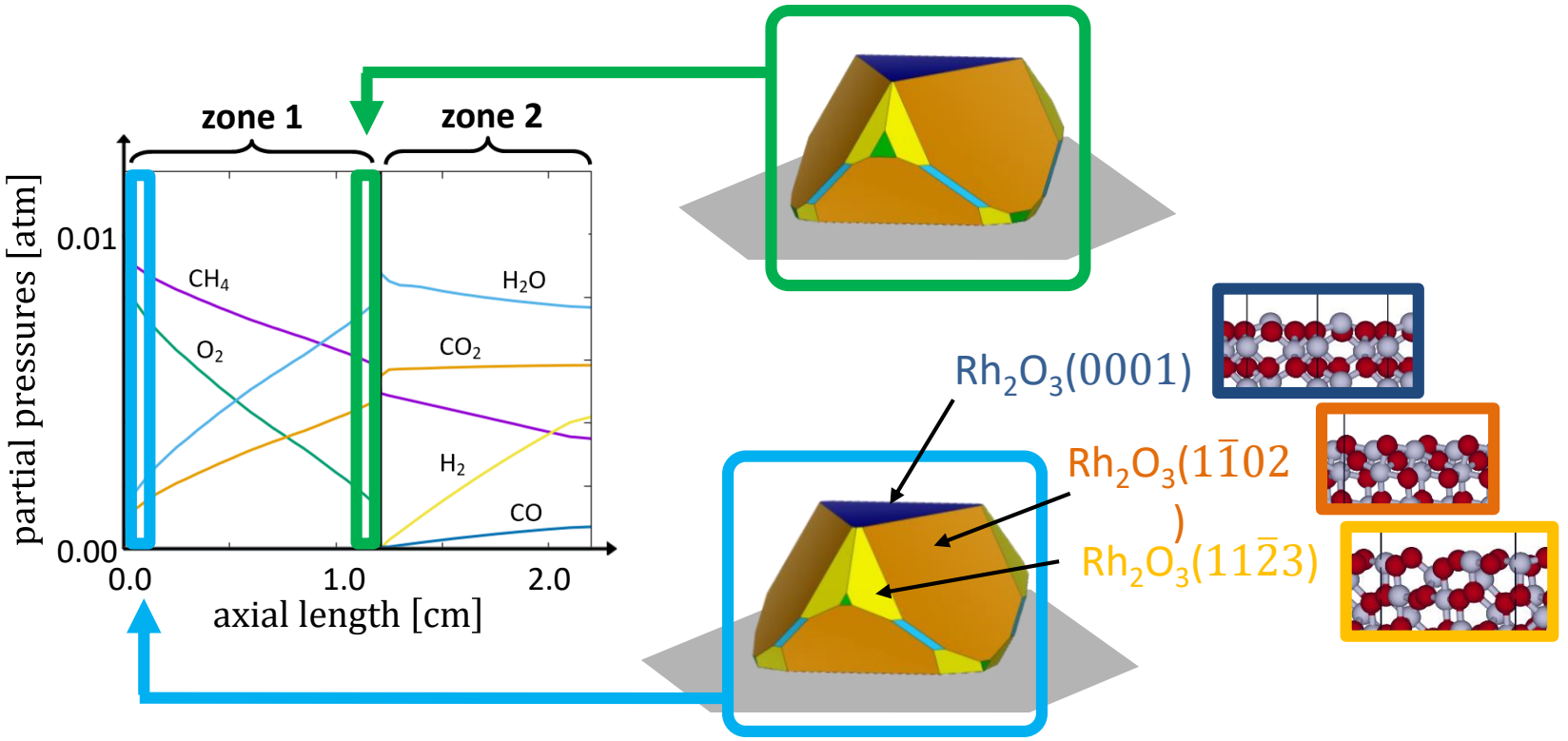


Surface terminations of Rh_2O_3 facets

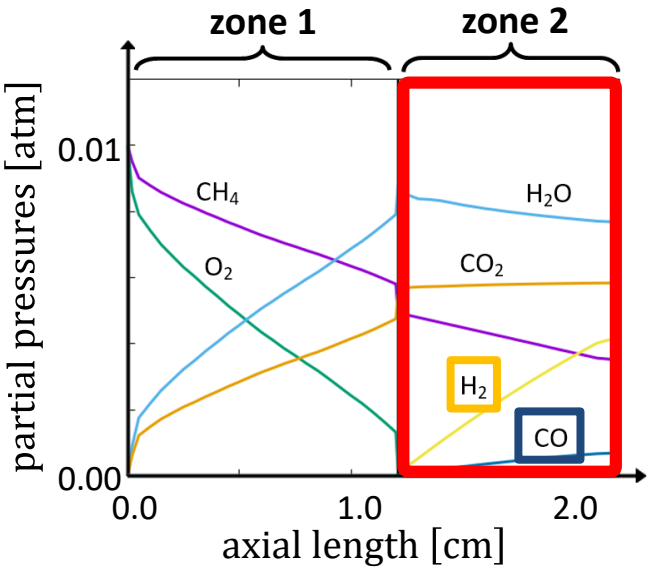


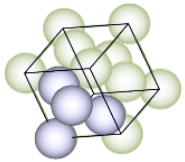


Rh_2O_3 catalyst morphology in zone 1 of the reactor

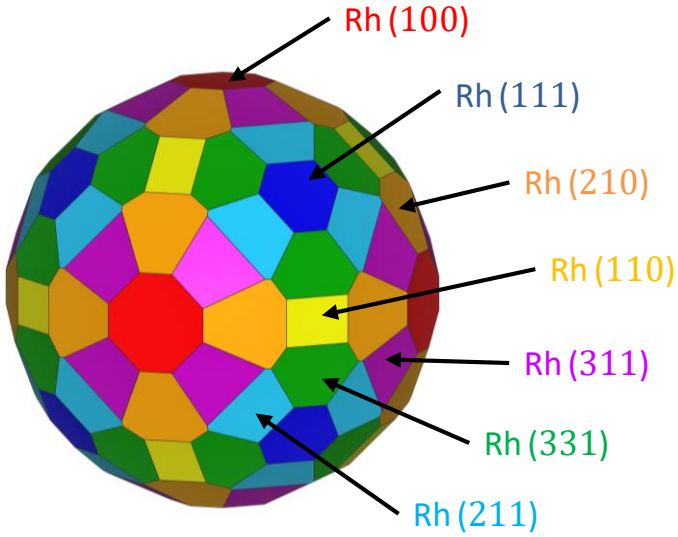


Rh_2O_3 catalyst morphology in zone 2 of the reactor

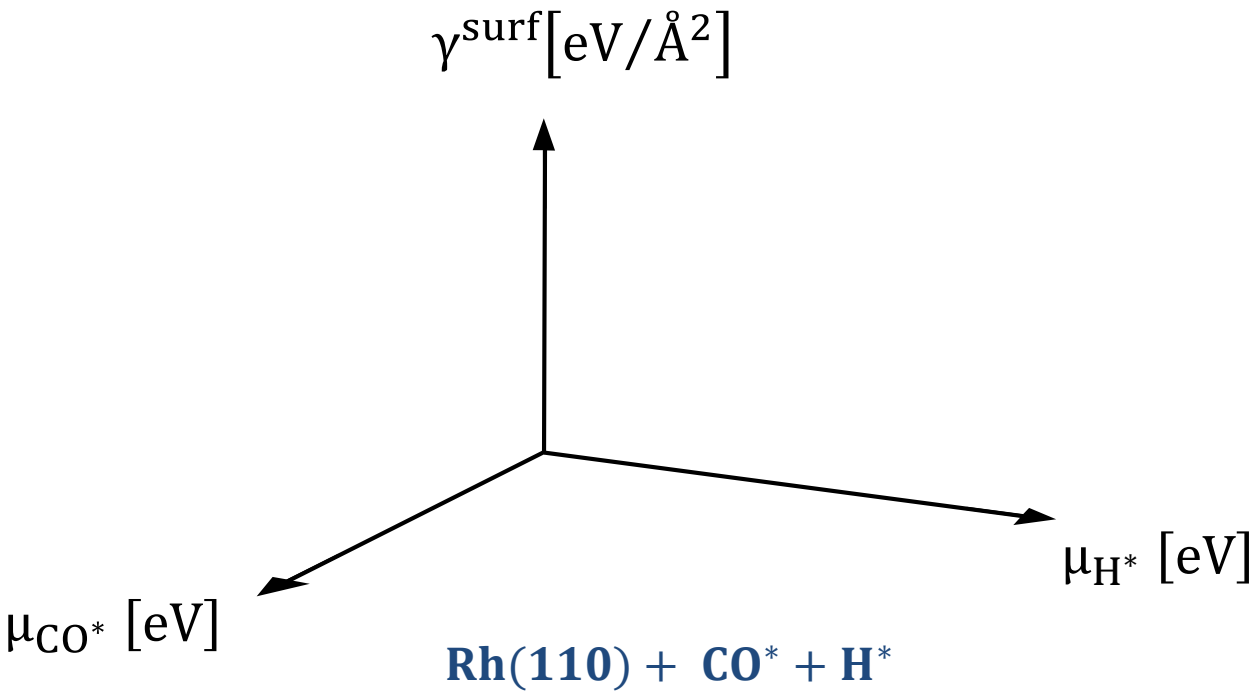




fcc Rh



How CO and H* affect the surface free energy*



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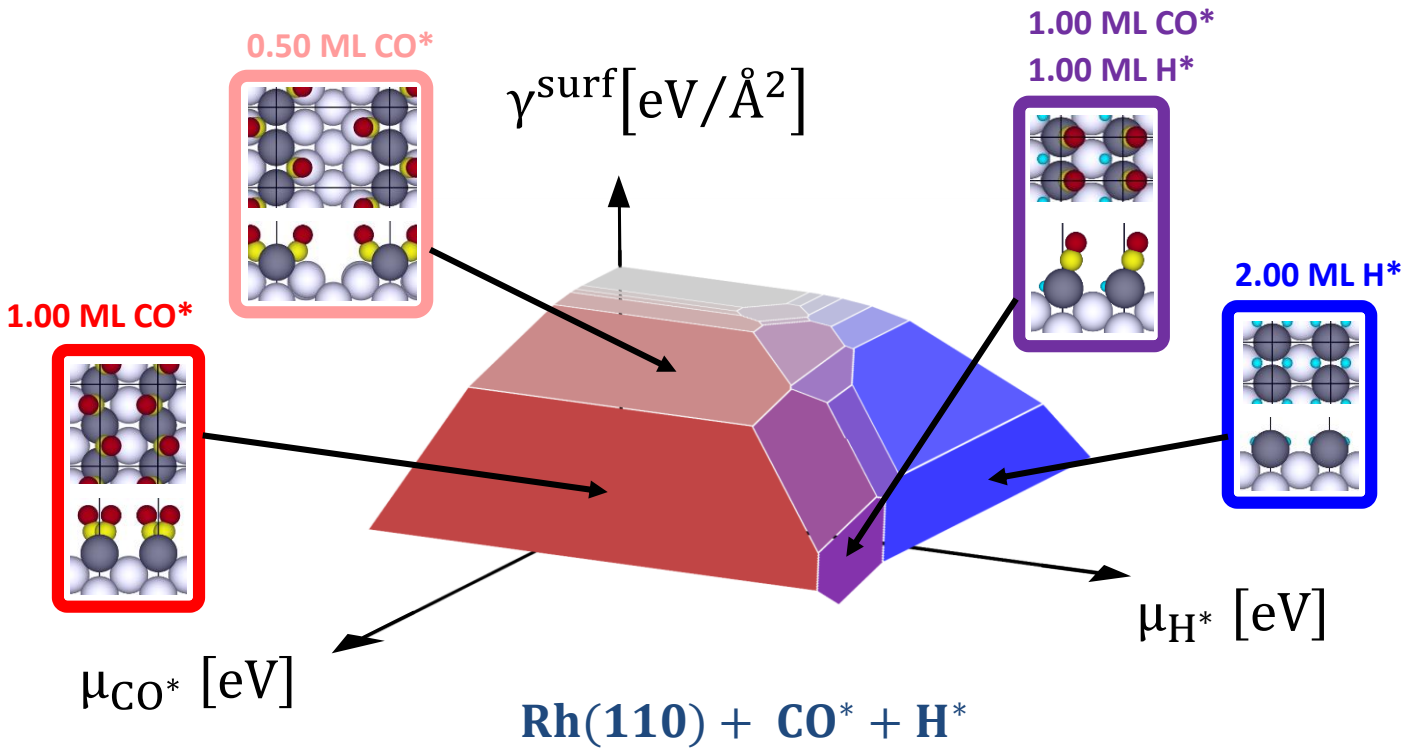
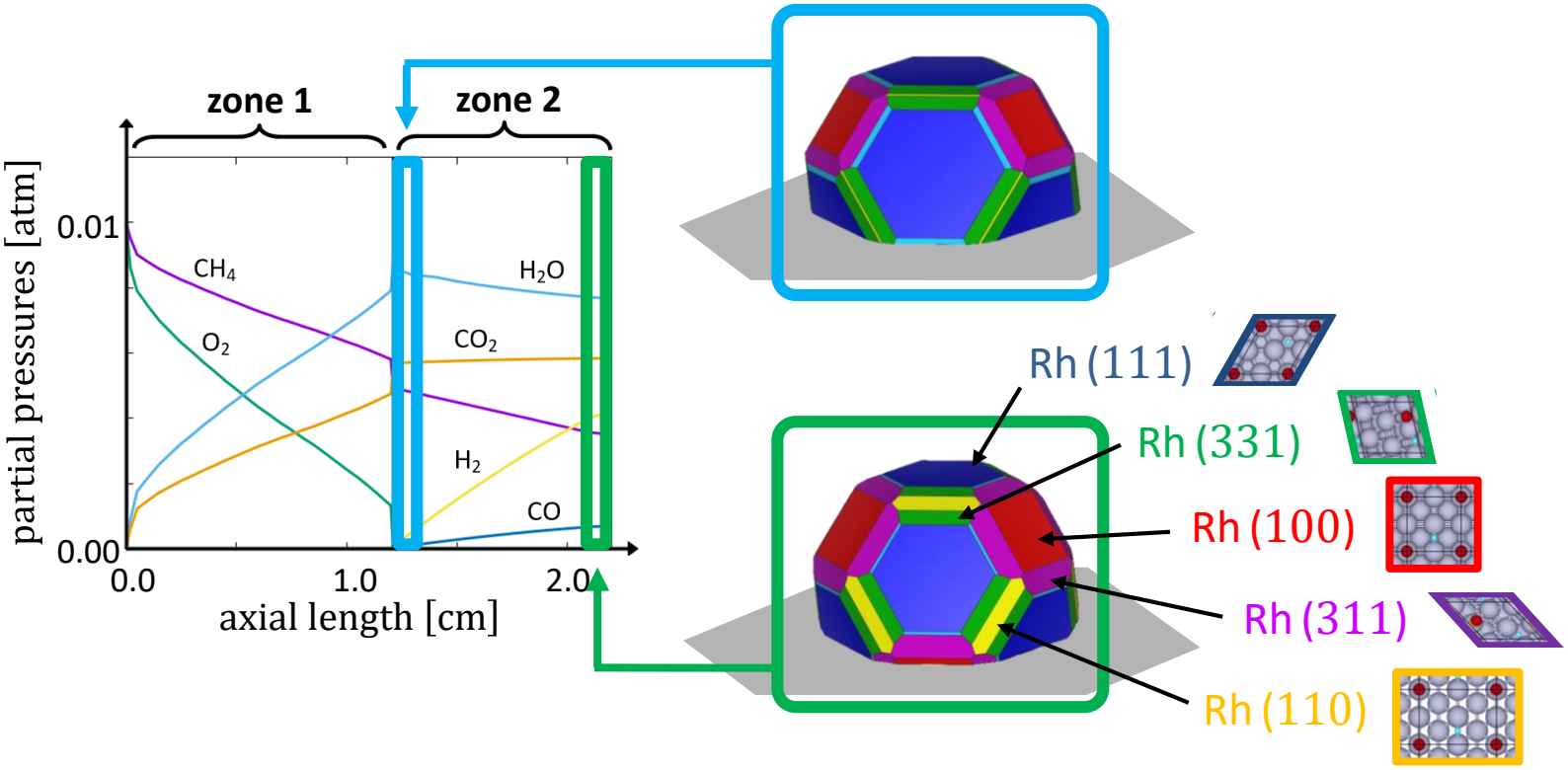


Rh_2O_3 catalyst morphology in zone 2 of the reactor



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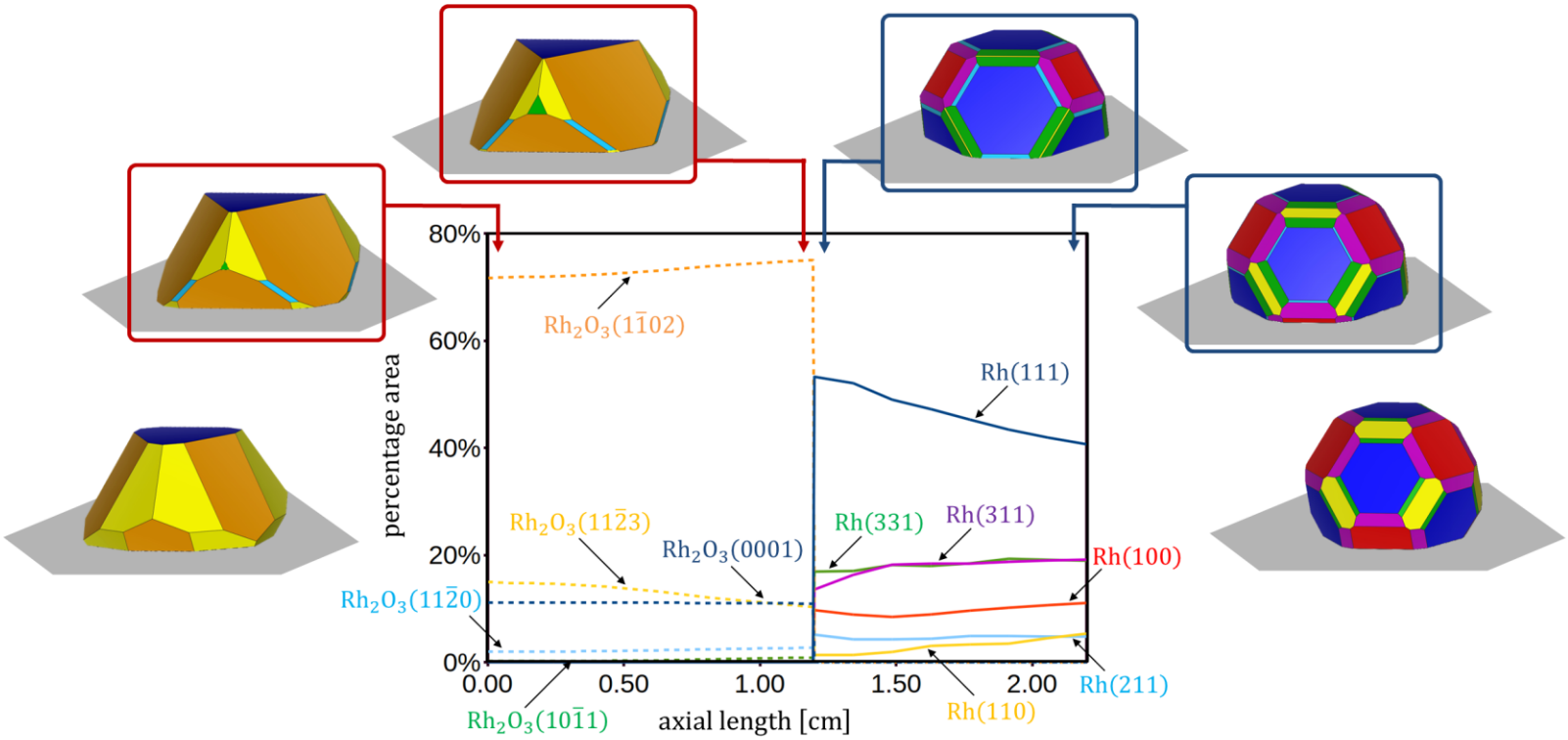
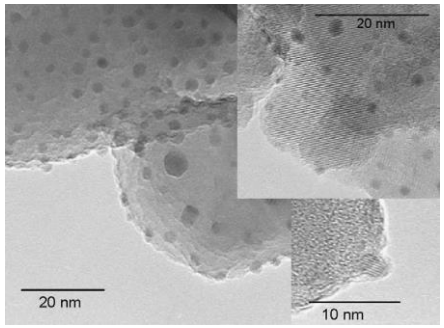
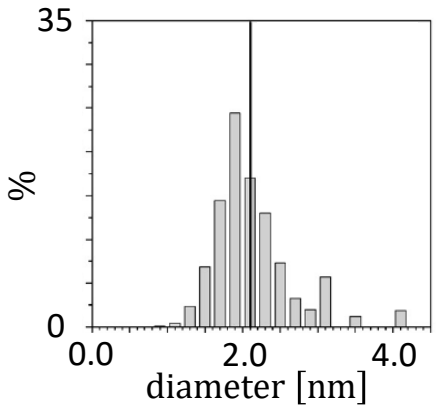


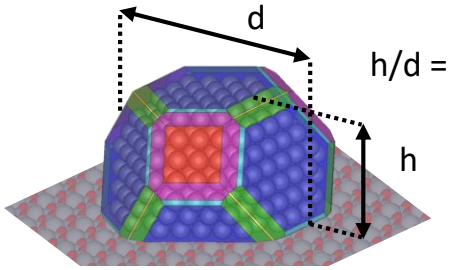
Comparison with characterization experiments



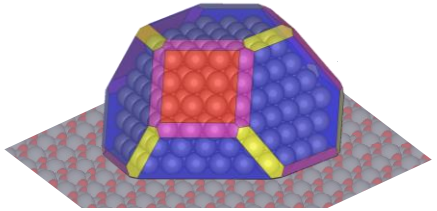


A. Beretta et al., App. Cat. B 83, 96-109 (2008)

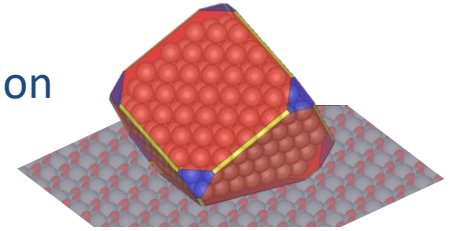
HRTEM



H_2 chemisorption



CO chemisorption



R. Cheula, A. Soon, M. Maestri, Cat. Sci. Tech., 2018

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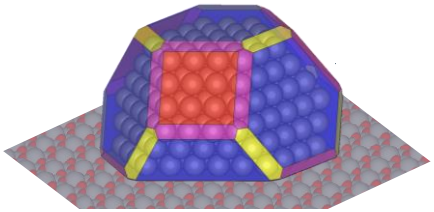


H_2 uptake

$$\text{dispersion} = 0.47\ \frac{H^*}{Rh_{tot}} \Big/ 1.00\ \frac{H^*}{Rh_{surf}} = 0.47\ \frac{Rh_{surf}}{Rh_{tot}}$$

Wulff-Kaishew construction:

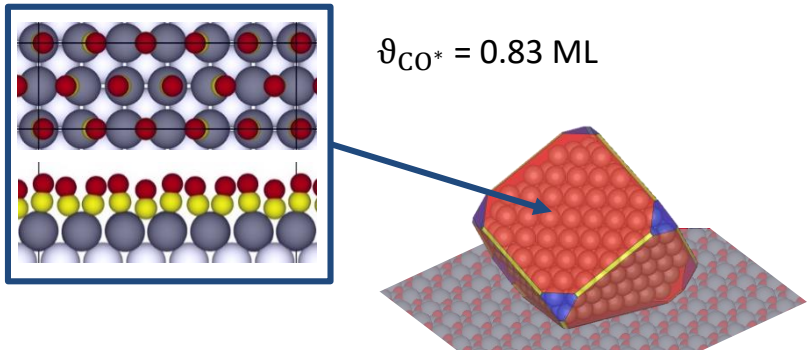
$$\text{dispersion} = 0.45\ \frac{Rh_{surf}}{Rh_{tot}}$$

CO uptake

$$\text{dispersion} = 0.38\ \frac{CO^*}{Rh_{tot}} \Big/ 0.83\ \frac{CO^*}{Rh_{surf}} = 0.46\ \frac{Rh_{surf}}{Rh_{tot}}$$

Wulff-Kaishew construction

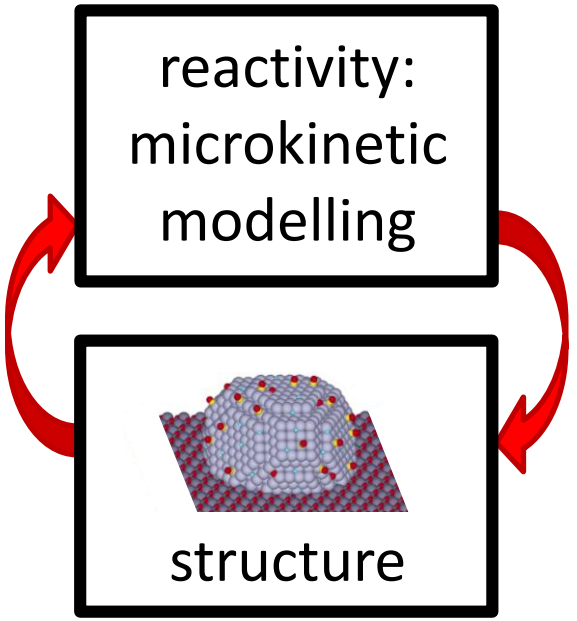
$$\text{dispersion} = 0.46\ \frac{Rh_{surf}}{Rh_{tot}}$$



R. Cheula, A. Soon, M. Maestri, Cat. Sci. Tech., 2018

Coupling microkinetic modeling and ab-initio thermodynamics

- ✓ Wulff construction and *ab initio* thermodynamics have been applied to predict morphological changes of catalyst material in reacting conditions
- ✓ The findings are in agreement with operando spectroscopy analysis and characterization analysis
- ✓ **This methodology paves the way for the development of structure-dependent microkinetic models**



R. Cheula, A. Soon, M. Maestri, Cat. Sci. Tech., 2018

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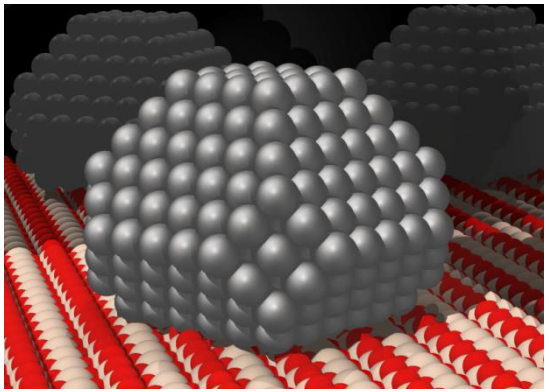
- ✓ Parametrization of kinetic parameters on different sites.
- ✓ Novel experimental tools: spectroscopy & kinetically relevant data.
- ✓ Confinement effects: «physical» catalysis

Structure-dependent microkinetic modeling

Assessment of BEP relations for hierarchical structure-dependent microkinetic modeling

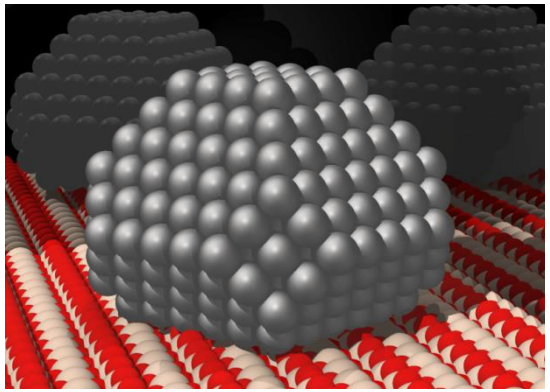


$$E_a = E_a^0 + \gamma_P \Delta H_r$$

Can BEP deal with the «complication» when «complexity» makes the higher level theories not applicable?

