Multi-scale simulation of heterogeneous catalysis reactions

From quantum *ab initio* calculations to experimentally validated kinetic models

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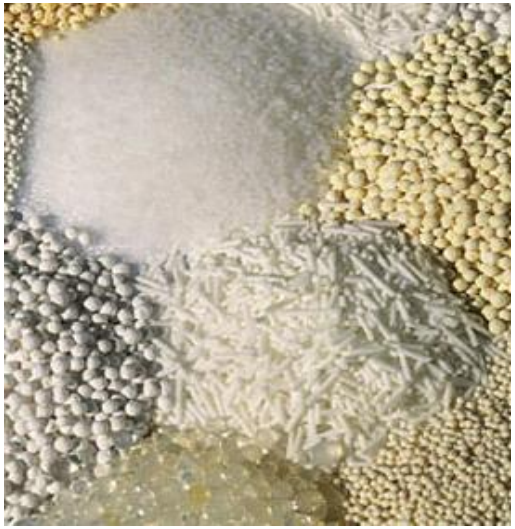
IFP Energies nouvelles
Catalysis and Separation Division

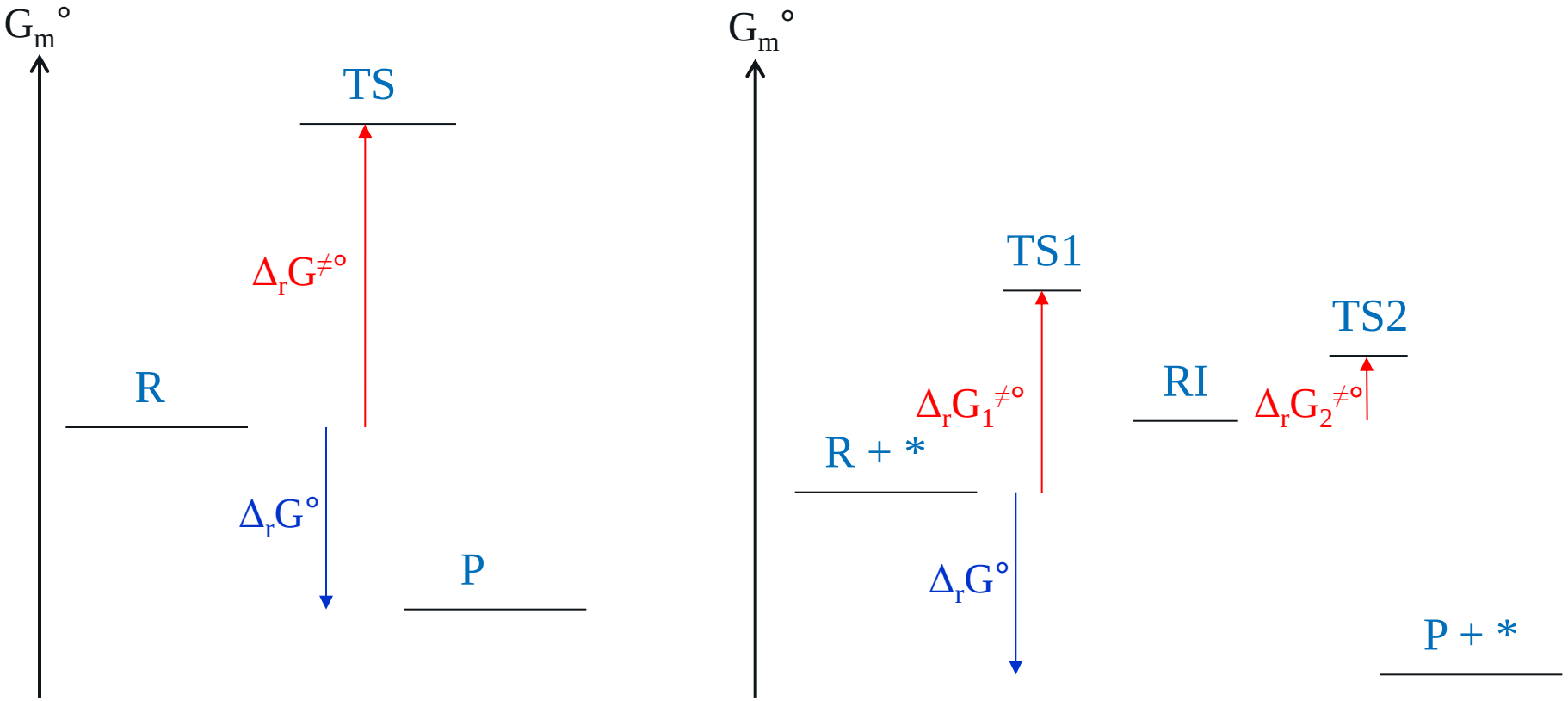


Role of the Catalysis and Separation Division:
discovering and developing new catalysts and adsorbents
For FUELS and CHEMICALS production processes

What is a catalyst ?

Chemical component which increases the RATE of a reaction

Without catalyst **R → P** With catalyst, active site = *

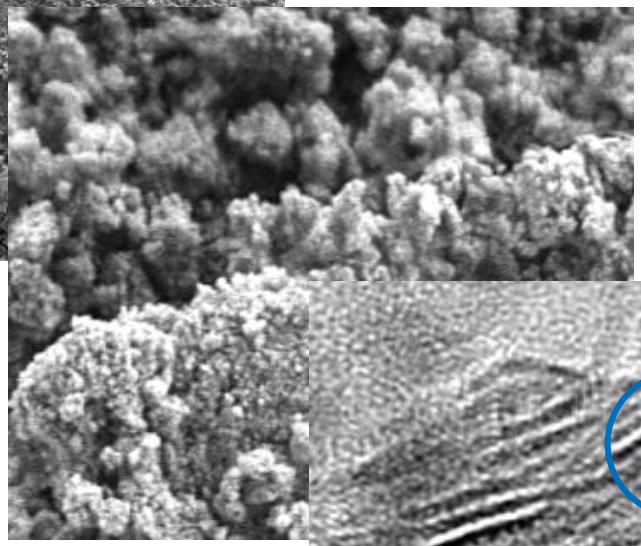


Eyring's law gives expression of the rate constant : $k = \frac{k_B T}{h} \times \exp\left(\frac{-\Delta_r G^{\neq °}}{RT}\right)$

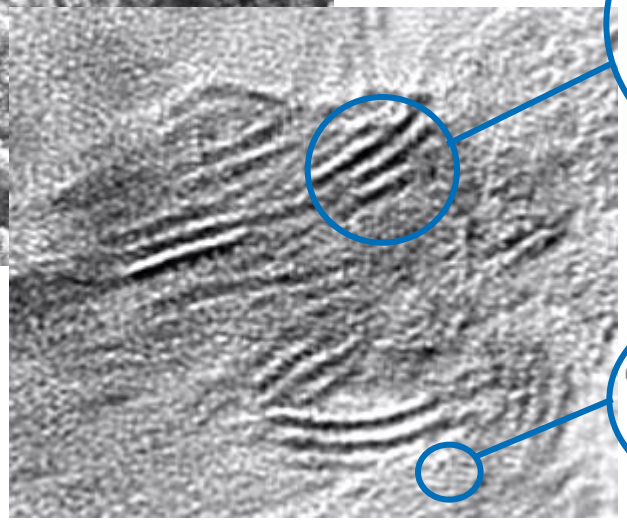
Zooming to the atomic scale of an heterogeneous catalyst

mm

μm

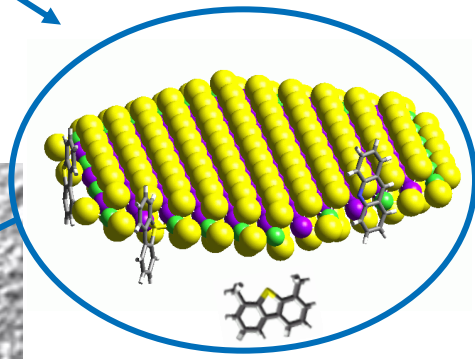


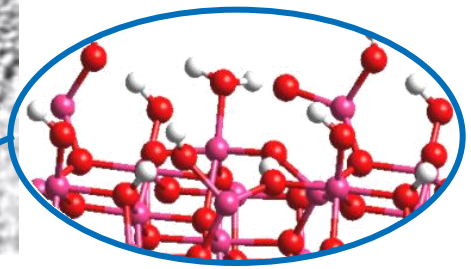
nm



Å

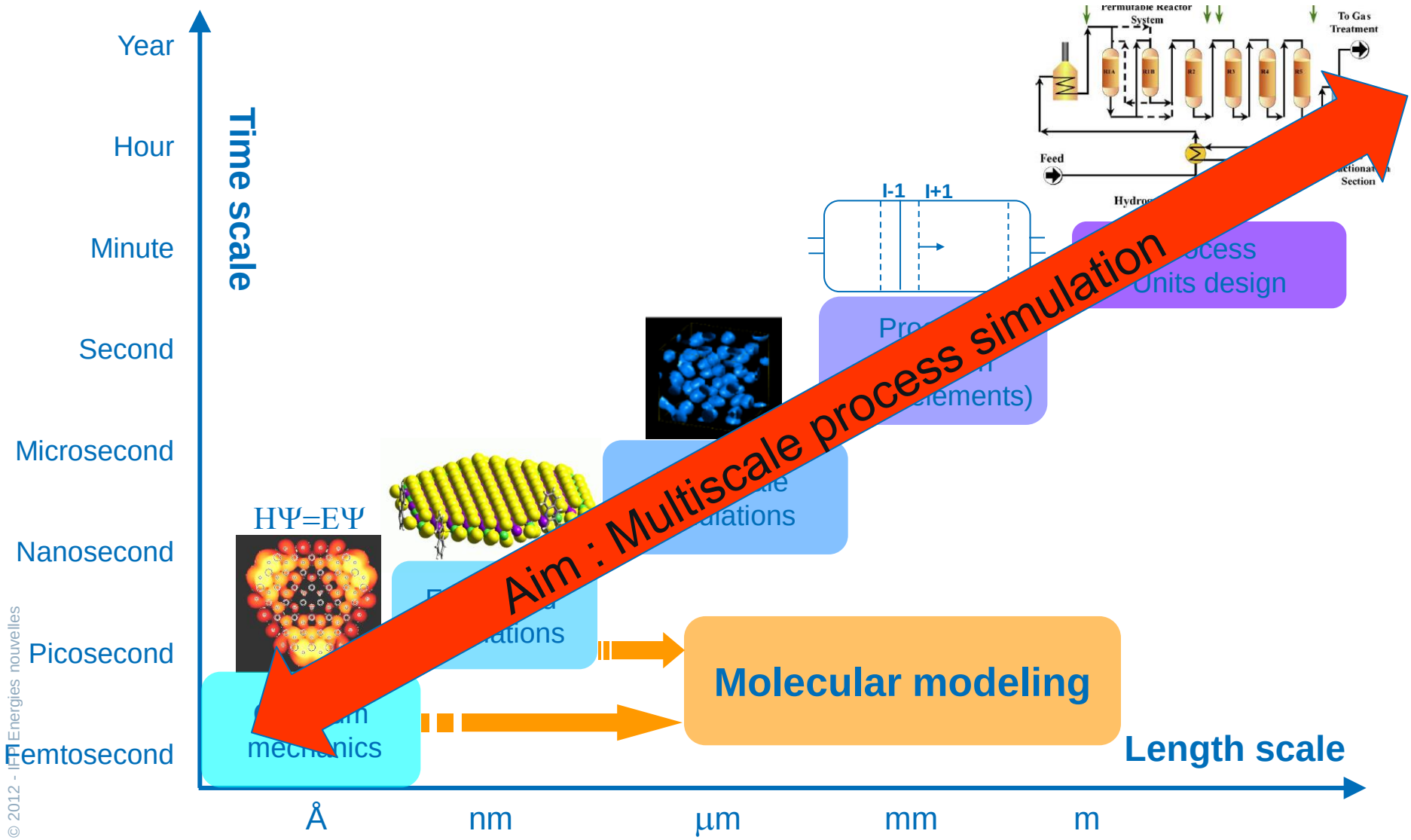
Co(Ni)MoS
<L>=3-4 nm





$Co(Ni)MoS/\gamma-Al_2O_3$

Process design simulation scales



Examples of industrial relevance : Outline

1. PETROCHEMISTRY

Butadiene selective hydrogenation on palladium

From ab initio calculations to CFD

With L. Briquet (ENS-Lyon), P. Raybaud (IFPEN), P. Sautet (ENS-Lyon), J.M. Schweitzer (IFPEN), J. Verstraete (IFPEN), A. Hammouti (IFPEN), A. Wachs (IFPEN), M. Rolland (IFPEN)

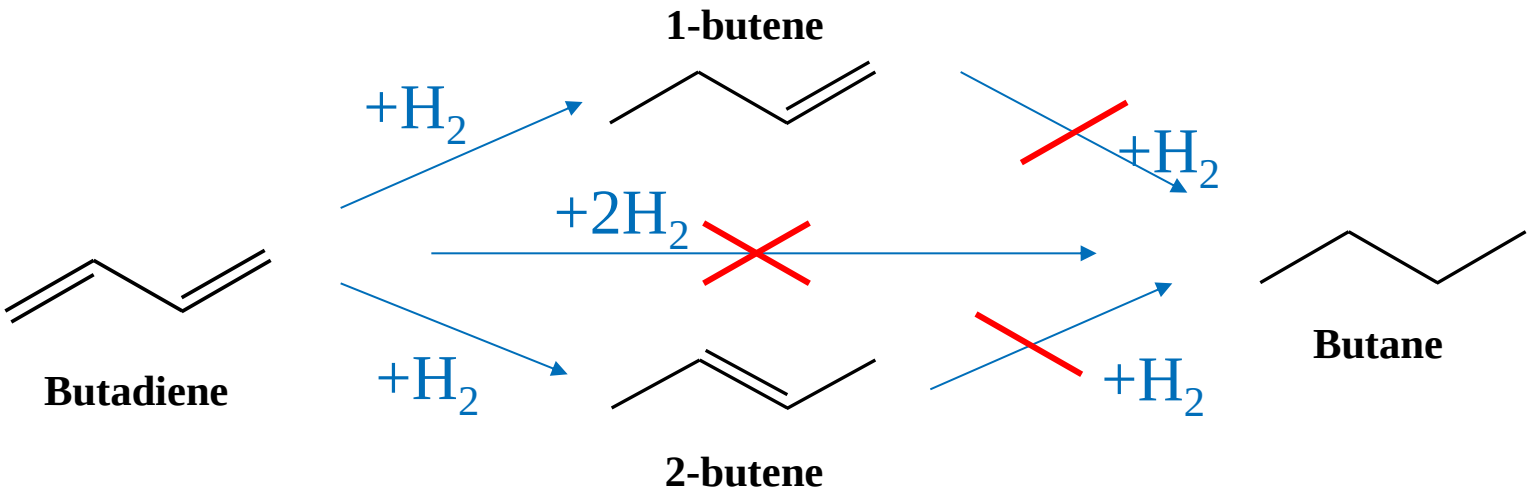
2. BIOMASS CONVERSION → CHEMICALS AND FUELS