Structure-dependent microkinetic modeling

Assessment of BEP relations for hierarchical structure-dependent microkinetic modeling



$$E_a = E_a^0 + \gamma_P \Delta H_r$$

From selected DFT calculations

Z.B. Ding, S. Guffanti, M. Maestri, submitted

Methodology: theory-to-theory comparison

Density Functional Theory Calculation

- Binding Energies
- Activation Energy: Climbing Image – Nudged Elastic Band

BEP assessment

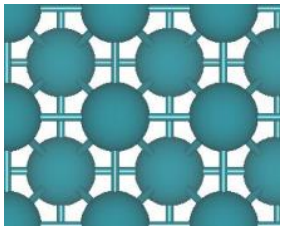
Dissociation Reactions:

- CO → C + O
- CH → C + H
- t-COOH→ CO_2 + H

Metal catalyst:

- Rh, Pt, Cu, Ag, Pd, Ni

Low index surfaces:



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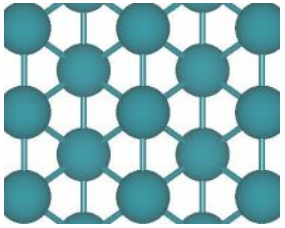

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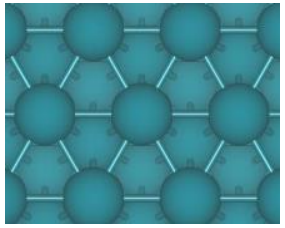

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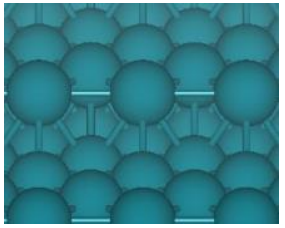


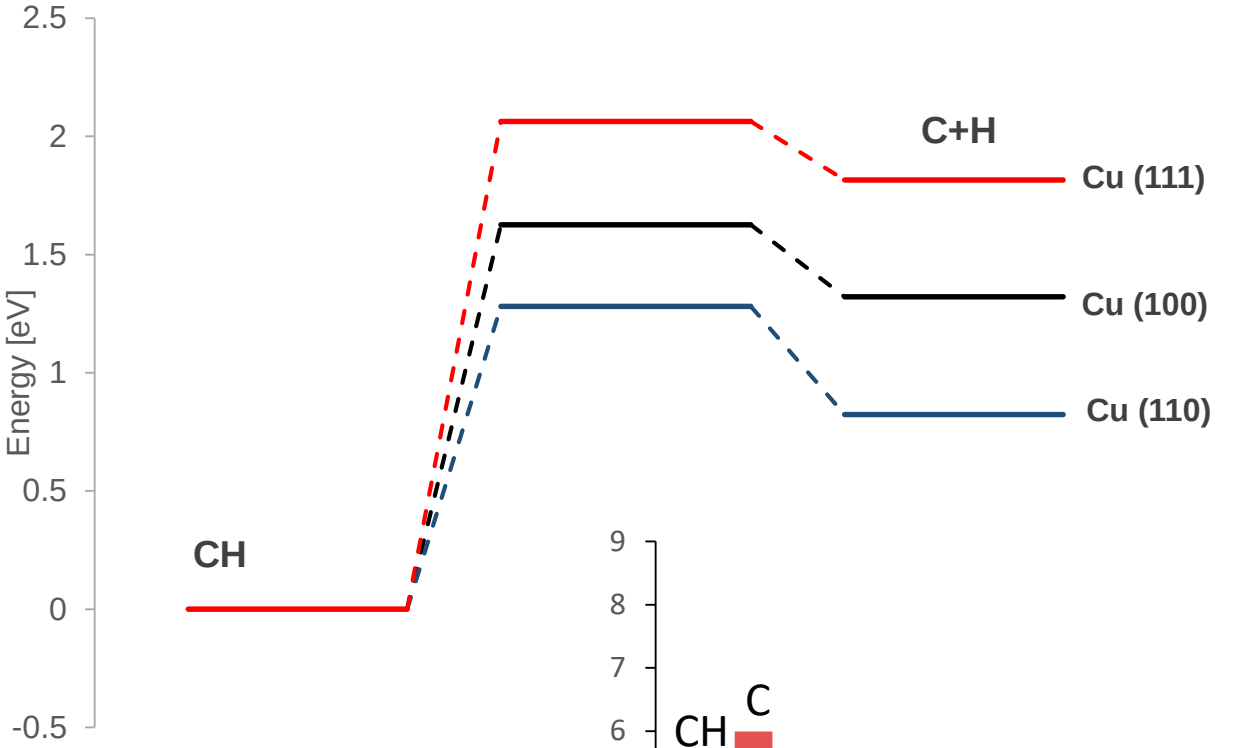
(211)

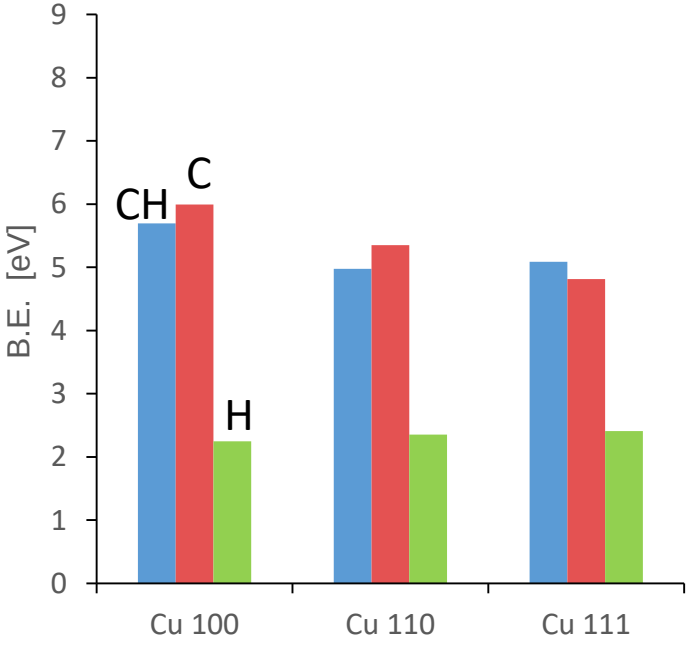
QUANTUMESPRESSO

QuantumEspresso code

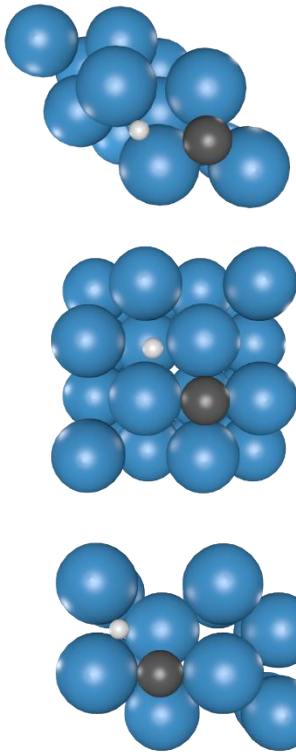
- Plane wave – uspp - PBE
- CI-NEB – 0.05 eV/A

$CH \rightarrow C + H$



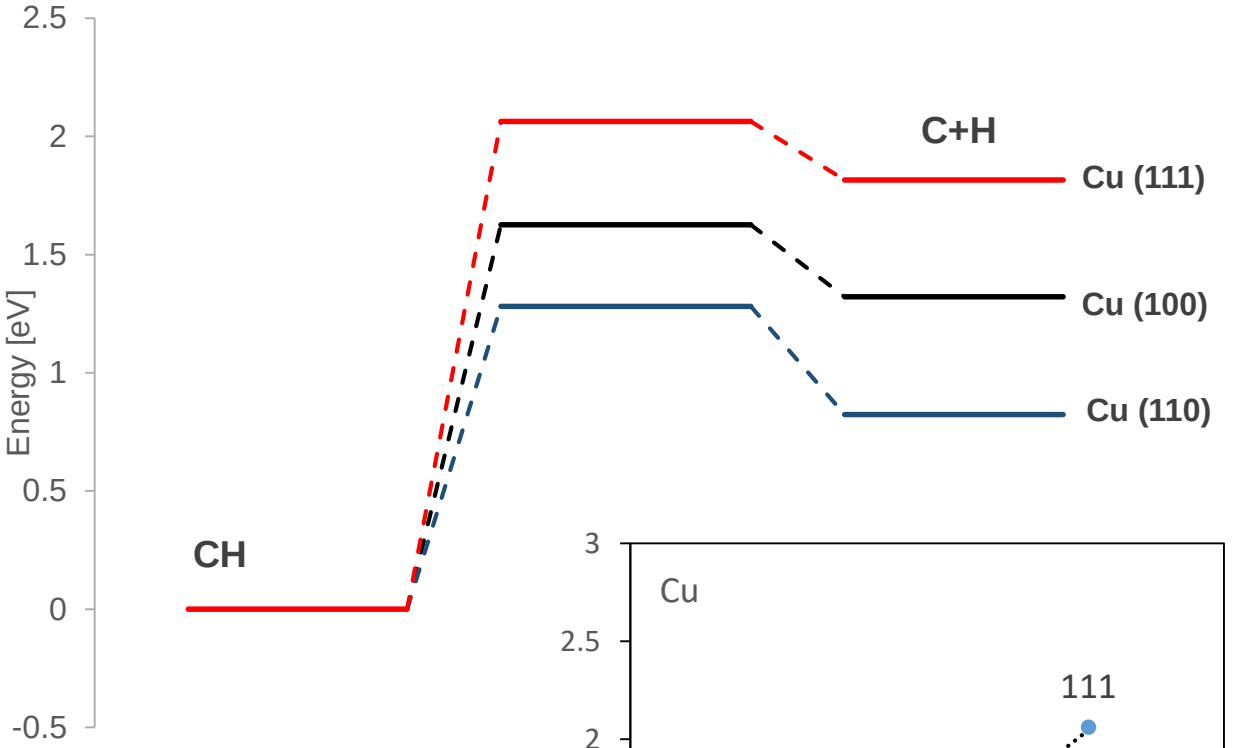


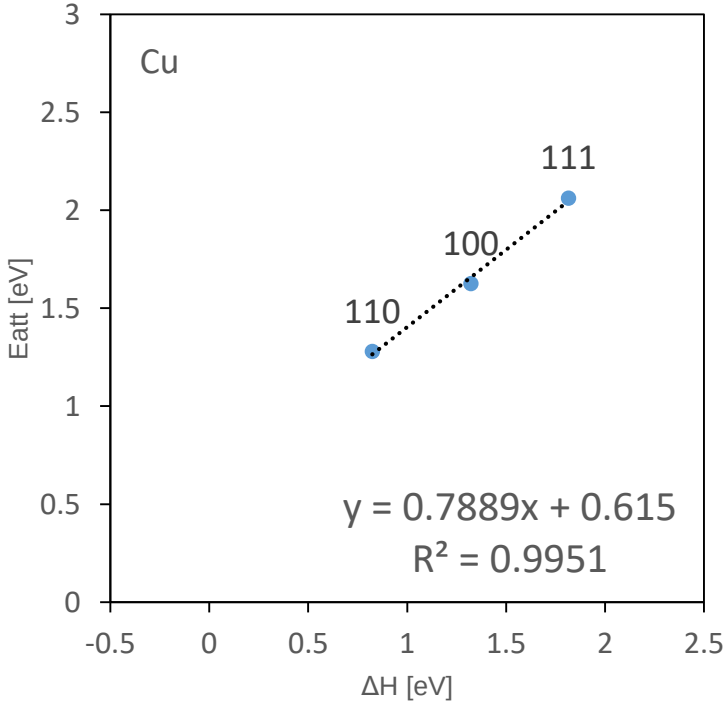
TS geometry

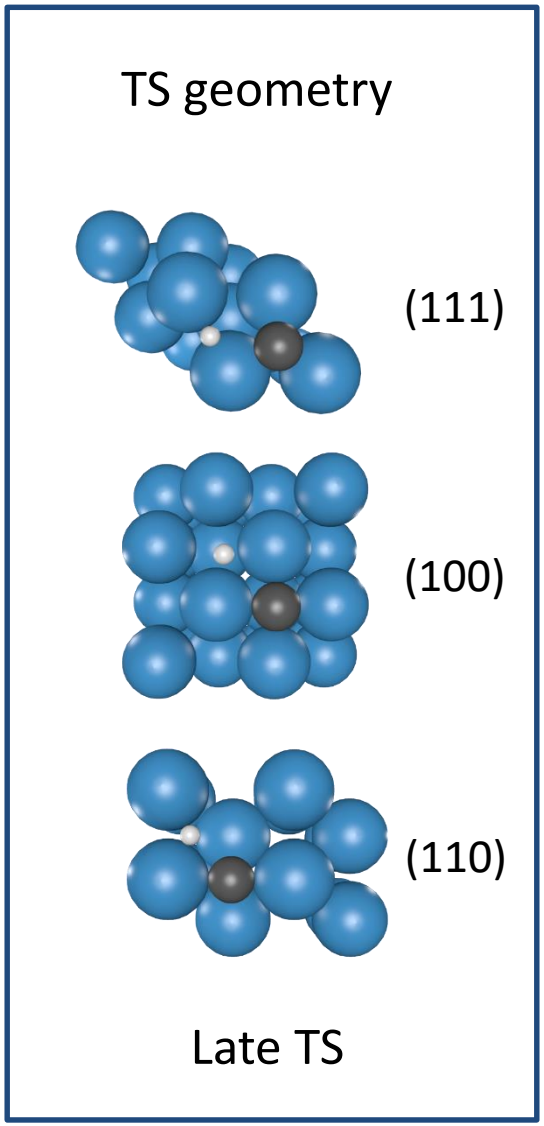


Late TS

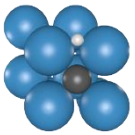
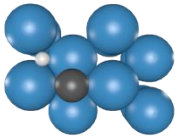
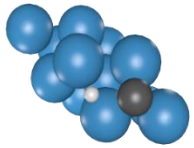
$CH \rightarrow C + H$



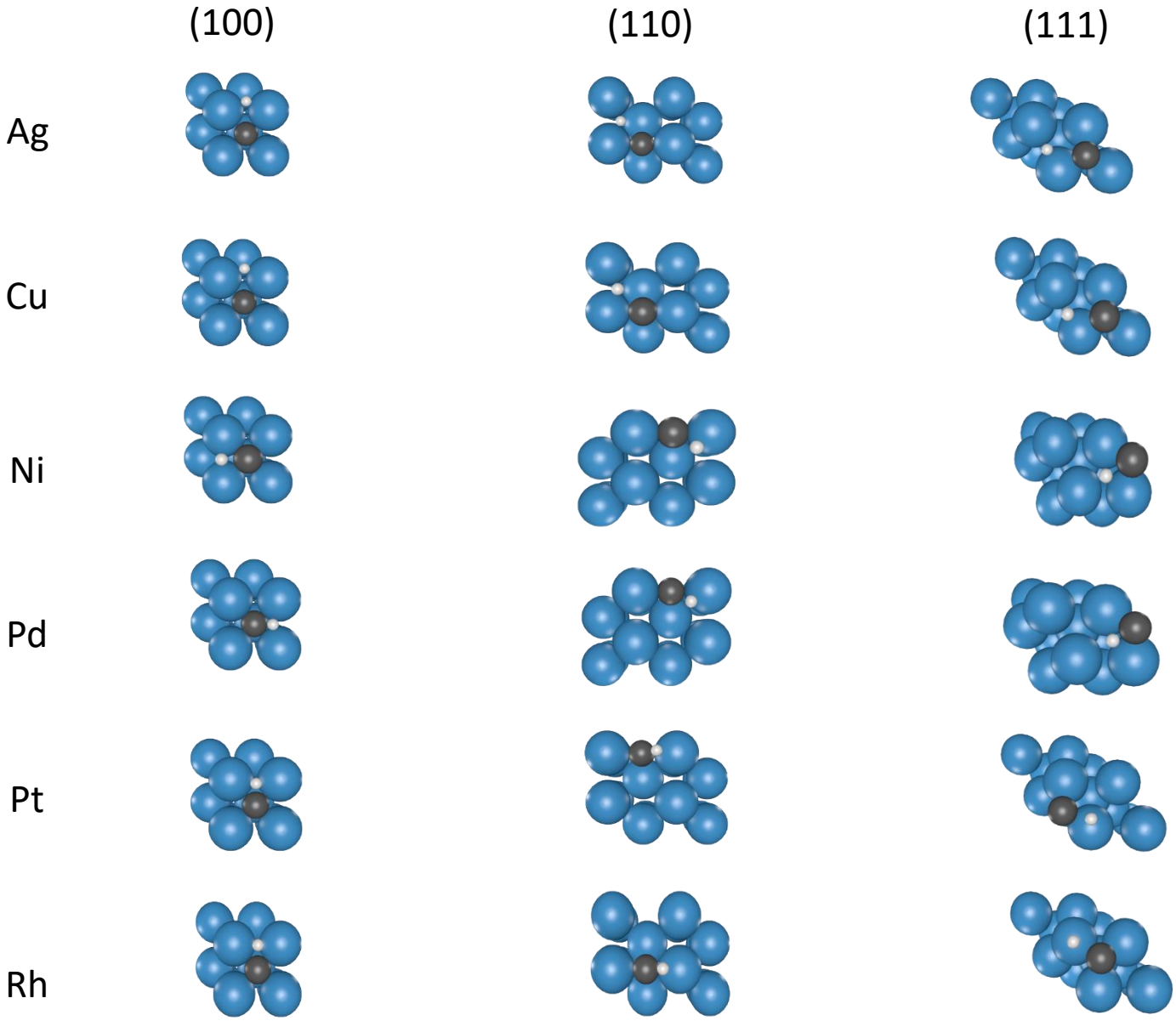




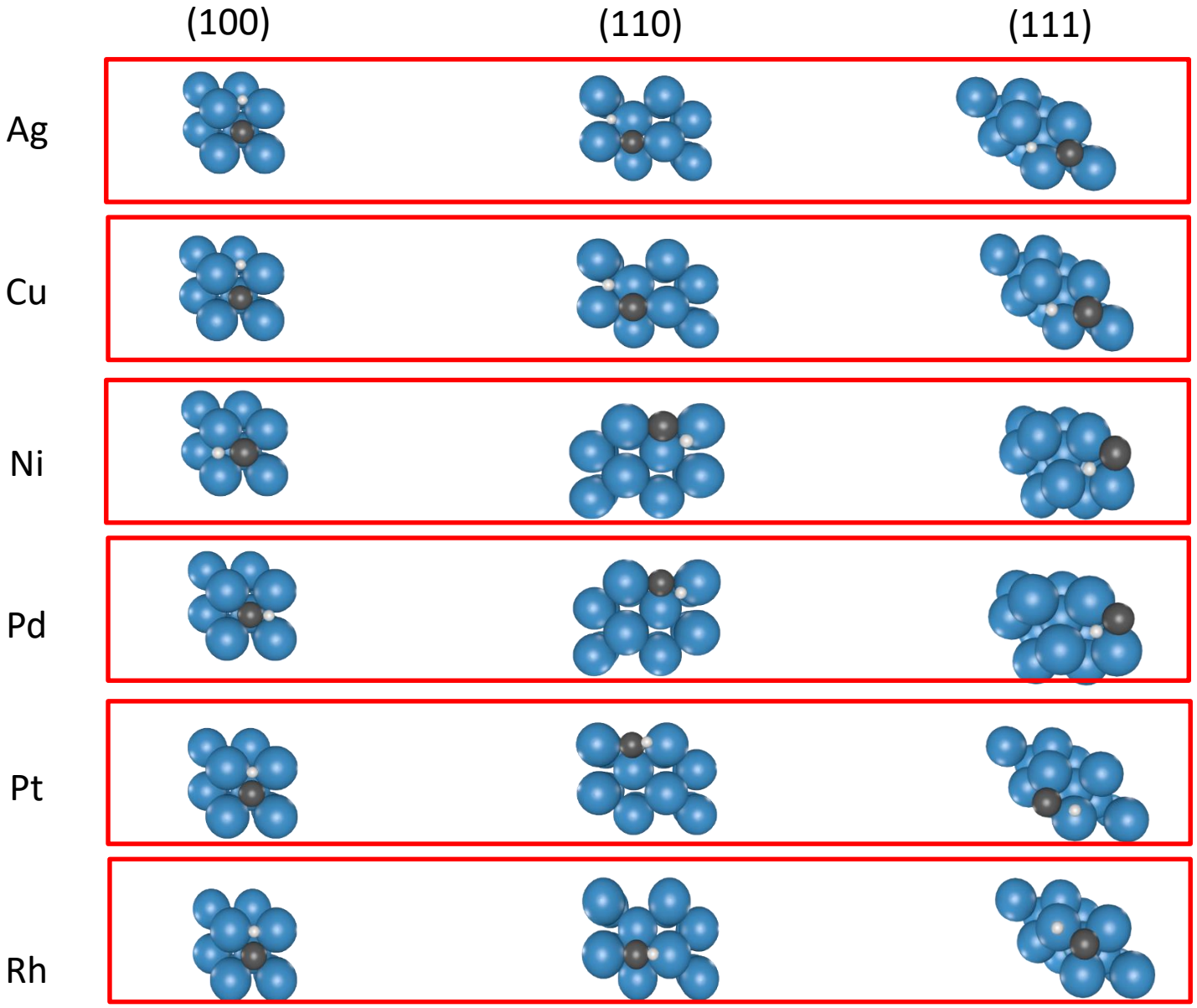
$CH \rightarrow C + H$

	(100)	(110)	(111)
Cu			

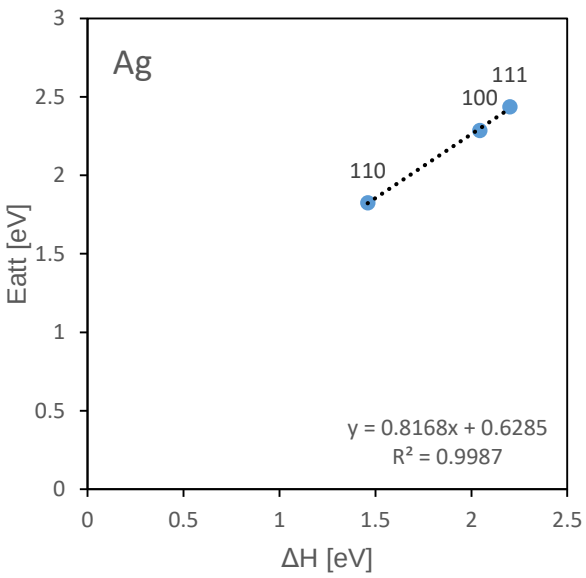
$CH \rightarrow C + H$

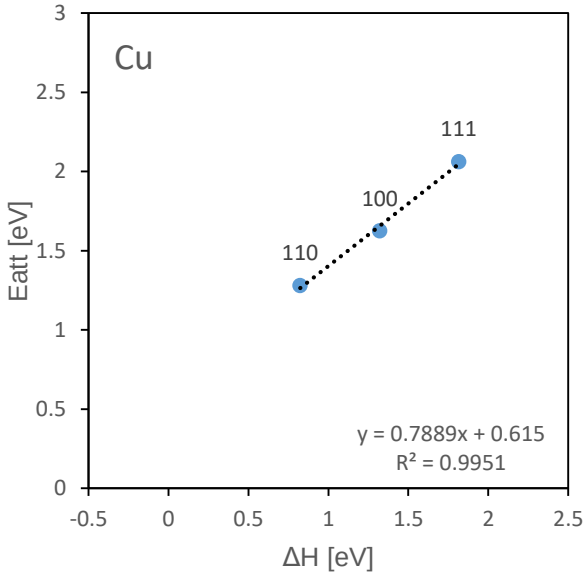


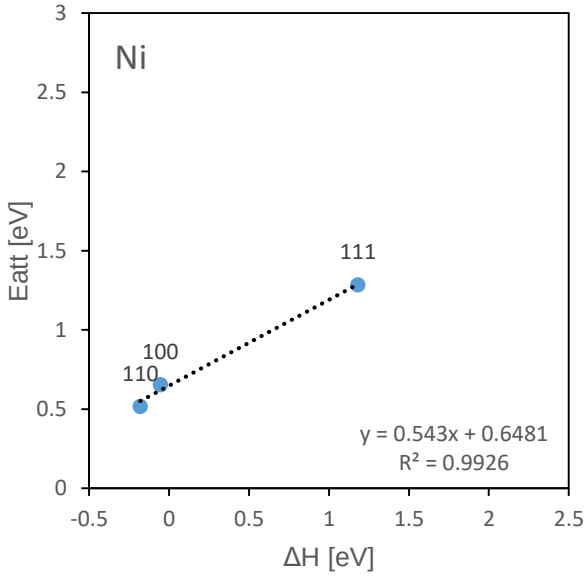
$CH \rightarrow C + H$

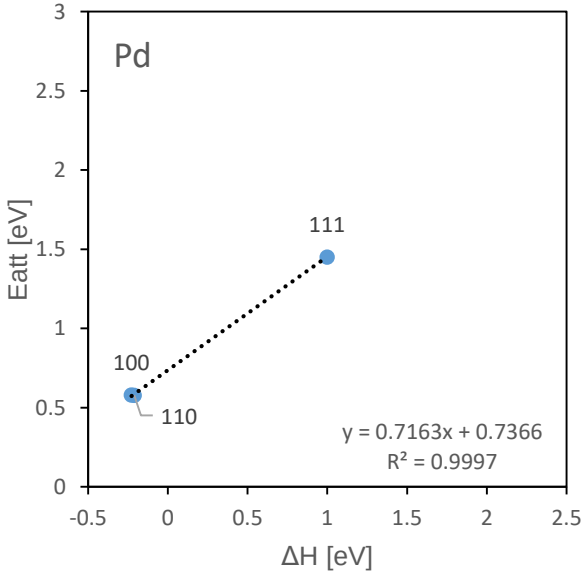


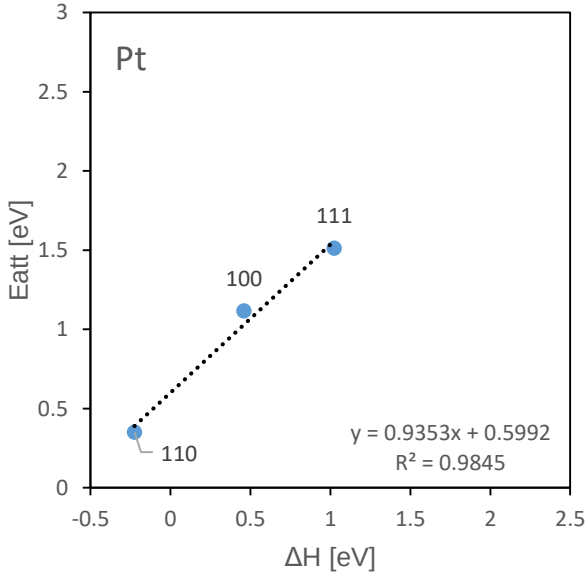
$CH \rightarrow C + H$

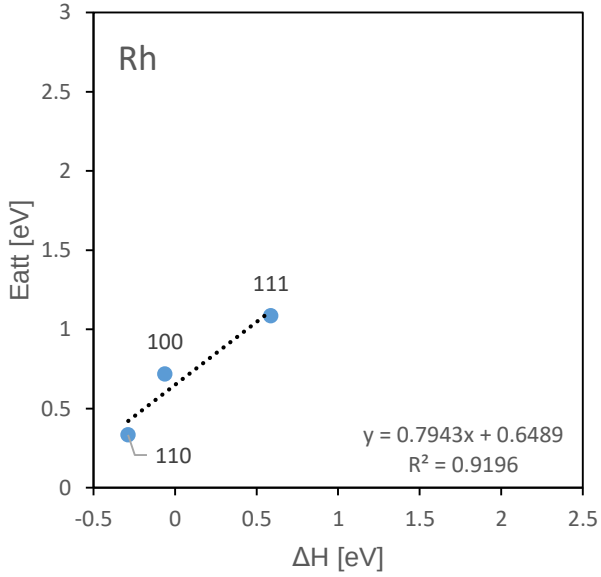




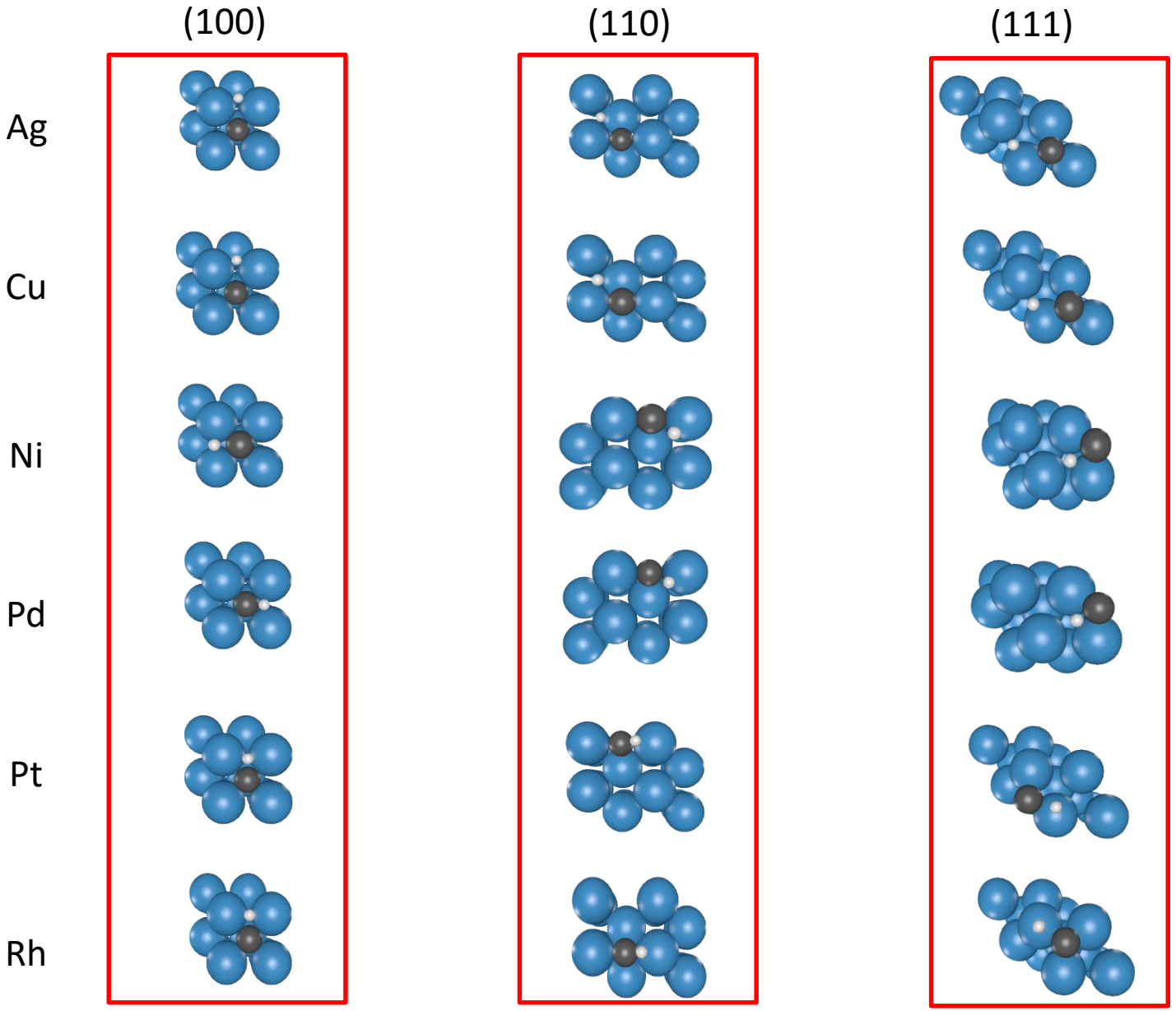




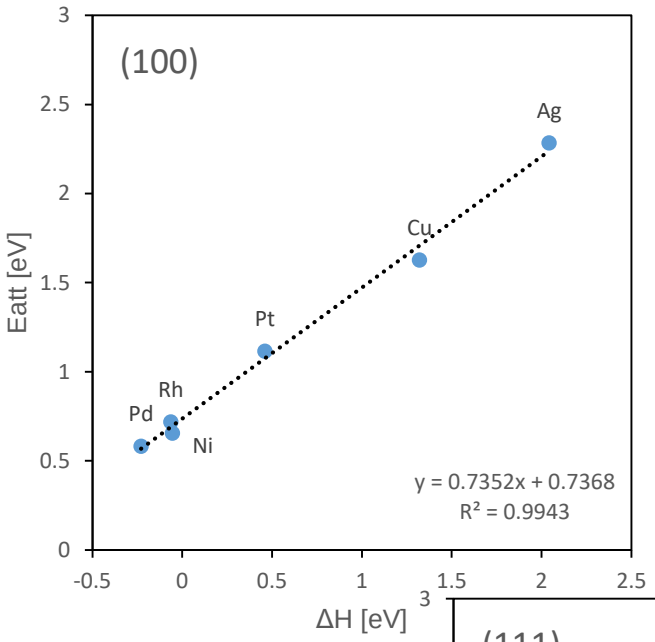


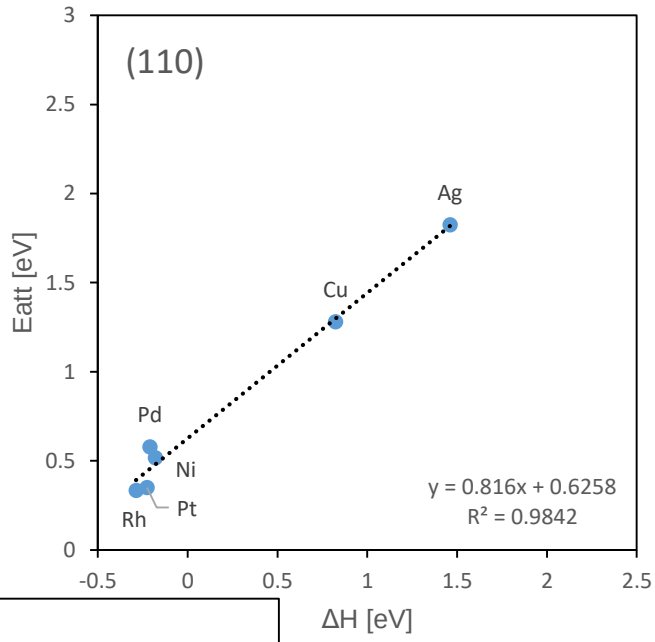


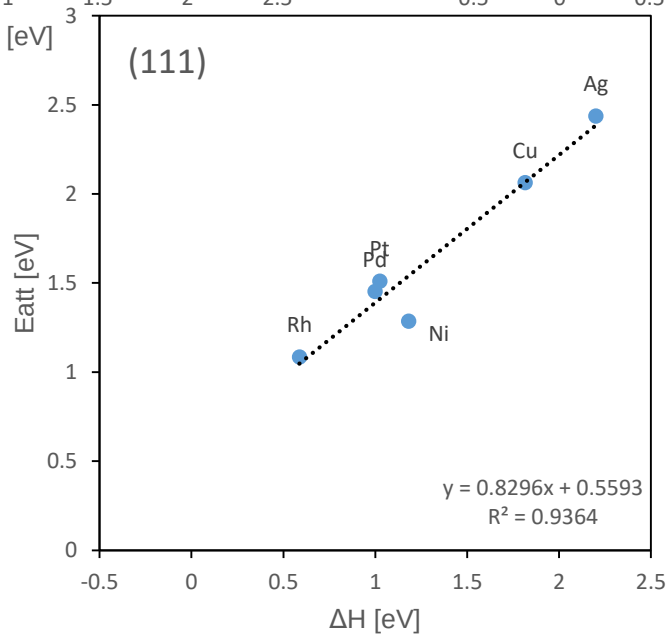
$CH \rightarrow C + H$



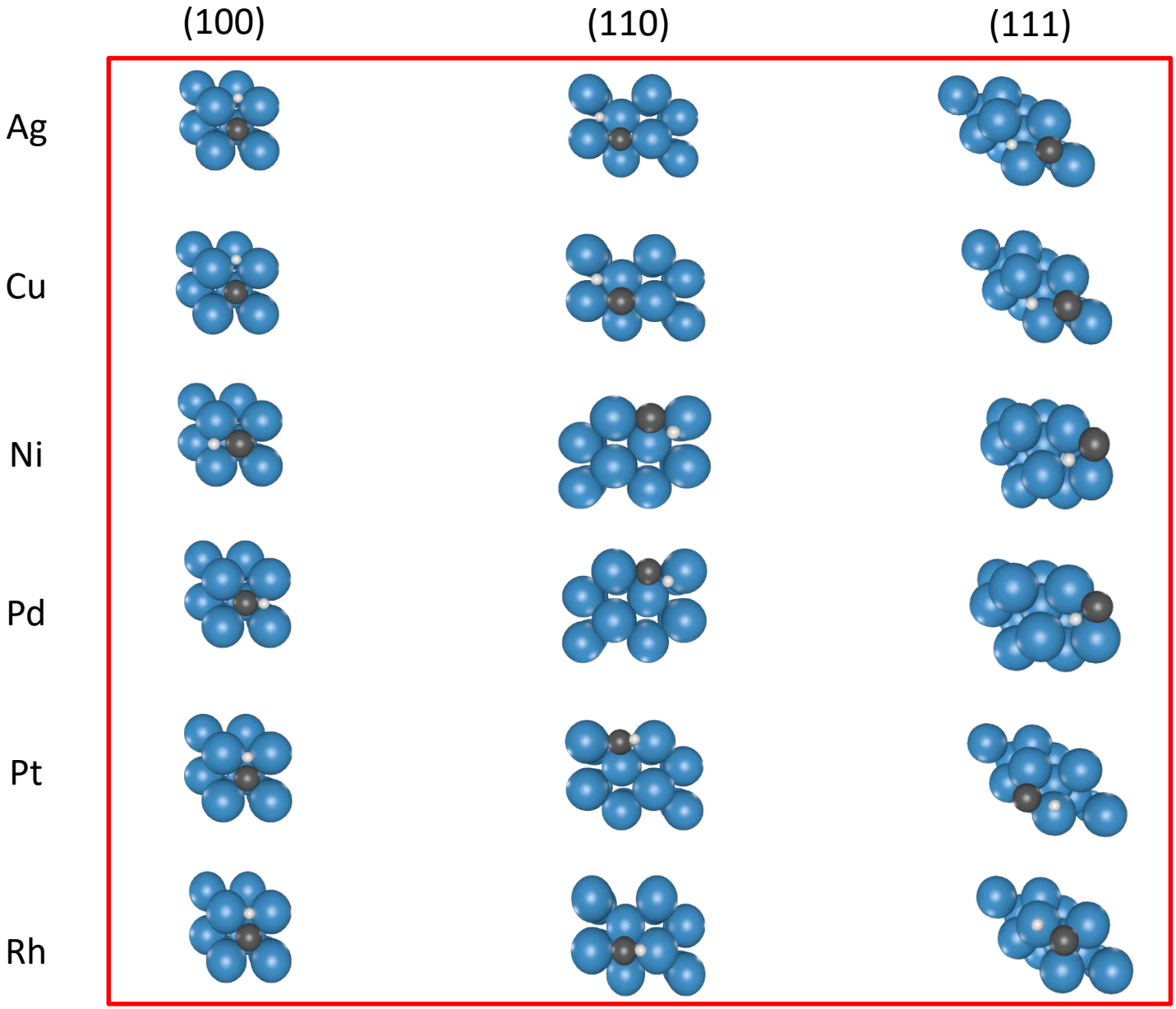
Different metals for each structure



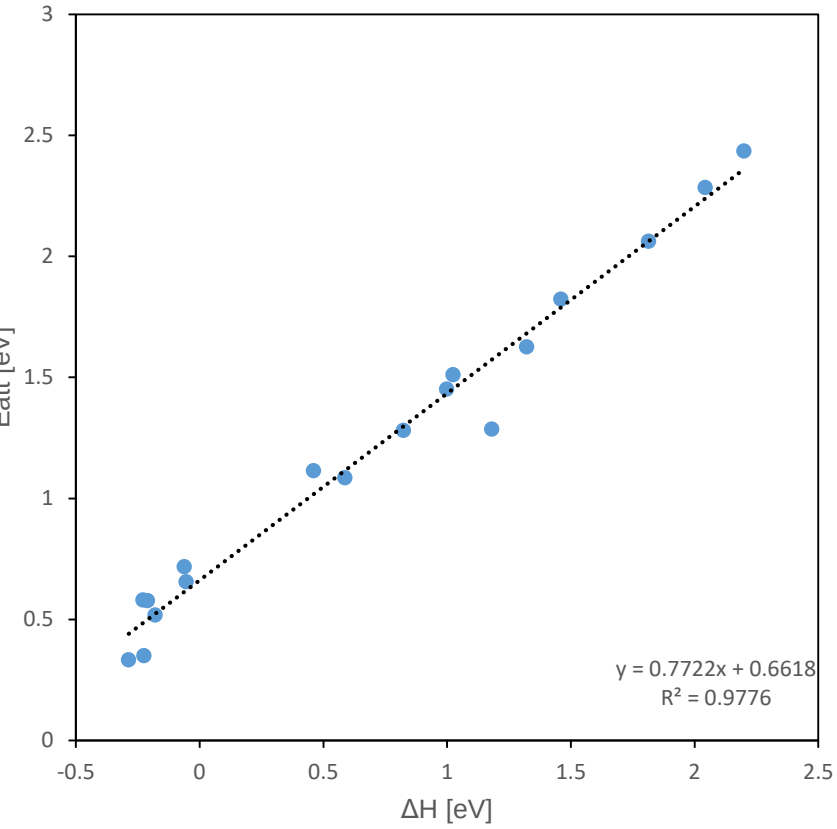


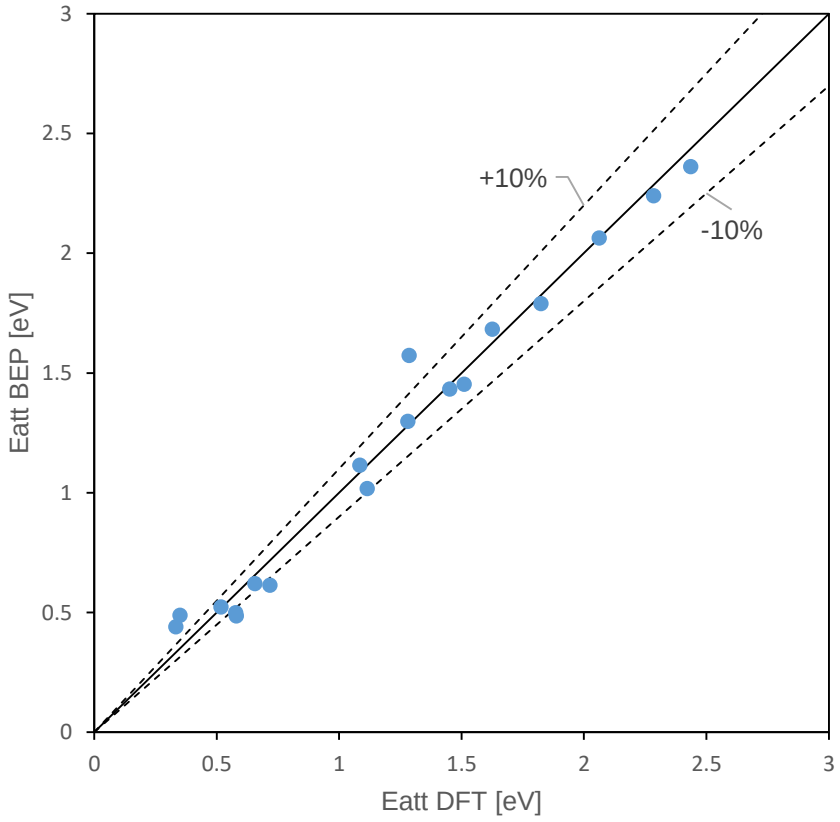


$CH \rightarrow C + H$

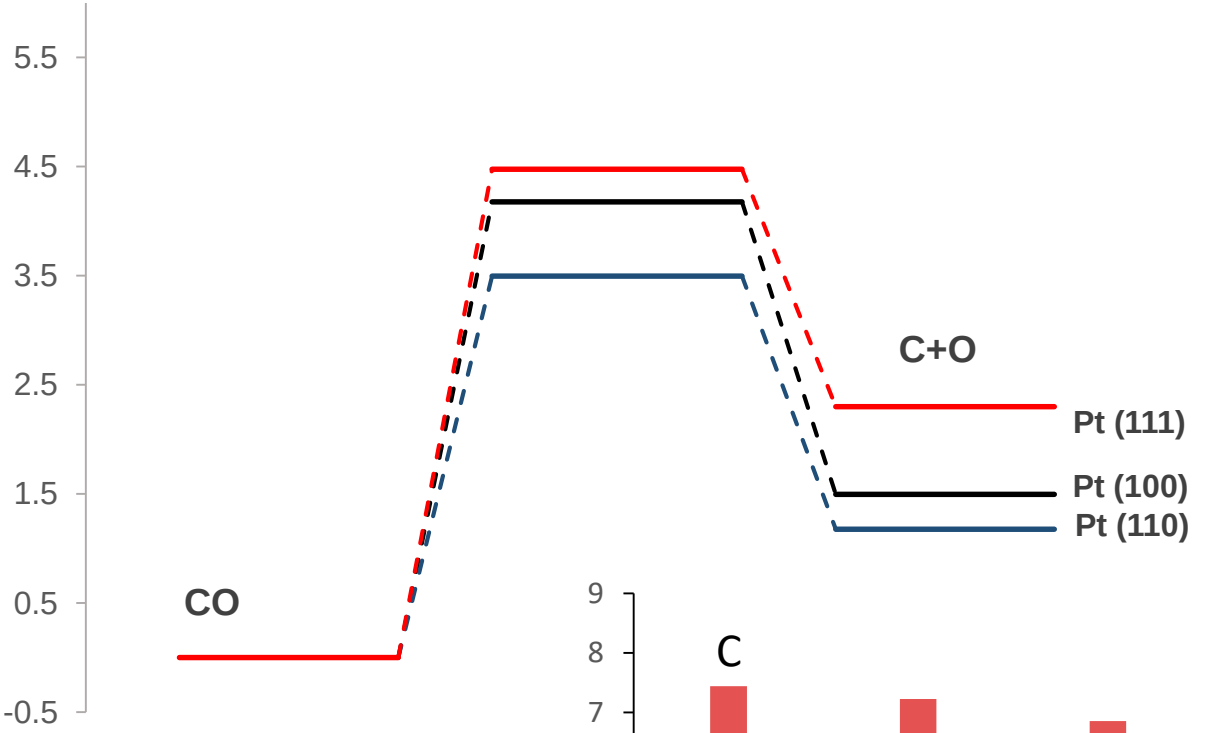


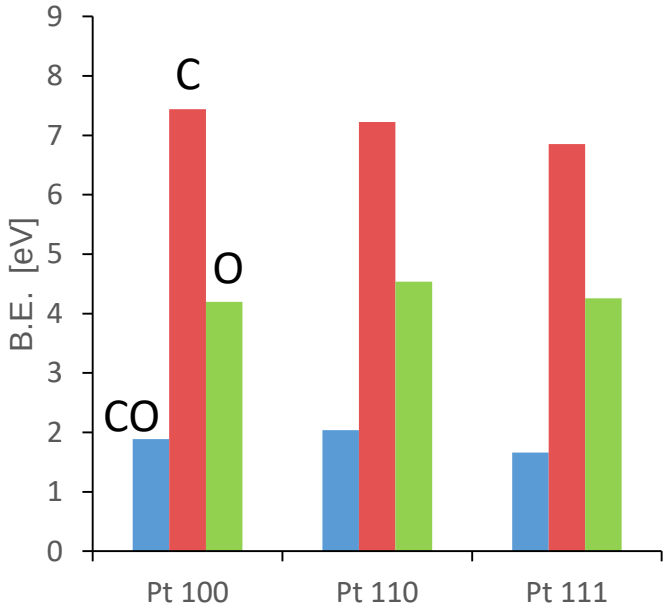
All structures – all metals





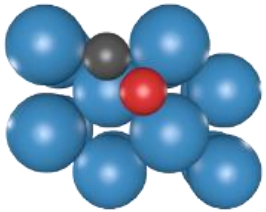
$CO \rightarrow C + O$





TS geometry

(111)



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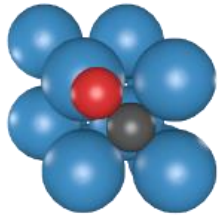
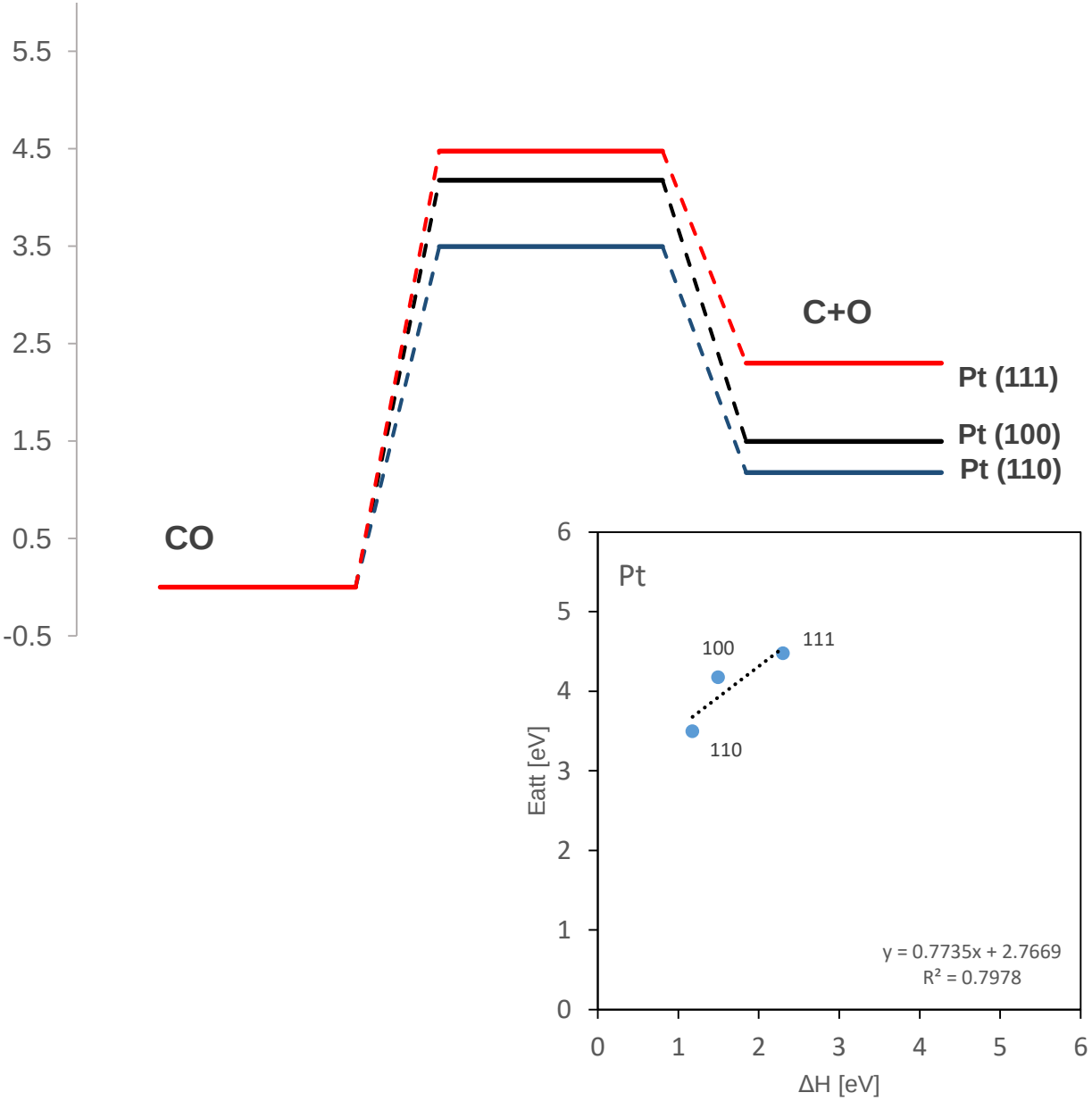


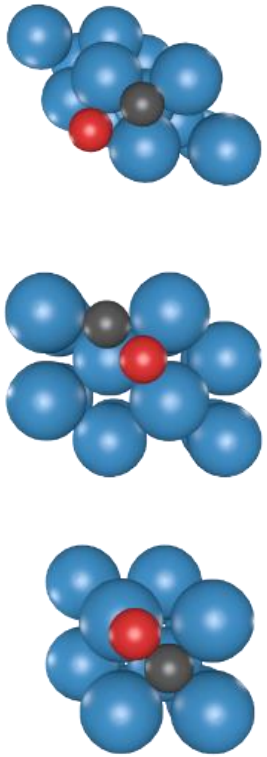
(110)

Late TS

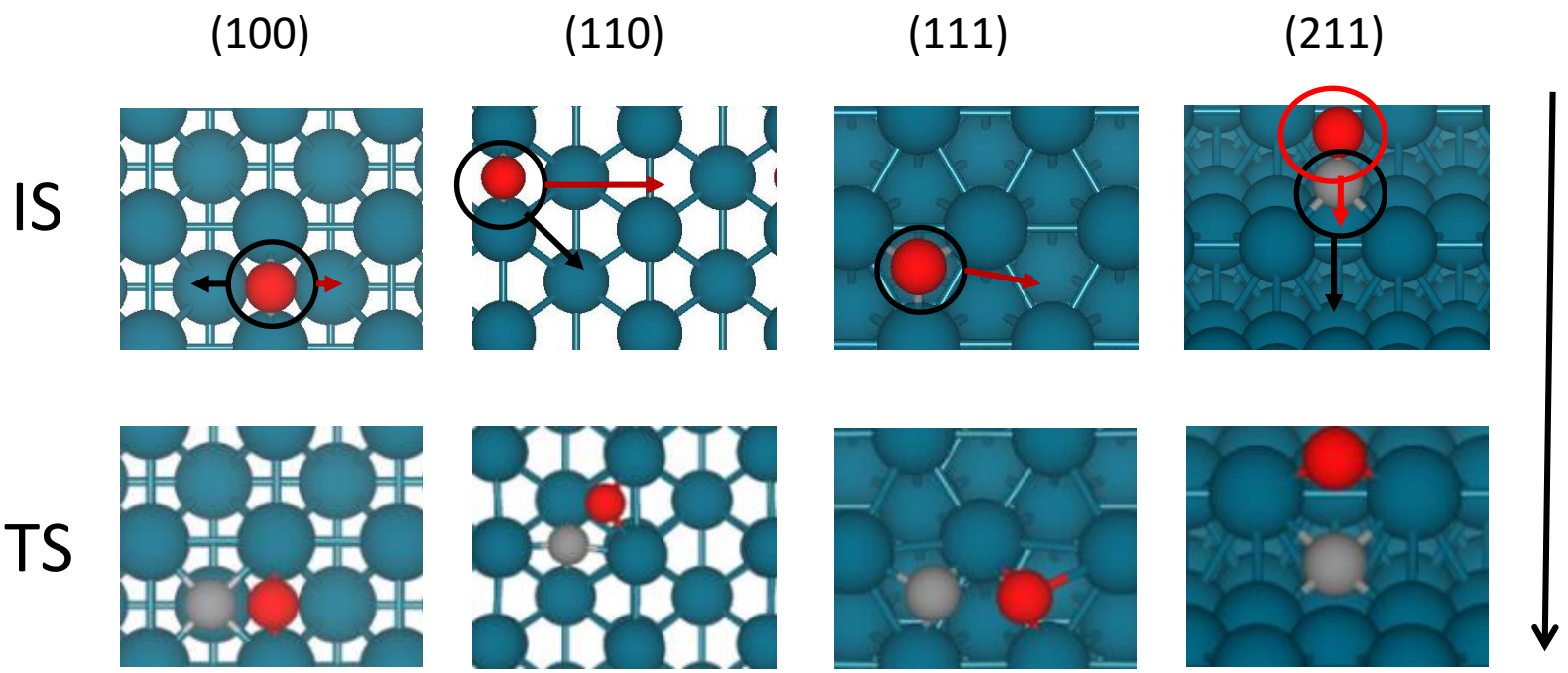
$CO \rightarrow C + O$



TS geometry



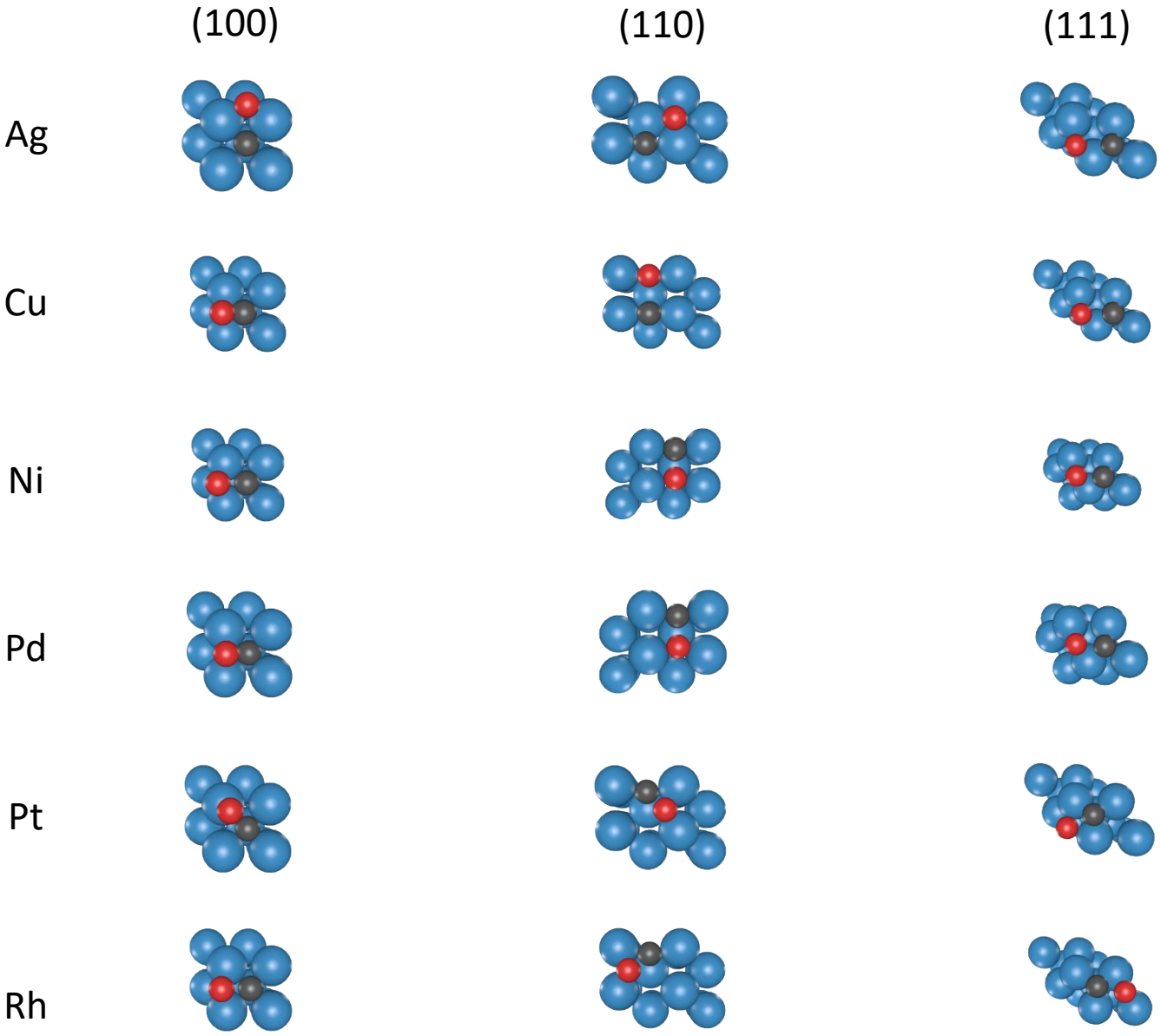
$CO \rightarrow C + O$



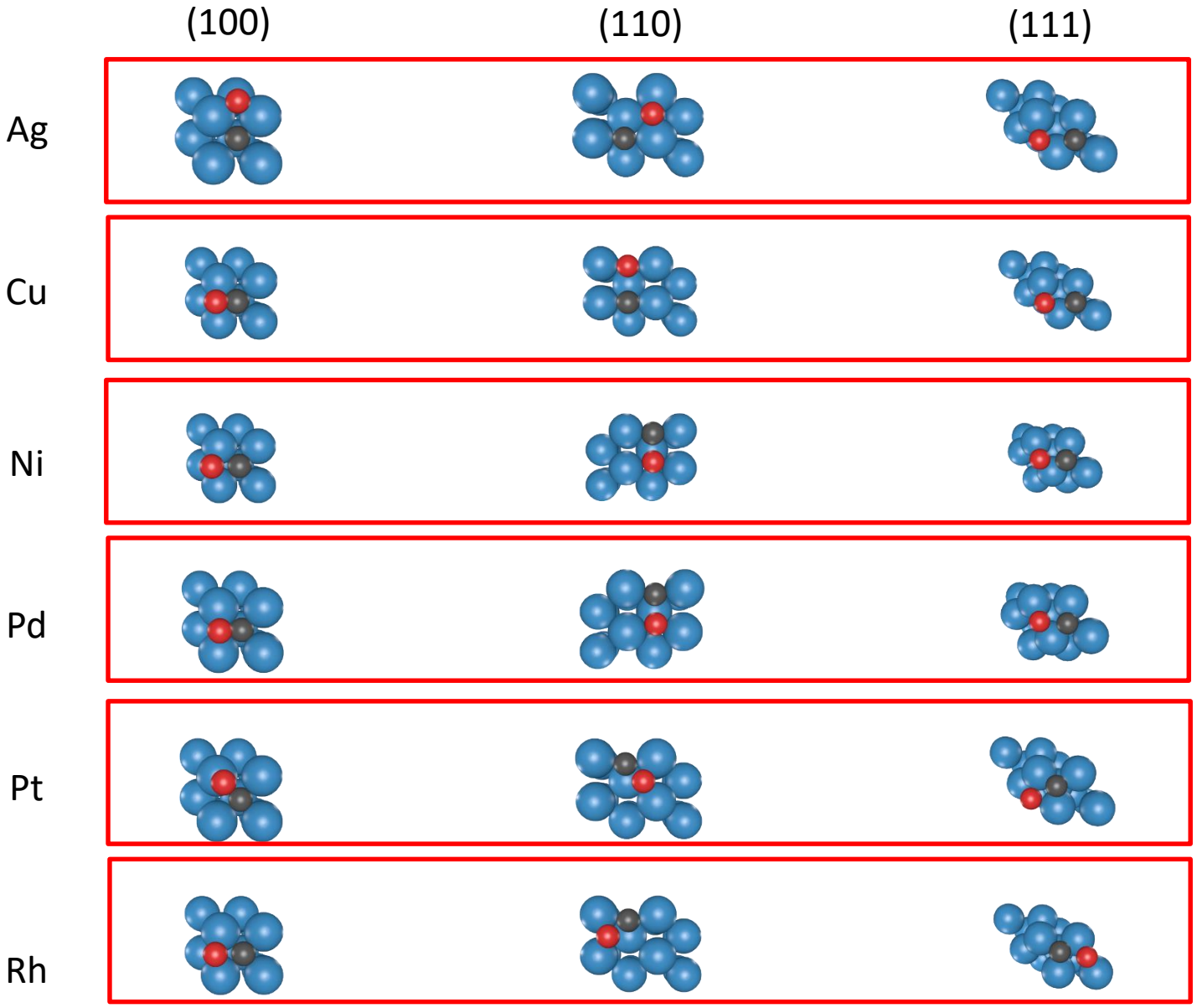
Dissociation sequence:
- CO migration
- CO bending
- C-O elongation