Dehydration of isopropanol on gamma-alumina

From ab initio calculations to kinetic modeling + experiments

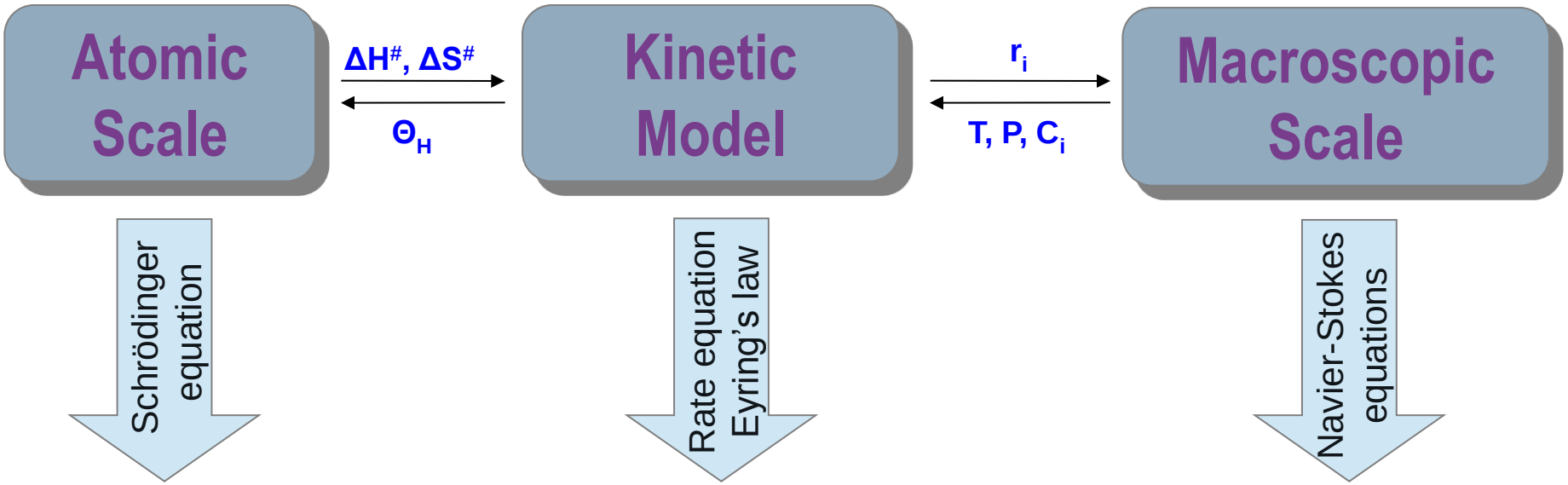
With K. Larmier (UPMC-IFPEN), H. Lauron-Pernot (UPMC), E. Marceau (UPMC), A. Nicolle (IFPEN), S. Maury (IFPEN), N. Cadran (IFPEN), AF. Lamic-Humblot (UPMC)

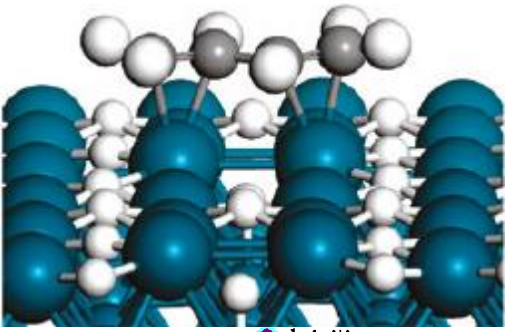
Selective hydrogenation of butadiene



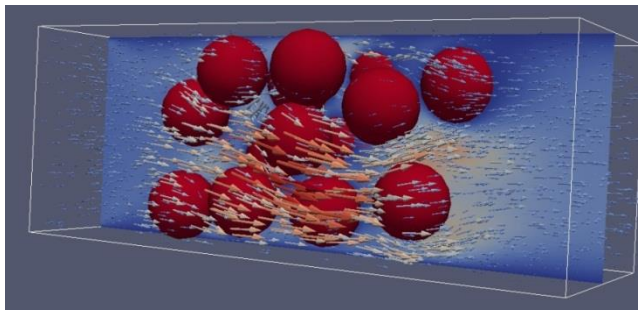
- Catalyst = Supported palladium particles
- Importance of reaction kinetics on selectivity
- Limitations by transport phenomena exist
  → Multiscale problem

Integrating First-Principles Calculations Into CFD Simulations





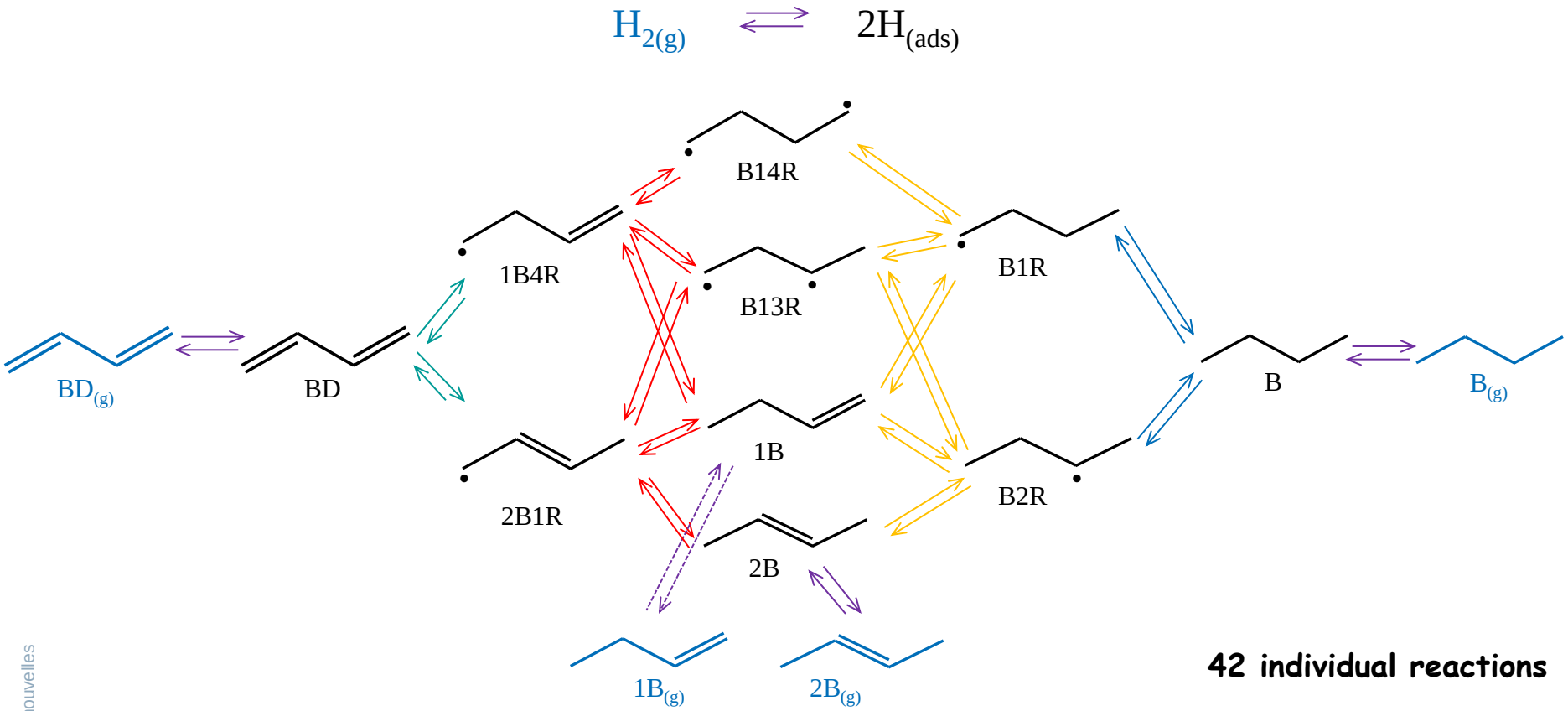
Home made code



b-initio VASP ackage imulation tenna

PeliGRIFF Parallel Efficient LIbrary for GRains In Fluid Flows

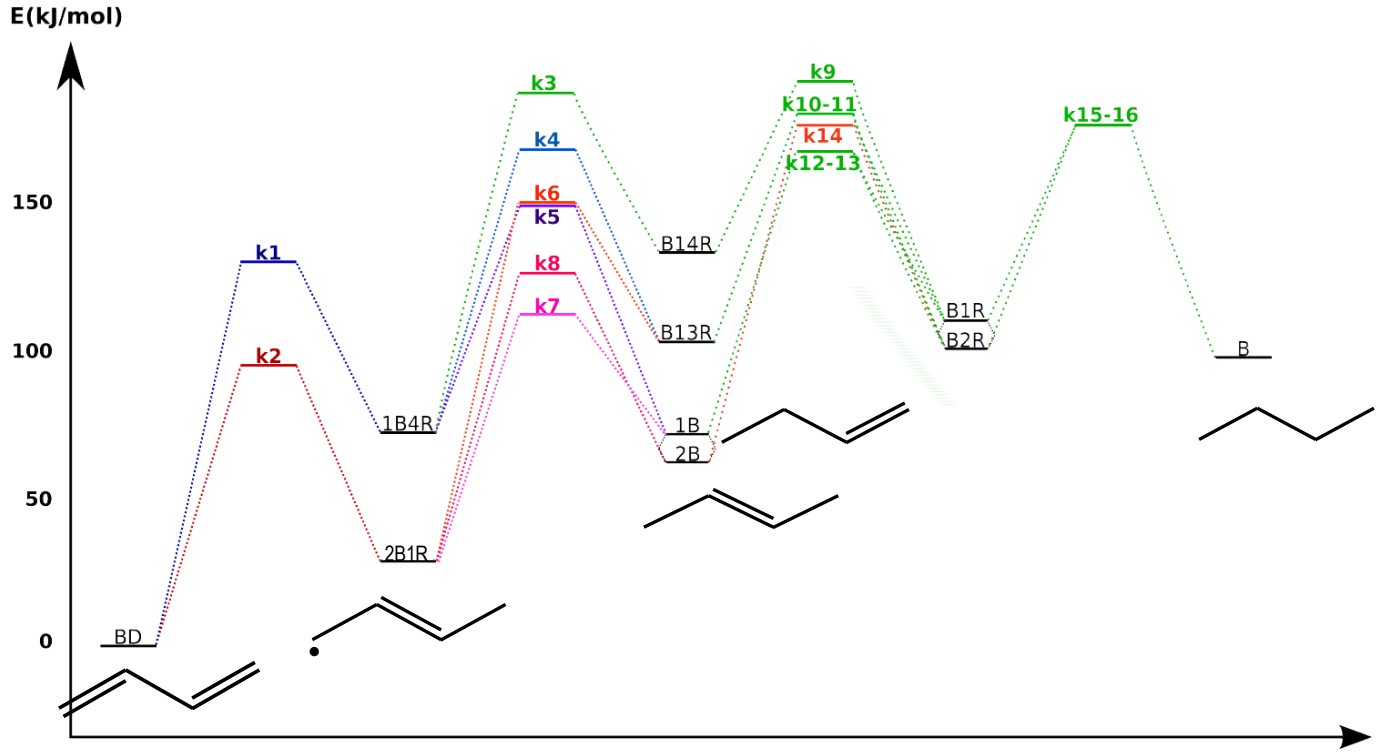
Horiuti – Polanyi reaction scheme



42 individual reactions

Adsorption	+1H	+2H	+3H	+4H	Desorption

Kinetic aspects at low hydrogen coverage



(2B1R) and butenes routes kinetically preferred over other routes

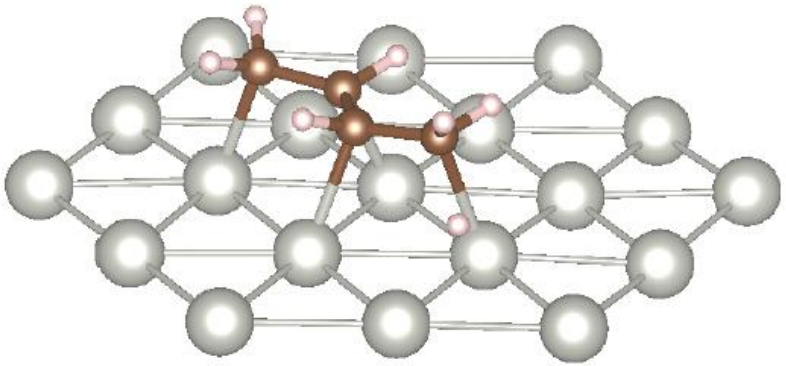
No clear conclusion regarding the competition between 1B and 2B

Will the formation of butane be quantitative ?