Determining factors:
- Anchoring C
- Lateness

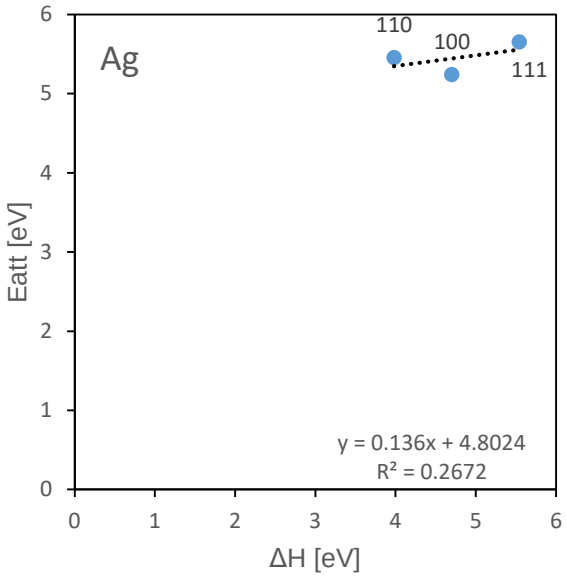
$CO \rightarrow C + O$

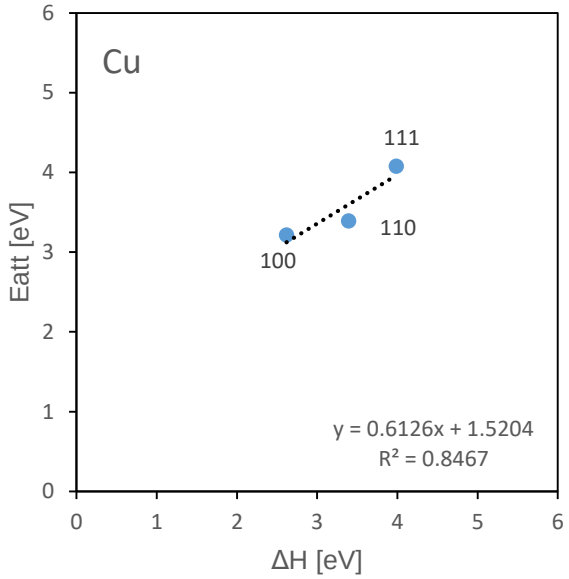


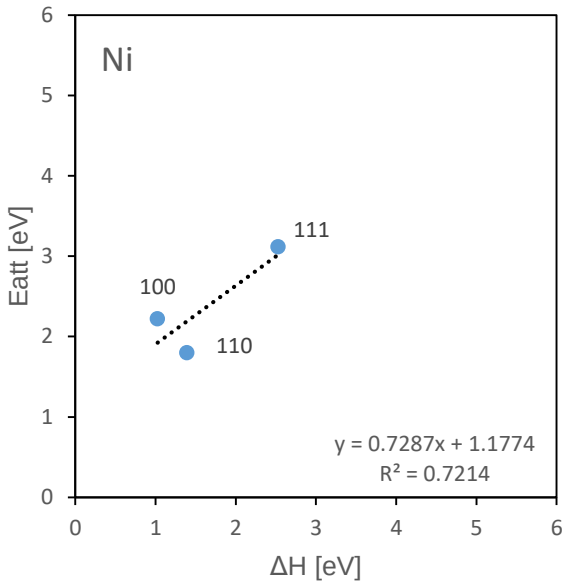
$CO \rightarrow C + O$

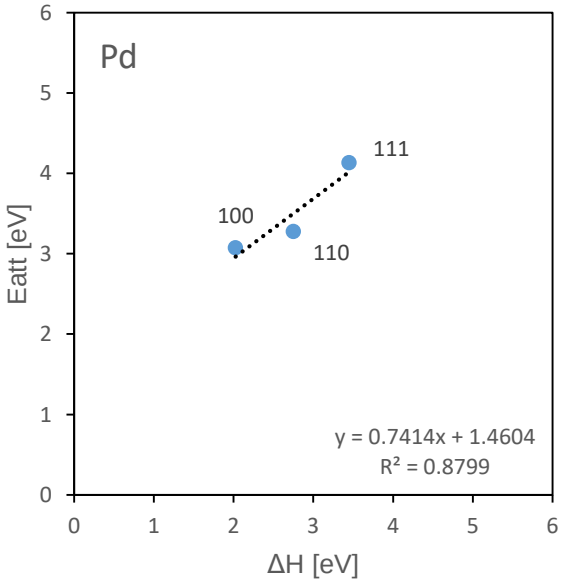


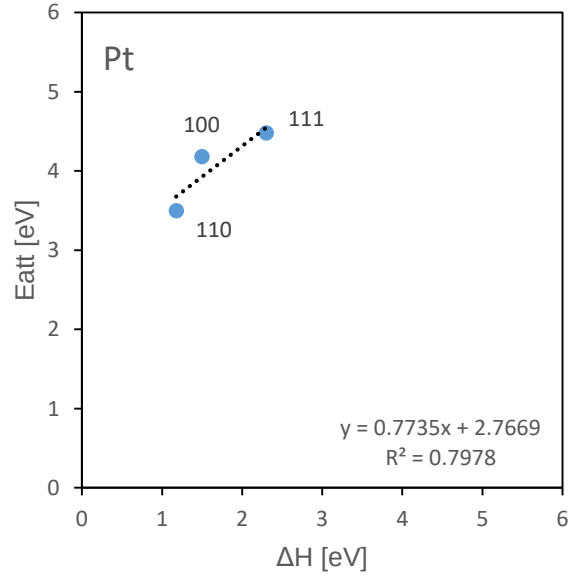
Different structures for each metal

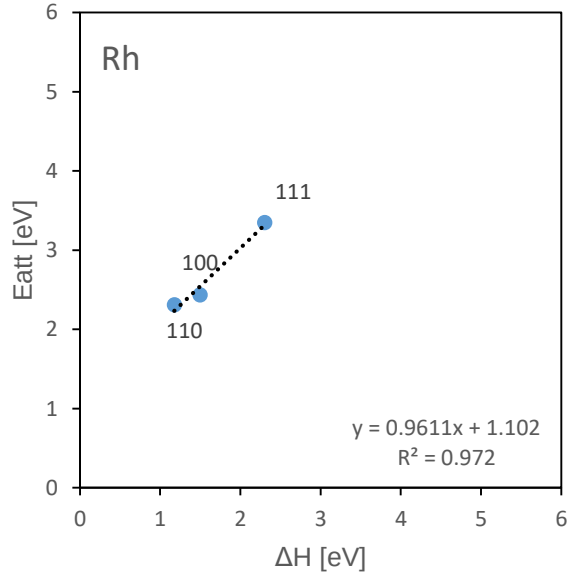






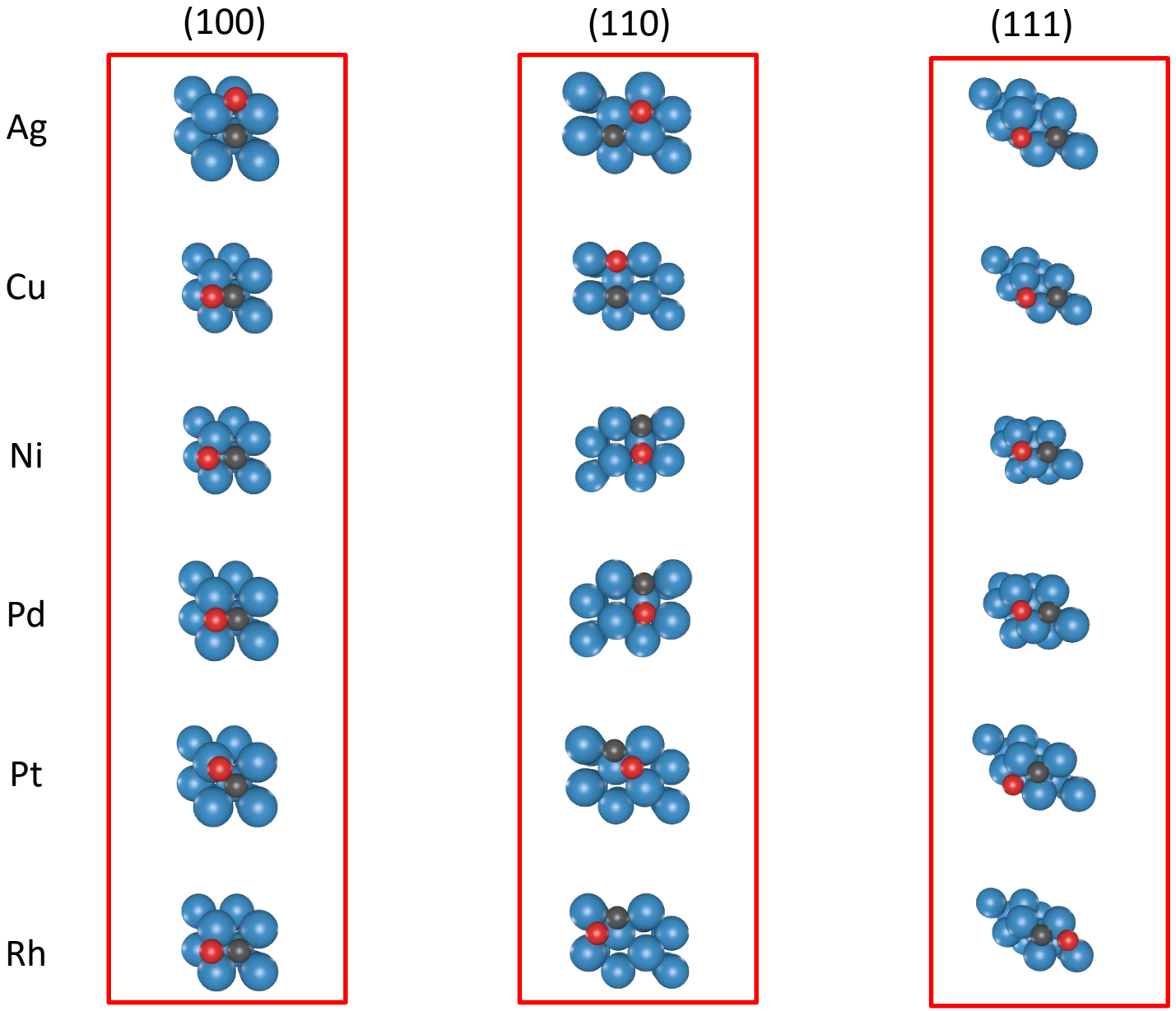




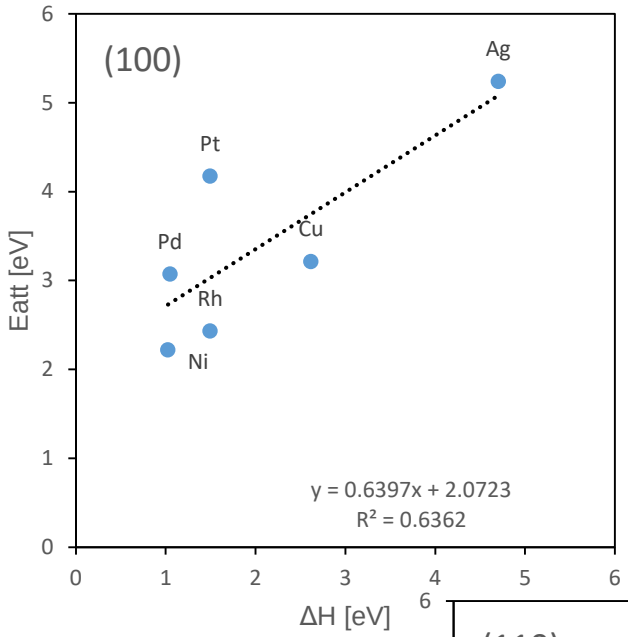


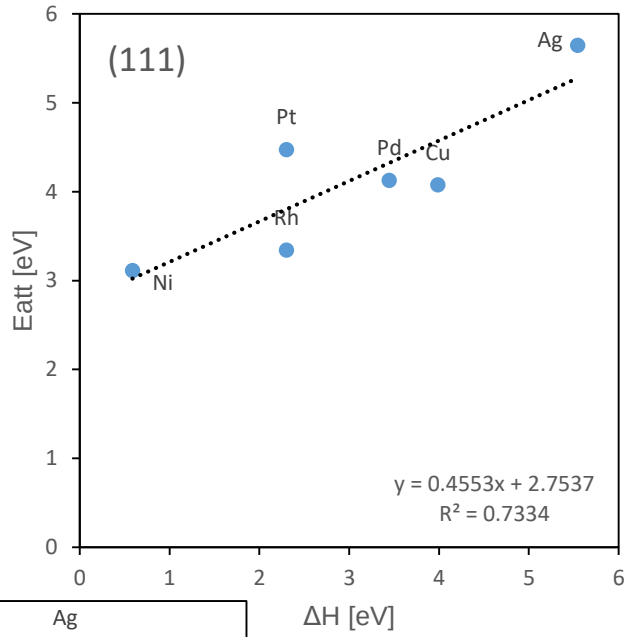
CO → C + O

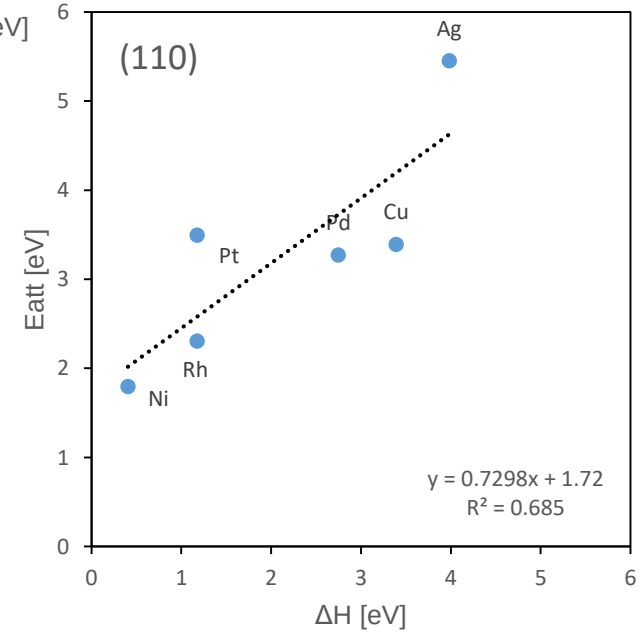
$CO \rightarrow C + O$



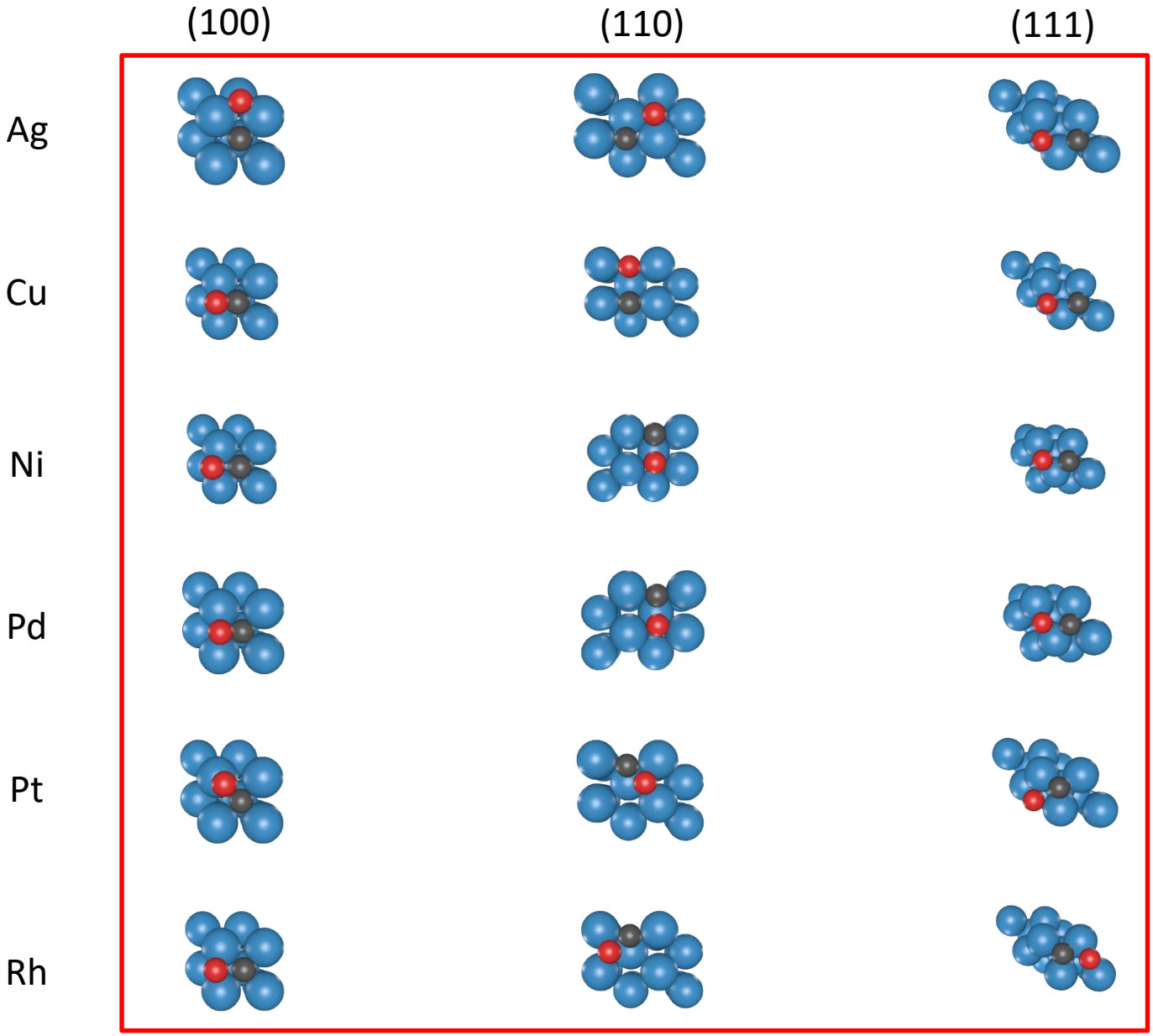
Different metals for each structure



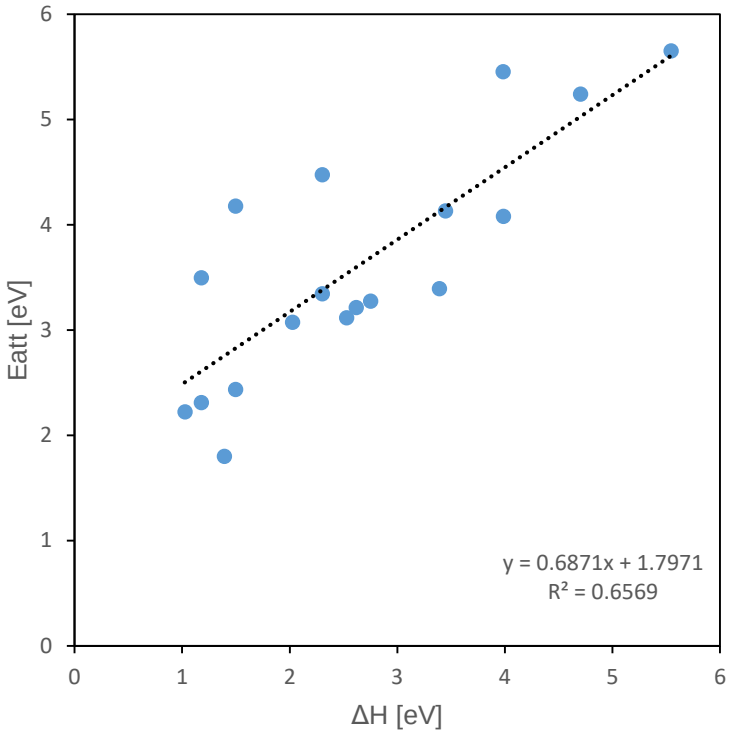


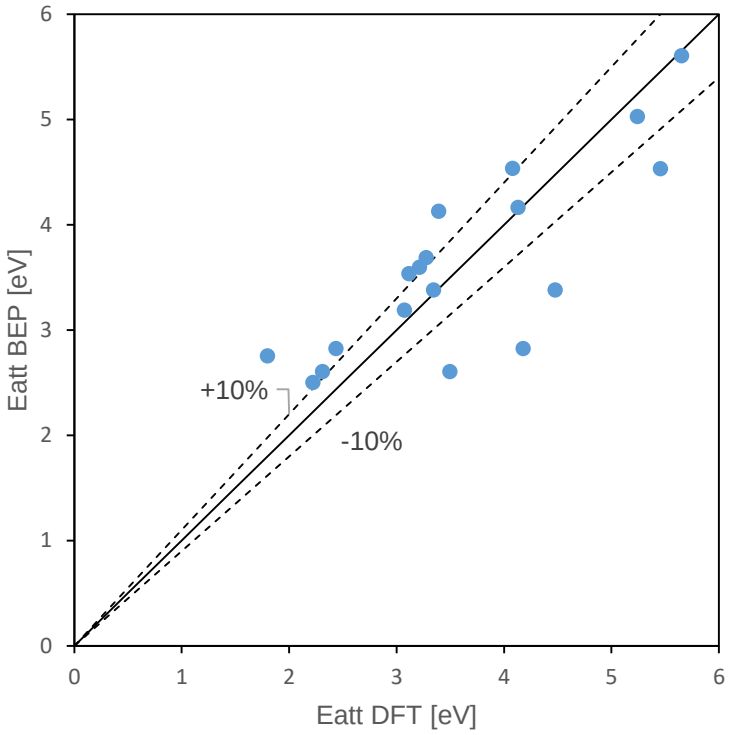


$CO \rightarrow C + O$

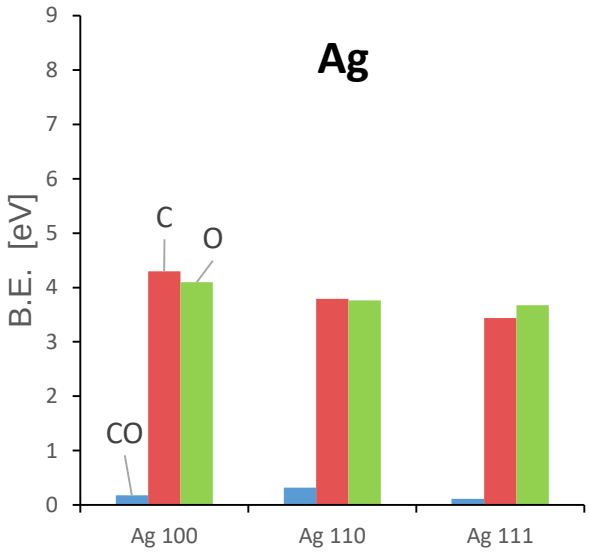


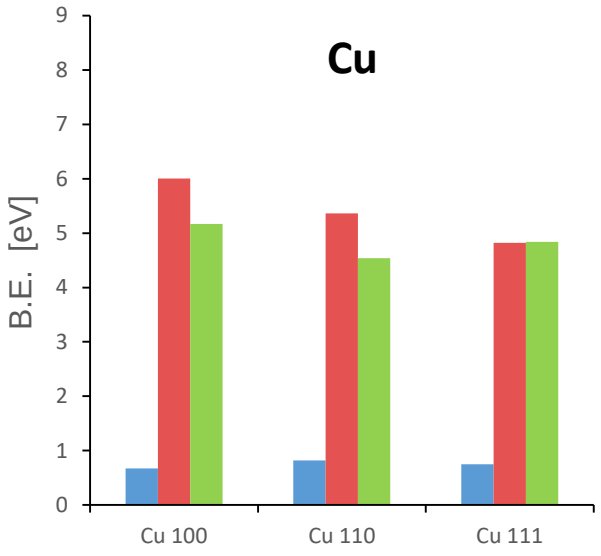
All structures – all metals

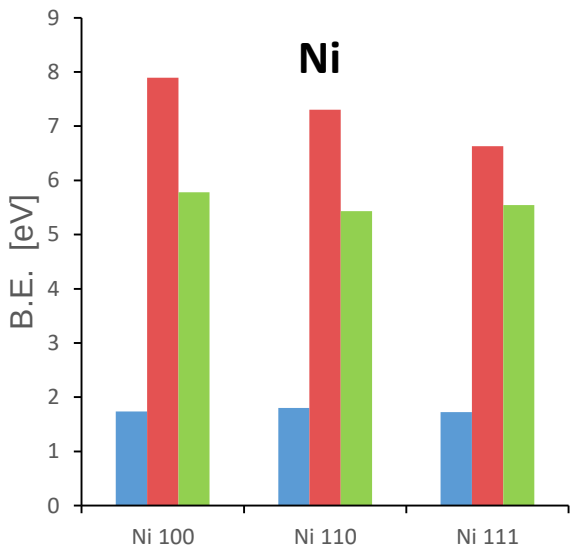


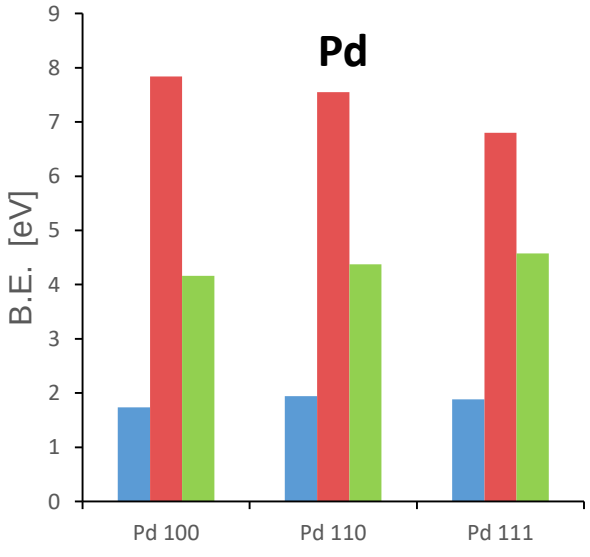


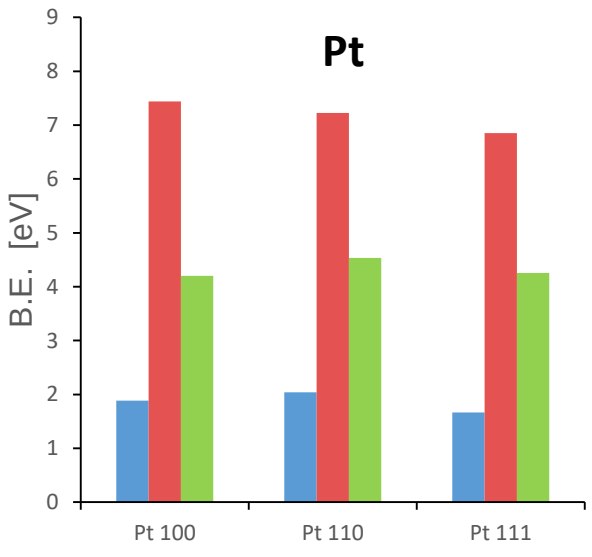
Reactant and products binding energies

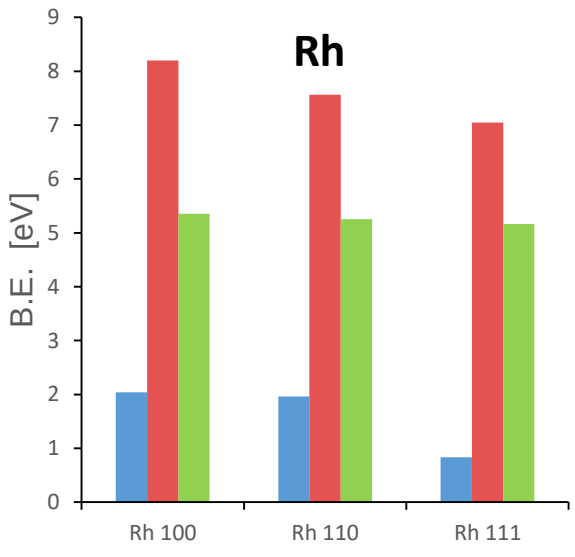






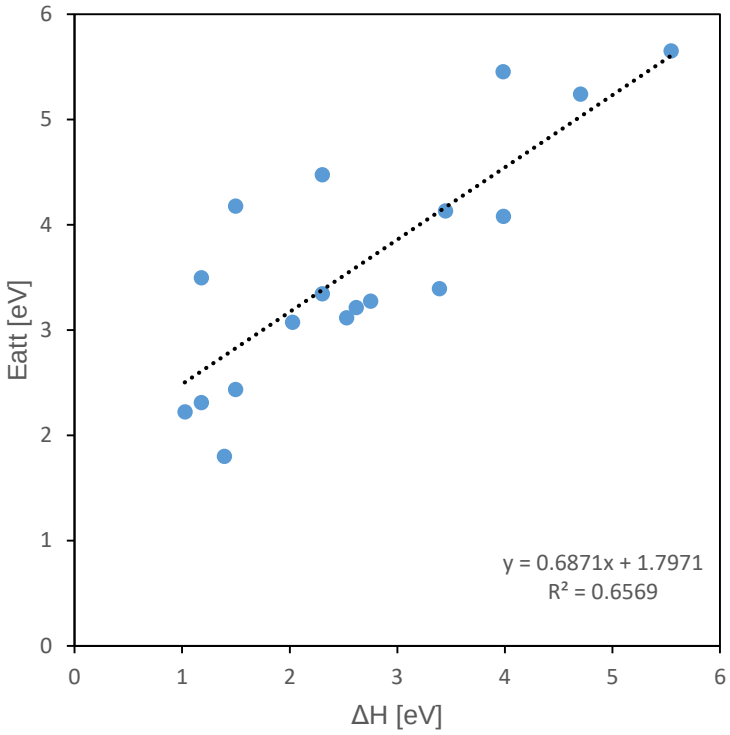


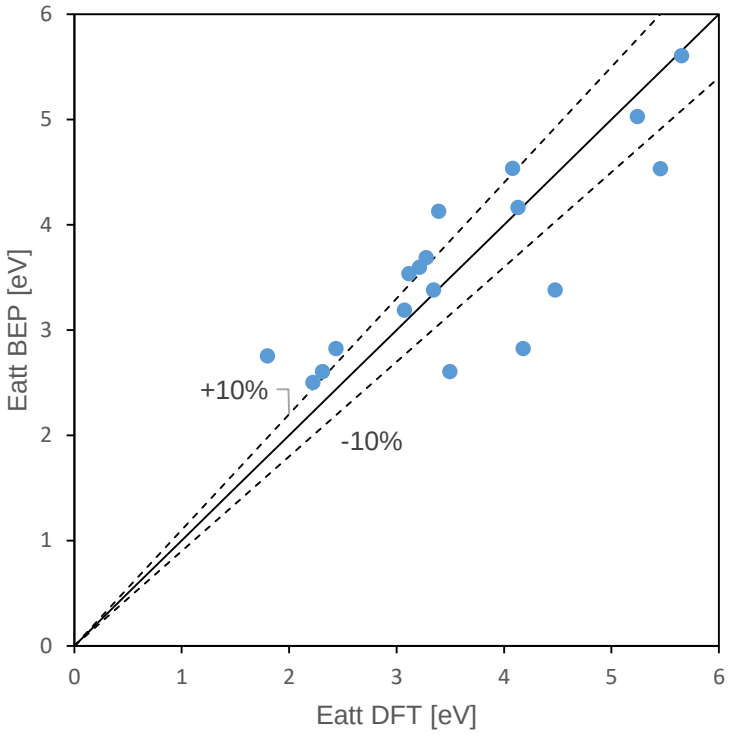




CO → C + O

All structures – all metals

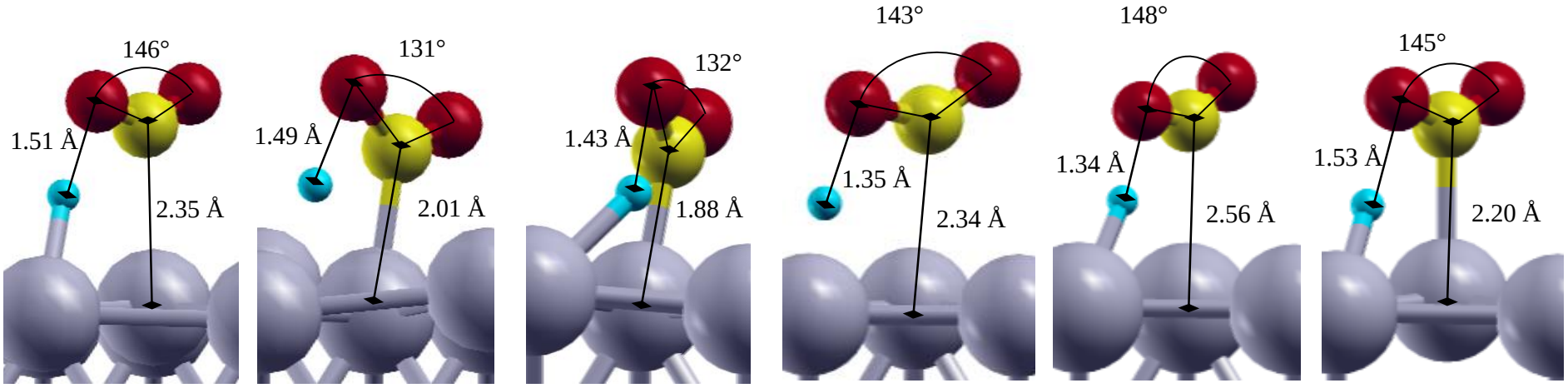




Different stabilities of reactants and products

and their concomitant effect on the TS can affect the BEP

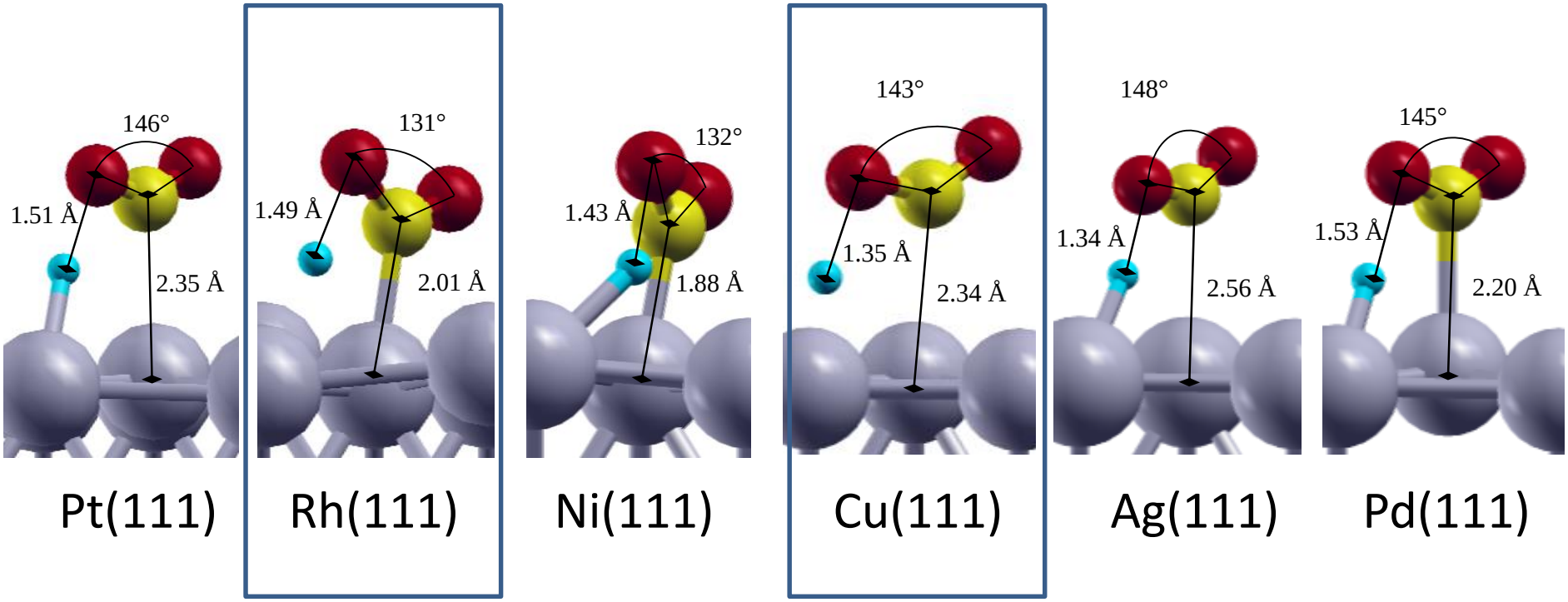
t-COOH → CO_2 + H



Pt(111) Rh(111) Ni(111) Cu(111) Ag(111) Pd(111)

Transition state geometry changes among the different metals.

$t\text{-}COOH \rightarrow CO_2 + H$



Transition state geometry changes among the different metals.

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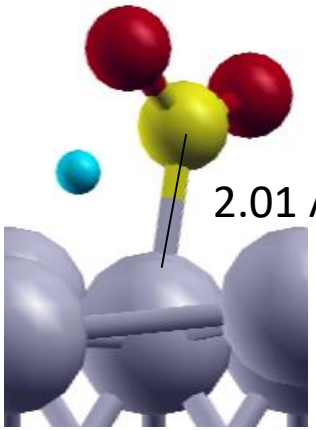