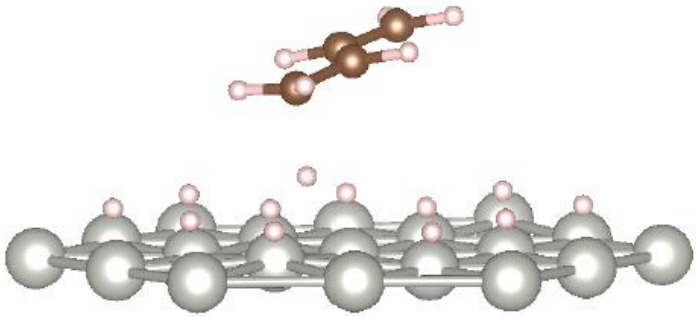
Impact of $P(H_2)$: kinetic aspects

C_1 attack

Θ_H: 0.1 ML



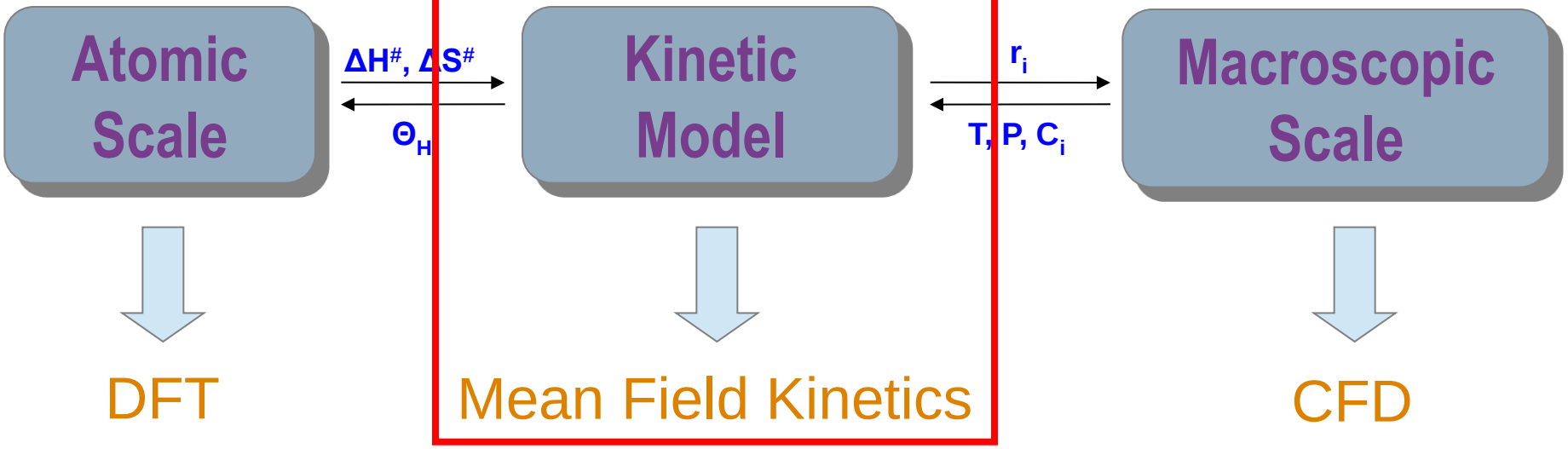
Θ_H: 1.0 ML

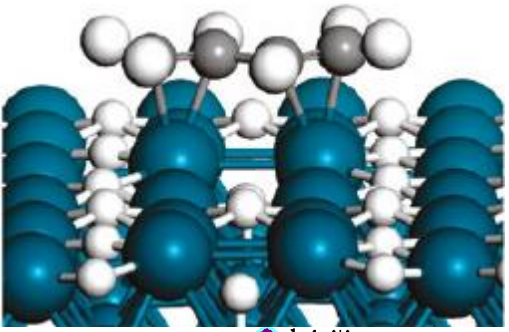


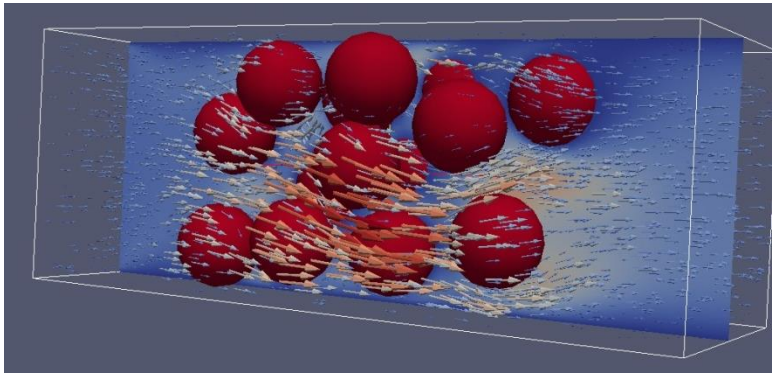
Horiuti – Polanyi type (Langmuir-Hinshelwood) → Eley-Rideal type

Briquet et al., *in preparation*

Integrating First-Principles Calculations Into CFD Simulations







b-initio VASP package Vienna simulation

PeliGRIFF Parallel Efficient LIbrary for GRains In Fluid Flows

Microkinetic modeling: Assumptions

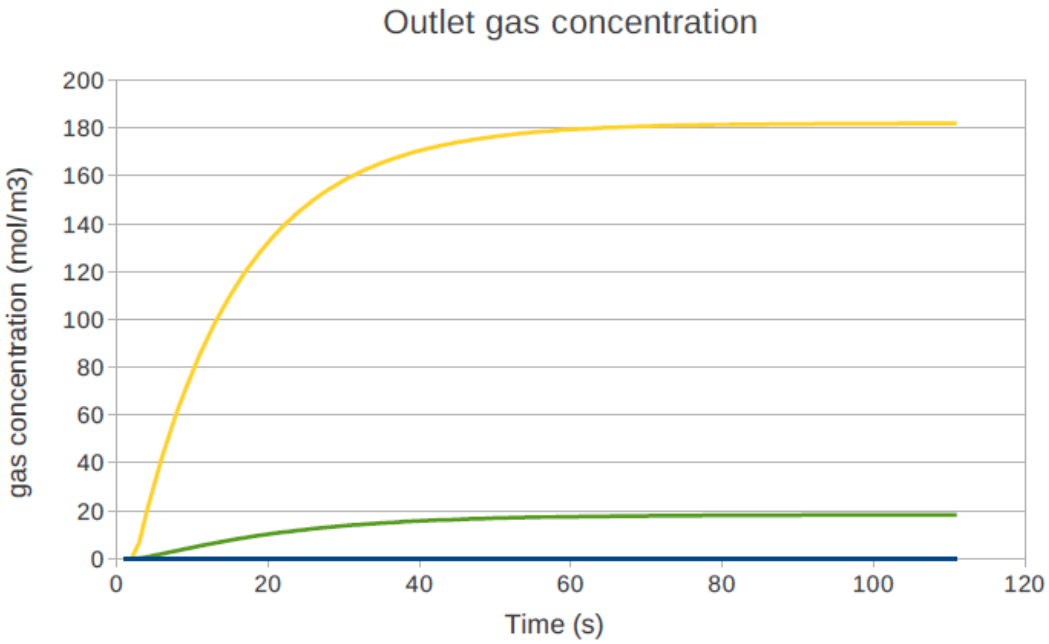
- **Dynamic simulation of a gas phase CSTR reactor using a mean field kinetic model (*)**
  - **species:**
    - **5 gas phase species + 11 surface species**
  - **42 elementary steps:**
    - **5 adsorption / desorption steps + 16 reversible surface reactions**
    - **reaction rates given by the mass action law**
    - **rate coefficients calculated from ab initio calculations at low H coverage ($\Delta_r H$, $\Delta_r S$, $\Delta H^{\#}$, $\Delta S^{\#}$) using Eyring's law**

$$k = \frac{k_B T}{h} \times \exp\left(\frac{-\Delta_r G^{\neq \circ}}{RT}\right)$$

From DFT

  - **full kinetic model**
    - **no assumption of rate determining steps**
    - **no quasi-steady state approximation**

Microkinetic modeling: Simulations



P= 10 bars
T = 300 K
N_{pd} = 333 mol.

Inlet $[H_2]/[BD] = 1$
Gas Flux = 100 m^3/h

$[BD]_{out} = [H_2]_{out} = [B]_{out} = 0$ %

$[1B]_{out} = 90.8$ %

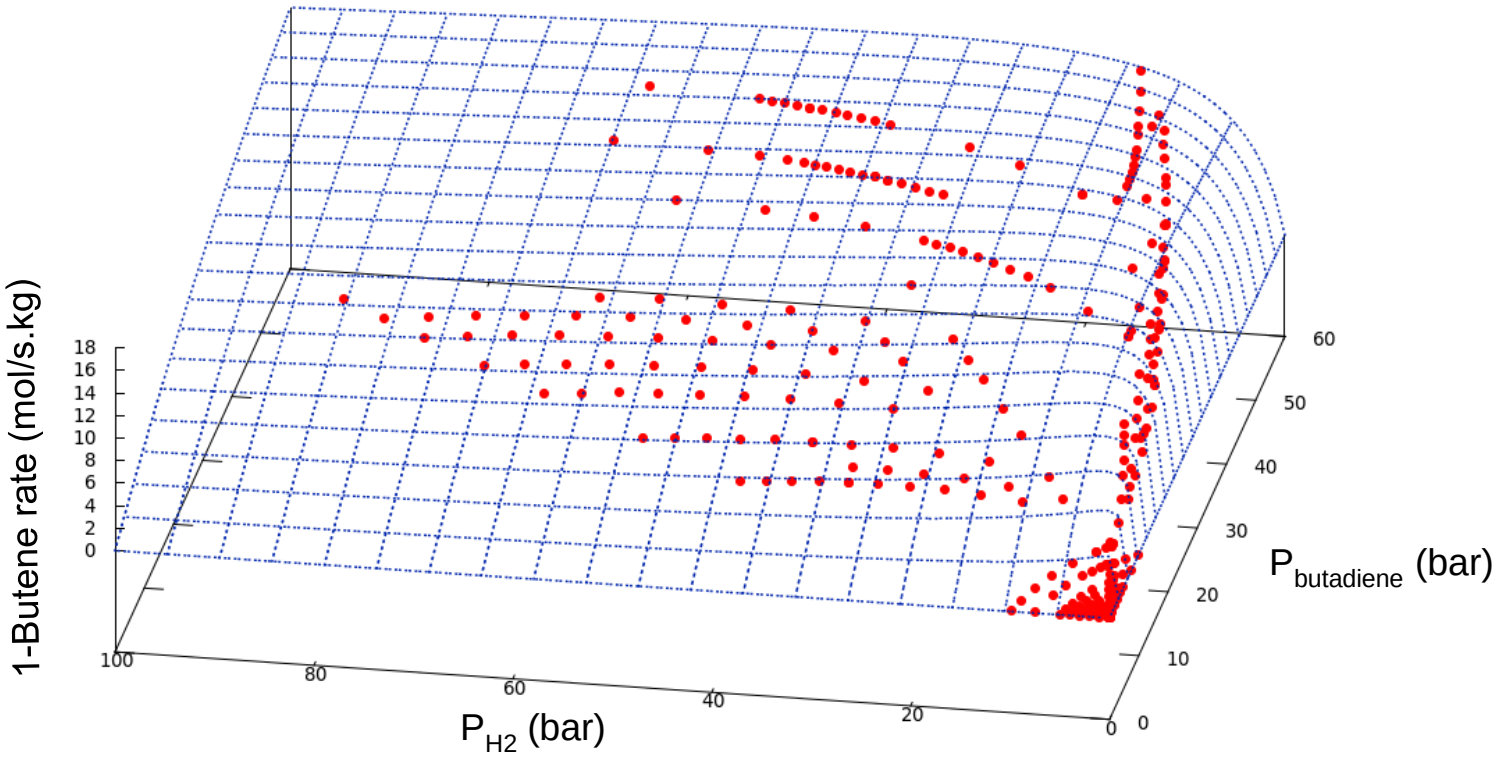
$[2B]_{out} = 9.2$ %

In these conditions,
- **full selectivity for butenes**
- **1B dominates over 2B**

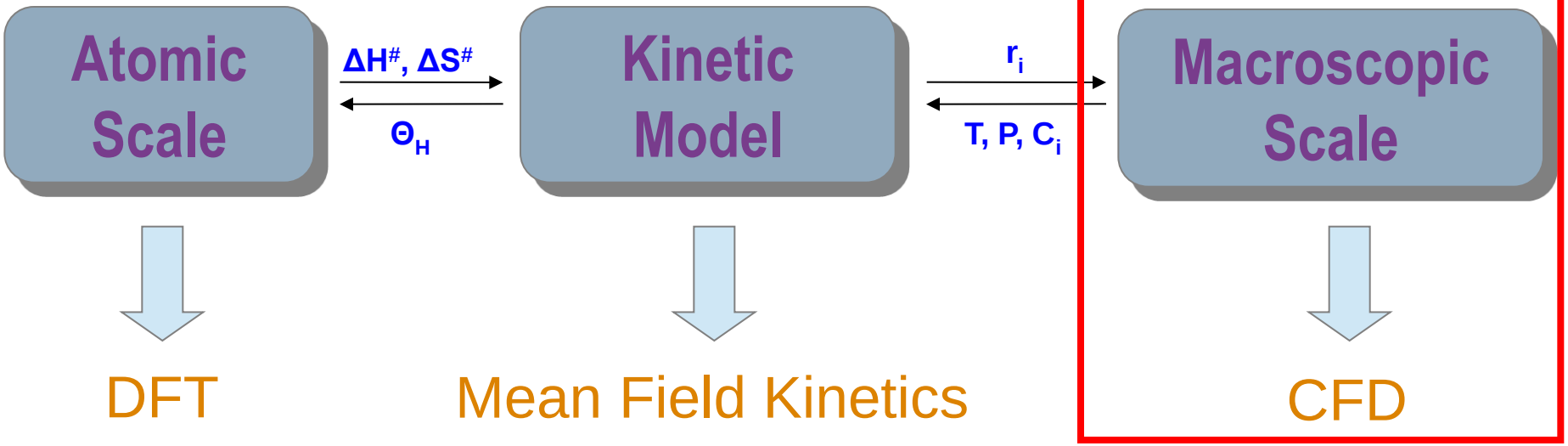
Microkinetic modeling: Deriving mean field kinetic rate equations

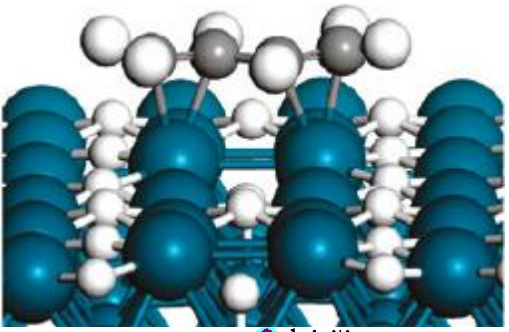
- **Approach**
  - **Rate limiting step depends on the operating conditions**
    - **H_2 adsorption**
    - **BD adsorption**

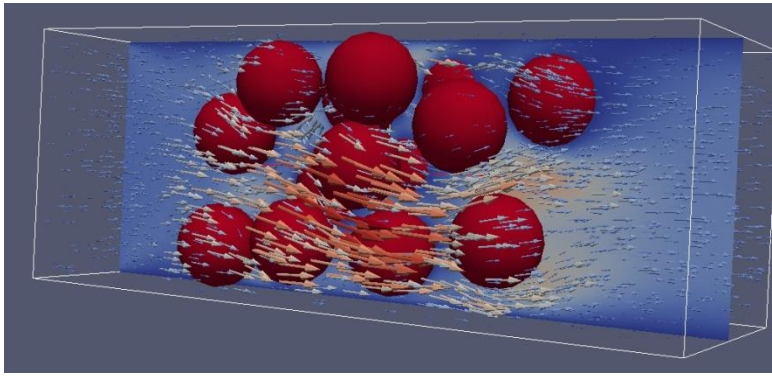
$$r = \frac{K_1 C_{BD} C_{H2}}{\left(1 + K_2 C_{BD} + K_3 \sqrt{C_{H2}}\right)\left(C_{H2} + K_4 C_{BD}\left(1 + K_2 C_{BD} + K_3 \sqrt{C_{H2}}\right)\right)}$$



Integrating First-Principles Calculations Into CFD Simulations





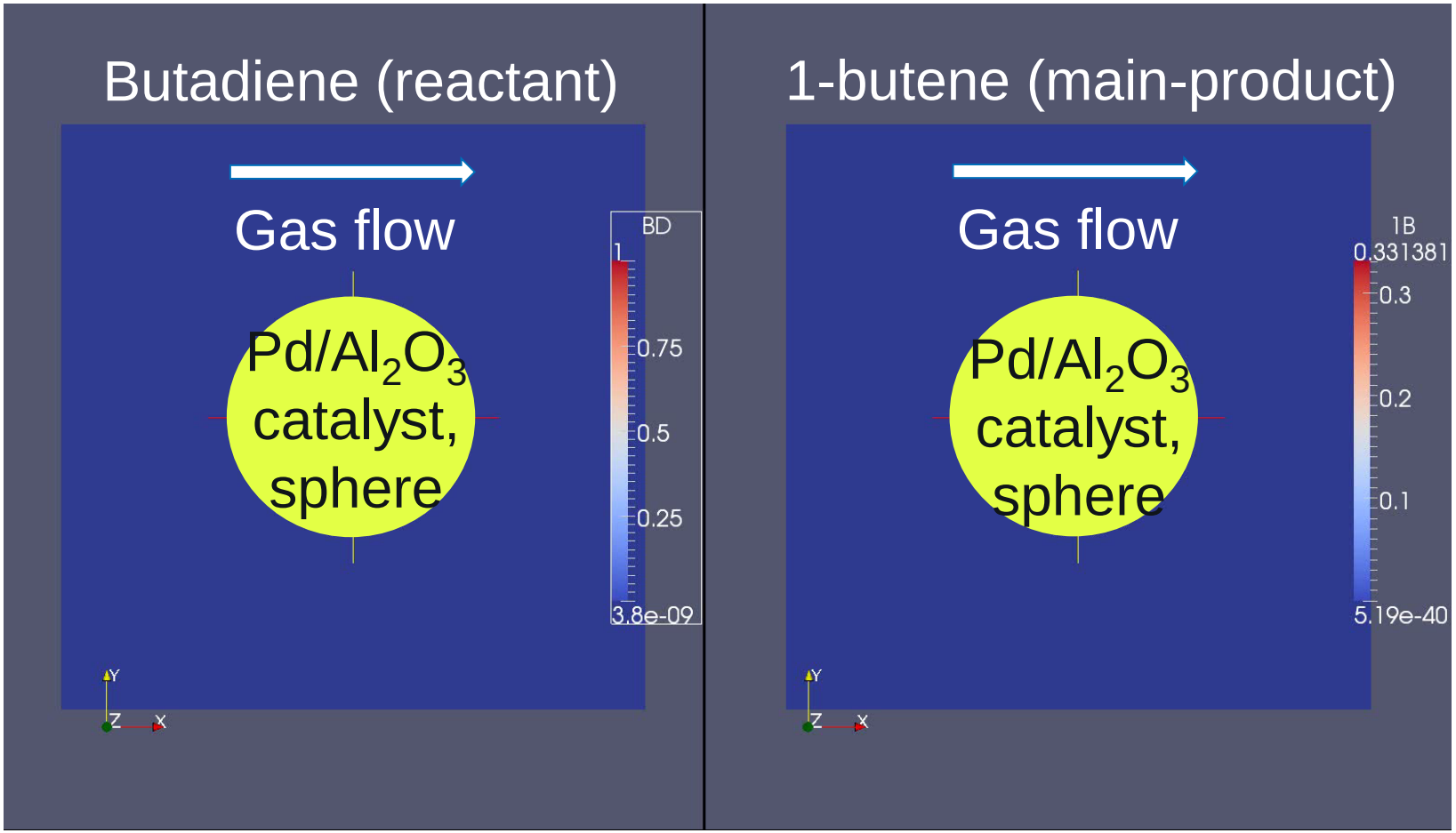


b-initio VASP ackage imulation tenna

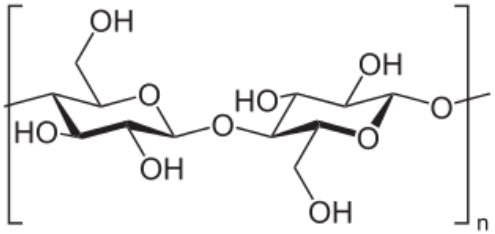
PeliGRIFF Parallel Efficient LIbrary for GRains In Fluid Flows

Flow around a single catalyst particle

$BD_{(g)}$ $1B_{(g)}$

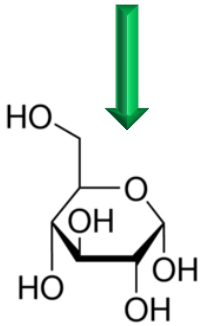


Alcohols conversion

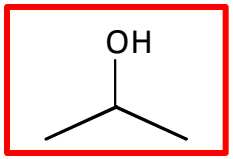


Cellulose

γ-alumina (acidic catalyst)



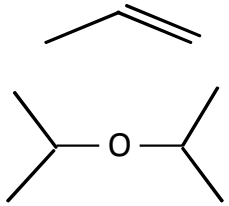
Glucose



Isopropanol

Intra-molecular dehydration

Inter-molecular dehydration



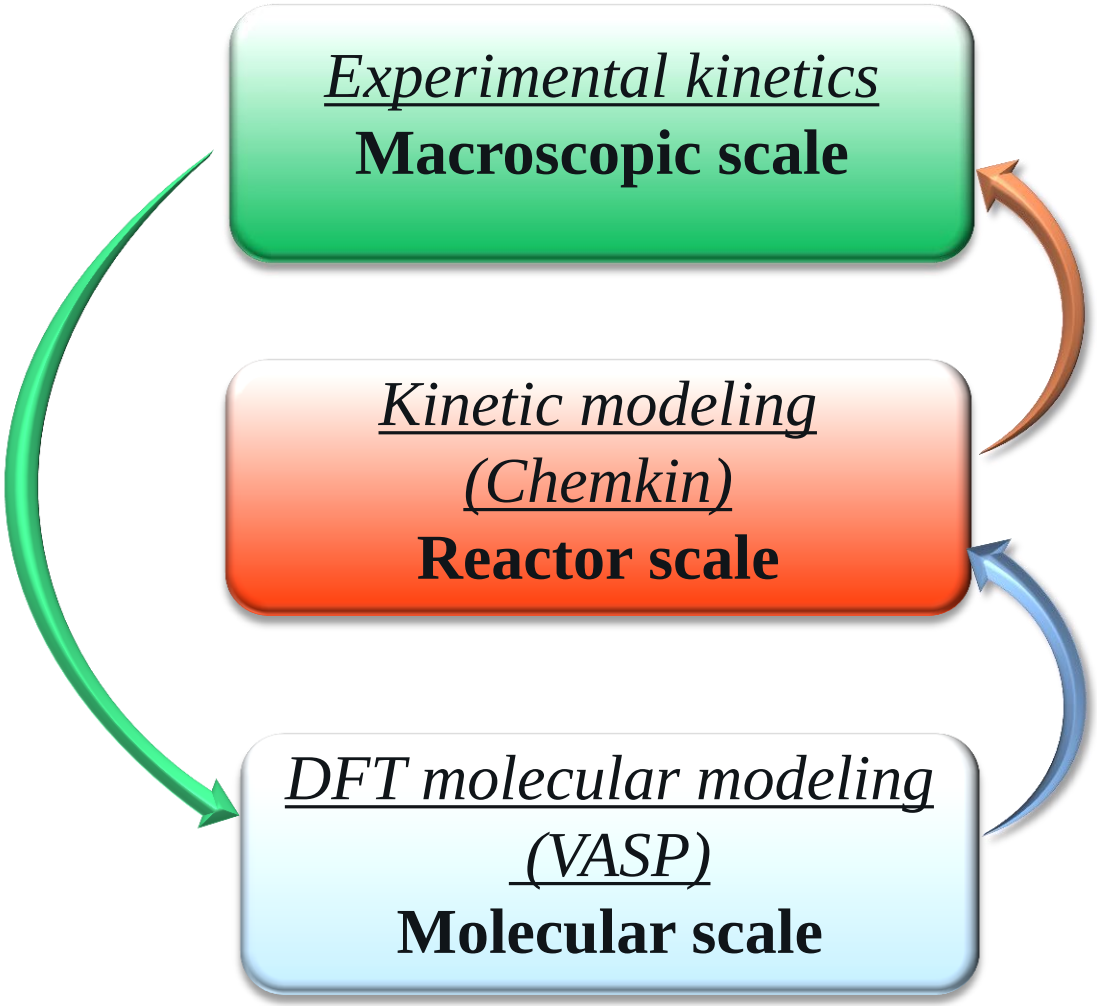
Propene

Diisopropylether

- **Can we predict where the active sites are located ?**
- **Can we predict the evolution of selectivity as a function of conversion ?**

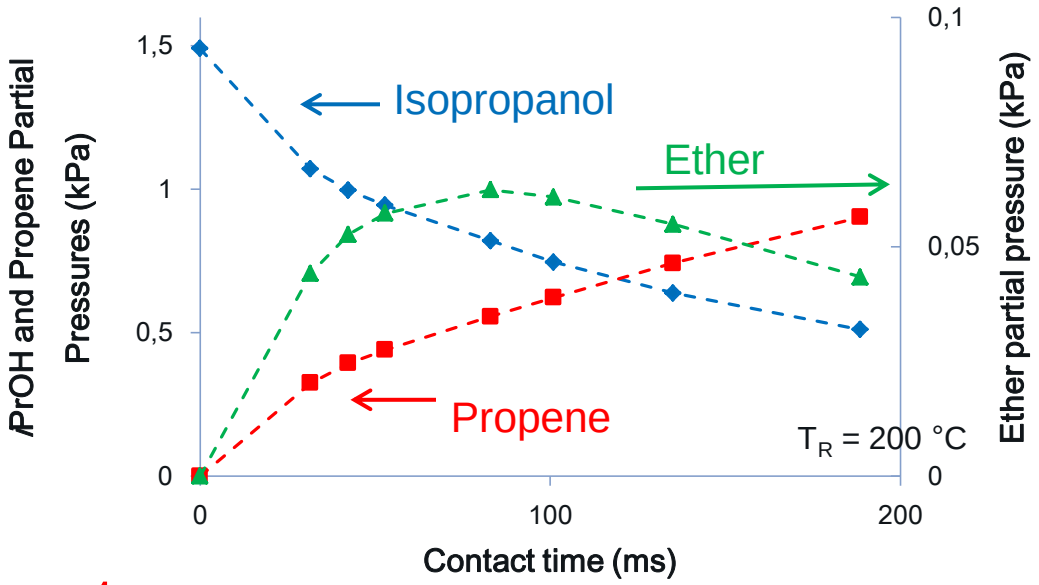
Aim : control of the activity and selectivity of the catalyst

Strategy



Kinetic measurements, steady-state conditions

- **Pure γ-alumina (145 m^2/g, Sasol Puralox), T_R = 200 °C**

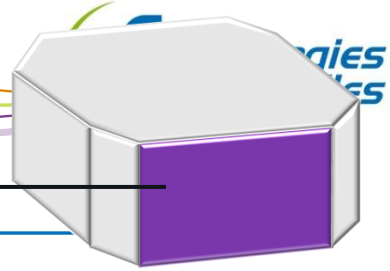


Fixed-bed open reactor
Initial P_{iPrOH} : 1.5 kPa
Flow rate: 6 - 60 $cc.min^{-1}$

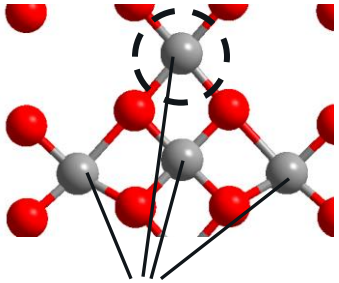
- **3 main routes**
  - **Direct formation of propene**
  - **Direct formation of diisopropylether**
  - **Conversion of diisopropylether into propene and isopropanol**

Larmier et al., *ACS Catalysis*, ***2015***, *5, 4423*

Molecular-scale modeling



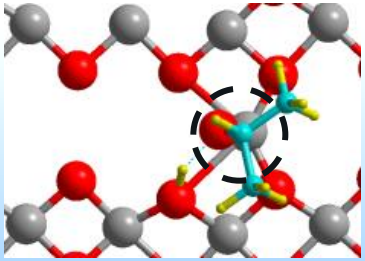
- **(100) facets – dehydrated : Lewis acidity at the origin of activity**

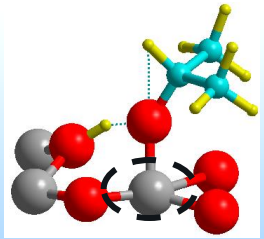


Lewis acidic Al

Common intermediate

Top view

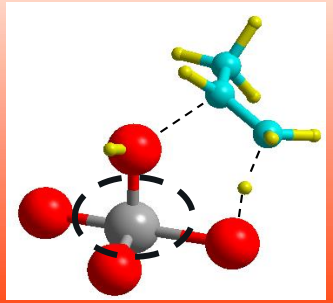




Side view

Mechanism E2

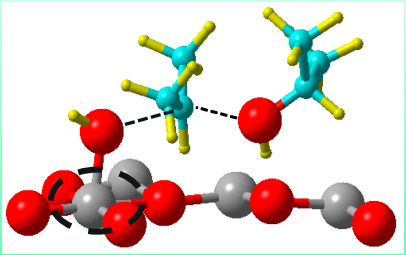
$\Delta_r H^{\ddagger} = 125$ kJ.mol^{-1}