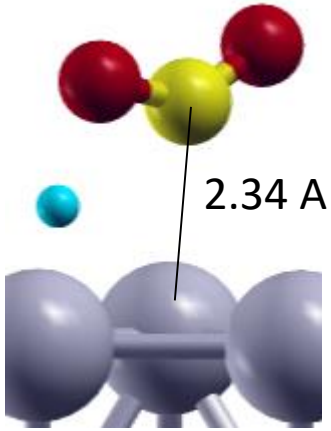


2.01 A (1.98 A)

Rh(111)

H b.e. = 2.85 eV

t-COOH b.e. = 3.08 eV



2.34 A (1.95 A)

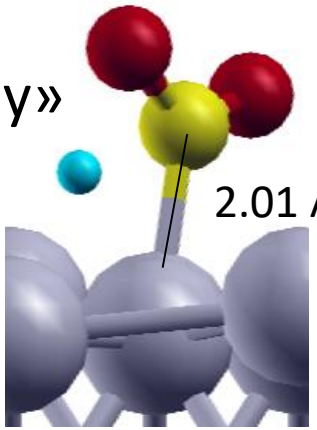
Cu(111)

H b.e. = 2.58 eV

t-COOH b.e. = 2.12 eV

$t\text{-}COOH \rightarrow CO_2 + H$

TS
«more early»

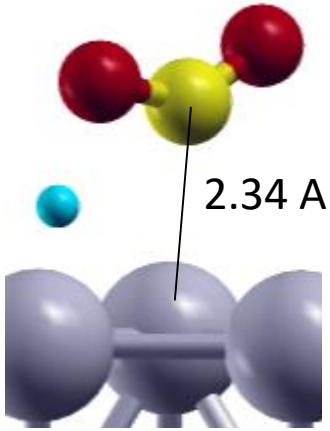


Rh(111)

H b.e. = 2.85 eV

t-COOH b.e. = 3.08 eV

TS
«more late»



Cu(111)

H b.e. = 2.58 eV

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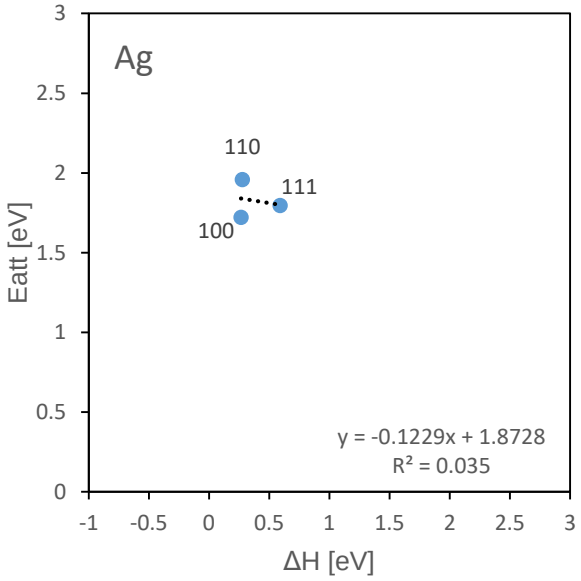
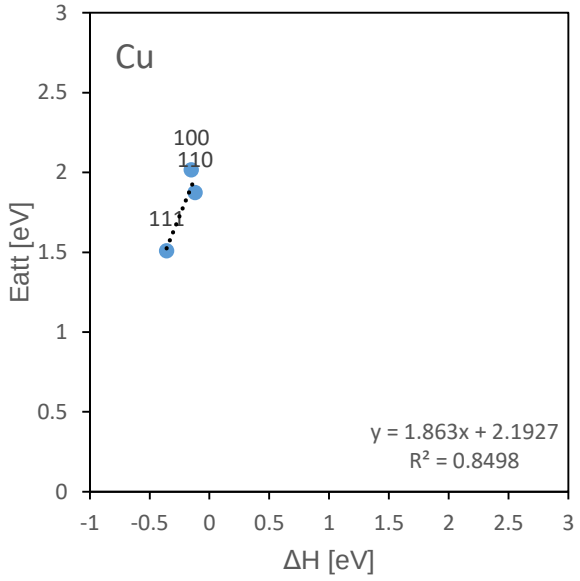
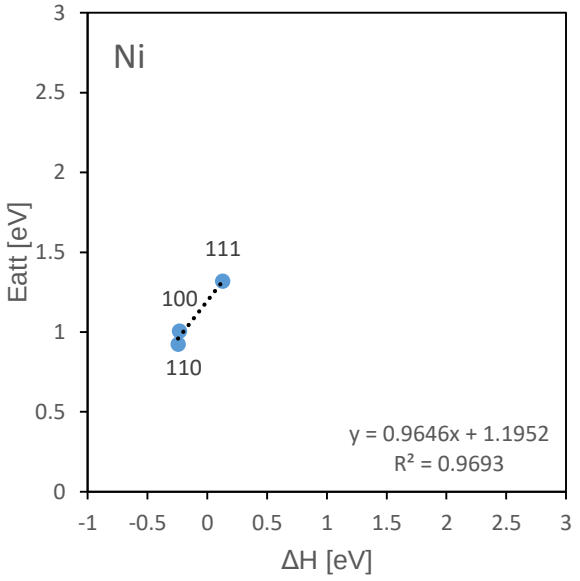
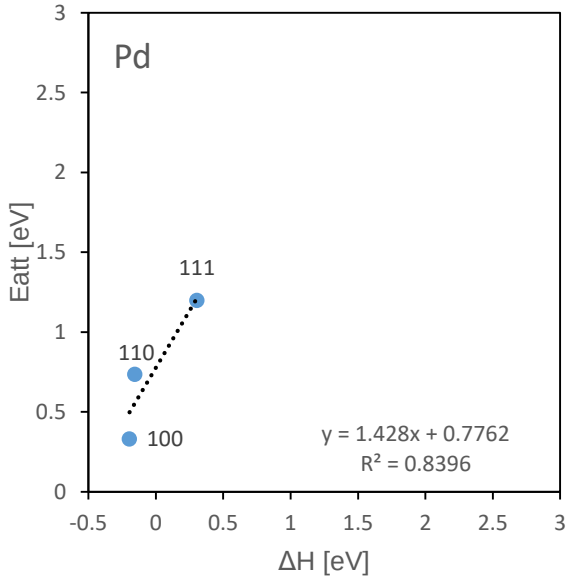
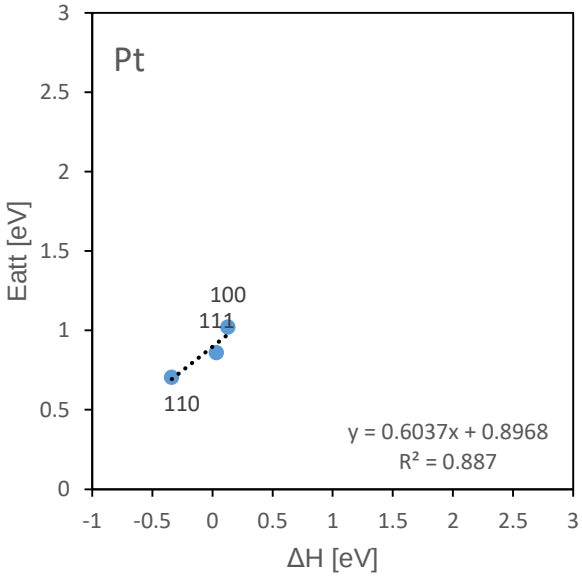
Different structures for all metals

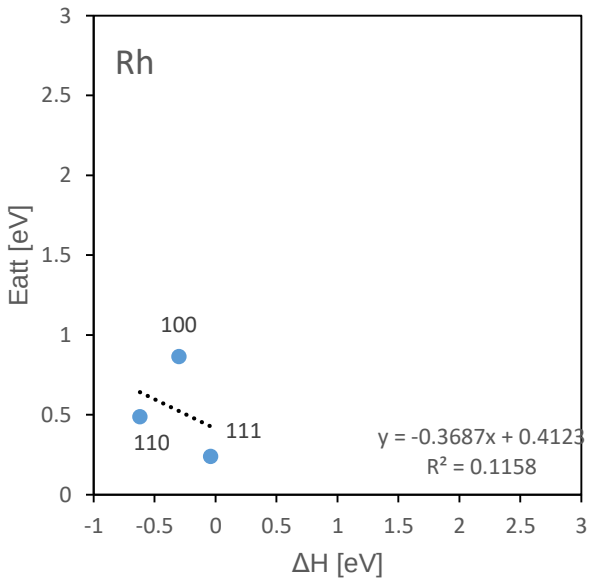




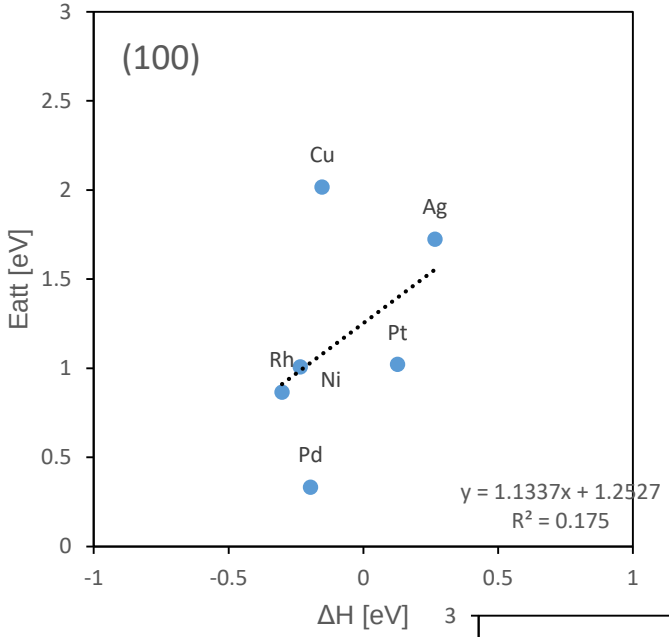


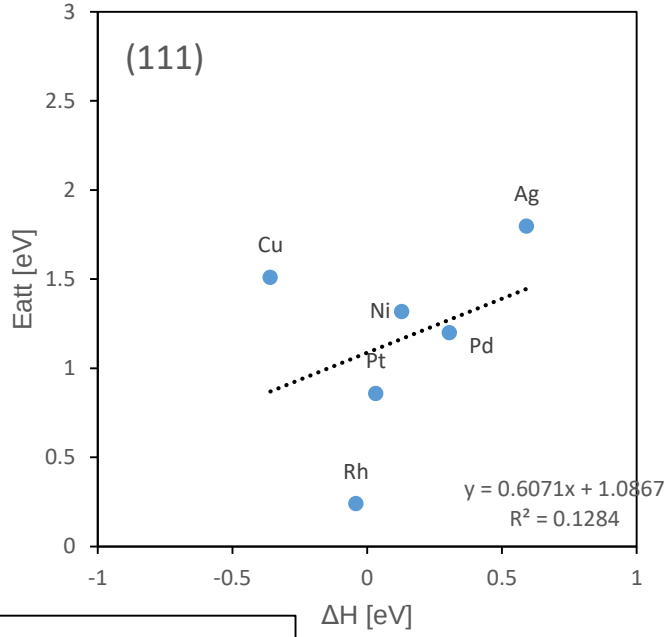


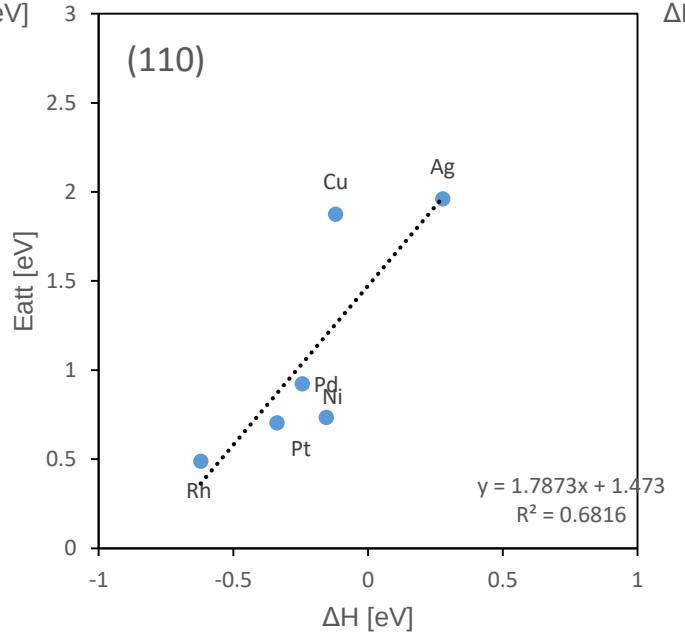




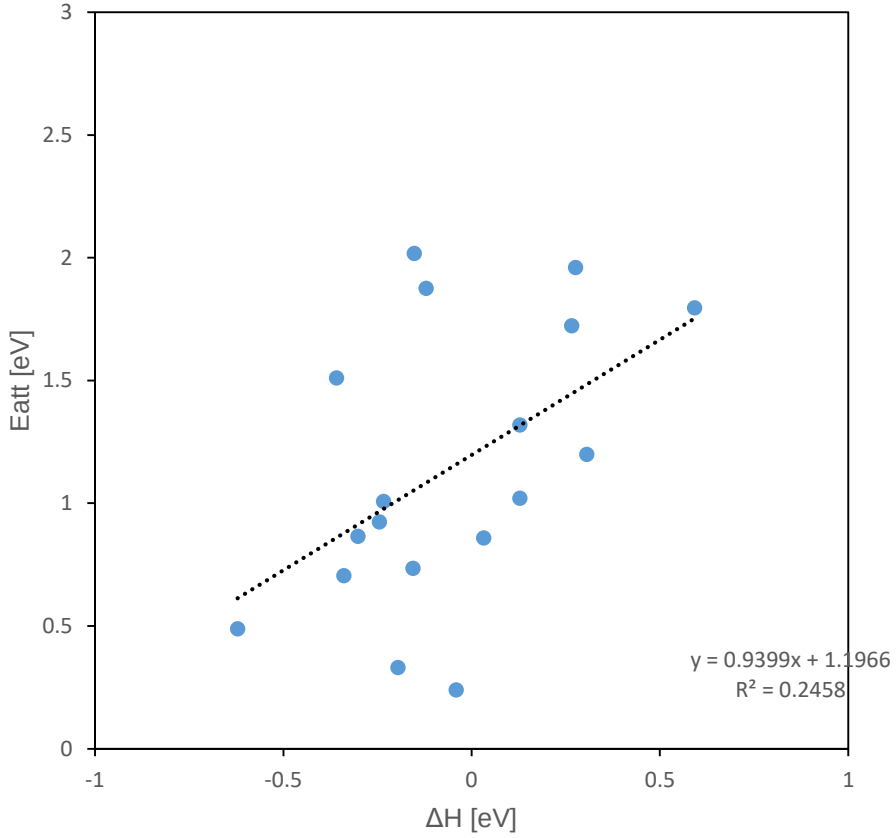
Different metals for each structure

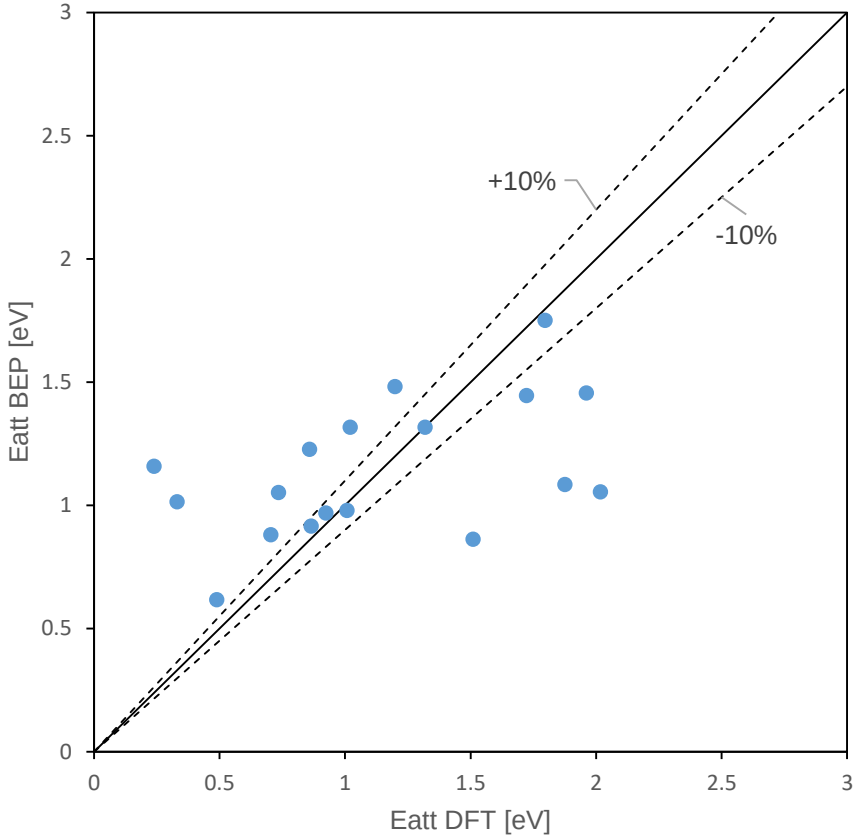






All structures – all metals





Conclusions on BEP

a) A first-principles assessment of BEP relations to be used in hierarchical modeling for the development of structure-dependent microkinetic models.

b) The problem is not about their use as an alternative to higher level theories, but about their reliability where higher level theories are ruled out by complexity: **are they able to deal with the «complication» when «complexity» makes the higher level theories not applicable?**

c) Information on the TS is crucial.

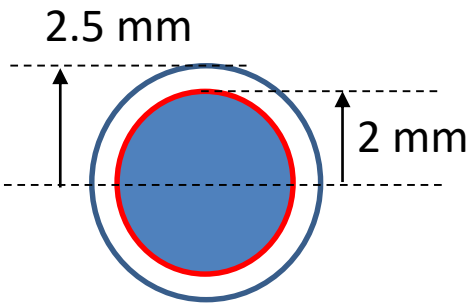
d) The differences in the interactions between reactants/products and the surface affect the nature of the TS and this limits the applicability of the BEP relation.

Outline

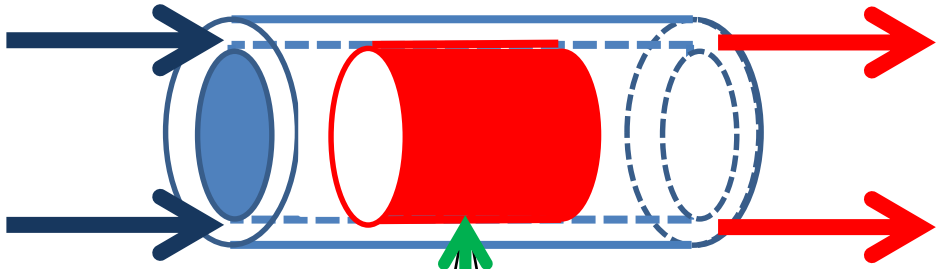
- ✓ Theoretical methods for the prediction of dynamic changes of nanoparticles and phase transformation.
- ✓ Parametrization of kinetic parameters on different sites.
- ✓ Novel experimental tools: spectroscopy & kinetically relevant data.
- ✓ Confinement effects: «physical» catalysis

Monitoring activity and structure

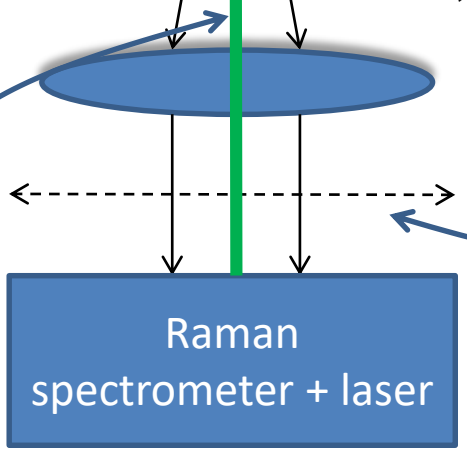
Annular Reactor



Minimization of the mutual invasiveness of the two techniques is a requirement.



- ✓ Optimization of the **optic system** to allow for an efficient collection of the back-scattering signal
- ✓ Proper integration of the Raman with the **heating system**
- ✓ Calibration (< 1 mW/μm^2) of the laser **power** to avoid interaction with the chemistry
- ✓ Excitation laser in the blue-green (e.g., 457 nm) to avoid **black-body effect at the high reaction temperature** (800°C)



Raman Spectrometer

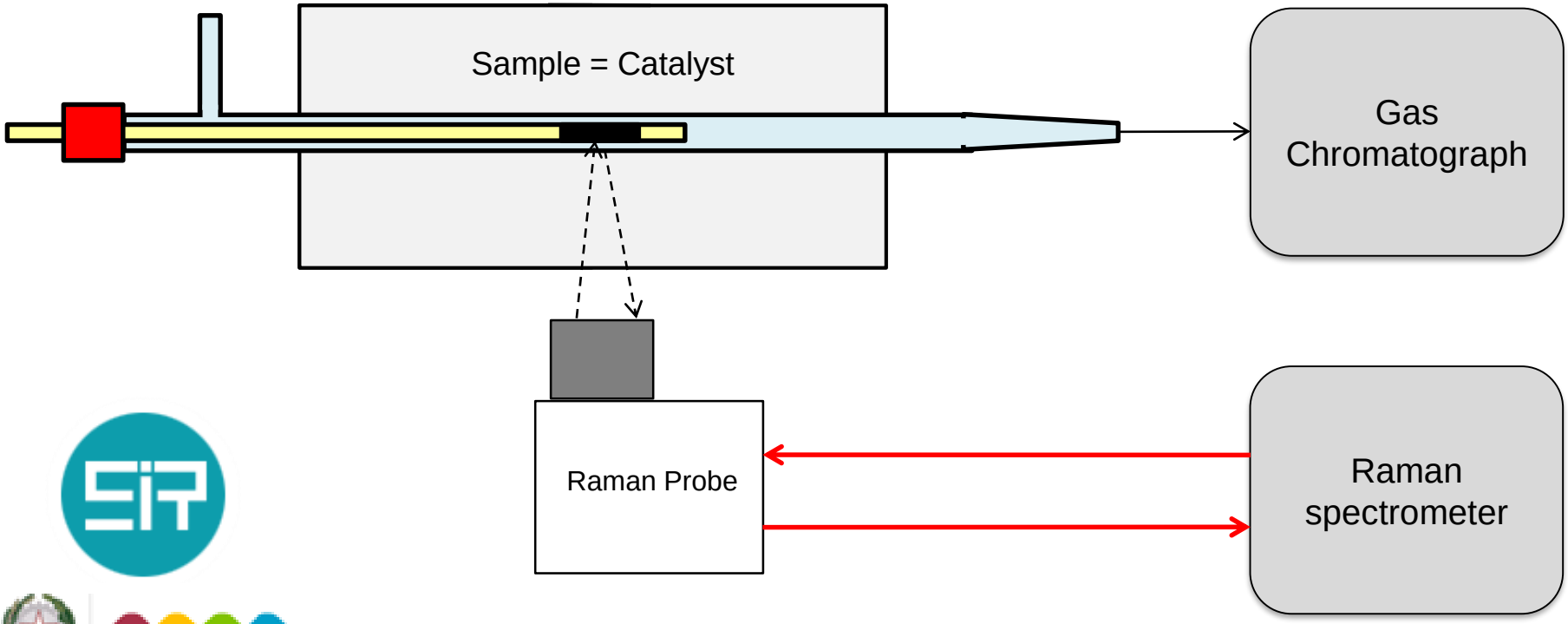
- ✓ Connection with fiber-optics to allow spatially-resolved measurement

Coupling is more than «plug&play»

Optical constraints

Kinetic constraints

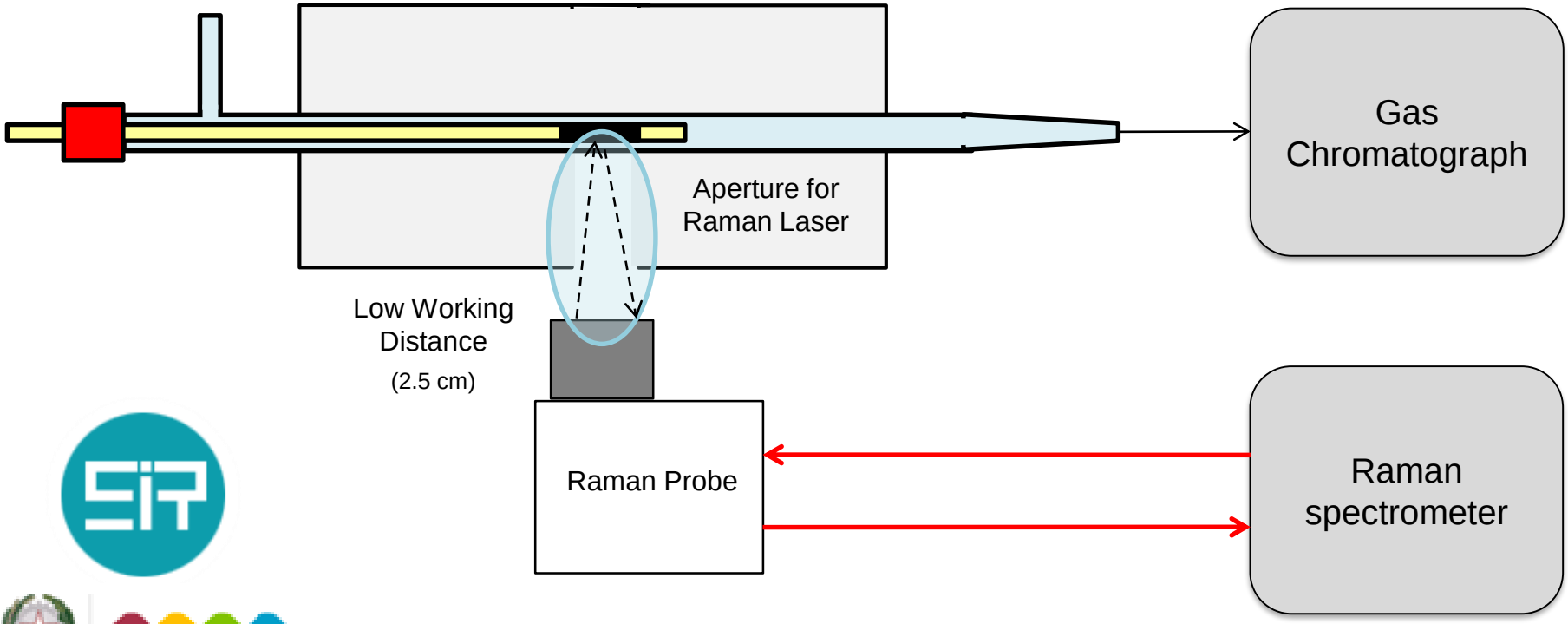
Material constraints



A. Maghsoumi, … and M. Maestri, Reaction Chemistry and Engineering, 2017

Coupling is more than «plug&play»

Optical constraints



A. Maghsoumi, … and M. Maestri, Reaction Chemistry and Engineering, 2017

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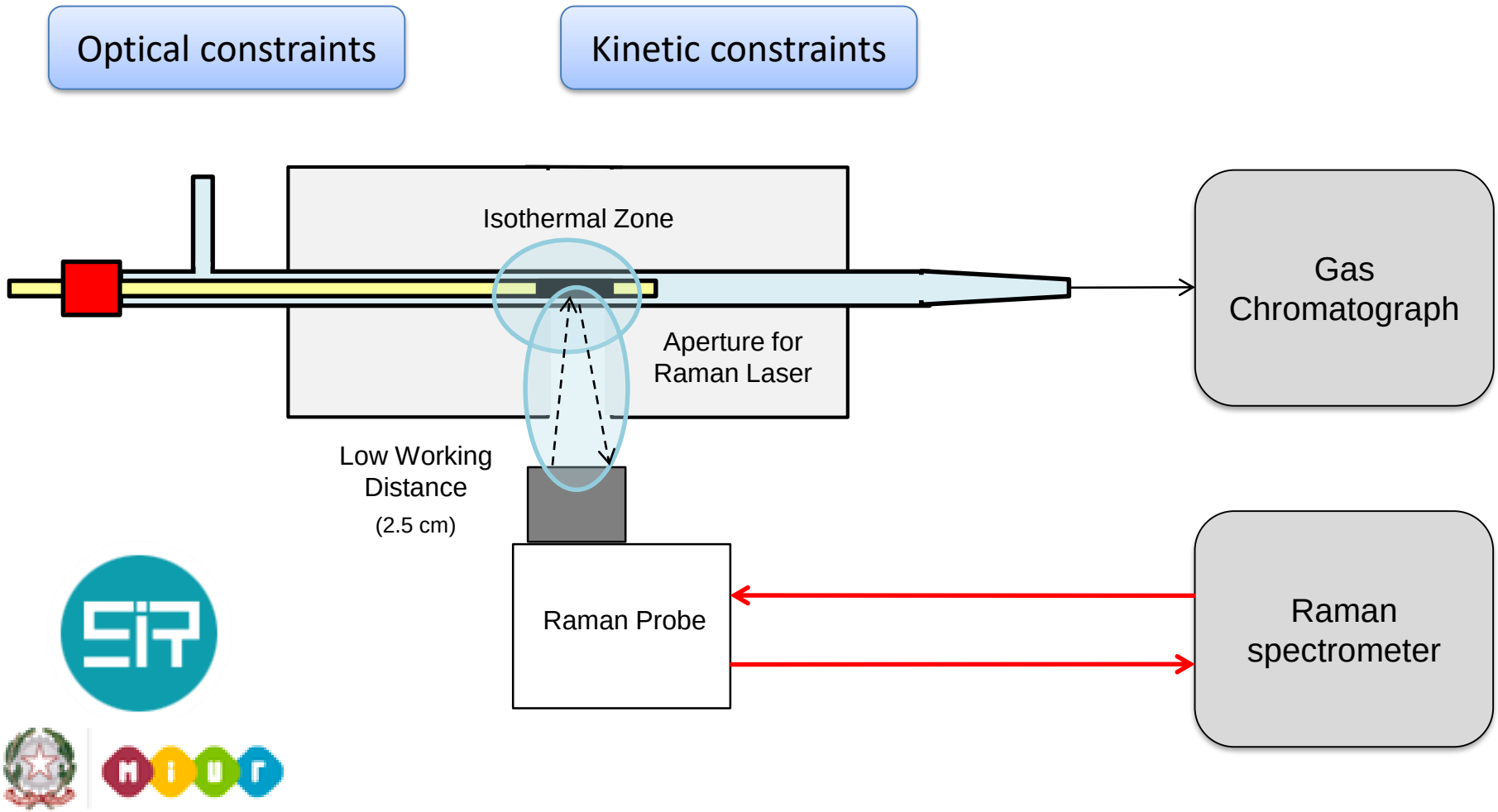

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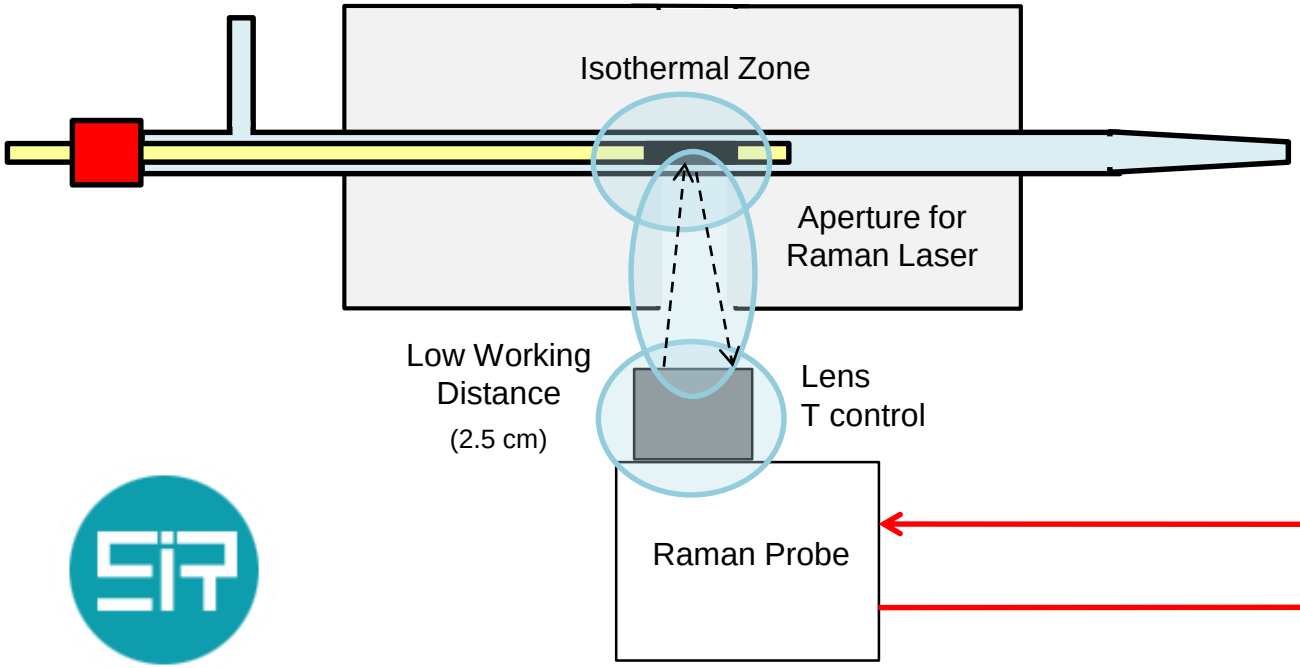
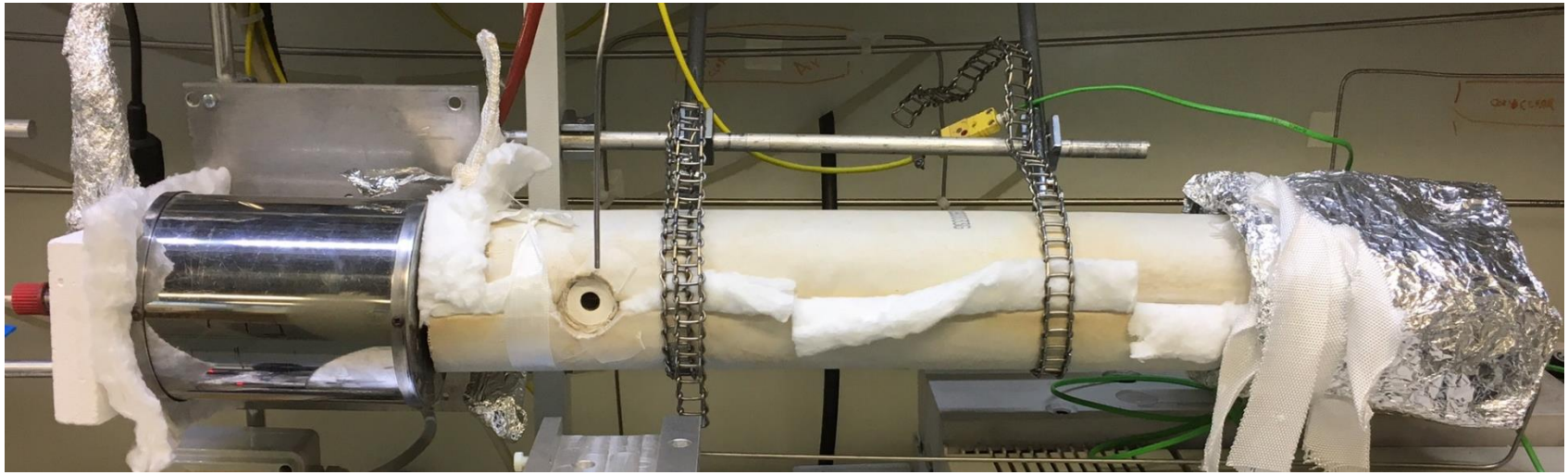


Gas Chromatograph

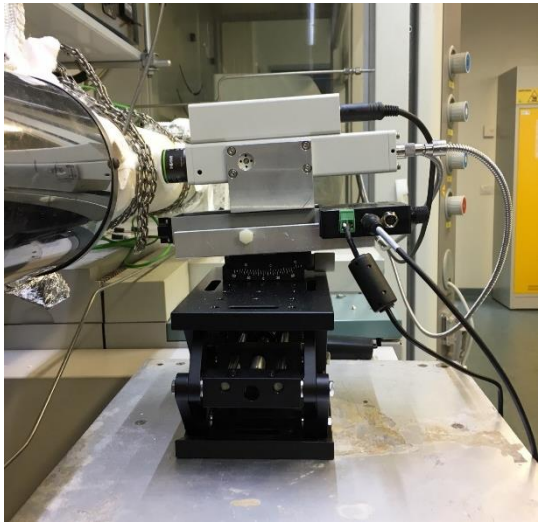
Raman spectrometer

A. Maghsoumi, … and M. Maestri, Reaction Chemistry and Engineering, 2017

Spectro-annular reactor.



- ✓ Spectroscopic & kinetic measurements
- ✓ conditions of T, P, and concentration relevant to catalysis



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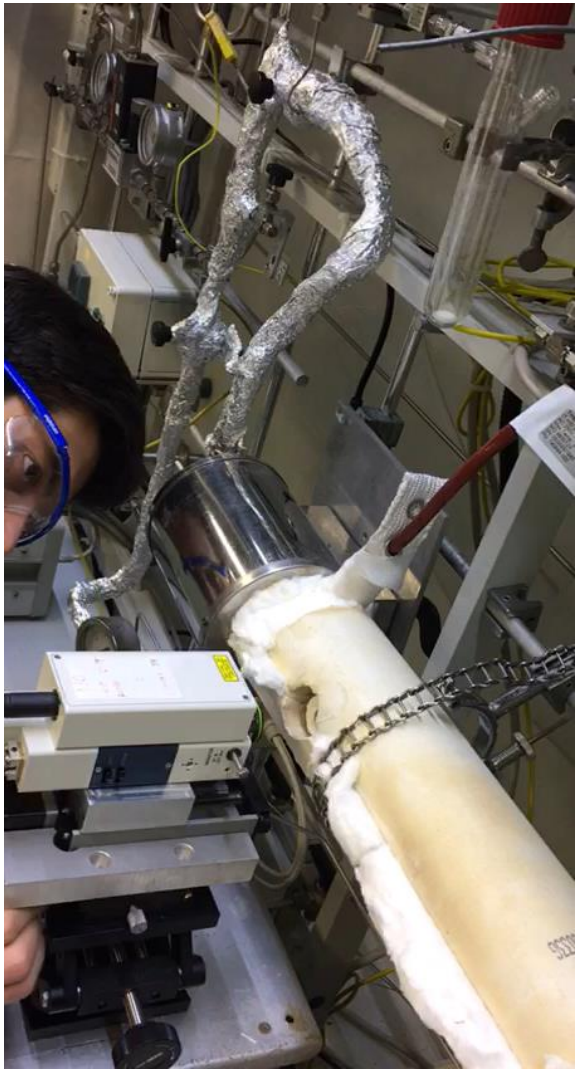
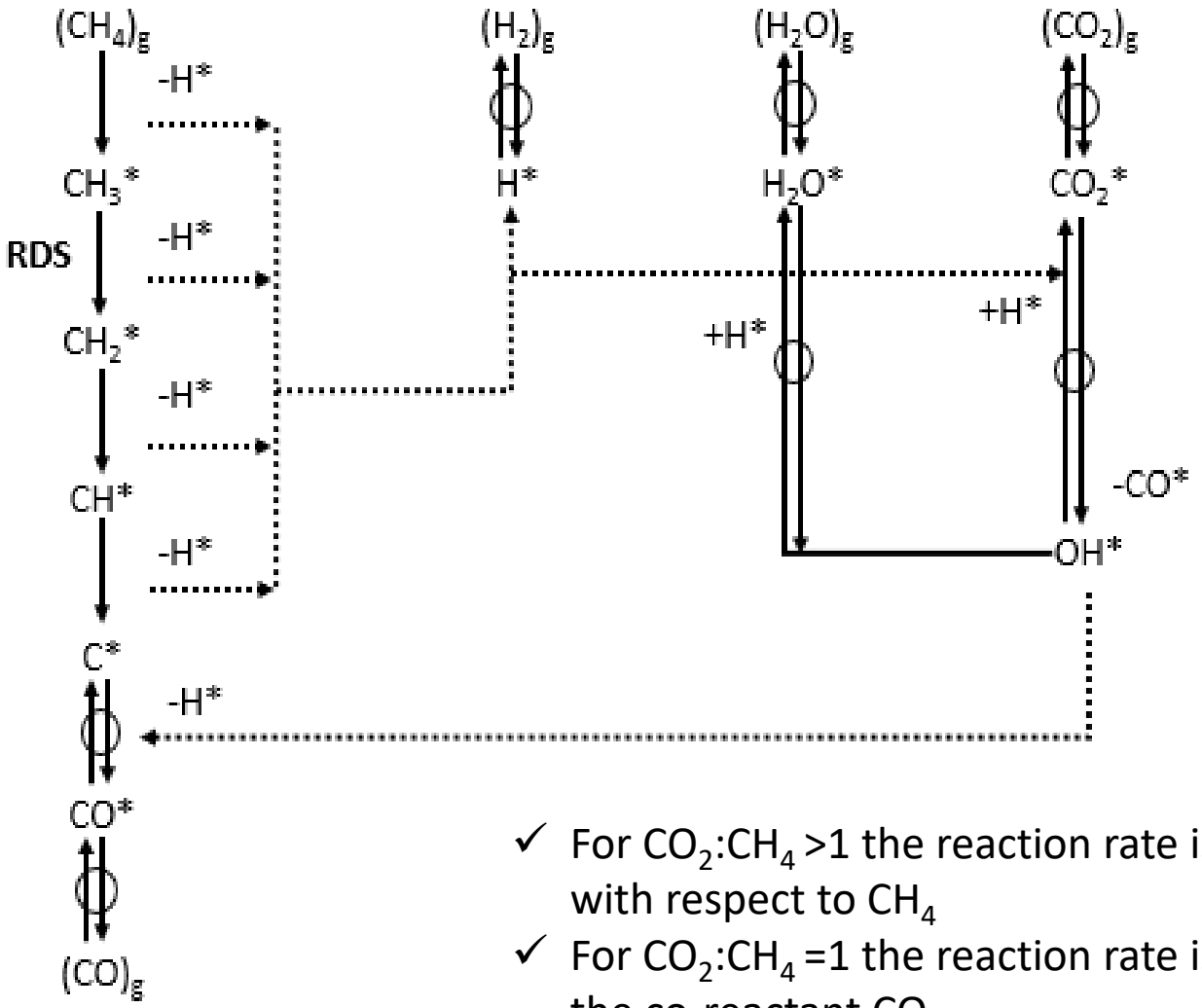


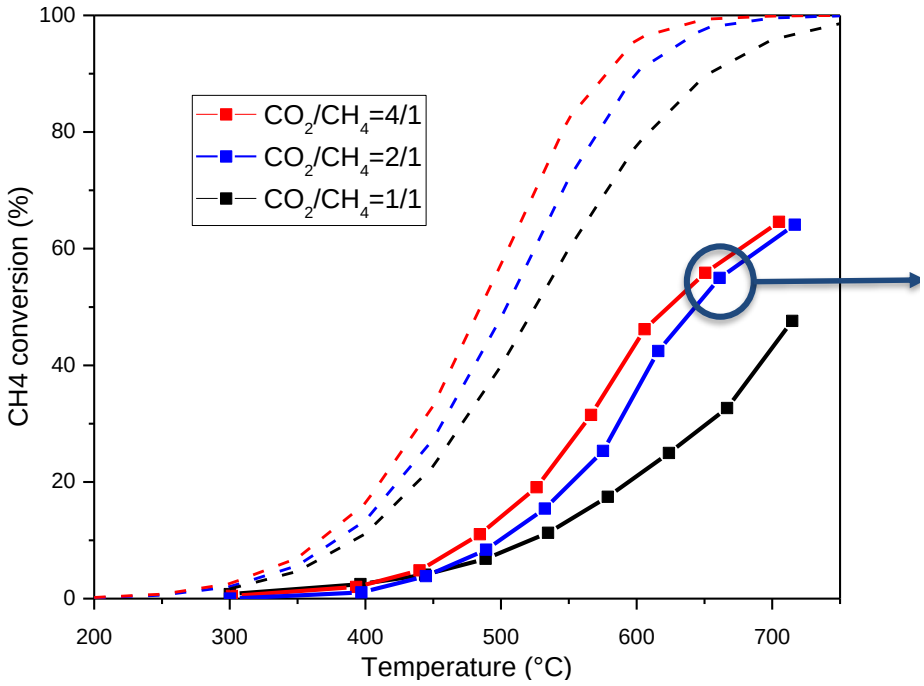
Dry-reforming of methane on Rh

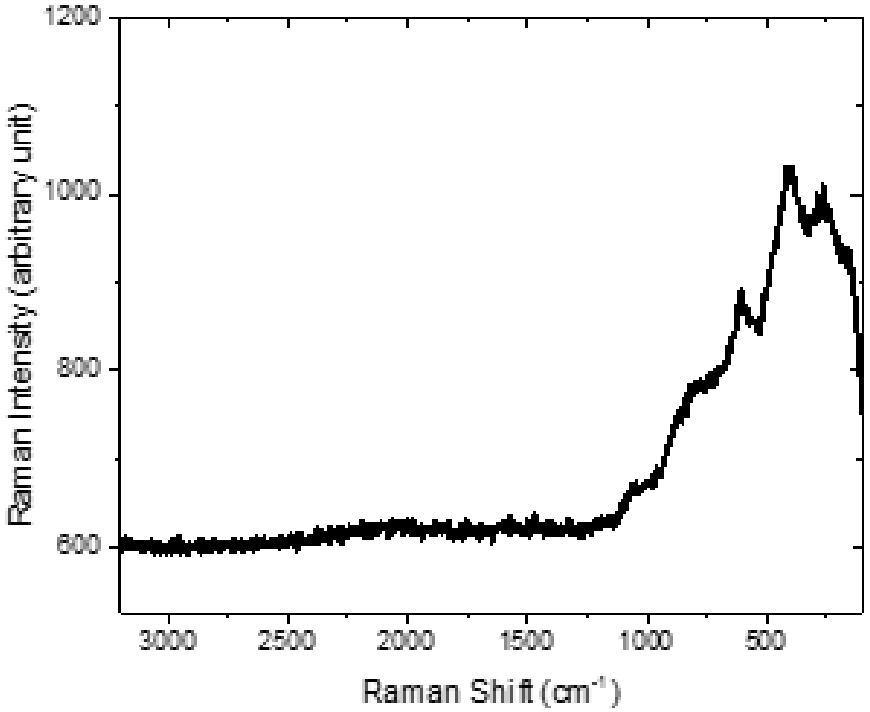


- ✓ For CO_2:CH_4 >1 the reaction rate is first order with respect to CH_4
- ✓ For CO_2:CH_4 =1 the reaction rate is dependent on the co-reactant CO_2