Propene formation

Mechanism S_N2

$\Delta_r H^{\ddagger} = 112$ kJ.mol^{-1}



Diisopropylether formation

Aluminum

Carbon

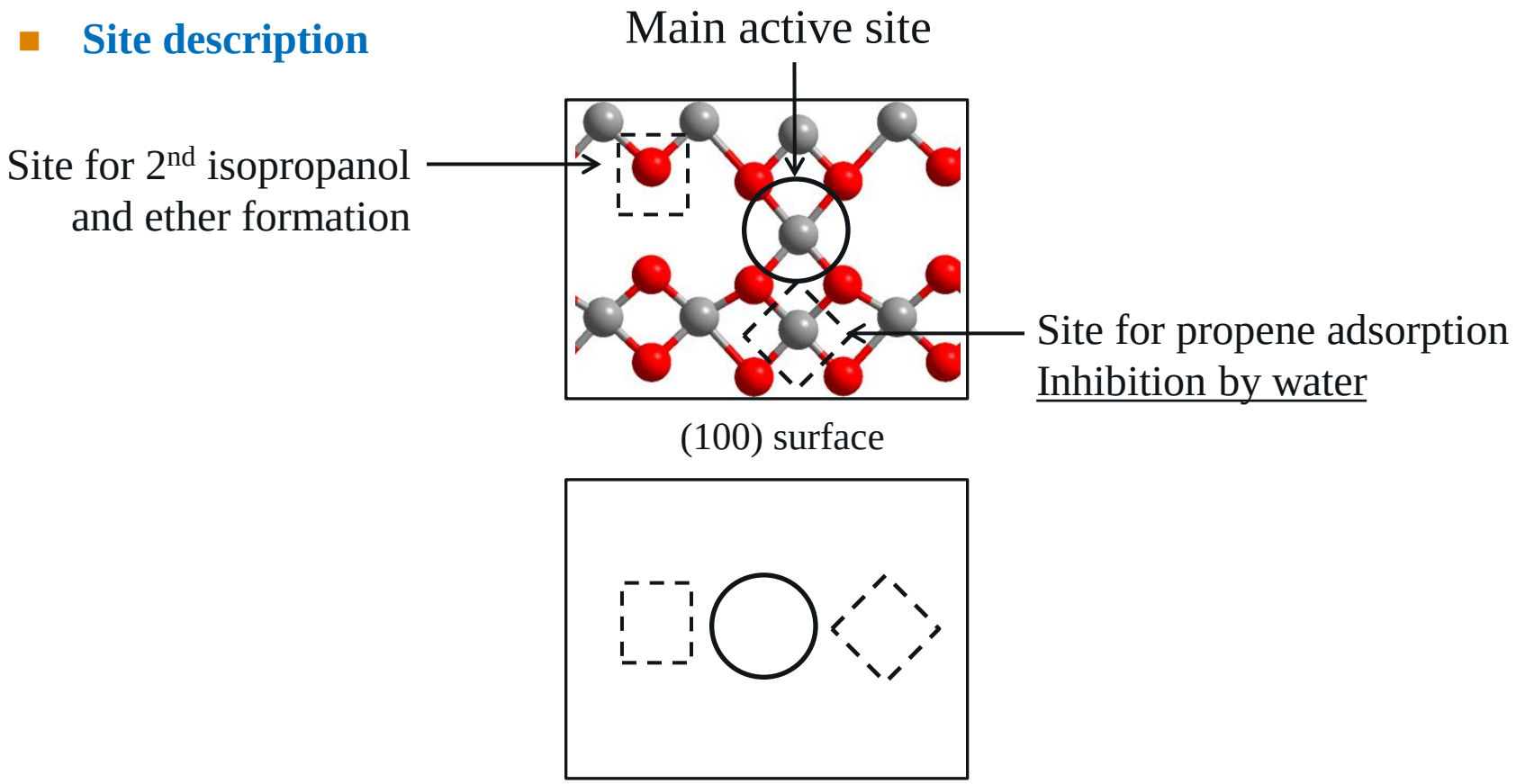
Oxygen

Hydrogen

All reactions occur on the same facet :
morphology of alumina platelets tunes the activity, but not the selectivity

Reactor-scale modeling

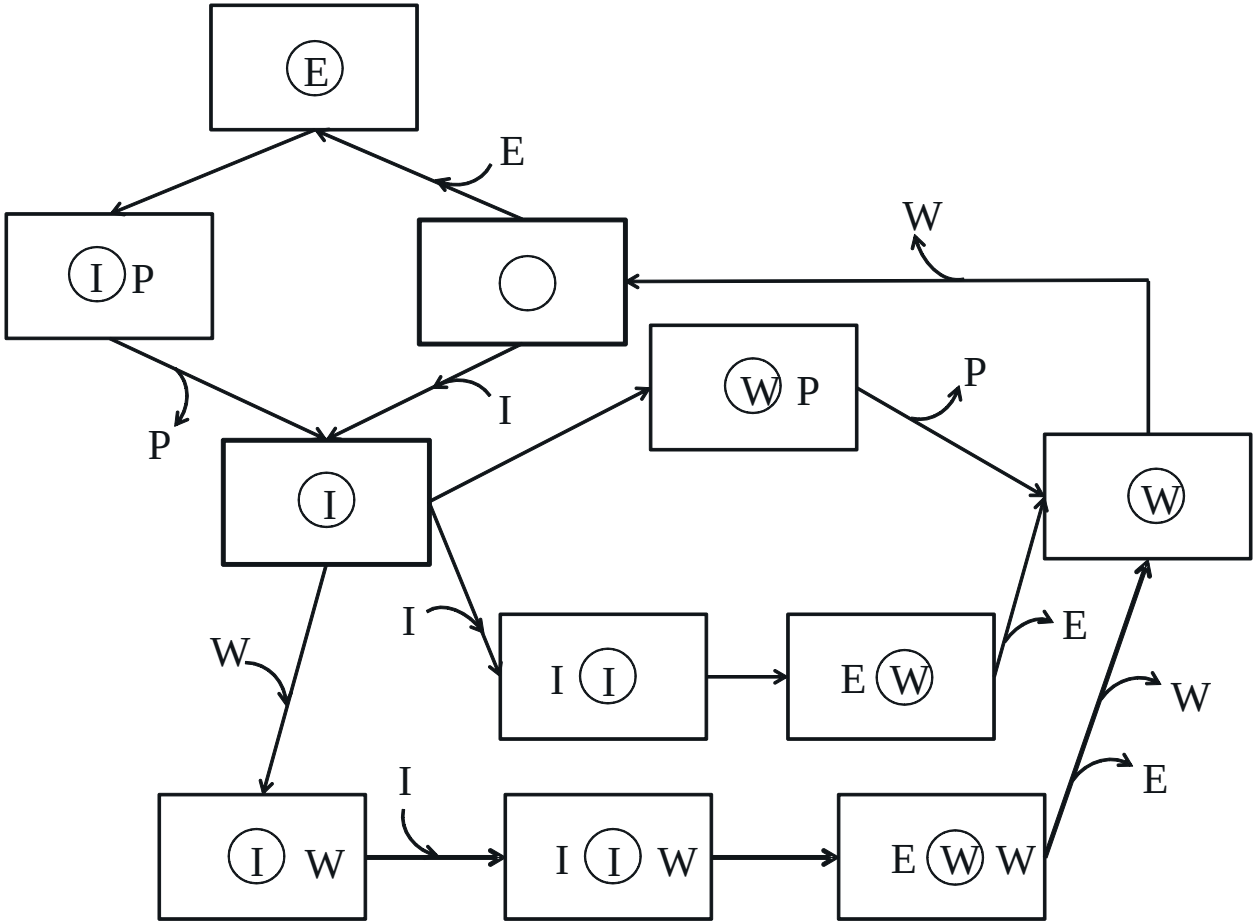
- **Site description**



- **Chemkin software**
- **Conditions : T_R = 200 °C, $P_{iPrOH}(0)$ = 1.5 kPa**

Reactor-scale modeling

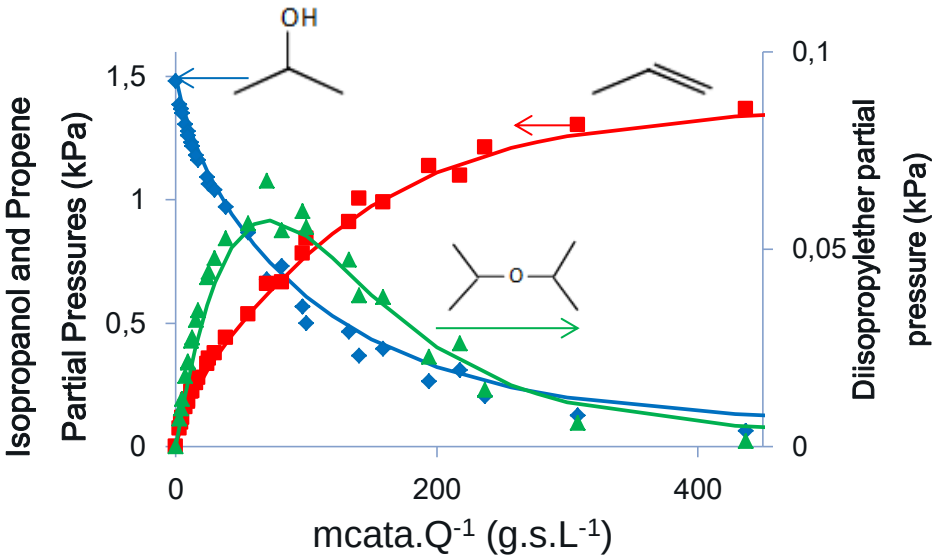
- **4 gas-phase species**
- **15 surface species**
- **34 reactions**

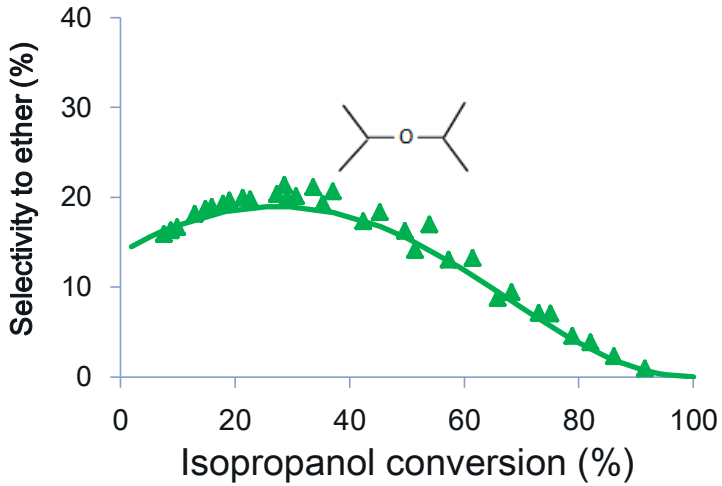


Larmier et al., *in preparation*

Reactor-scale modeling

- **Simulation results : very good agreement with experiments**
  - **Marks : experimental data**
  - **Lines : kinetic modeling (‘DFT model’)**





Larmier et al., *in preparation*

Conclusions and perspectives

- Reactor simulations, including CFD aspects, can be built on the basis of quantum ab initio calculations
  - Proof of concept
- Extend this method to other fields of refining, petrochemistry, depollution, etc.
  - A research project is devoted to this at IFPEN
- Make the bridge between multiple scales smoother
  - Towards the integration of methods ?

Acknowledgements

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H. Lauron-Pernot

Calculation time and funding

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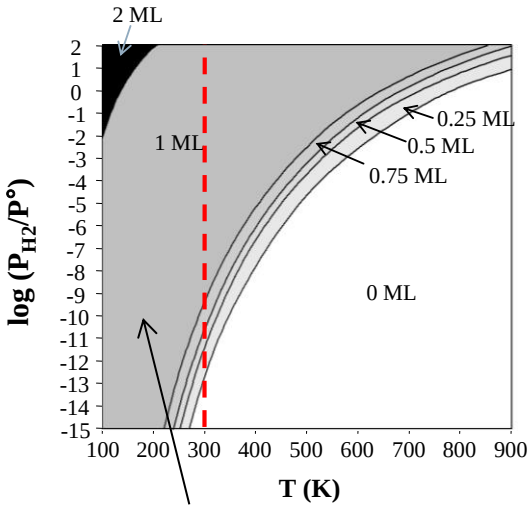
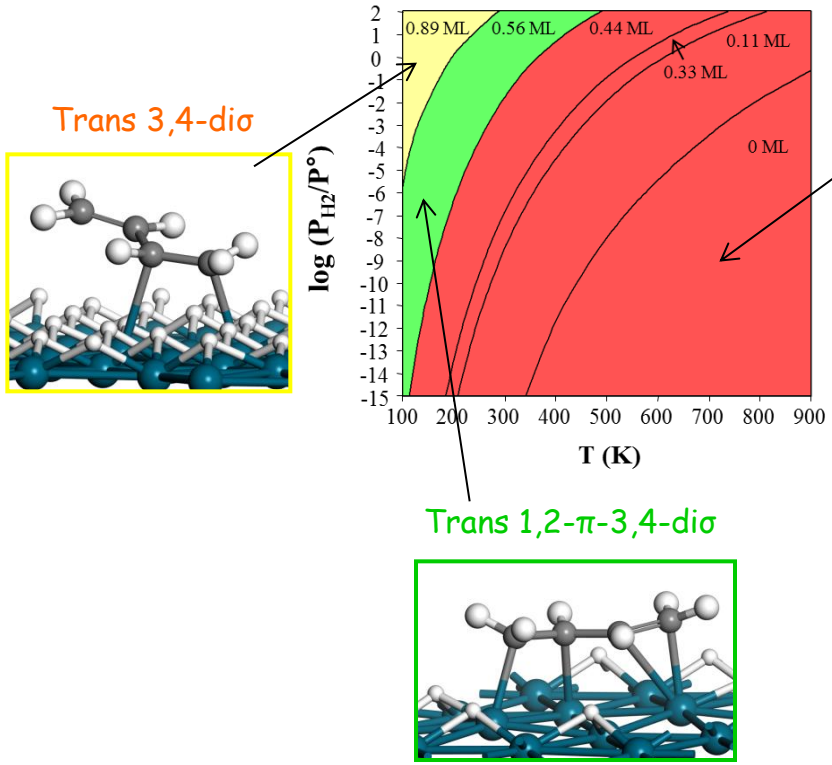
Impact of $P(H_2)$: thermodynamic aspects