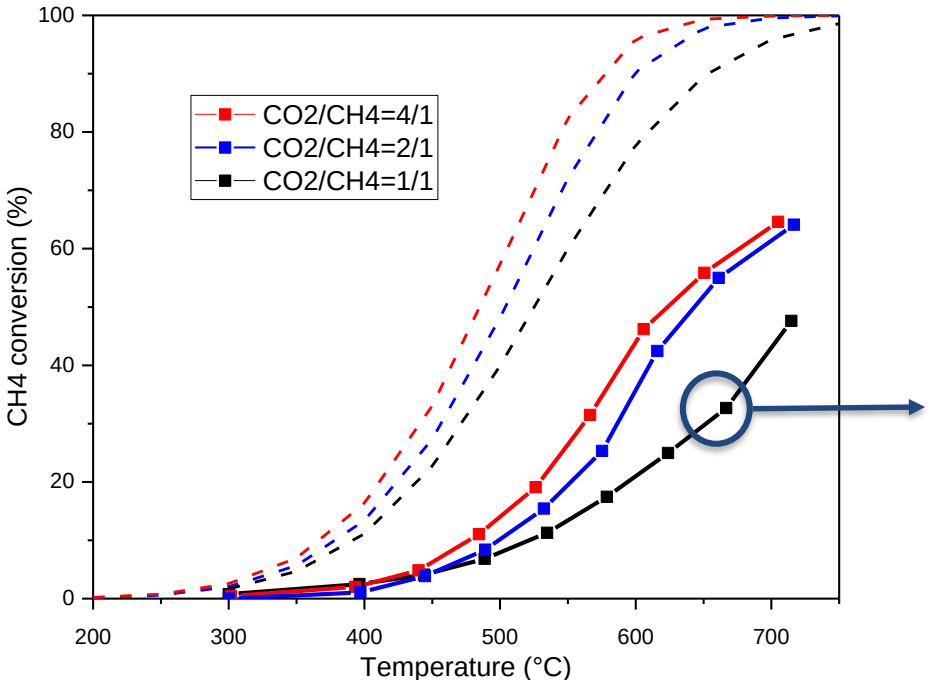
M. Maestri, D.G. Vlachos, et al., J. Catal. 2008

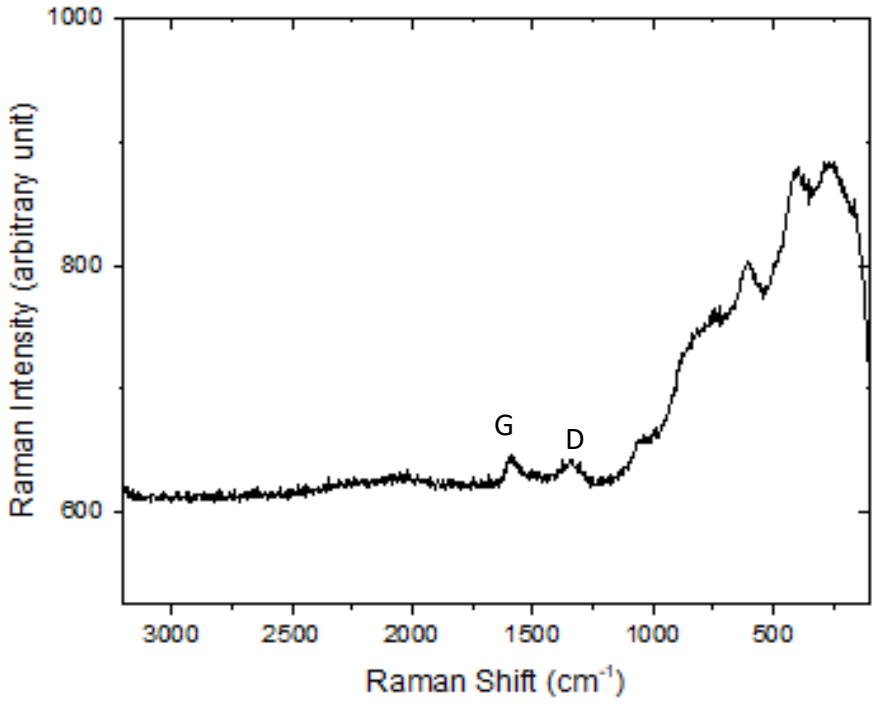
CH_4=4% CO_2/CH_4=2:4



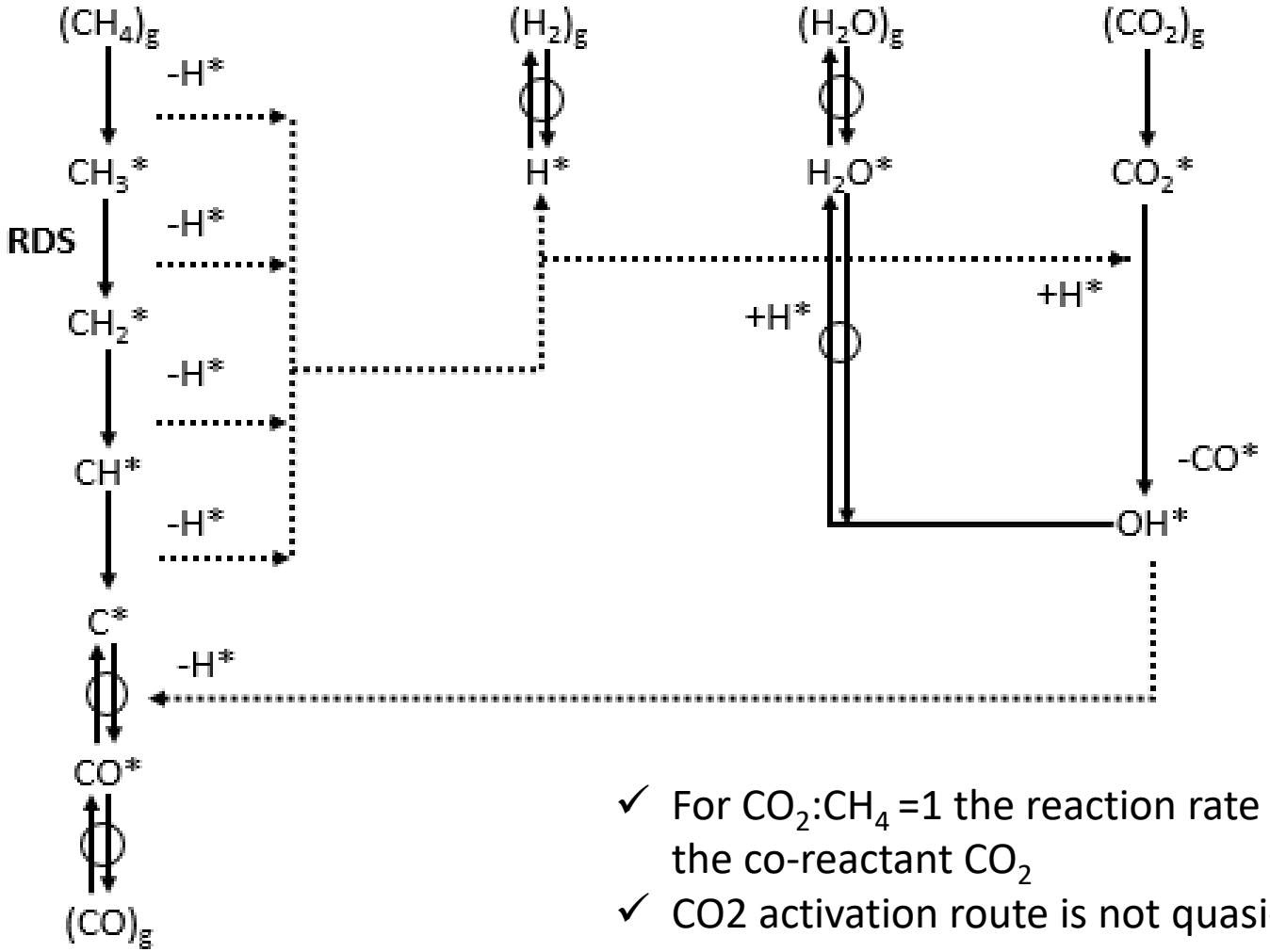


DR: CH_4=4% CO_2/CH_4=1





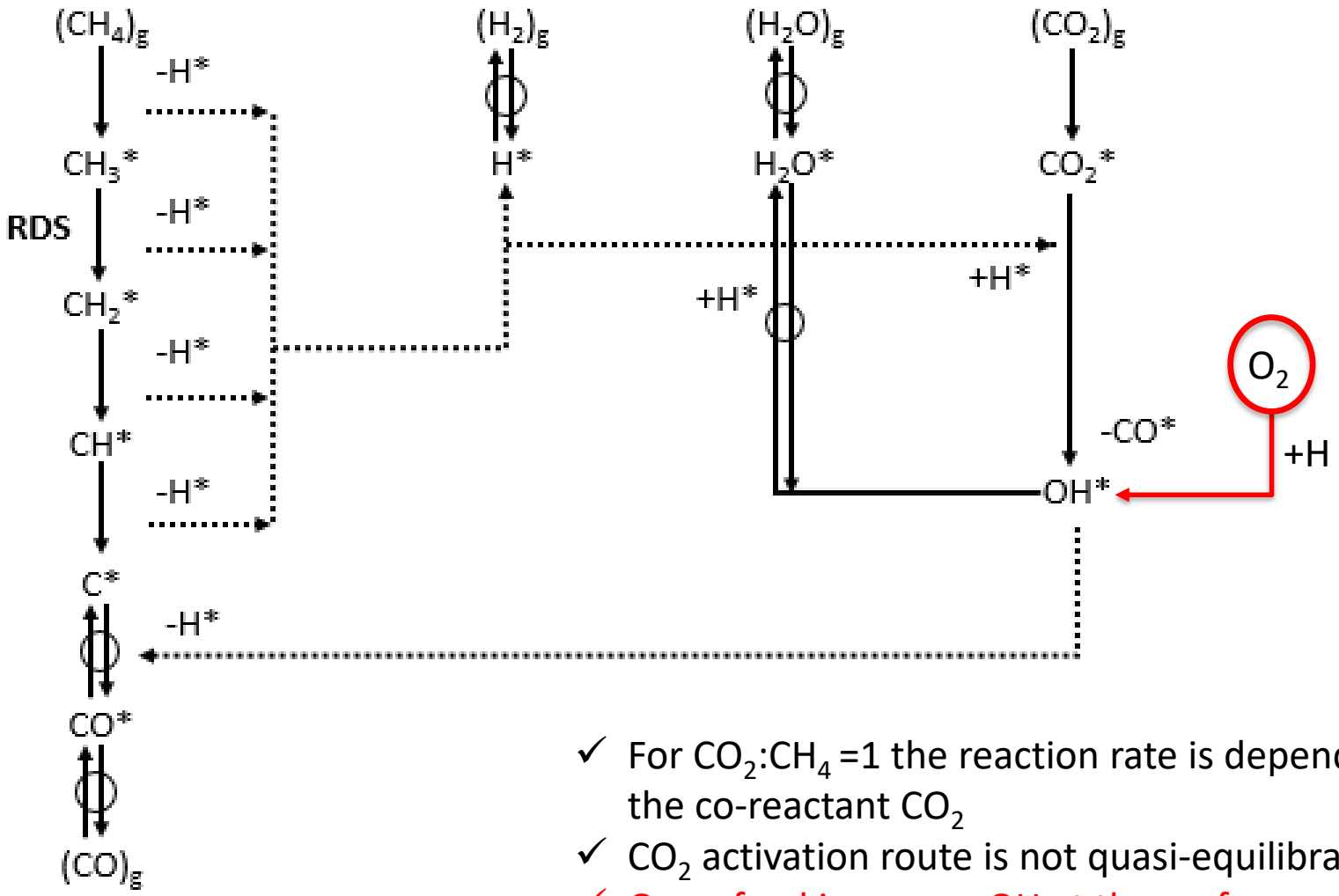
DR: CH_4=4% CO_2/CH_4=1



- ✓ For CO_2:CH_4 =1 the reaction rate is dependent on the co-reactant CO_2
- ✓ CO2 activation route is not quasi-equilibrated

M. Maestri, D.G. Vlachos, et al., J. Catal. 2008

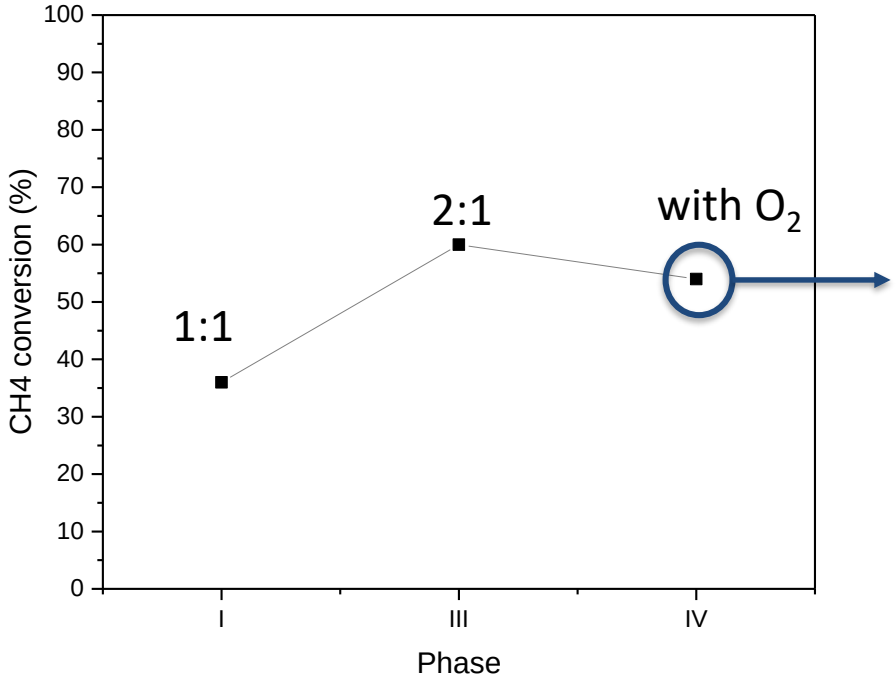
DR: CH_4=4% CO_2/CH_4=1

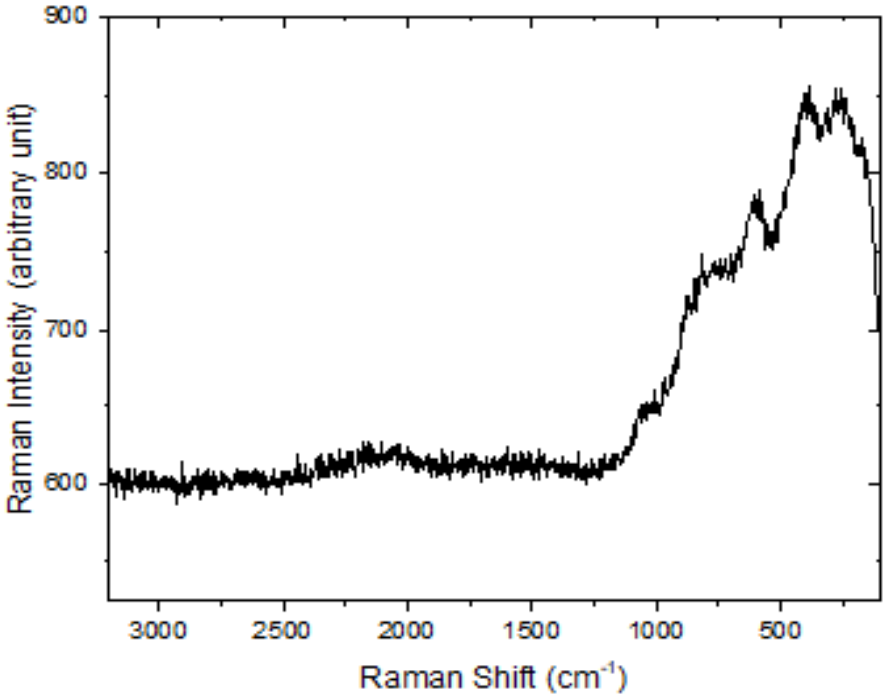


- ✓ For CO_2:CH_4 =1 the reaction rate is dependent on the co-reactant CO_2
- ✓ CO_2 activation route is not quasi-equilibrated
- ✓ O_2 co-feed increases OH at the surface

M. Maestri, D.G. Vlachos, et al., J. Catal. 2008

DR with O_2: CH_4=4% $CO_2/CH_4/O_2$=1/1/0.1





Outline

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- ✓ Novel experimental tools: spectroscopy & kinetically relevant data.
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First-principles assessment of catalysis by confinement: NO oxidation on pure silica frameworks with voids of molecular dimensions

Laboratory of Catalysis and Catalytic Processes LCCP

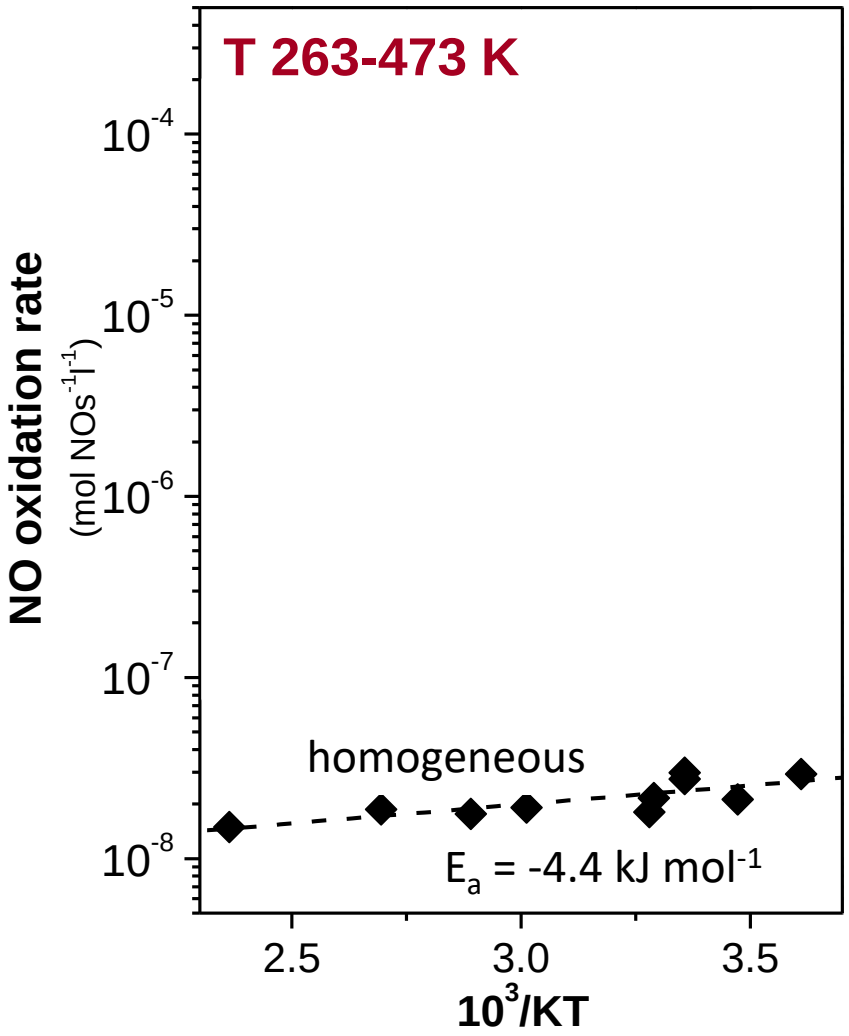
POLITECNICO MILANO 1863

LSAC Laboratory for the Science and Applications of Catalysis

M. Maestri and E. Iglesia, PCCP, 2018

Catalytic Consequences of Confinement

NO oxidation rate on microporous and mesoporous PURE SILICA materials



$$r = k_{eff}(NO)^2(O_2)$$

Artioli, Lobo and Iglesia, J. Phys. Chem. C, 2013

Catalytic Consequences of Confinement

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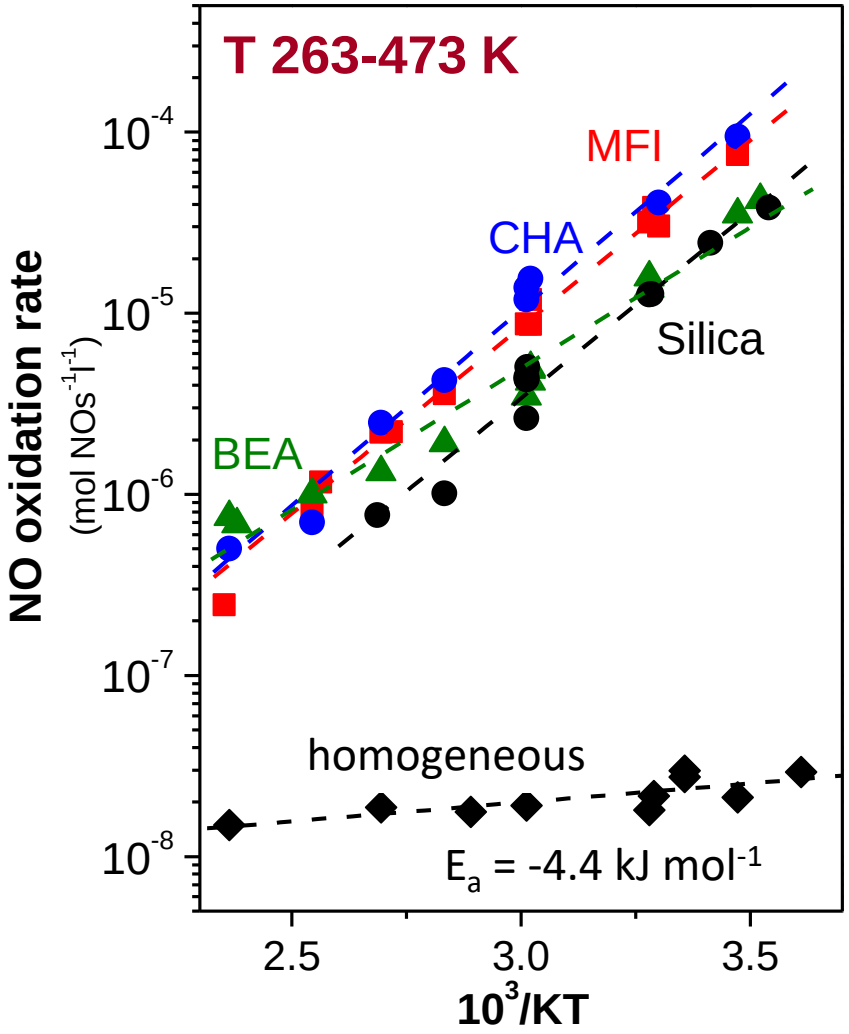

Same NO and O_2 kinetic dependences in the constrained and unconstrained volumes:

$$r = k_{eff}(NO)^2(O_2)$$

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Catalytic Consequences of Confinement

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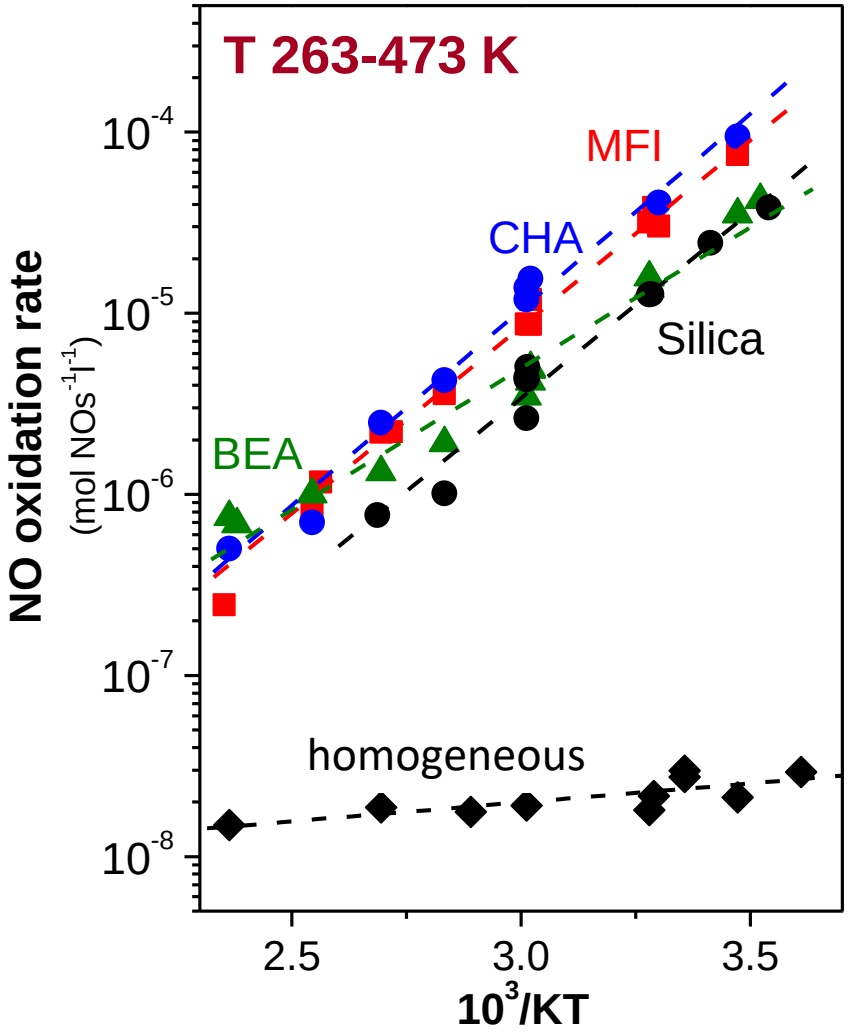


Microporous structures influence the Gibbs free energy of specific transition states by their mere confinement,
without the specific involvement of distinct binding sites.

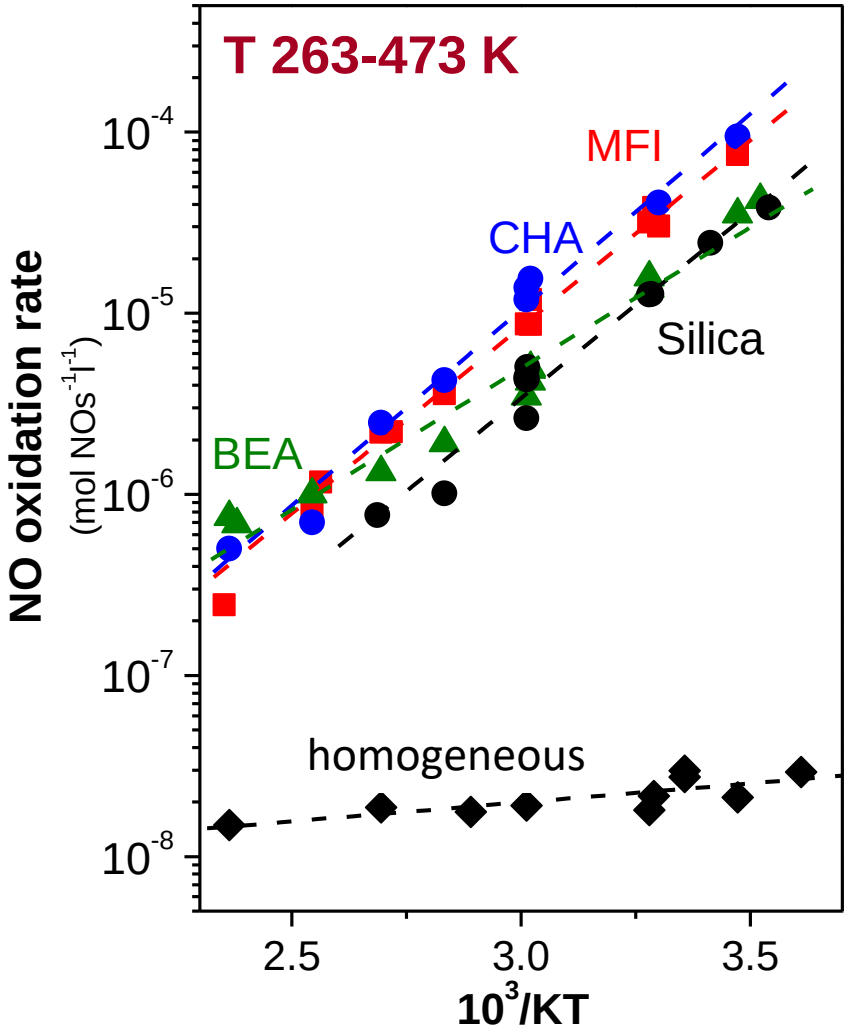
Same NO and O_2 kinetic dependences in the constrained and unconstrained volumes:

$$r = k_{eff}(NO)^2(O_2)$$

Artioli, Lobo and Iglesia, J. Phys. Chem. C, 2013

Catalytic Consequences of Confinement

Rigorous mechanistic interpretations using theory are required



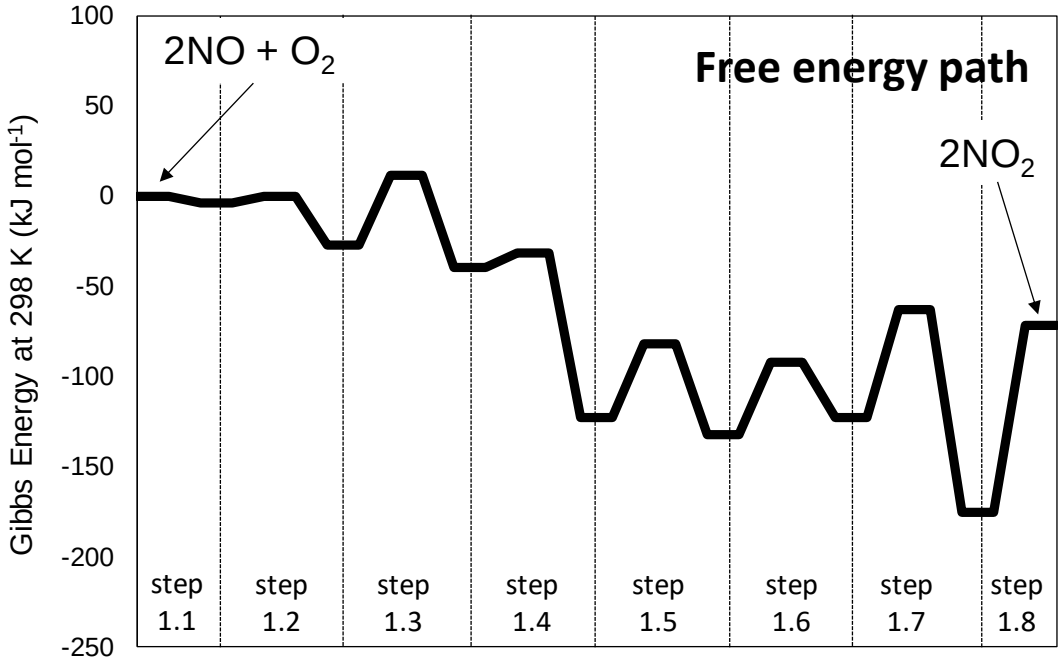
How the TS structures that mediate homogeneous reactions in unconfined spaces can be stabilized relative to their precursors by their mere "adsorption" within voids?

Theoretical methods

Energy:
DFT: PBE,B3LYP(QEspresso/Gaussian09)
vdW scheme: Grimme-D2
MP2 (Gaussian09)
TS search: CI-NEB/Berny algorithm
Enthalpy/Entropy:
Statistical thermodynamics/ideal gas

Artioli, Lobo and Iglesia, J. Phys. Chem. C, 2013

Assessment of NO oxidation pathway in unconfined space



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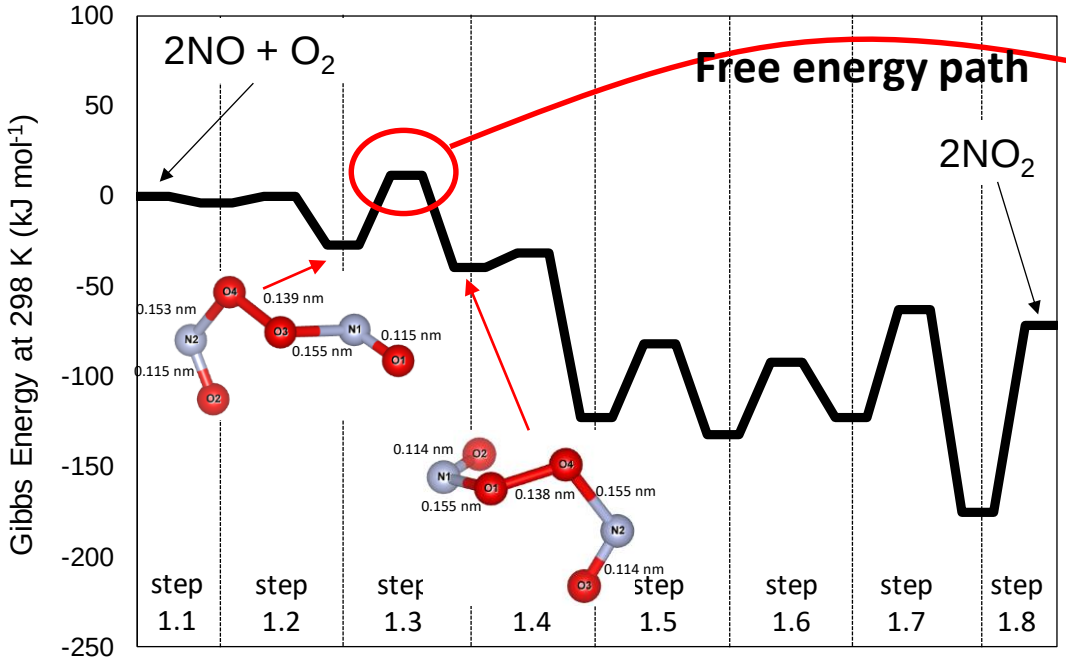
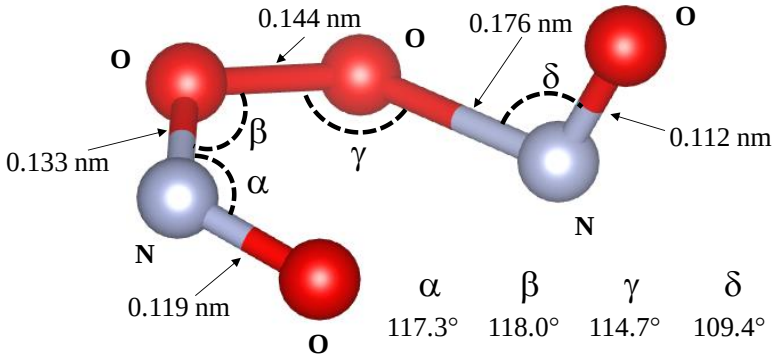


Kinetically relevant TS



cis- to trans-NOO_2NO isomerization

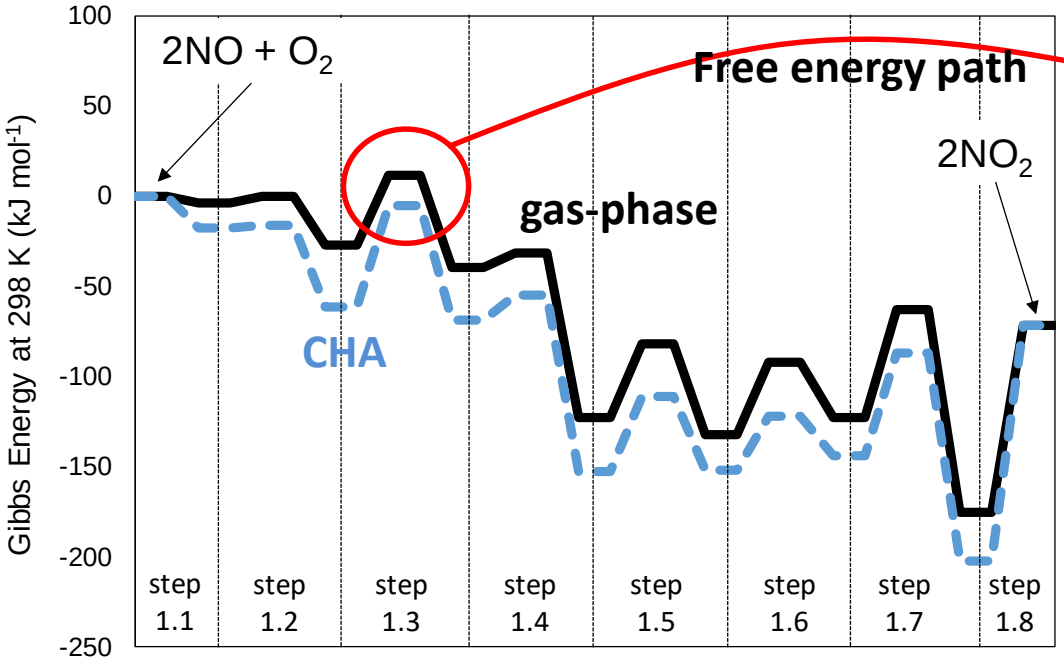
$$r = \vec{k}_{1.3}\frac{\vec{k}_{1.1}}{\overleftarrow{k}_{1.1}}\frac{\vec{k}_{1.2}}{\overleftarrow{k}_{1.2}}(NO)^2(O_2) = \vec{k}_{1.3}K_{1,1}K_{1,2}(NO)^2(O_2)$$

$$r = 2\frac{k_B T}{h}exp\left(-\frac{\Delta G_{app}}{RT}\right)(NO)^2(O_2)$$

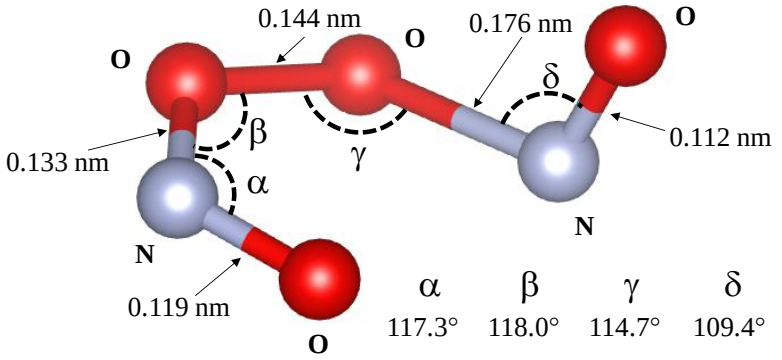
$$\Delta H_{app} = H^{\ddagger}_{1.3} - 2H_{NO} - H_{O_2}$$

$$\Delta S_{app} = S^{\ddagger}_{1.3} - 2S_{NO} - S_{O_2}$$

Assessment of NO oxidation pathway in confined space



Kinetically relevant TS



cis- to trans-NOO_2NO isomerization

$$r = \vec{k}_{1.3,conf}\frac{\vec{k}_{1.1,conf}}{\overleftarrow{k}_{1.1,conf}}\frac{\vec{k}_{1.2,conf}}{\overleftarrow{k}_{1.2,conf}}(NO)^2(O_2) = \vec{k}_{1.3,conf}K_{1,1,conf}K_{1,2,conf}(NO)^2(O_2)$$

$$\Delta H_{app,conf} = H^{\ddagger}_{1.3,conf} - 2H_{NO} - H_{O_2}$$

$$\Delta S_{app,conf} = S^{\ddagger}_{1.3,conf} - 2S_{NO} - S_{O_2}$$

Functional form of the rate equation same as the one in gas-phase, but different kinetic and thermodynamic parameters

Effect of confinement on ΔH‡ and ΔS‡

$$r = 2\frac{k_B T}{h}\exp\left(-\frac{\Delta G_{app}}{RT}\right)(NO)^2(O_2)$$

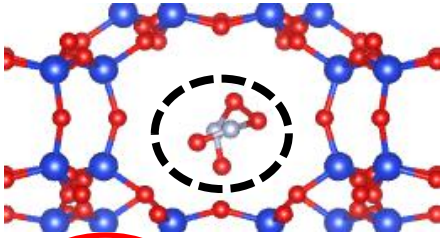
$$\Delta G_{app} = \Delta H_{app} - T\Delta S_{app}$$

Unconfined space

$$\Delta H_{app} = H^{\ddagger}_{1.3,gas} - 2H_{NO,gas} - H_{O_2,gas}$$

$$\Delta S_{app} = S^{\ddagger}_{1.3,gas} - 2S_{NO,gas} - S_{O_2,gas}$$

Confined space



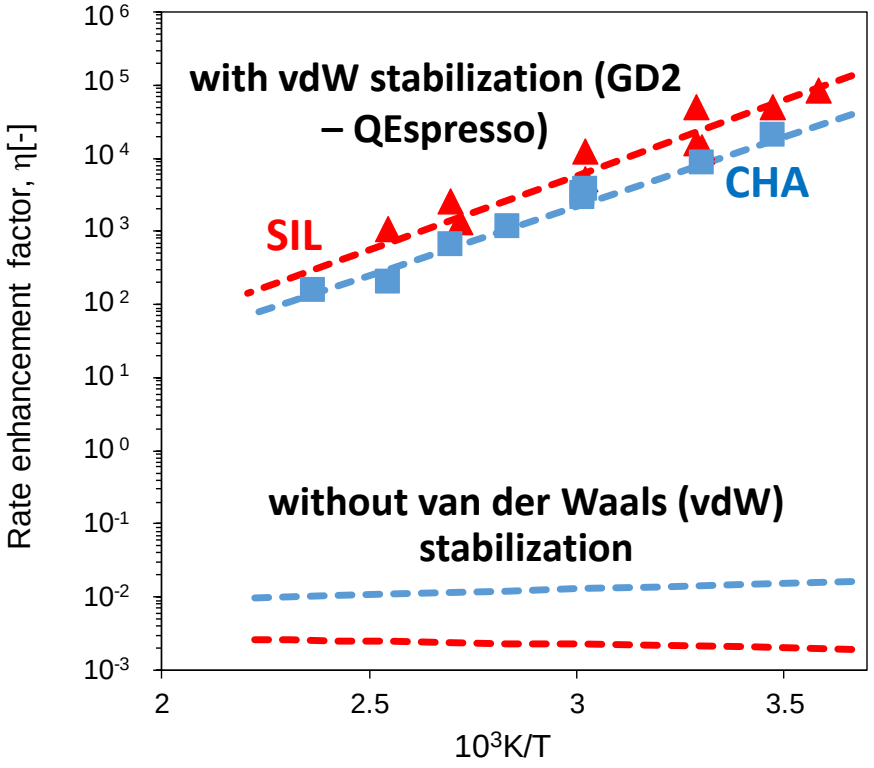
$$\Delta H_{app,conf} = H^{\ddagger}_{1.3,conf} - 2H_{NO,gas} - H_{O_2,gas}$$

$$\Delta S_{app,conf} = S^{\ddagger}_{1.3,conf} - 2S_{NO,gas} - S_{O_2,gas}$$

Rate-enhancement factor

$$\eta = \frac{r_{confined}}{r_{unconfined}} = exp\left(\frac{S^{\ddagger}_{1.3,conf} - S^{\ddagger}_{1.3,gas}}{R}\right) exp\left(-\frac{H^{\ddagger}_{1.3,conf} - H^{\ddagger}_{1.3,gas}}{RT}\right)$$

Effect of confinement on ΔH‡ and ΔS‡



Enthalpic stabilization of the TS:

- ✓ dominates over entropy stabilization
- ✓ stabilization due to non-specific van der Waals interactions upon confinement

Entropic stabilization of the TS:

- ✓ associated with the loss of translational entropy due to the restricted mobility of the transition states

M. Maestri and E. Iglesia, PCCP, 2018

Rate-enhancement factor

$$\eta = \frac{r_{confined}}{r_{unconfined}} = exp\left(\frac{S^{\ddagger}_{1.3,conf} - S^{\ddagger}_{1.3,gas}}{R}\right) exp\left(-\frac{H^{\ddagger}_{1.3,conf} - H^{\ddagger}_{1.3,gas}}{RT}\right)$$

Effect of confinement: «physical» catalysis

- ✓ DFT methods that account for **dispersive forces** show how voids of molecular dimensions enhance reaction rates by confining the transition states that mediate homogeneous routes, **without requiring specific binding sites.**

- ✓ The enthalpic stabilization of TS **provided by vdW** dispersion forces **more than compensates the loss of entropy upon confinements at the low temperatures**, thus **leading to lower free energy of activation** than for the homogeneous reaction.

M. Maestri and E. Iglesia, PCCP, 2018

Conclusions

- ✓ Inclusion of the effect of **structure** and **dynamic of catalyst surface** with changing reaction environment is key

- ✓ Several issues limit the use of first-principles calculations and hamper a direct application (**complication** and **complexity** traps)

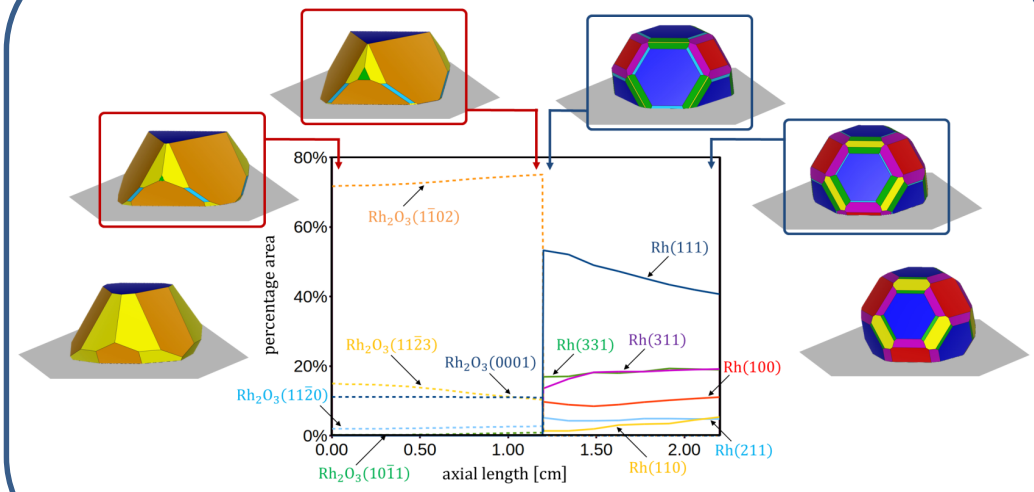
- ✓ Semi-empirical methods can effectively be employed in conjunction with first-principles studies for the **exploration of complex reaction networks using hierarchical multiscale approaches**

- ✓ The problem **is not about their use as an alternative to higher level theories**, but about their **reliability where higher level theories are ruled out by complexity**: are they able to deal with the «complication» when «complexity» makes the higher level theories not applicable?

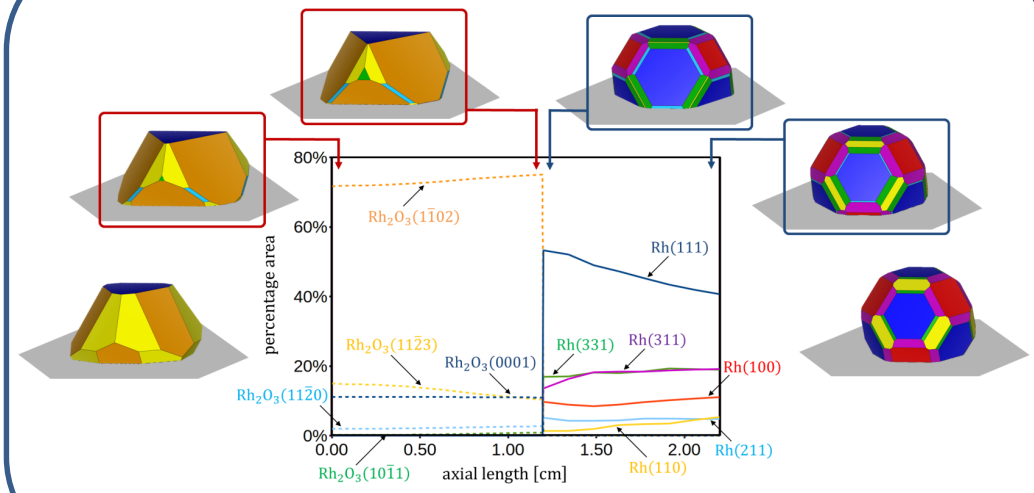
- ✓ **Complementary** information from **theory** and **experiments** is **essential**:
  correlation of observations to mechanistic insights
  Fill the gaps to complexity and practical performances

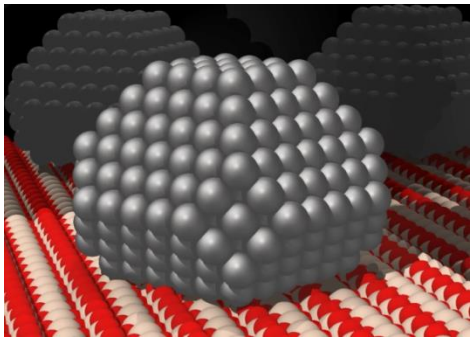
Conclusions

Conclusions



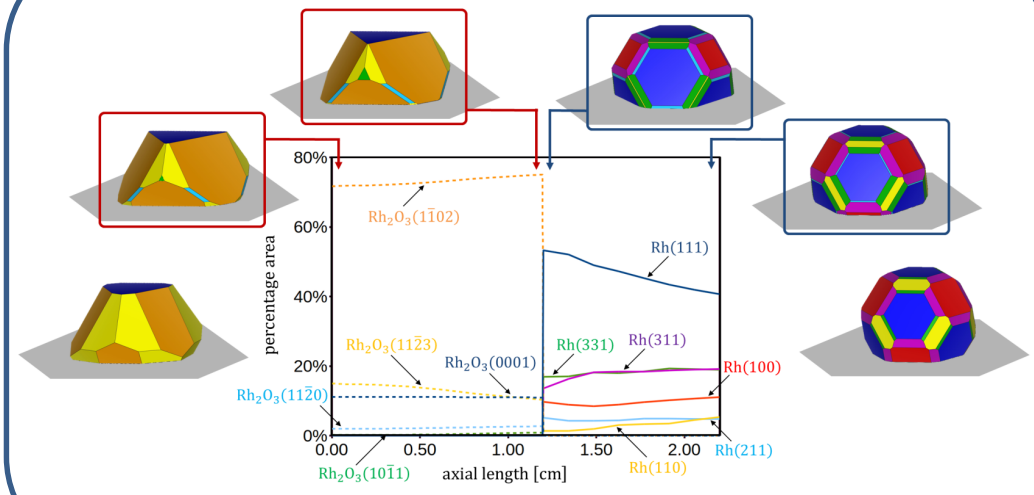
Conclusions

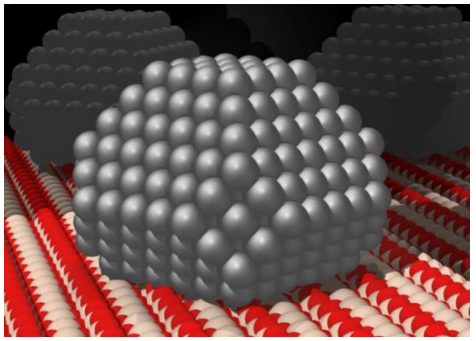




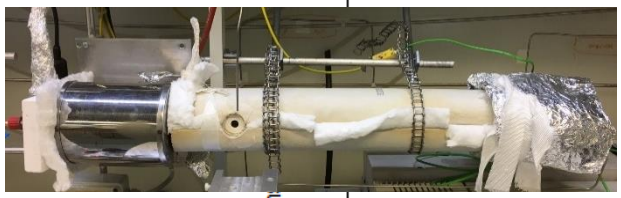
$$E_a = E_a^0 + \gamma_P \Delta H_r$$

Conclusions

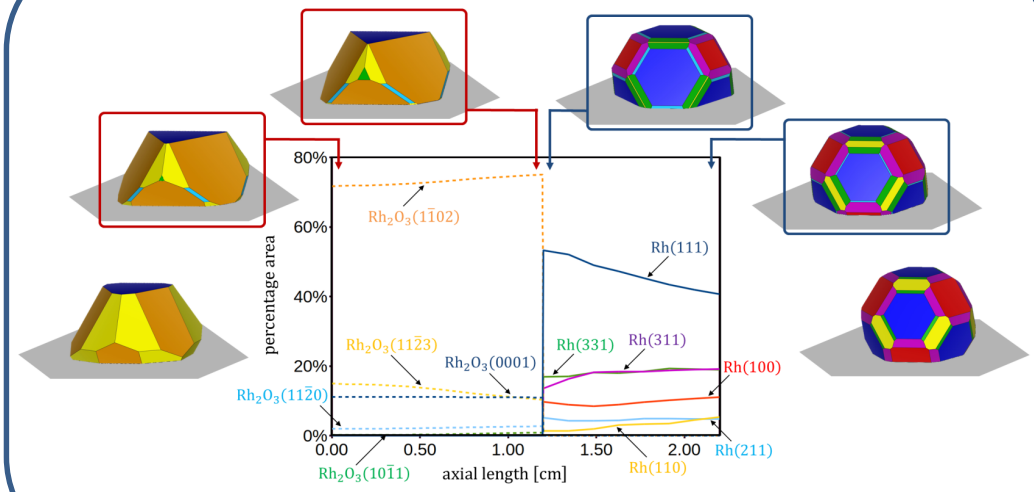


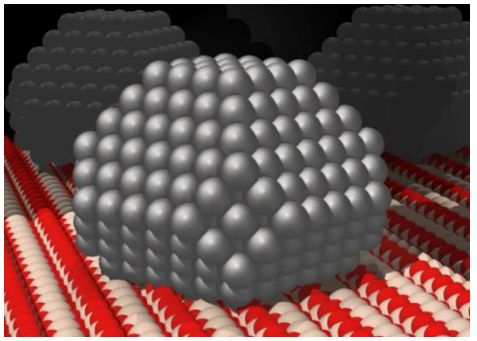


$$E_a = E_a^0 + \gamma_P \Delta H_r$$

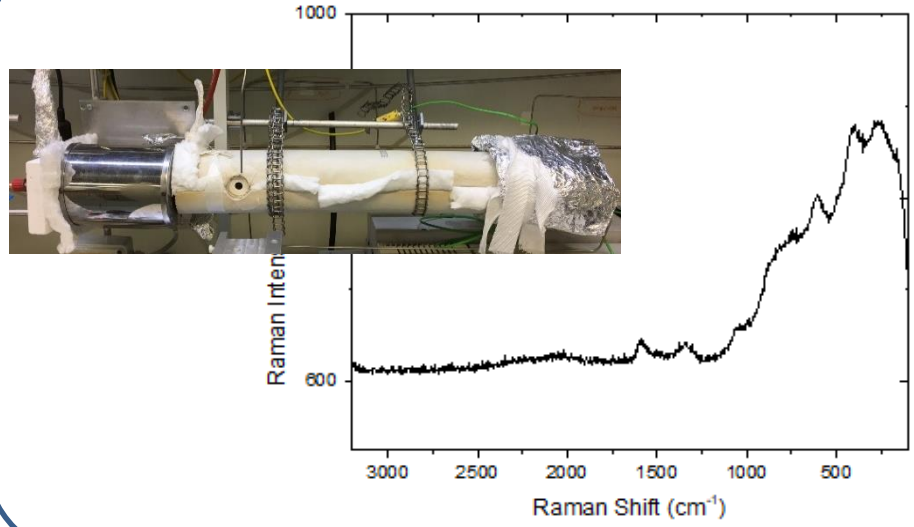


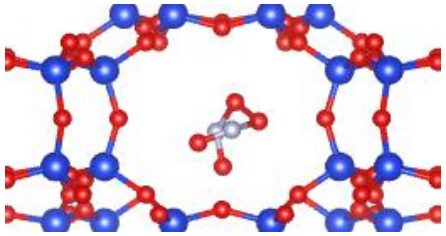
Conclusions





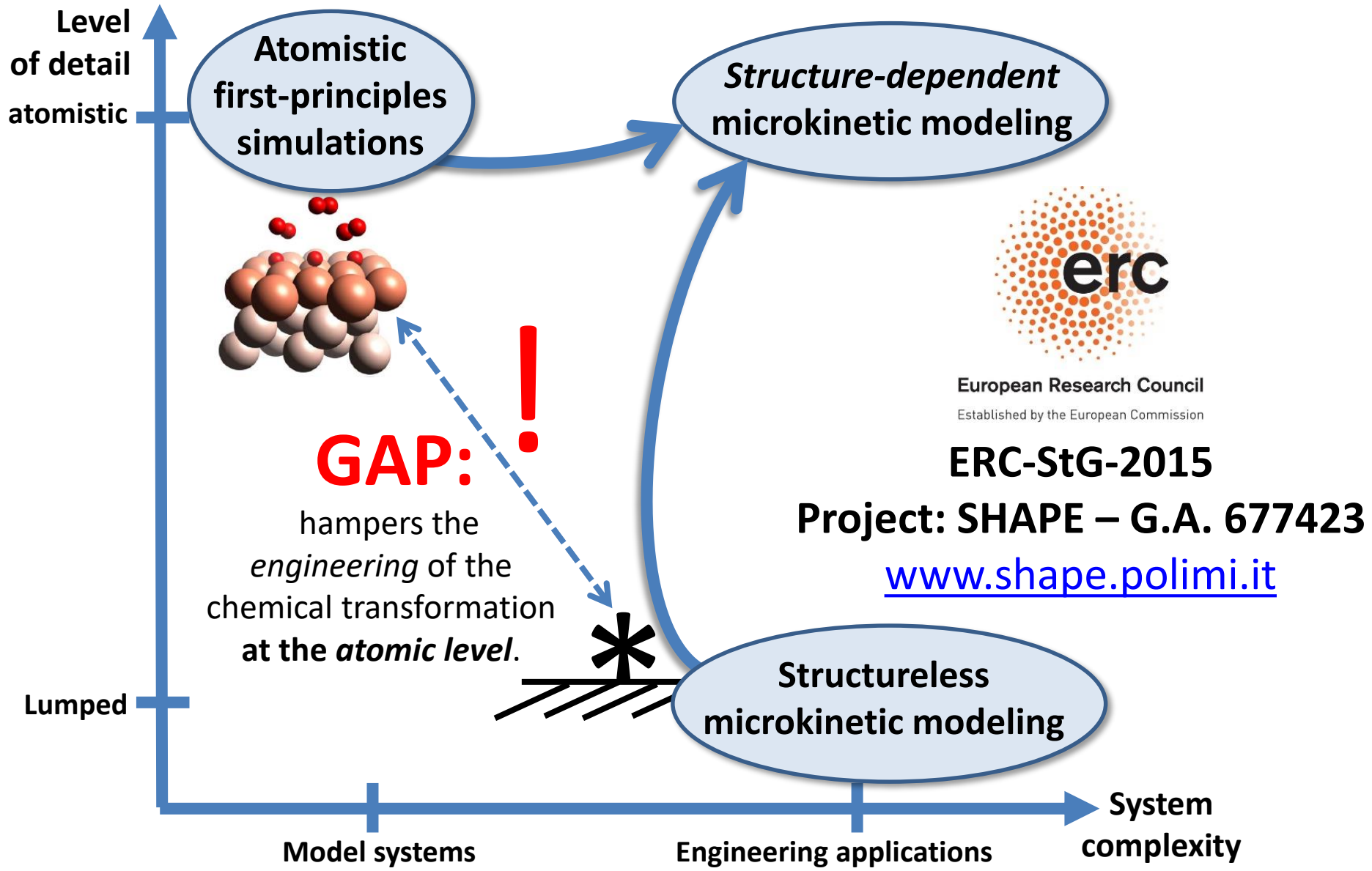
$$E_a = E_a^0 + \gamma_P \Delta H_r$$





$$\Delta G_{app} = \Delta H_{app} - T\Delta S_{app}$$

Structure-dependent microkinetic modeling



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matteo.maestri@polimi.it

«*As researchers, we are doing 'things' that are meant to be scientific, not necessarily practical. They will end up in practical applications as the result of having done them well*»