H / Pd(111)



Higher θ_H expected

Butadiene / H / Pd(111)

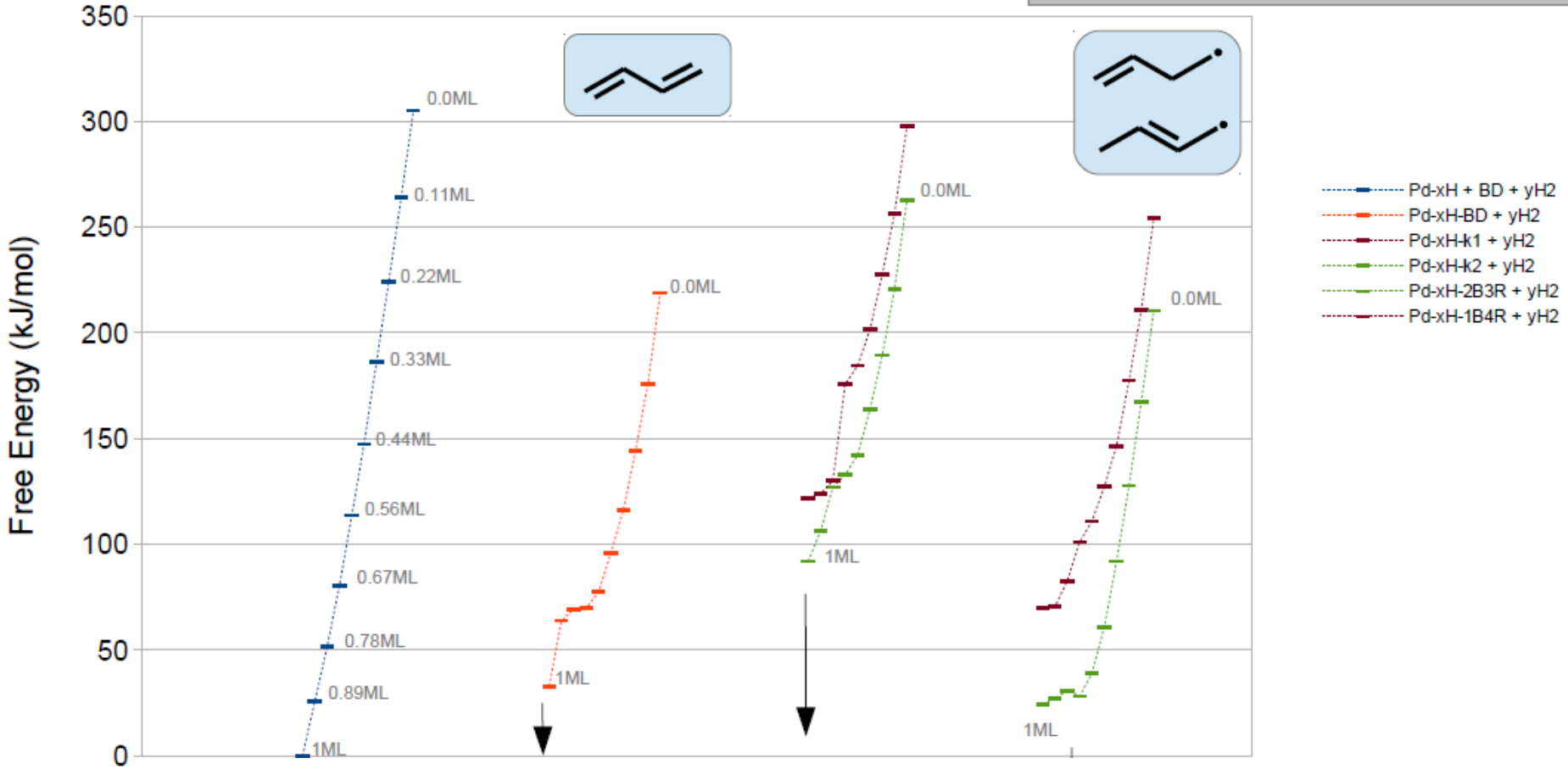


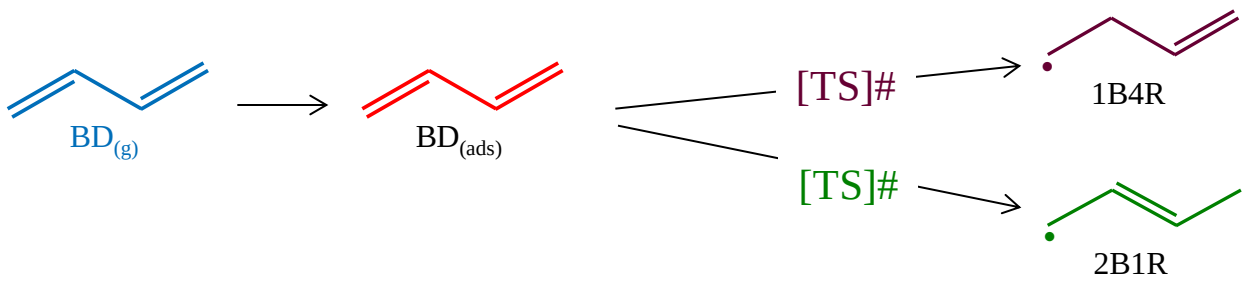
Impact of θ_H on the adsorption mode of butadiene

Chizallet, C.; Bonnard, G.; Krebs, E.; Bisson, L.; Thomazeau, C.; Raybaud, P., *J. Phys. Chem. C* **2011**, *115*, 12135.

Impact of $P(H_2)$: intermediates and transition states

T = 300K	$P(1B)=10^{-3}$ bar
P(H2)=5 bar	$P(2B)=10^{-3}$ bar
P(BD)=5 bar	$P(B)=10^{-3}$ bar

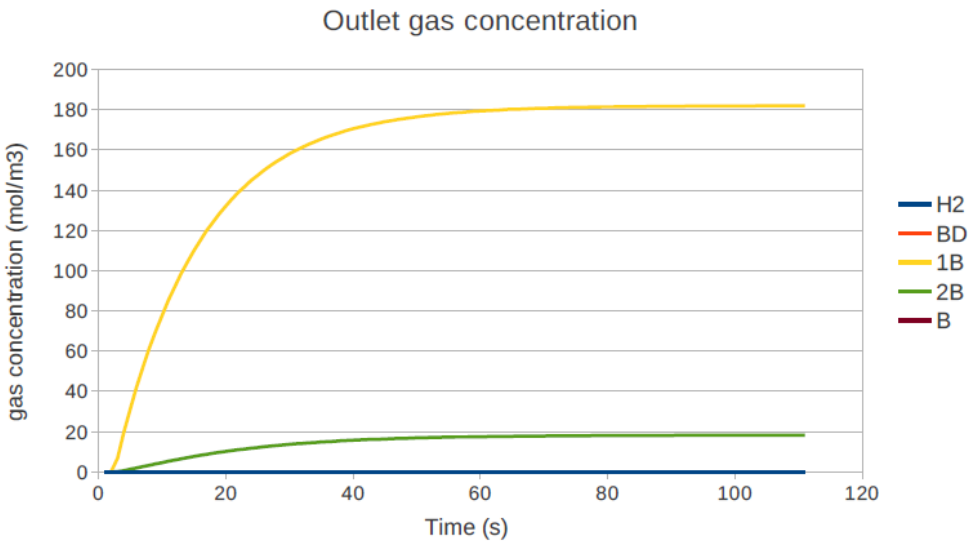


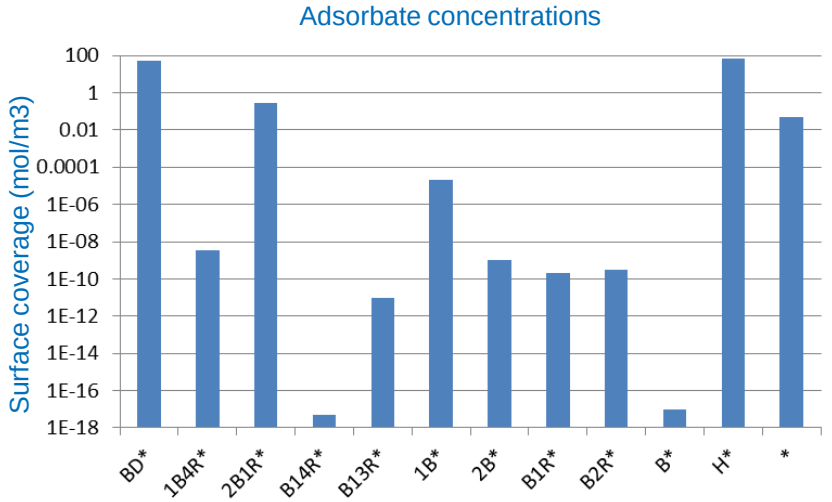


Microkinetic modeling: Simulations

P= 10 bars
T = 300 K
N_{pd} = 333 mol.

Inlet $[H_2]/[BD]$ = 1
Gas Flux = 100 m^3/h





$[BD]_{out} = [H_2]_{out} = [B]_{out} = 0$ %

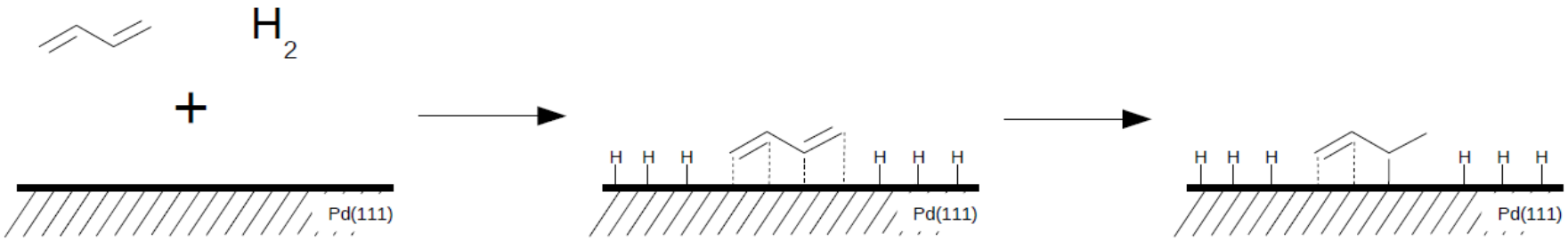
$[1B]_{out} = 90.8$ %

$[2B]_{out} = 9.2$ %

In these conditions,
full selectivity for butenes
1B dominates over 2B
MASI: H* > BD* >>> ...

Micro-Kinetic Model at High Θ_H

Langmuir-Hinshelwood mechanism

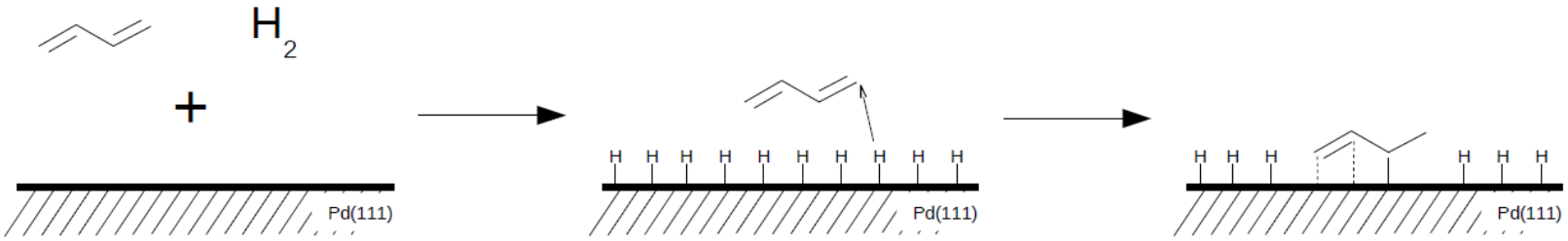


P= 50 bar
T = 300 K
N_{pd} = 333 mol.
Inlet $[H_2]/[BD] = 1$
Gas Flux = 100 m^3/h

	P_{out} (bar)	X_{HC} (%)	r (mol/s.kg)
H_2	25.00	-	0.00
Butadiene	25.00	100.00	0.00
1-Butene	0.00	0.00	0.00
2-Butene	0.00	0.00	0.00
Butane	0.00	0.00	0.00

Micro-Kinetic Model at High Θ_H

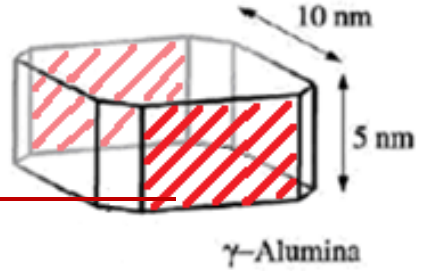
Eley-Rideal mechanism



P= 50 bar
T = 300 K
N_{pd} = 333 mol.
Inlet $[H_2]/[BD] = 1$
Gas Flux = 100 m^3/h

	P_{out} (bar)	X_{HC} (%)	r (mol/s.kg)
H_2	0.01		-3.15
Butadiene	0.01	0.04	-3.15
1-Butene	49.11	98.21	3.09
2-Butene	0.87	1.75	0.06
Butane	0.00	0.00	0.00

II – Modélisation moléculaire



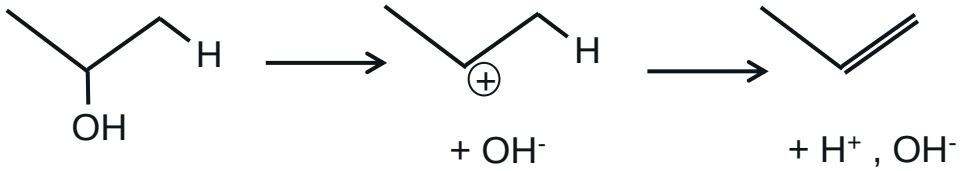
2 – Surface (100) – Formation du propène

Surface d'alumine non représentée

- **Formation du propène - mécanismes envisageables :**

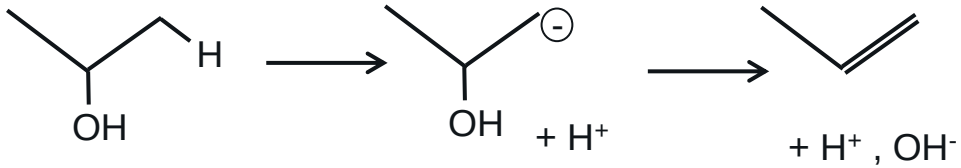
Carbocation

- **Mécanisme E1 :**
  - **Rupture liaison C-O**
  - **Puis rupture liaison C-H**
  - **Intermédiaire : carbocation**



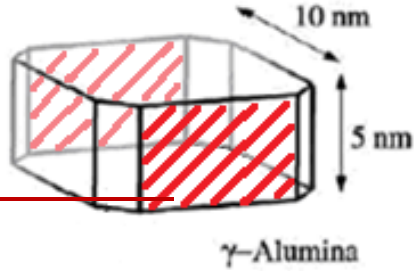
Carbanion

- **Mécanisme E1cb :**
  - **Rupture liaison C-H**
  - **Puis rupture liaison C-O**
  - **Intermédiaire : carbanion**

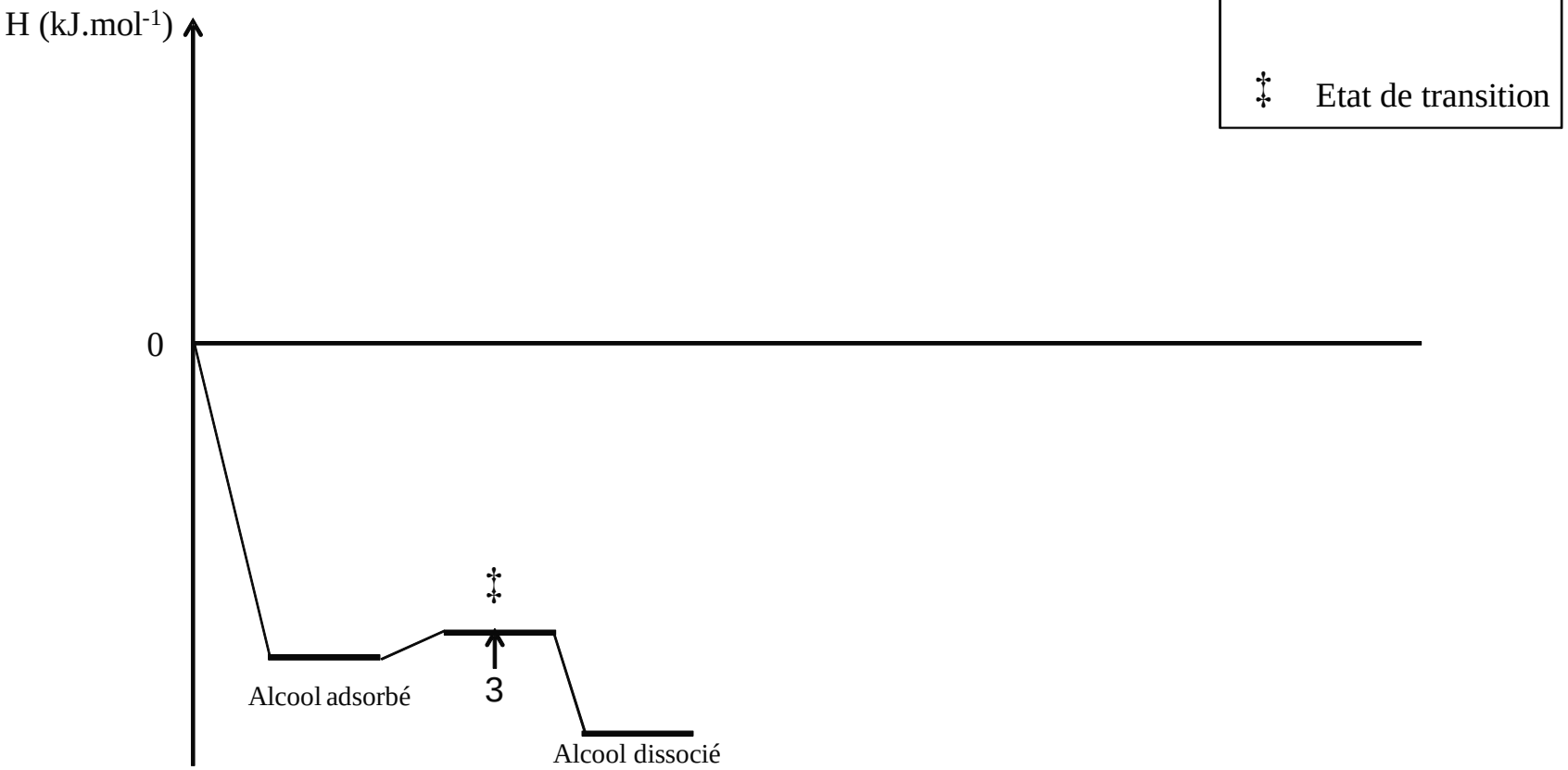


- **Mécanisme E2 :**
  - **Rupture C-H et C-O simultanée**
  - **Pas d'intermédiaire**

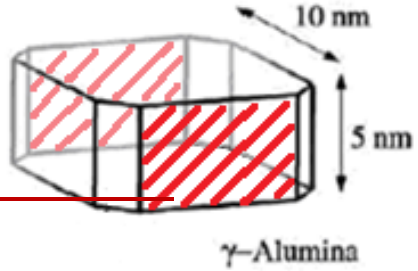
II – Modélisation moléculaire



2 – Surface (100) – Formation du propène

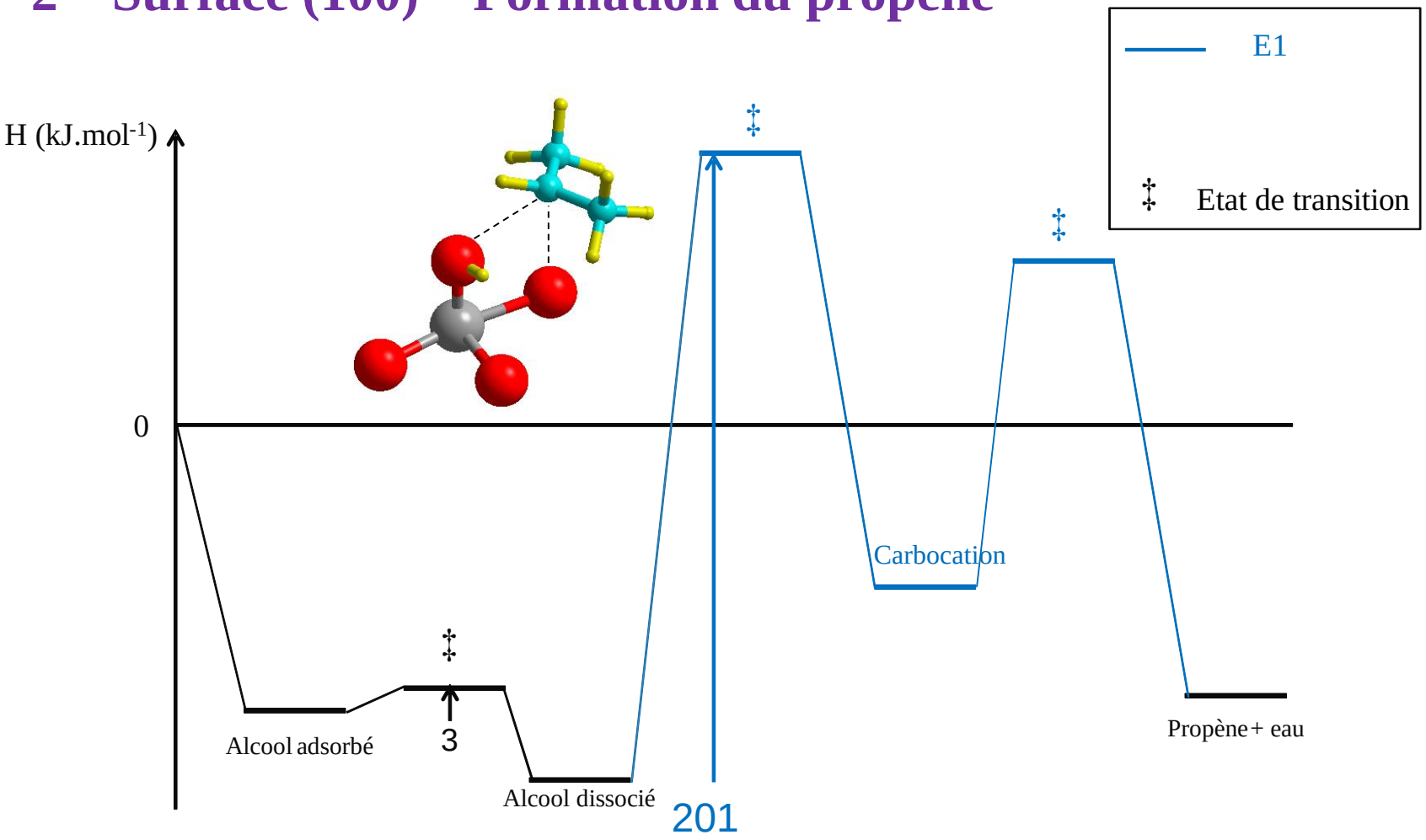


II – Modélisation moléculaire

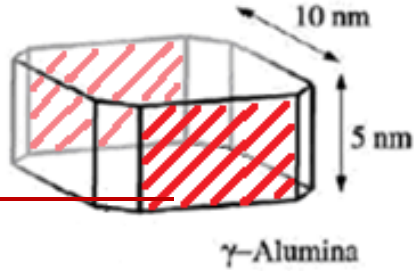


(100)

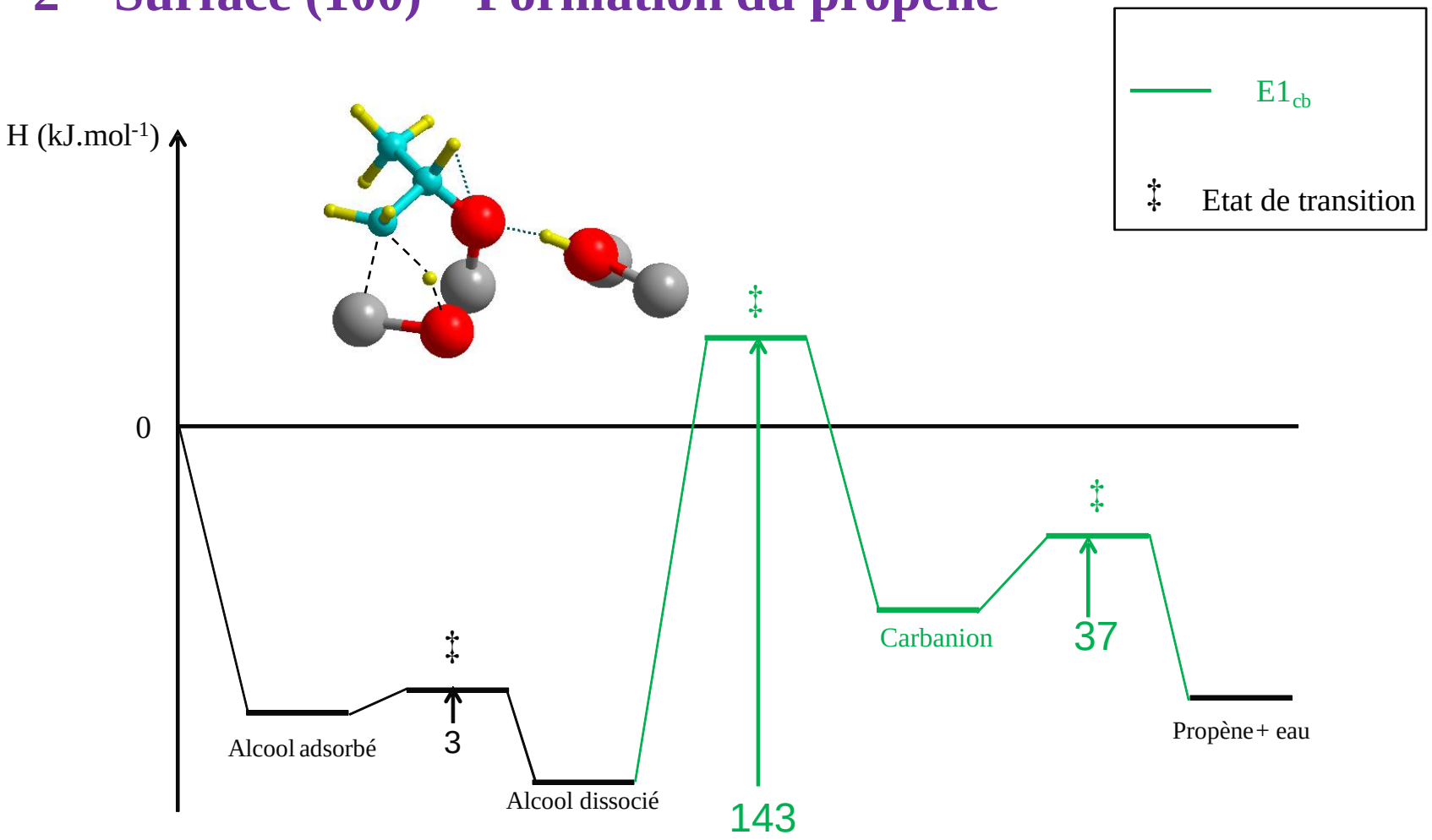
2 – Surface (100) – Formation du propène



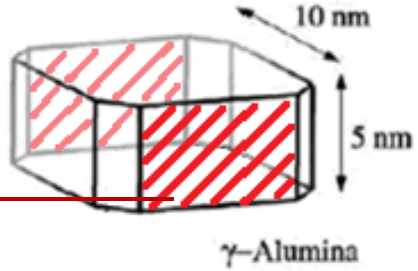
II – Modélisation moléculaire



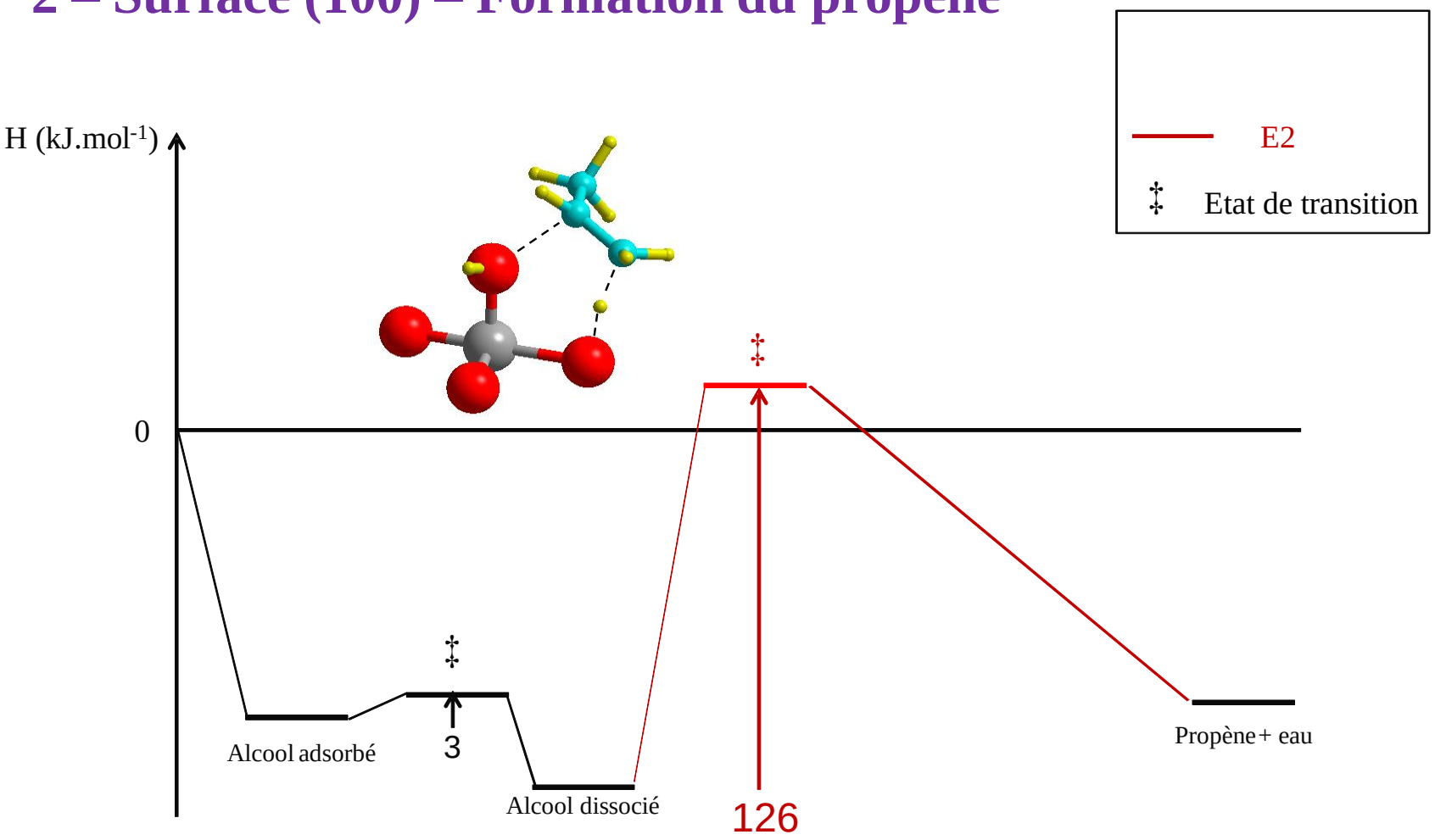
2 – Surface (100) – Formation du propène



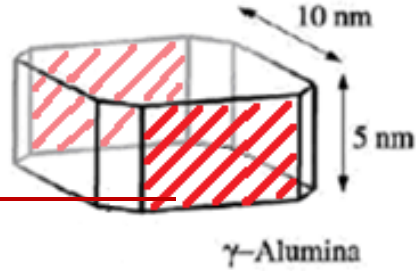
II – Modélisation moléculaire



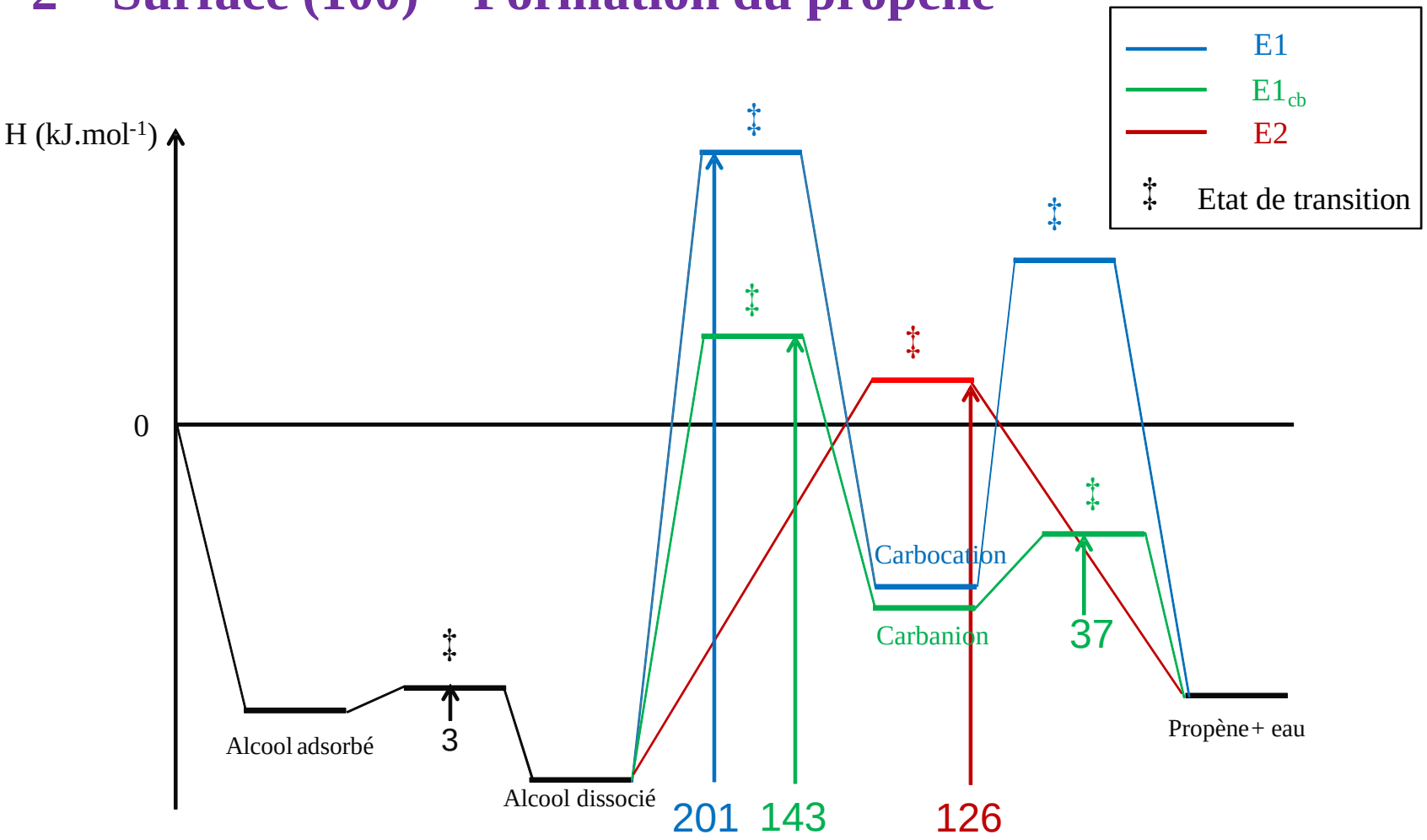
2 – Surface (100) – Formation du propène



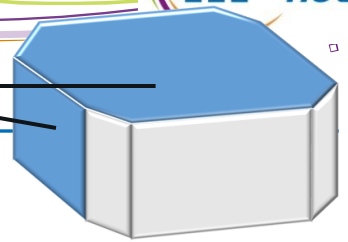
II – Modélisation moléculaire



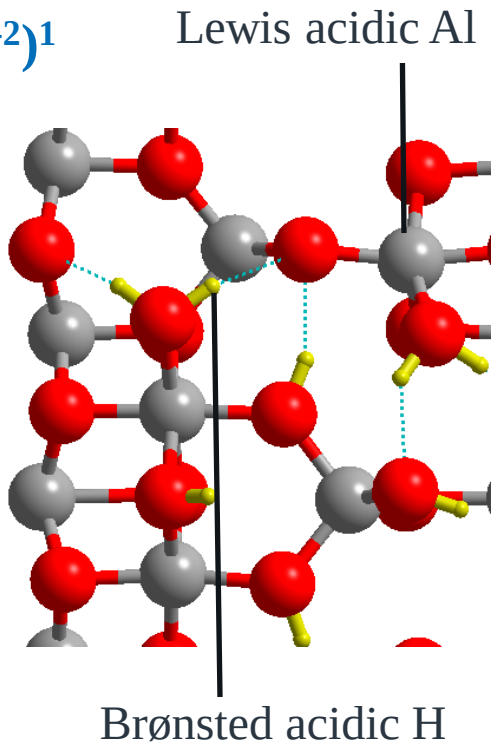
2 – Surface (100) – Formation du propène



Molecular-scale modeling



- **(110) facets – partially hydrated ($\theta_{OH} \approx 9.0$ OH.nm^{-2})[1]**
- **Propene formation**
  - **Lewis mechanism: E2, $\Delta_r H^{\ddagger} = 158$ kJ.mol^{-1}**
  - **Brønsted mechanism: $\Delta_r H^{\ddagger} > 200$ kJ.mol^{-1}**
- **Ether formation**
  - **Lewis mechanism : S_N2, $\Delta_r H^{\ddagger} = 140$ kJ.mol^{-1}**
  - **Brønsted mechanism : not possible**



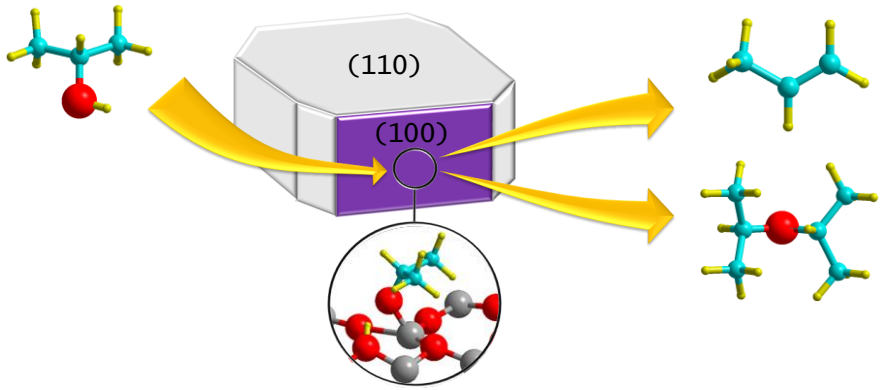
$$\text{Rate constants (110)} = \frac{\text{Rate constants (100)}}{1000}$$

(110) facets less reactive than (100) facets

[1] Raybaud et al. *Journal of Physics - Condensed Matter*, **2008**

Molecular-scale modeling

- **One common active site on the (100) surface for both reactions**



- **Comparison with experimental results ($\Delta_r H^{\ddagger}$ in kJ.mol^{-1})**

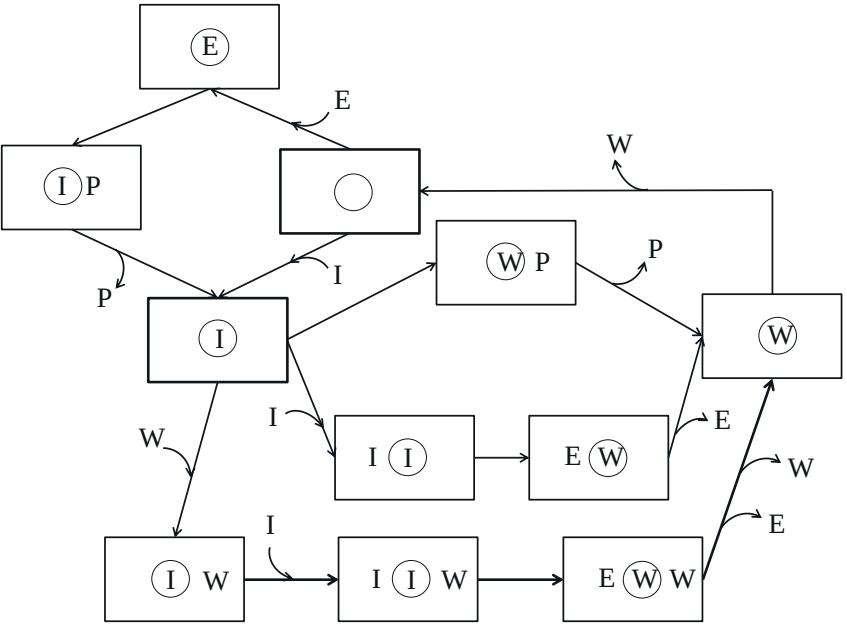
Reaction	Active facets	Modeling		Experiments*
		$\Delta_r S^{\ddagger}$	$\Delta_r H^{\ddagger}$	$\Delta_r H^{\ddagger}$
Propene formation	(100)	-8	126	128 ± 5
Ether formation	(100)	-36	112	118 ± 5

- **Propene formation activation entropically favored**

* Conversion < 10 %
Temperature : 165 to 210 °C
Initial *i*PrOH partial pressure : 1.5 kPa
Flow rate: 60 cc.min^{-1}

Reactor-scale modeling

- **"DFT model" – explicit site description**
  - **4 gas-phase species**
  - **15 surface species**
  - **34 reactions …**



- **"Analytic model" – implicit site description**
  - **4 gas-phase species**
  - **0 surface specie**
  - **3 reactions only**

*i*PrOH => Propene + H_2O $\quad r_1 = \frac{L_0}{\Gamma} k_1 \left[K_1 \left(\frac{P_I}{P^0} \right) + K_2 \left(\frac{P_I}{P^0} \right)^2 \right]$

*2 i*PrOH => DIPE + H_2O $\quad r_2 = \frac{L_0}{\Gamma} k_2 \left[K_2 \left(\frac{P_I}{P^0} \right)^2 + K_4 \left(\frac{P_I}{P^0} \right)^2 \left(\frac{P_W}{P^0} \right) \right]$

DIPE => Propene + *i*PrOH $\quad r_3 = \frac{L_0}{\Gamma} k_3 \left[K_5 \left(\frac{P_E}{P^0} \right) \right]$

Inhibitions :

$$\Gamma = 1 + K_1 \left(\frac{P_I}{P^0} \right) + K_2 \left(\frac{P_I}{P^0} \right)^2 + K_3 \left(\frac{P_I}{P^0} \right) \left(\frac{P_W}{P^0} \right) + K_4 \left(\frac{P_I}{P^0} \right)^2 \left(\frac{P_W}{P^0} \right) + K_5 \left(\frac{P_E}{P^0} \right)$$